## The Catalytic Hydrolysis of Isocyanic Acid (HNCO) in the Urea-SCR Process

## A dissertation submitted to the SWISS FEDERAL INSTITUTE OF TECHNOLOGY ZURICH for the degree of DOCTOR OF TECHNICAL SCIENCES

presented by

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To my parents

We must never feel disarmed: nature is immense and complex, but it is not impermeable to intelligence; we must circle around it, pierce and probe it, looking for the opening or making it.

**Primo Levi** (1919-1987)

# Table of Contents

Acknowledgements	VII	
Summary	IX	
Sommario	XI	
Chapter 1: Introduction	1	
1.1 The origin of <i>Smog</i>	1	
1.2 Diesel engines and air pollution	2	
1.2.1 Diesel engine emissions: NOx and PM	3	
1.2.2 NOx and PM effect on health and environment	4	
1.2.3 European emission standards for heavy duty diesel vehicles	6	
1.3 NOx reduction in heavy duty diesel vehicles	8	
1.3.1 Chemistry of the urea-SCR process	8	
1.3.2 Catalytic hydrolysis of isocyanic acid	10	
1.4 Scope of the thesis	11	
1.5 Notes on the supply of urea	12	
Chapter 2: Experimental	15	
2.1 Experimental set-up	15	
2.1.1 Dosing system	16	
2.1.2 HNCO generator	17	
2.1.3 Reactors	19	
2.1.3.1 Tubular glass reactors	19	
2.1.3.2 Plug flow glass micro-reactor	20	
2.1.3.3 Plug flow stainless-steel micro-reactor	20	
2.1.4 FTIR Spectrometer	21	
2.1.4.1 Gas cell	21	
2.1.4.2 DRIFT cell	22	

2.1.5 Ion analyzer	22
2.2 Catalyst characterization methods	22
2.2.1 Diffuse Reflectance Infrared Spectroscopy (DRIFT)	23
2.2.2 Additional applied characterization techniques	24
2.2.2.1 BET surface analysis	24
2.2.2.2 X-Ray Diffraction (XRD)	24
2.2.2.3 Temperature Programmed Desorption of $NH_3$ ( $NH_3$ TPD)	24
2.2.2.4 Electron Paramagnetic Resonance Spectroscopy (EPR)	24
2.2.2.5 Inductively Coupled Plasma - Atomic Emission Spectroscopy (ICP - AES)	25
2.2.2.6 <sup>27</sup> Al Magic-Angle Spinning Nuclear Magnetic Resonance Spectroscopy	
$(^{27}Al-NMR)$	25
2.3 Data Evaluation	25
2.3.1 Conversion and yield	25
2.3.2 GHSV	26
2.3.3 Mole and mass balances in adsorption/desorption experiments	26
2.3.4 Symbols	27
Chanter 3. Catalyst Screening	
Chapter 5. Catalyst bertenning	29
3.1 Introduction	<b>29</b> 29
3.1 Introduction 3.2 Experimental	<b>29</b> 29 30
3.1 Introduction 3.2 Experimental 3.2.1 Specialized Hydrolysis Catalyst	<ul> <li>29</li> <li>29</li> <li>30</li> <li>30</li> </ul>
<ul> <li>3.1 Introduction</li> <li>3.2 Experimental</li> <li>3.2.1 Specialized Hydrolysis Catalyst</li> <li>3.2.2 SCR-Hydrolysis Catalyst</li> </ul>	<ul> <li>29</li> <li>29</li> <li>30</li> <li>30</li> <li>31</li> </ul>
<ul> <li>3.1 Introduction</li> <li>3.2 Experimental</li> <li>3.2.1 Specialized Hydrolysis Catalyst</li> <li>3.2.2 SCR-Hydrolysis Catalyst</li> <li>3.3 Results: Specialized Hydrolysis Catalyst</li> </ul>	<ul> <li>29</li> <li>29</li> <li>30</li> <li>30</li> <li>31</li> <li>33</li> </ul>
<ul> <li>3.1 Introduction</li> <li>3.2 Experimental</li> <li>3.2.1 Specialized Hydrolysis Catalyst</li> <li>3.2.2 SCR-Hydrolysis Catalyst</li> <li>3.3 Results: Specialized Hydrolysis Catalyst</li> <li>3.3.1 Hydrolysis Properties</li> </ul>	29 29 30 30 31 33 33
<ul> <li>3.1 Introduction</li> <li>3.2 Experimental</li> <li>3.2.1 Specialized Hydrolysis Catalyst</li> <li>3.2.2 SCR-Hydrolysis Catalyst</li> <li>3.3 Results: Specialized Hydrolysis Catalyst</li> <li>3.3.1 Hydrolysis Properties</li> <li>3.3.2 Correlation between acidity and activity</li> </ul>	29 30 30 31 33 33 35
<ul> <li>3.1 Introduction</li> <li>3.2 Experimental</li> <li>3.2.1 Specialized Hydrolysis Catalyst</li> <li>3.2.2 SCR-Hydrolysis Catalyst</li> <li>3.3 Results: Specialized Hydrolysis Catalyst</li> <li>3.3.1 Hydrolysis Properties</li> <li>3.3.2 Correlation between acidity and activity</li> <li>3.4 SCR-Hydrolysis Catalyst</li> </ul>	29 30 30 31 33 33 35 36
<ul> <li>3.1 Introduction</li> <li>3.2 Experimental</li> <li>3.2.1 Specialized Hydrolysis Catalyst</li> <li>3.2.2 SCR-Hydrolysis Catalyst</li> <li>3.3 Results: Specialized Hydrolysis Catalyst</li> <li>3.3.1 Hydrolysis Properties</li> <li>3.3.2 Correlation between acidity and activity</li> <li>3.4 SCR-Hydrolysis Catalyst</li> <li>3.4.1 Hydrolysis properties</li> </ul>	29 30 30 31 33 33 35 36 36
<ul> <li>3.1 Introduction</li> <li>3.2 Experimental <ul> <li>3.2.1 Specialized Hydrolysis Catalyst</li> <li>3.2.2 SCR-Hydrolysis Catalyst</li> </ul> </li> <li>3.3 Results: Specialized Hydrolysis Catalyst <ul> <li>3.3.1 Hydrolysis Properties</li> <li>3.3.2 Correlation between acidity and activity</li> </ul> </li> <li>3.4 SCR-Hydrolysis Catalyst <ul> <li>3.4.1 Hydrolysis properties</li> <li>3.4.2 DeNOx properties</li> </ul> </li> </ul>	29 30 30 31 33 35 36 36 38
<ul> <li>3.1 Introduction</li> <li>3.2 Experimental</li> <li>3.2.1 Specialized Hydrolysis Catalyst</li> <li>3.2.2 SCR-Hydrolysis Catalyst</li> <li>3.3 Results: Specialized Hydrolysis Catalyst</li> <li>3.3.1 Hydrolysis Properties</li> <li>3.3.2 Correlation between acidity and activity</li> <li>3.4 SCR-Hydrolysis Catalyst</li> <li>3.4.1 Hydrolysis properties</li> <li>3.4.2 DeNOx properties</li> <li>3.4.3 Correlation between acidity and activity</li> </ul>	29 30 30 31 33 35 36 36 36 38 39
<ul> <li>3.1 Introduction</li> <li>3.2 Experimental</li> <li>3.2.1 Specialized Hydrolysis Catalyst</li> <li>3.2.2 SCR-Hydrolysis Catalyst</li> <li>3.3 Results: Specialized Hydrolysis Catalyst</li> <li>3.3.1 Hydrolysis Properties</li> <li>3.3.2 Correlation between acidity and activity</li> <li>3.4 SCR-Hydrolysis Catalyst</li> <li>3.4.1 Hydrolysis properties</li> <li>3.4.2 DeNOx properties</li> <li>3.4.3 Correlation between acidity and activity</li> <li>3.4.4 Comparison with conventional V<sub>2</sub>O<sub>5</sub>/WO<sub>3</sub>-TiO<sub>2</sub> SCR catalysts</li> </ul>	29 30 30 31 33 35 36 36 36 38 39 41

Chapter 4: HNCO Adsorption on TiO <sub>2</sub>	43	
4.1 Introduction	43	
4.2 TiO <sub>2</sub> anatase, background	44	
4.3 Experimental	46	
4.4 Catalyst characterization	47	
4.4.1 NH <sub>3</sub> -TPD	47	
4.4.2 DRIFT investigation of the fresh sample	47	
4.4.3 DRIFT investigation of NH <sub>3</sub> adsorption	49	
4.4.4 DRIFT investigation of CO adsorption	51	
4.4.5 XRD pattern	52	
4.5 Adsorption of HNCO	53	
4.5.1 DRIFT investigation of HNCO adsorption	53	
4.6 Discussion	57	
4.7 Conclusions	58	
Chapter 5: HNCO Adsorption on Fe-ZSM5	61	
5.1 Introduction	61	
5.2 Fe-ZSM5 zeolite background	62	
5.3 Experimental	62	
5.4 Results	63	
5.4.1 Characterization of iron exchanged catalysts	63	
5.4.2 HNCO adsorption on Fe-ZSM5 $_1$ and Fe-ZSM5 $_2$	65	
5.4.3 Adsorption of HNCO on H-ZSM5 and its constituents	67	
5.4.4 Adsorption of HNCO on Fe <sub>2</sub> O <sub>3</sub> , Fe/Al <sub>2</sub> O <sub>3</sub> , and Fe/SiO <sub>2</sub>	69	
5.5 Discussion	71	
5.6 Conclusions	72	
Chapter 6: Reaction Mechanism	73	
6.1 Introduction	73	
6.2 Experimental	74	
6.3 Hydrolysis with $TiO_2$ anatase	74	

6.3.1 Reactivity of NCO species in the presence of water	74
6.2.2 Adaption of U.O. on TiO	74
$6.3.2 \text{ Adsorption of } H_2O \text{ on } HO_2$	73
6.3.3 Adsorption of $CO_2$ on $IIO_2$	/8
$6.3.4$ HNCO hydrolysis over $11O_2$	79
6.3.5 Discussion	80
6.4 Hydrolysis with Fe-ZSM5	81
6.5 Conclusions	83
Chapter 7: Influence of NO <sub>2</sub>	85
7.1 Introduction	85
7.2 Experimental	86
7.3 HNCO hydrolysis with in the presence of NO <sub>2</sub>	87
7.3.1 TiO <sub>2</sub> anatase	87
7.3.2 Fe-ZSM5	88
7.4 Role of NO <sub>2</sub>	89
7.4.1 TPD of $NH_3$ and $NO_2$	89
7.4.2 Combined TPD/TR experiments	90
7.4.3 DRIFT experiments	94
7.5 Discussion	97
7.6 Conclusions	98
Chapter 8: Influence of NH <sub>3</sub> , NO and SO <sub>2</sub>	99
8.1 Introduction	99
8.2 Experimental	100
8.3 Results: $TiO_2$ anatase	101
8.3.1 Influence of $NH_3$ and NO on the catalytic activity	101
8.3.2 DRIFT investigation of the HNCO/NH <sub>3</sub> competitive adsorption	102
8.4 Results: Fe-ZSM5 <sub>1</sub>	103
8.4.1 Influence of NH <sub>3</sub> and NO on the catalytic activity	103
8.4.2 Influence of $SO_2$	104
8.5 Conclusions	105

Chapter 9: Kinetics of the HNCO Hydrolysis	107	
9.1 Introduction	107	
9.1.1 Analysis methods	107	
9.1.2 Symbols	110	
9.1.3 Review of the analysis method	110	
9.2 Determination of the reaction orders	111	
9.2.1 Reaction order for $CO_2(\gamma)$	112	
9.2.2 Reaction order for $NH_3(\delta)$	112	
9.2.3 Reaction order for HNCO ( $\alpha$ )	113	
9.2.4 Reaction order for $H_2O(\beta)$	114	
9.2.5 Reproducibility of the data	115	
9.3 Activation energy under typical diesel exhaust conditions	116	
9.3.1 Considerations on mass transfer and reactor ideality	118	
9.3.1.1 Criteria	119	
9.3.1.2 Calculations	120	
9.3.2 Symbols	122	
9.4 Conclusions	123	
Chapter 10: Conclusions and Outlook	125	
10.1 Conclusions	125	
10.2 Outlook	128	
Bibliography	131	
List of Publications	143	
Curriculum Vitae	145	

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# Summary

The selective catalytic reduction of  $NO_x$  with urea (*urea-SCR*) in diesel exhaust gases is an emerging technology that most European truck manufacturers have recently started to employ. One fundamental step of this process is the decomposition of urea into ammonia. This occurs via two reactions: the thermolysis of urea into ammonia and isocyanic acid (HNCO), and the following catalytic hydrolysis of isocyanic acid. The purpose of this thesis was to investigate, under real conditions, the catalytic hydrolysis of isocyanic acid:

$$HNCO + H_2O \rightarrow NH_3 + CO_2$$

Not much information is available about this reaction and the goals of this work were to identify active hydrolysis catalysts, investigate their possibilities and limits in typical diesel exhaust conditions, and acquire a deeper understanding of the reaction mechanism. The results presented in this thesis deal with the following main topics:

- selection of catalysts active for the HNCO hydrolysis. Two different approaches were adopted: the study of a catalyst specialized for the HNCO hydrolysis, and the development of a SCR catalyst also active for the hydrolysis reaction,
- elucidation of the reaction mechanism by means of analytic and spectroscopic methods,
- investigation of the effects of compounds inevitably present in diesel exhaust gases (NH<sub>3</sub>, NO, SO<sub>2</sub> and NO<sub>2</sub>) on the activity of the catalysts,
- kinetics investigation.

Among a number of tested materials,  $TiO_2$  in the anatase phase showed the best hydrolysis properties and was therefore selected for more detailed investigations. The hydrolysis properties of Fe-ZSM5, a catalyst from the SCR family, were also studied, revealing a very high activity for the HNCO hydrolysis. Moreover, the test of these different materials suggested that hydrolysis properties are related to Lewis acidity.

The interaction of isocyanic acid with  $TiO_2$  was investigated by means of DRIFT spectroscopy. Isocyanic acid adsorbed dissociatively on  $TiO_2$  to yield isocyanate (–NCO) groups, bound to  $Ti^{4+}$  sites, and hydroxyl (–OH) groups. The stability of the –NCO groups decreased with increasing temperature and at T > 200 °C they were very easily removed from the surface. The adsorption of HNCO on Fe-ZSM5 was also investigated in detail by DRIFT spectroscopy and compared to the adsorption on H-ZSM5, Al<sub>2</sub>O<sub>3</sub>, SiO<sub>2</sub>, Fe/Al<sub>2</sub>O<sub>3</sub> and Fe/SiO<sub>2</sub>. At 150 °C, HNCO adsorbed dissociatively on Fe-ZSM5 producing principally isocyanate species (–NCO) adsorbed on Al and Fe sites.

In the presence of water, hydrolysis of the -NCO groups to  $NH_3$  was observed on both  $TiO_2$  and Fe-ZSM5. The reactivity of isocyanate species toward water increased with temperature, in agreement with the activity of the catalysts. This suggested that -NCO groups are likely intermediate species in the hydrolysis of HNCO.

Investigation of the influence of NH<sub>3</sub> and NO<sub>2</sub> on the catalyst activities revealed that for both catalysts, the rate of hydrolysis was considerably reduced in the presence of NH<sub>3</sub> and NO<sub>2</sub> at temperatures below 200 °C. DRIFT investigations revealed that, at these temperatures, the adsorption of NH<sub>3</sub> on the surface hinders the formation of –NCO species. Transient low temperature investigations of the reaction, TPD experiments and DRIFT investigations showed that in the presence of NO<sub>2</sub>, part of it adsorbed strongly on the surface while part reacted with NH<sub>3</sub> to form ammonium nitrate on the catalyst surface. Both of these effects hinder the formation of –NCO species on the surface. Since at high temperatures NH<sub>3</sub> and NO<sub>2</sub> were desorbed and NH<sub>4</sub>NO<sub>3</sub> was decomposed, the catalytic activity was completely restored by thermal treatment at 450 °C.

The effect of  $SO_2$  and NO on the activity of  $TiO_2$  and Fe-ZSM5 was also investigated. The results showed that sulfur dioxide led to little or no variation in the catalytic properties. On the contrary, the presence of NO increased the catalytic activity of Fe-ZSM5 at low temperature, while  $TiO_2$  did not show variations in its hydrolysis properties. In view of the assumption of competitive adsorption between NH<sub>3</sub> and HNCO, this effect is attributed to the partial removal of adsorbed NH<sub>3</sub> from the surface by reaction with NO (SCR reaction). No similar effect was observed for  $TiO_2$ , owing to the poor SCR activity of this material.

The kinetics of the HNCO hydrolysis on  $TiO_2$  at low temperature was studied and reaction orders and the activation energy were determined. In particular, the reaction order for NH<sub>3</sub> decreased with decreasing temperature, proving the inhibition effect of ammonia. The reaction order for HNCO, CO<sub>2</sub>, and H<sub>2</sub>O were calculated to be 1, 0, and 1, respectively. However, in the presence of excess water (i.e., typical diesel exhaust conditions), the H<sub>2</sub>O reaction order reduced to zero, thus suggesting that the surface was covered with water. In typical diesel exhaust conditions, the activation energy was calculated to be ~  $40 \pm 4$  kJ/mol in the low temperature region.

# Sommario

La riduzione catalitica selettiva degli ossidi di azoto per mezzo di urea (urea-RCS) è una tecnica di trattamento dei gas di scarico che i maggiori produttori europei di mezzi pesanti hanno recentemente cominciato ad applicare nei loro veicoli. Uno dei passaggi principali di questa tecnica è l'ottenimento di ammoniaca a partire da urea. Questo avviene attraverso due reazioni: la decomposizione termica dell'urea in ammoniaca e acido isocianico (HNCO) e la successiva idrolisi catalitica dell'acido isocianico. Lo scopo di questa tesi è stato lo studio dettagliato di questa seconda reazione:

$$HNCO + H_2O \rightarrow NH_3 + CO_2$$

In letteratura sono disponibili solo pochi studi dedicati all'idrolisi catalitica dell'acido isocianico e l'obbiettivo di questo lavoro è stato quello di coprire questa mancanza selezionando catalizzatori attivi per questa reazione, studiandone le possibilità e limiti in condizioni reali e analizzando il possibile meccanismo di reazione. I risultati contenuti in questa tesi possono essere suddivisi in tre argomenti principali:

- la selezione di catalizzatori attivi per l'idrolisi dell'acido isocianico. In questo senso sono state considerati due approcci: quello di selezionare un catalizzatore attivo in maniera specifica per la razione di idrolisi e quello di sviluppare un catalizzatore RSC in grado di favorire anche l'idrolisi dell'acido isocianico,
- lo studio del meccanismo di reazione attraverso l'utilizzo di metodi analitici e tecniche spettroscopiche,
- l'indagine accurata dell'effetto che componenti tipici del gas di scarico prodotto da un motore diesel, quali NH<sub>3</sub>, NO, SO<sub>2</sub> and NO<sub>2</sub>, hanno sull'attività dei catalizzatori,
- lo studio della cinetica di reazione.

Il confronto di numerosi materiali ha portato alla selezione di  $TiO_2$  in fase anatasio, per le sue ottime proprietà catalitiche nei confronti della reazione di idrolisi, e degli zeoliti ZSM5 contenenti ferro, per la loro notevole attività nei confronti di entrambe le reazioni di RCS degli ossidi di azoto e di idrolisi dell'acido isocianico. I risultati ottenuti hanno inoltre evidenziato una relazione tra l'acidità (acidità di Lewis) dei catalizzatori e la loro attività nei confronti della reazione di idrolisi.

L'interazione dell'acido isocianico con  $TiO_2$  è stata studiata per mezzo di spettroscopia DRIFT. I risultati hanno rivelato che l'acido isocianico assorbe sul biossido di titanio in maniera dissociativa formando specie isocianato (–NCO) e grouppi OH. I gruppi –NCO hanno inoltre dimostrato una stabilità decrescente in funzione di un aumento della temperatura, diventando facilmente rimuovibili dalla superficie per T > 200 °C.

Anche l'assorbimento dell'acido isocianico su Fe-ZSM5 è stato studiato in modo dettagliato attraverso spettroscopia DRIFT. Il confronto dei risultati ottenuti con quelli risultanti dall'assorbimento di HNCO su H-ZSM5, Al<sub>2</sub>O<sub>3</sub>, SiO<sub>2</sub>, Fe/Al<sub>2</sub>O<sub>3</sub> e Fe/SiO<sub>2</sub> ha permesso di stabilire che, a 150 °C, l'acido isocianico assorbe anche su Fe-ZSM5 in maniera dissociativa formando specie isocianato legate agli atomi di alluminio e di ferro presenti sulla superficie del catalizzatore.

I risultati ottenuti hanno inoltre dimostrato che, in presenza di acqua, le specie isocianato idrolizzano formando ammoniaca con una reattività crescente al crescere della temperatura, in accordo con l'attività dei catalizzatori. Questo risultato suggerisce un ruolo di intermedi di reazione nell'idrolisi dell'acido isocianico per le specie –NCO.

L'indagine dell'effetto di NH<sub>3</sub>, NO<sub>2</sub> e NO sull'attività dei catalizzatori ha dimostrato che la velocità di reazione riduce sensibilmente in presenza di NH<sub>3</sub> e NO<sub>2</sub> per temperature minori di 200 °C. Esperimenti di spettroscopia DRIFT hanno rivelato che a bassa temperatura la presenza di ammoniaca riduce la formazione delle specie isociananto a causa del suo assorbimento competitivo sulla superficie. Studio della reazione in presenza di NO<sub>2</sub>, esperimenti di desorbimento programmato (TPD) e analisi di spettroscopia DRIFT hanno invece dimostrato che la presenza di NO<sub>2</sub> comporta non solo il suo assorbimento sulla superfice, ma anche la formazione nitrato d'ammonio attraverso reazione con l'ammoniaca. La formazione di quest'ultimo sulla superficie del catalizzatore impedisce l'assorbimento dell'acido iscianico causando una effetto di disattivazione. Tuttavia, poiché ad elevate remperature NO e NH<sub>3</sub> desorbono dalla superficie e il nitrato d'ammonio decompone, il trattamento dei catalizzatori a 450 °C ha permesso di rigenerarne completamente l'attività.

Ulteriori esperimenti hanno dimostrato che l'anidride solforosa  $(SO_2)$  ha un'influenza trascurabile sull'attività catalitica di TiO<sub>2</sub> e Fe-ZSM5. Al contrario, esperimenti condotti in

presenza di monossido d'azoto (NO) hanno rivelato un aumento dell'attività di Fe-ZSM5 a bassa temperatura (T < 175 °C). Questo risultato conferma l'ipotesi di assorbimento competitivo da parte di ammoniaca e HNCO sui catalizzatori. Nel caso di Fe-ZSM5 l'ammoniaca assorbita sulla superficie reagisce con il monossido d'azoto (reazione RCS), lasciando liberi siti attivit per l' assorbimento dell'acido isocianico. Con TiO<sub>2</sub> quest'effetto non è stato osservato a causa delle sue trascurabili proprietà RCS.

Lo studio della cinetica dell'idrolisi dell'acido isocianico catalizzata da TiO<sub>2</sub> ha permesso di stimare un ordine di reazione per l'ammoniaca negativo a bassa temperatura, e nullo per T > 150 °C. Questo risultato conferma ancora una volta l'effetto di inibizione dell'amoniaca a basse temperature. Gli ordini di reazione per HNCO, CO<sub>2</sub> e H<sub>2</sub>O, sono invece risultati rispettivamente 1,0 e 1. Tuttavia, esperimenti realizzati in presenza di un eccesso di acqua, hanno rivelato che, in queste condizioni, l'ordine di reazione per H<sub>2</sub>O si riduce a zero (la superficie del catalizzatore è satura d'acqua). A basse temperature e per condizioni tipiche di un gas dis scarico prodotto da un motore diesel (cioè in presenza di un eccesso d'acqua) è stata calcolata un'energia di attivazione pari a ~ 40 ± 4 kJ/mol.

# 1

# Introduction

"...he said it required no science to see that there was something produced in great cities which was not found in the country, and that was smoky fog, or what was known as `smog"

"Daily Graphic", 26 July 1905, citing Henry Antoine des Voeux.

## 1.1 The origin of Smog

In 1905 a member of the London's Coal Smoke Abatement Society, Henry Antoine des Voeux, coined a new word: *smog*. He introduced this expression in his paper "Fog and Smoke", presented in a meeting of the Public Health Congress in London; it was originated by combining the words *smoke* and *fog* [*AHD* (2000)]. However, the first recognized episodes of smog attributed to automotive emissions occurred in Los Angeles in the 1940s.



Figure 1.1: Los Angeles during the episode of air pollution in 1943. Source [AQDM].

In summer 1943 the citizens of Los Angeles complained that the visibility was drastically reduced and people were suffering from burning eyes, respiratory problems, nausea, and vomiting. The phenomenon was termed as "smog", using the definition given in 1905 by H. A. des Voeux. Nevertheless, it was necessary to wait until the 1950s before suspicions about the contribution of motor vehicles to the air pollution problem of the area were raised. In 1952 Dr. A. J. Haagen-Smit demonstrated that the smog problem observed in Los Angeles resulted from reaction of nitrogen oxides and hydrocarbon exposed to sunlight [*Haagen-Smit (1952)*]. These reactions produced secondary pollutants that caused eye and throat irritation and reduced the visibility in the town. Following studies made clear that the vehicles were a major contributor of nitrogen oxides and hydrocarbons, as well as the main source of carbon monoxide in urban areas. As a result, California became the testing ground for pioneer legislation and emission control devices. In the late 1960s the first emission standards were introduced nationwide in the United States. In succeeding years Japan and Europe followed the United States' example. In 2005 China also introduced emission standards for heavy duty trucks [*SEPA*].

## **1.2 Diesel engines and air pollution**

There are many sources of air pollution but the main contributing sectors are transport, power generation, industry, agriculture and heating. All of these sources produce a variety of air pollutants, such as sulfur dioxide, nitrogen oxides, ammonia, volatile organic substances and par-

ticulate matter (European emission database [*EED*]). In urban areas vehicle emissions are among the most predominant source of air pollution and in particular, diesel engines are a significant source of particulate matter as well as nitrogen oxides. However, diesel engines are also the primary power source used in heavy duty applications. Thanks to their efficiency, reliability and durability (it is not uncommon for a diesel engine to have an about 10 times larger life time than a comparable gasoline engine [*Heck et al. (2002)*]), they are also winning an increasing share of the light duty vehicle and passenger car markets worldwide. According to Bosch, in 2004 nearly 52% of newly registered cars in Western Europe were equipped with diesel engines (36% in 2001) [*BOSCH*]. Besides, the policy of several European countries is to keep the price of diesel fuel lower than that of gasoline, which further adds to the promotion of diesel vehicles.

#### 1.2.1 Diesel engine emissions: NOx and PM

Combustion in diesel engines contributes significantly to the emissions of nitrogen oxides and particular matter. Nitrogen oxides, also called NOx, emitted from diesel engines consist of nitric oxide (NO) and only a small amount of nitrogen dioxide (NO<sub>2</sub>). The main source of nitrogen oxides in the exhaust of diesel engines is the oxidation of atmospheric nitrogen [*Heywood* (1988)]. However, if the fuel contains nitrogen compounds, the oxidation of these compounds is an additional source of nitrogen oxides. Particulate matter (PM) is a term used to describe particles with a diameter of less than 10 $\mu$ m. Particulate matter is a complex mixture that consists of "primary" and "secondary" particles. Primary particles are generated during the combustion process and consist of carbonaceous materials (soot) upon which some heavy hydrocarbons, sulfates and water might have been adsorbed. They result from incomplete burning of hydrocarbons, which occurs during combustion in regions with oxygen deficiency (i.e. under poor fuel mixing conditions) [*Heywood* (1988)]. Secondary particles are formed in the atmosphere upon chemical reaction of primary diesel engine emissions such NOx, and SO<sub>2</sub> (sulfur dioxide is formed by combustion of the sulfur present in the diesel blend).

The operation of diesel engines is characterized by low fuel/air ratios (*i.e.* an excess of air, termed 'lean' operation). Therefore the combustion process occurs in the presence of excess oxygen, allowing higher fuel conversion efficiency than in gasoline engines and resulting in reduction of CO emissions. Lean operation would also permit cooler combustion which results in reduced production of nitrogen oxides emissions. However, there is an upper limit to the further

addition of air, since a too lean mixture excessively reduces the combustion temperature, increasing the emission of particulates. In addition, problems controlling the fuel/air mixture can occur. These facts highlight the linkage between formation of nitrogen oxides and particulate emissions. Unfortunately they are inversely related: cooler engine operation produces less nitrogen oxides but more particulates, but at higher temperature operation the combustion is more complete, which produces less particulates but more nitrogen oxides. This is referred to as the *NOxparticulate trade-off*.

#### 1.2.2 NOx and PM effect on health and environment

Exposure to high concentration of air pollutants leads to reduced life expectancy and causes premature death and widespread aggravation to health. It has been estimated that Europe loses 200 million working days a year for air pollution-related illness and that 6.4 % of deaths and illnesses in young European children are caused by outdoor pollution [*EEA* (2005)]. Also the ecosystem suffers the negative effects of air contamination [*Bouble et al.* (1994)]. Nitrogen oxides and soot contribute to a large extent to the negative health and environmental effects of air pollution (Figure 1.2).



Figure 1.2: Schematic of the negative effects of NOx and PM.

NOx contribute to the ozone depletion in upper atmosphere (stratosphere). However, they have several detrimental effects also in the lower atmosphere (troposphere). Nitric oxide (NO, major component of NOx) takes part to the formation of elevated ozone concentrations present at ground level via reaction with volatile organic compounds (VOCs) in the presence of sunlight. Although ozone is beneficial in the stratosphere because it adsorbs ultraviolet radiations, it poses health hazard to humans in the troposphere because it inflames respiratory tracts and damages lungs. Ozone is thought to hasten the deaths of up to 20000 people in the EU each year [EEA (2005)]. In addition, ozone negatively affects ecosystems and agricultural crops resulting in visible plants damage and in the reduction in crop yield and seed production. Nitric oxide participates also in the formation of acid rain via formation of nitric acid. Acid rain erodes buildings and statue and causes lakes and rivers to become acidic and unsuitable for many fishes. An additional detrimental effect of nitric oxide is the eutrophication of aquatic ecosystems via addition of excess nitrogen. Eutrophication is a consequence of an excess input of nutrients that disturb the ecosystem. A common outcome is the formation of an excessive amount of algae in surface waters. Finally, nitric oxide contributes to the generation of fine particulate via formation of secondary particulates such as ammonium nitrate, with resulting health impacts and contributions to regional haze.

Nitrogen dioxide (NO<sub>2</sub>), is a reddish brown toxic gas. The potential toxicity of NO<sub>2</sub> has long been recognized and demonstrated [*Holgate (ed) et al. (1999); Buick et al. (1999)*]. Inhalation of high concentrations of NO<sub>2</sub> (on the order of a few hundred parts per million) is fatal [*Guidotti (1978); Elsayed (1994)*]. Moreover, NO<sub>2</sub> is implicated in the production of ozone via photochemical interactions and it contributes to a general reduction of visibility because it adsorbs light in the visible wavelength region. NOx contributes also to the ozone depletion in the ozonosphere.

Particulate matter (PM) has significant health hazardous effects for the respiratory system and is considered as a potential and probable human carcinogen [*Bouble et al. (1994); Marley et al. (2006)*]. In particular, very small particles (diameter < 5  $\mu$ m) are highly hazardous since they are not filtered out by the upper respiratory tract and therefore can penetrate deeply into the respiratory system [*WHO (2000); EEA (2005); Marley et al. (2006)*].

#### 1.2.3 European emission standards for heavy duty diesel vehicles

As evident from paragraph 1.2.2, the negative effects of NOx and PM emissions are well known and the need to improve air quality has been recognized in the European Union for a long time. The impact of air pollution on human beings has been the major factor motivating its control. In the past years EU countries focused on establishing minimum quality standards for ambient air [*WHO (2000)*]. In order to meet these standards, legislation has been steadily introduced containing gradually more stringent emission limits for harmful pollutants. In particular, Table 1.1 summarizes NOx and PM limits in present and upcoming European standards for heavy duty diesel powered vehicles. As this table indicates, considerable restrictions have been legislated in recent years. PM limits refer to particles directly emitted by diesel engines (primary particles, i.e. soot). The formation of secondary particles in the atmosphere is also reduced through the introduction of NOx emissions regulations.

	Year	NOx [g/kWh]	PM [g/kWh]
Euro 2	1997	7	0.15
Euro 3	2000	5	0.1
Euro 4	2005	3.5	0.02
Euro 5	2008	2	0.02

Table 1.1: past and future European regulatory limits for PM and NOx in heavy duty diesel vehicles.

Along with NOx and PM emissions control, legislation also focused on an improvement of fuel quality via reduction of the amount of sulfur contained in diesel oils. Two mandatory deadlines were introduced which fixed the maximum sulfur content in diesel fuels at 50 ppm for 2005 and 10 ppm for 2009. This measure is expected to have a dual positive impact: it will reduce the emissions of sulfur dioxides (toxic to humans, and also a further source of particulate matter due to conversion to sulfates) and it will enable the introduction of more sophisticated catalytic systems. Many European countries have introduced incentives to accelerate the use of low and zero-sulfur fuels even ahead of the deadlines [*EEA* (2005)].

Switzerland has decided to conform to the European Union legislation, thus obtaining a decrease in the emission of most air pollutants over the past years. Nevertheless, high concentration of ground level ozone, particulate matter and nitrogen oxides are still reported on regular basis [*EEA (2005)*]. As an example, Figure 1.3 reports the trend of NOx annual mean concentration measured in Switzerland from 1988 to 2004.

The NOx-particulate trade-off represents a significant challenge for engine manufacturers. An enormous amount of research was necessary to develop technologies able to reduce both NOx and PM emissions. It has been estimated that in the absence of emission regulations and technological developments, Europeans would have had to reduce their driving by 90% in order to maintain the today levels of air quality. However, the increasing volume of transport, (30% for goods transportation and 20% for passengers over the past 10 years) has counterbalanced the significant technological improvements and resulted in not overall reduction in emissions [*EEA* (2005)]. Therefore, further strengthening of the legislation is projected for 2008 (Euro 5) and 2010 (Euro 6). It is estimated that manufacturers of heavy-duty diesel vehicles will need after-treatment techniques for cleaning the exhaust gases to accomplish the new limits.



**Figure 1.3:** trend of NOx annual mean in Switzerland in the years 1988-2004. ( $\Box$ ) urban roads, ( $\bullet$ ) urban parks, ( $\blacktriangle$ ) suburban, (x) rural, ( $\circ$ ) alpine foothills /Jura mountains, ( $\Delta$ ) Alps, (--) quality air standard. Data source [*BAFU*].

## **1.3 NOx reduction in heavy duty diesel vehicles**

Owing to their operation with an excess of oxygen, diesel engines require different after emission control technologies than gasoline engines, which operate at stoichiometric air-fuel ratios. In order to meet the Euro IV regulations, the manufacturers of heavy duty vehicles have looked into various possibilities, two of which are most promising: <u>exhaust gas recirculation</u> (EGR) [*Zheng et al.* (2004)] and <u>selective catalytic reduction with urea (urea-SCR) [*Koebel et al.* (2000); *Gabrielsson* (2004)]. The first technique is based on diluting the air/fuel mixture with exhaust gases in order to reduce the combustion temperature below the point at which NOx are formed. In the second technique the nitrogen oxides are catalytically reduced by means of a reducing compound (urea). Most leading European manufacturers of heavy-duty vehicles (DAF, Iveco, Mercedes-Benz, Renault and Volvo) have either totally or primarily opted for SCR technology (information available at [*DIDRV*]). However, Scania is offering both systems and MAN strongly advocates EGR technology (information available at [*SM*]).</u>

#### 1.3.1 Chemistry of the urea-SCR process

Removal of NOx by selective catalytic reduction with ammonia is a well known technique widely used for stationary applications [*Heck (1999); Forzatti (2000); Srivastava et al. (2005)*]. The term "selective" refers to the ability of ammonia to react selectively with NOx instead of being oxidized to  $N_2$ ,  $N_2O$  or NO by oxygen. The general SCR reactions with ammonia are represented by equations (1.1, 1.2):

$$4NO + 4NH_3 + O_2 \rightarrow 4N_2 + 6H_2O \qquad (standard-SCR) \qquad (1.1)$$

$$2NO + 2NO_2 + 4NH_3 \rightarrow 4N_2 + 6H_2O \qquad (fast-SCR) \qquad (1.2)$$

Since the nitrogen oxides of a diesel exhaust gas are mainly composed of NO, the main reaction occurring on the SCR catalyst is the "standard-SCR" reaction involving NO and ammonia (1.1). However, a more desired pathway is represented by reaction (1.2), called "fast-SCR" reaction. This reaction is very fast, but requires equal amounts of NO and NO<sub>2</sub> in the exhaust gas. The reactions of ammonia with NO and  $NO_2$  in the absence of oxygen (1.3, 1.4) are very slow and are not relevant under lean conditions.

$$6NO + 4NH_3 \rightarrow 5N_2 + 6H_2O \tag{1.3}$$

$$6NO_2 + 8NH_3 \rightarrow 7N_2 + 12H_2O \tag{1.4}$$

When the SCR technique is applied to diesel vehicles, the use of ammonia as reducing agent becomes unacceptable, since ammonia is toxic and difficult to handle. This problem can be solved by using compounds that decompose to ammonia in the exhaust. Urea is an ideal solution because it is non-toxic and easy to handle. Replacing ammonia with urea, the overall NOx reduction process is represented by reactions (1.5) and (1.6):

$$2NH_2 - CO - NH_2 + 4NO + O_2 \rightarrow 4N_2 + 4H_2O + 2CO_2$$
(1.5)

$$2NH_2 - CO - NH_2 + 2NO_2 + 2NO \rightarrow 4N_2 + 4H_2O + 2CO_2$$
(1.6)

In SCR systems urea is usually atomized as an aqueous solution directly into the exhaust gas (at ambient temperature and pressure, urea is a solid that readily dissolves with water). The decomposition to ammonia takes place in the hot exhaust via three steps: the first step is the evaporation of water from the urea solution, thus leading to solid or molten urea (1.7). Pure urea then heats up and thermally decomposes yielding equimolar amounts of isocyanic acid (HNCO) and ammonia (1.8). Finally, isocyanic acid reacts with water vapor (present in the exhaust gas as combustion product) giving equimolar amounts of ammonia and carbon dioxide (1.9).

$$NH_2 - CO - NH_{2(aq)} \rightarrow NH_2 - CO - NH_{2(sol)} + H_2O_{(gas)}$$
(1.7)

$$NH_2 - CO - NH_{2(sol)} \rightarrow NH_{3(gas)} + HNCO_{(gas)}$$
(1.8)

$$HNCO_{(gas)} + H_2O \to NH_3 + CO_{2(gas)}$$
(1.9)

The overall urea decomposition process is represented by reaction (1.10) and produces two moles of ammonia and one of  $CO_2$  for each mole of urea:

$$NH_2 - CO - NH_2 + H_2O \rightarrow 2NH_3 + CO_2 \tag{1.10}$$

Reactions (1.7) and (1.8) are endothermic and occur already in the gas phase ahead of the SCR catalyst. However, the hydrolysis of isocyanic acid (1.9) as well as the SCR reactions (1.1-1.2) require a catalyst to proceed. A schematic of the urea-SCR process is shown in Figure 1.4.



Figure 1.4: Schematic of the urea SCR process.

#### 1.3.2Catalytic hydrolysis of isocyanic acid

The hydrolysis of isocyanic acid (1.9) is an exothermic reaction ( $\Delta H^0 = -95.9$  kJ) and the Gibbs free energy is strongly negative, so that the equilibrium lies completely on the right side. However, HNCO is quite stable in the gas phase even under humid conditions and hydrolysis only occurs in the presence of a catalyst. As observed in the previous section, the selective catalytic reduction (SCR) of NOx with ammonia (1.1-1.2) also proceeds only in the presence of a catalyst. Among the various catalysts which have been tested V<sub>2</sub>O<sub>5</sub>/WO<sub>3</sub>-TiO<sub>2</sub> gained wide technical application [*Busca et al. (1998)*]. This catalyst was observed to perform very well also for the HNCO hydrolysis and it has been shown that its hydrolysis activity is much higher than its SCR activity [*Kleemann et al. (2000)*]; this allows a vehicle manufacturer to omit a specialized hydrolysis catalyst. However, a mobile SCR system usually permits only a short distance between the engine exhaust (where urea might be injected) and the catalyst entrance. This leads to a short residence time of urea in this section and therefore the decomposition might not be completed at the catalyst entrance [*Koebel et al. (2000*]]. Moreover, HNCO is known to easily polymerize to cyanuric acid or to react with urea and ammonia to form long chain compounds if

condensed on cold surfaces [*Belson et al. (1982); Koebel et al. (1996)*]. If the temperature is high enough, the products of these reactions should again decompose into smaller molecules (NH<sub>3</sub>, H<sub>2</sub>O, HNCO, CO<sub>2</sub>) [*Koebel et al. (2000)*]. Nevertheless, the risk to have these long chain compounds in the exhaust gas should be minimized, since they can lead to deposit buildup on the surfaces of the exhaust passages. In order to avoid problems with the decomposition of urea droplets on the SCR catalyst, slip of isocyanic acid through the catalyst, and formation of long chain compounds, system designs which include a specialized hydrolysis catalyst have been also proposed [*Jacob (1999)*]. Titania in the anatase modification proved to be a suitable hydrolysis catalysts [*Kleemann et al. (2000); Koebel et al. (2000)*]. However, the introduction of a dedicated hydrolysis catalyst is disadvantageous because it complicates the urea-SCR catalytic system. Therefore there is still a debate whether such complex systems will be the general solution for every application, or if specific situations exist in which a system containing just the SCR catalysts will perform equally well.

### **1.4 Scope of the thesis**

In the literature only one detailed investigation dealing with the catalytic hydrolysis of HNCO under typical diesel exhaust conditions has been published [*Kleemann et al. (2000)*]. This investigation studied the hydrolysis properties of the vanadia based SCR catalyst ( $V_2O_5/WO_3$ -TiO<sub>2</sub>) and its constituents (pure TiO<sub>2</sub> and TiO<sub>2</sub>/WO<sub>3</sub> mixtures). This single investigation is in contrast to the growing interest in HNCO catalytic hydrolysis required for the development of mobile urea-SCR systems. The purpose of this work was to fill this gap and acquire a deeper understanding of this catalytic reaction.

Both concepts, the specialized hydrolysis catalyst and the SCR catalyst (also active for the hydrolysis reaction) were explored. Pure metal oxides were investigated as dedicated hydrolysis catalysts, while the hydrolysis properties of Fe-ZSM5 were studied for a combined SCR-Hydrolysis catalyst. The latter choice was motivated by the interest that Fe-ZSM5 received in recent years as potential alternative to vanadia based SCR catalysts [*Ma et al.* (1999); Long et al. (1999); Ramachandran et al. (2000); Delahay et al. (2005); Qi et al. (2005); Sullivan et al. (2005)]. The use of a SCR catalyst different from the conventional V<sub>2</sub>O<sub>5</sub>/WO<sub>3</sub>-TiO<sub>2</sub> catalyst would have the advantage of decreasing the use of this highly toxic material. However, despite

this growing interest for Fe-ZSM5 as SCR catalyst, little information is reported in the literature about the hydrolysis properties of Fe-ZSM5 [*Jones et al.* (2004)].

The present work concentrates on model gas investigations which mimic the conditions in a real diesel engine exhausts. The exhaust gas temperature of diesel engines is usually low because of the lean operation, and varies significantly depending on driving conditions and on the position within the exhaust system. Typically, the exhaust gas temperature can vary between 150-550 °C. In addition, diesel exhaust contains a significant amount of oxygen and water as well as NO<sub>2</sub> and sulfur oxides, characteristics that must be taken into account for the selection of suitable catalysts. The material contained in this thesis is structured as follows:

- *Chapter 2* summarizes the experimental setup and defines the characterization techniques used throughout the investigations. Since many results were obtained by means of vibrational spectroscopy (FTIR and DRIFT), a brief introduction to these technique is also given.

- *Chapter 3* summarizes the catalyst screening used to select catalysts for further investigations. Among the tested catalyst TiO<sub>2</sub> in anatase modification was chosen for the concept of a dedicated hydrolysis catalyst and Fe-ZSM5 was chosen as SCR catalyst also active for the HNCO hydrolysis.

- *Chapter 4 and 5* describe the surface characteristics of the  $TiO_2$  anatase and Fe-ZSM5 samples used and report the investigation of the HNCO adsorption of these materials.

- *Chapter 6* discusses the possible mechanism of the HNCO catalytic hydrolysis.

- *Chapter 7 and 8* summarize the effects of compounds inevitably present in diesel exhaust (NH<sub>3</sub>, NO, SO<sub>2</sub> and NO<sub>2</sub>) on the catalyst activity of the tested materials.

- *Chapter 9* presents some results of kinetic studies on the HNCO hydrolysis over  $TiO_2$  anatase.

- *Chapter 10* contains the conclusions and the outlook of this work.

## **1.5** Notes on the supply of urea

Urea is a commodity produced worldwide in large scale for the food processing and fertilizer industries, obtained from reaction between ammonia and carbon dioxide [*Fable et al.* (2002)]. For the urea-SCR system, urea is carried on board the vehicle as a water solution contained in a separate tank. Therefore, the vehicle requires regular refueling of the urea solution just as it does for fuel. Typically, a concentration of 32.5 wt% of urea is used. Obviously, higher concentrations would reduce the weight required to be carried on board. However, at this concentration the mixture is eutectic with a minimum freezing point of -11 °C, therefore lending itself for use in many countries throughout the year without further modification of the carrying system. Options to prevent freezing of the solution in colder areas could include the use of additives which can further reduce the freezing temperature of the solution, or heating of the onboard storage tank and tubes. The use of solid urea has also been proposed, but control of the dosage of solid urea is more difficult. Although some patents exists [*Jacob et al. (1994); Kaefer et al.* (2004)], adequate dosing systems have not yet been realized.

Recently an industry-standard solution for urea-SCR applications has been introduced into the market under the name *AdBlue*. There are already several producers of AdBlue present on the market, the most notable including GreenChem, Yara and Univar. The price of AdBlue is estimated to be about half the price of diesel fuel [*AdBlue*]. Heavy-duty vehicles consume approximately 5% per volume of diesel use for Euro IV and 6% for Euro V (1.5 l of AdBlue per 100 km [*AdBlue*]). Therefore, in order to fill the diesel and the AdBlue tanks together, the latter should have ~ 1/20 of the diesel tank volume. At the moment AdBlue is not widely available, since the distribution network is still under construction. However stations are already up and running in Germany and more are opening in numerous other locations. Detailed studies to estimate the potential demand for urea, the costs of the associated production and distribution infrastructure and assessment of the environmental impact related to the use of urea-SCR are also available [*Fable et al.* (2002)].

# 2

# Experimental

## 2.1 Experimental set-up

The experimental set-up used for the laboratory tests is schematically illustrated in Figure 2.1. It was composed of a gas dosing system, a generator to produce isocyanic acid, a reactor for catalyst testing, an ion analyzer for measuring the HNCO and NH<sub>3</sub> concentration, and an FTIR spectrometer equipped either with a gas cell for the quantification of the gases or a DRIFT cell for surface investigations. A valve system allowed to bypass the reactor for measuring the gas feed composition. All the connecting pipes were heated to 150 °C in order to avoid water condensation and HNCO polymerization.



**Figure 2.1:** Experimental setup: 1) water reservoir; 2) mass flow controllers; 3) peristaltic pump; 4) water evaporator; 5) HNCO generator; 6) reactor; 7) ion analyzer; 8) flow meter; 9) filter; 10) diaphragm pump; 11) spectrometer accessory.

#### 2.1.1 Dosing system

The feed gas was obtained by mixing highly concentrated gases (supplied by Carbagas, specifications given in Table 2.1) with a carrier gas (N<sub>2</sub>) by means of five mass flow controllers (Brooks 5850s). The maximum total flow rate was 450  $l_N/h$ . Water was added in different modes, depending on the concentration required. High water concentrations (i.e. 5%) were obtained using a manually controlled peristaltic pump. Low water concentrations (0.02-2.5%) were achieved by saturating the N<sub>2</sub> flow with water (either the entire flow or just a portion of it, depending on the required concentration). Water was always passed through a water evaporator before entering the feed gas.

Gas species	Concentration	Purity
$N_2$	100%	99.999%
<b>O</b> <sub>2</sub>	100%	99.5%
NH <sub>3</sub>	5% in N <sub>2</sub>	99.999%
NO <sub>2</sub>	1% in synthetic air	99%
NO	5% in N <sub>2</sub>	99.9%
СО	5% in N <sub>2</sub>	99.997%
CO <sub>2</sub>	14% in N <sub>2</sub>	99%
SO <sub>2</sub>	1%	0.99%

Table 2.1: specifications of the gases used for laboratory experiments.

#### 2.1.2 HNCO generator

Isocyanic acid was produced by depolymerization of cyanuric acid via reaction (2.1).

$$3 \text{ HNCO } \leftrightarrow \overset{O}{\underset{H}{\overset{HN}{\overset{}}}}_{\overset{NH}{\overset{}}}_{\overset{O}{\overset{}}}_{\overset{HN}{\overset{}}}_{\overset{HN}{\overset{}}}_{\overset{O}{\overset{}}}_{\overset{HN}{\overset{}}}_{\overset{HN}{\overset{}}}_{\overset{O}{\overset{}}}_{\overset{HN}{\overset{}}}_{\overset{HN}{\overset{}}}_{\overset{O}{\overset{}}}_{\overset{HN}{\overset{}}}_{\overset{O}{\overset{}}}_{\overset{HN}{\overset{}}}_{\overset{O}{\overset{}}}_{\overset{HN}{\overset{}}}_{\overset{O}{\overset{}}}_{\overset{HN}{\overset{}}}_{\overset{O}{\overset{}}}_{\overset{HN}{\overset{}}}_{\overset{O}{\overset{}}}_{\overset{HN}{\overset{}}}_{\overset{O}{\overset{}}}_{\overset{HN}{\overset{}}}_{\overset{O}{\overset{}}}_{\overset{HN}{\overset{}}}_{\overset{O}{\overset{}}}_{\overset{HN}{\overset{}}}_{\overset{O}{\overset{}}}_{\overset{HN}{\overset{}}}_{\overset{O}{\overset{}}}_{\overset{HN}{\overset{}}}_{\overset{HN}{\overset{}}}_{\overset{O}{\overset{}}}_{\overset{HN}{\overset{}}}_{\overset{HN}{\overset{}}}_{\overset{O}{\overset{}}}_{\overset{HN}{\overset{}}}_{\overset{HN}{\overset{}}}_{\overset{O}{\overset{}}}_{\overset{HN}{\overset{}}}_{\overset{HN}{\overset{}}}_{\overset{O}{\overset{}}}_{\overset{HN}{\overset{}}_{\overset{HN}{\overset{}}}_{\overset{HN}{\overset{}}}_{\overset{HN}{\overset{}}_{\overset{HN}{\overset{}}}_{\overset{HN}{\overset{}}}_{\overset{HN}{\overset{}}_{\overset{HN}{\overset{}}}_{\overset{HN}{\overset{}}_{\overset{HN}{\overset{}}}_{\overset{HN}{\overset{}}_{\overset{HN}{\overset{}}}_{\overset{HN}{\overset{}}}_{\overset{HN}{\overset{}}_{\overset{HN}{\overset{}}}_{\overset{HN}{\overset{}}_{\overset{HN}{\overset{}}_{\overset{HN}{\overset{}}}_{\overset{HN}{\overset{}}_{\overset{HN}{\overset{}}}_{\overset{HN}{\overset{}}_{\overset{HN}{\overset{}}_{\overset{HN}{\overset{}}}_{\overset{HN}{\overset{}}}_{\overset{HN}{\overset{}}_{\overset{HN}{\overset{}}}_{\overset{HN}{\overset{}}_{\overset{HN}{\overset{}}}_{\overset{HN}{\overset{}}_{\overset{HN}{\overset{}}}_{\overset{HN}{\overset{}}_{\overset{HN}{\overset{}}}_{\overset{HN}{\overset{}}_{\overset{HN}{\overset{}}}_{\overset{HN}{\overset{}}}_{\overset{HN}{\overset{}}_{\overset{HN}{\overset{}}}_{\overset{HN}{\overset{}}_{\overset{HN}{\overset{}}}_{\overset{HN}{\overset{}}_{\overset{HN}{\overset{}}}_{\overset{HN}{\overset{}}}_{\overset{HN}{\overset{}}_{\overset{HN}{\overset{}}}_{\overset{HN}{\overset{}}}_{\overset{HN}{\overset{}}_{\overset{HN}{\overset{}}}_{\overset{HN}{\overset{}}}_{\overset{HN}{\overset{}}_{\overset{HN}{\overset{}}}_{\overset{HN}{\overset{}}_{\overset{HN}{\overset{}}_{\overset{HN}{\overset{}}}_{\overset{HN}{\overset{}}}_{\overset{HN}{\overset{}}_{\overset{HN}{\overset{}}}_{\overset{HN}{\overset{}}}_{\overset{HN}{\overset{}}_{\overset{HN}{\overset{}}}_{\overset{HN}{\overset{}}}_{\overset{HN}{\overset{}}}_{\overset{HN}{\overset{}}}_{\overset{HN}{\overset{}}}_{\overset{HN}{\overset{}}}}_{\overset{HN}{\overset{}}}}_{\overset{HN}}_{\overset{HN}{\overset{}}_{\overset{HN}{\overset{}}}_{\overset{HN}{\overset{}}}_{\overset{HN}{\overset{}}}_{\overset{HN}}}_{\overset{HN}{\overset{}}}_{\overset{HN}{\overset{}}}_{\overset{HN}{\overset{}}}_{\overset{HN}{\overset{}}}_{\overset{HN}{\overset{}}}_{\overset{HN}{\overset{}}_{\overset{HN}{\overset{}}}_{\overset{HN}{\overset{}}}_{\overset{HN}{\overset{}}}_{\overset{HN}{\overset{}}}_{\overset{HN}{}}}_{\overset{HN}{\overset{}}_{\overset{HN}{\overset{}}}_{\overset{HN}{\overset{}}}_{\overset{HN}{}}}_{\overset{HN}{\overset{}}}_{\overset{HN}{\overset{}}}_{\overset{HN}{\overset{}}$$

The thermolysis of cyanuric acid to isocyanic acid was first observed by Liebig and Wöhler in 1846 [*Liebig et al.* (1846)]. The reaction was then used to produce gaseous HNCO for laboratory use [*Herzberg et al.* (1950)]. The HNCO generator used is shown in Figure 2.2 and it allowed the production of a continuous flow of HNCO for direct use in the laboratory tests.



Figure 2.2: Schematic of the HNCO generator.

The reactor was constructed from a stainless steel cylinder 600 mm long, with a 27 mm inner diameter. The carrier gas (N<sub>2</sub>) was fed into the generator at a flow of 14 l<sub>N</sub>/h. The reactor was divided into a pre-heating zone and a secondary heating zone whose respective temperatures were controlled by two separate heating coils. The pre-heating zone was further divided into a first section, filled with steatite pearls, and a second section containing a mixture of cyanuric acid and stainless steel nuts. The secondary heating zone was just filled with stainless steel nuts. The first section was heated to a temperature of 280-360 °C. By varying the temperature in this range the concentration of isocyanic acid in the carrier gas stream could be adjusted in the range from 50 to 1000 ppm. The secondary-heating section was heated to 420 °C in order to obtain complete depolymerization of cyanuric acid. The HNCO concentration in the feed gas was measured using the FTIR analyser (equipped with the gas cell) or using the ion analyzer (section 2.1.5). The generator also produced small amounts of by-products (CO, CO<sub>2</sub> and NH<sub>3</sub>) in proportion with HNCO of the type HNCO : NH<sub>3</sub> : CO<sub>2</sub> : CO = 1000 : 25 : 20: 10. For experiments where further
removal of ammonia was required (DRIFT experiments of HNCO adsorption), the feed gas flow was passed through a bed of phosphorus pentaoxide. The concentration of the remaining ammonia was only  $\sim 0.4\%$  of the HNCO concentration.

The depolymerization reaction of cyanuric acid to isocyanic acid is reversible. In order to avoid formation of cyanuric acid via HNCO polymerization, the HNCO generator was directly connected with the heated gas line.

### 2.1.3 Reactors

#### 2.1.3.1 <u>Tubular glass reactors</u>

The reactor used for testing monolithic catalysts and for TPD/TR experiments was a tubular glass reactor with internal diameter of 28mm (Figure 2.3). The reactor consisted of a pre-heating section filled with steatite pearls and of a second section containing the monolithic catalyst. Two separate heating tapes were connected with individual temperature controllers. The temperature was regulated using two thermocouples (TIC) placed just behind the pre-heating section and at the end of the catalyst section as shown in the drawing. A third thermocouple (TI), located just ahead of the catalyst, was used for monitoring purposes.



Figure 2.3: Schematic of the tubular glass reactor.

For TPD/TR experiments the powder sample was held between two quartz wool plugs with a thickness of about 6-7 mm.

#### 2.1.3.2 Plug flow glass micro-reactor

The catalytic activity of powder samples were tested in a plug flow glass micro-reactor (Figure 2.4). The reactor consisted of a pre-heating zone of about 200 mm length filled with glass pearls and a second zone containing the sample. The inner diameter was 6.5 mm. The reactor was heated by a heating coil with the temperature being controlled via a thermocouple positioned at the end of the catalytic bed. The powder sample was positioned between two quartz wool layers with a thickness of 3-4 mm.



Figure 2.4: Schematic of the plug-flow glass micro-reactor.

#### 2.1.3.3 <u>Plug flow stainless-steel micro-reactor</u>

A stainless steel micro-reactor for tests with powder samples (Figure 2.5) was used in order to compare results of the present thesis with results of a previous work [*Kleemann et al. (2000)*]. It consisted of a tube with an inner diameter of 6.5 mm and a preheating zone with a length of  $\sim$  70 cm in spiral configuration. The catalyst was placed between two layers (3-4 mm) of quartz wool. A thermocouple was inserted into the quartz wool for measuring the temperature at the

catalyst outlet. The micro-reactor was placed into a stainless steel cylinder heated by a heating tape.



Figure 2.5: Schematic of the plug-flow stainless steel micro-reactor.

## 2.1.4 FTIR Spectrometer

The FTIR spectrometer (Thermo Nicolet Nexus 860, equipped with and MTC detector) was used with two different analysis modules: a multi-path gas cell for continuous/in-line gas analysis and a DRIFT cell for surface investigations.

### 2.1.4.1 Gas cell

The gas cell allowed fast and simultaneous measurements of several gas species concentrations. It was constructed of nickel-coated aluminum and employed gold coated aluminum mirrors and ZnSe windows. The volume was 200 ml and the total path was 2m. The cell was suitable for use in both ambient and elevated temperatures (20 °C to 185 °C). In order to avoid water condensation and HNCO polymerization a fixed temperature of 185 °C was employed. The gas cell was operated with the OMNIC software for qualitative and quantitative gas analysis and was initially calibrated to quantify NO,  $H_2O$ ,  $NO_2$ ,  $N_2O$ , CO,  $CO_2$ , HNCO and  $NH_3$ . The OMNIC software allowed continuous online measurement of the outlet gases. Spectra were collected with 16 scans per spectrum and 0.4 cm<sup>-1</sup> resolution.

#### 2.1.4.2 DRIFT cell

Diffuse Reflectance Infrared Fourier Transform (DRIFT) spectra were recorded with a Thermo-Nicolet DRIFT cell equipped with ZnSe windows. About 25 mg of catalyst powder were used for the tests. All spectra were collected with 200 scans and a resolution of 4 cm<sup>-1</sup>.

#### 2.1.5 Ion analyzer

The working principle of the ion analyser is discussed in [*Kröcher et al.* (2005)]. Briefly, a constant gas flow is withdrawn from the FTIR gas cell and mixed with a buffered absorption solution. Ammonia and HNCO are dissolved in the buffer. After the separation of the gas flow the absorption solution is made alkaline by the addition of 0.7 M caustic soda solution and the NH<sub>3</sub> concentration is measured by an ammonia-sensitive electrode. To determine the concentration of isocyanic acid, a part of the absorption solution after the gas separator is taken and HNCO is hydrolyzed to NH<sub>3</sub> by an acidic solution. The ammonia produced is then measured as previously described. Thus, the second sensor of the instrument measures the sum of NH<sub>3</sub> and HNCO in the gas. This method was used for measurement of the HNCO concentration in the gas feed during DRIFT investigations and for preliminary calibration of the gas cell.

## 2.2 Catalyst characterization methods

Different techniques were used for catalysts characterization, which are listed in the following. More details about the experimental procedure are given in the coming chapters. Since many results presented in this thesis were obtained by infrared spectroscopy, and in particular with Diffuse Reflactance Infrared Spectroscopy (DRIFT) a brief introduction to this technique is also given. More general information about infrared spectroscopy are available in many textbook [*Hair* (1967); *George et al.* (1987); *Fadini et al.* (1989); *Stuart* (2004)], as well as the basic principles of the other applied techniques [*Niemantsverdriet* (1995)].

## 2.2.1 Diffuse Reflectance Infrared Spectroscopy (DRIFT)

When the infrared radiation is directed onto the surface of a solid sample, two types of reflections can occur, specular and diffuse reflectance. The specular component is the radiation, which directly reflects off the sample surface. The diffused component is the radiation that penetrated the sample and then emerges. A Diffuse Reflectance Infrared Spectroscopy accessory is designed so as to maximize the diffused component and minimize the specular component. The optics collects the scattered radiation and directs it to the infrared detector. The infrared absorption spectrum is described by the Kubelka-Munk function (2.2), that transform the measured spectrum  $R_m(v)$  into the adsorption spectrum K(v).

$$\frac{K}{S} = \frac{(1 - R_{\infty})^2}{2R_{\infty}}$$
(2.2)

where K = Absorption coefficient (function of the frequency)

S = Scattering coefficient

 $R_{\infty}$  = Reflectivity of a sample of infinite thickness, measured as a function of the frequency

This technique is useful for highly scattering particulate samples (e.g., powder catalysts) and for strongly absorbing samples. Moreover, sampling is fast and easy because little or no sample preparation is required. However, particle size is a key variable. Large particles will result in the scattering of energy, leading to a shift of the spectrum baseline and a broadening of IR bands. Since in DRIFT measurements the infrared light travels in the sample for a long period and the optics collects a large portion of the distorted energy, it is important to use very fine particles.

DRIFT spectroscopy was used to study the species adsorbed on the surface of the catalysts. Adsorption of probe molecules was applied used in order to investigate the surface acidity. CO adsorption was used to examine the Lewis acidity. Ammonia adsorption was used to investigate both the Lewis and the Brønsted acid sites. Carbon monoxide is a weakly basic molecule with a pronounced soft electronic character. Because of this weak basicity, the interaction with electronically hard solid acids is usually very weak. When CO is adsorbed at room temperature it is possible to estimate the coordination that occurs with Lewis acid sites [*Payen et al. (2002)*]. The small size of CO allows probing nearly all acid sites. Ammonia is a small molecule that adsorbs both as  $NH_4^+$  species on Brønsted acid sites and coordinatively bound  $NH_3$  on Lewis acid sites. The small size of  $NH_3$  allows probing nearly all acid sites.

## 2.2.2 Additional applied characterization techniques

#### 2.2.2.1 BET surface analysis

The surface area of the catalysts was measured via BET analysis. A Micromeritics ASAP 2000 analyzer was used to measure the  $N_2$  adsorption isotherms of the samples. The specific surface areas were determined from the BET plot. Prior to the experiments the sample was pre-treated overnight under vacuum at 250 °C.

#### 2.2.2.2 X-Ray Diffraction (XRD)

XRD analysis was used to identify the most prominent exposed crystal surfaces of the sample, and was performed with a Philips X-Pert – MPD diffractometer using Fe K $\alpha$  radiation at 1.936 Å. The intensity data were collected in the 2 $\theta$  range between 20° and 80° with a step size of 0.05° and a counting time of 5 s per step. The measurements were made without subjecting the sample to any special treatment.

#### 2.2.2.3 <u>Temperature Programmed Desorption of NH<sub>3</sub> (NH<sub>3</sub> TPD)</u>

NH<sub>3</sub>-TPD was used to study the surface acidity of the catalysts and it was performed with a TPD/TPR 2900 analyzer from Micromeritics. Since different experimental procedures were used, a detailed description is given in the specific chapter.

#### 2.2.2.4 <u>Electron Paramagnetic Resonance Spectroscopy (EPR)</u>

ESR measurements were used to study iron species loaded on Fe-zeolites samples. They were performed with an ELEXYS Bruker spectrometer (at X-band microwave frequency). The measurements were made without subjecting the sample to any special treatment.

#### 2.2.2.5 Inductively Coupled Plasma - Atomic Emission Spectroscopy (ICP - AES)

ICP-AES was used to measure the amount of iron loaded onto the Fe-zeolite samples and was performed with a Varian Vista AX spectrometer.

## 2.2.2.6 <sup>27</sup>Al Magic-Angle Spinning Nuclear Magnetic Resonance Spectroscopy (<sup>27</sup>Al-NMR)

 $^{27}$ Al MAS NMR was performed with a Bruker Ultrashield 500 spectrometer at a magnetic field of 11.7 T equipped with a 4 mm MAS head probe. The aluminum resonance frequency at this field strength is 130 MHz. The sample rotation speed was 12.5 kHz. The  $^{27}$ Al chemical shifts were referenced to a saturated Al(NO<sub>3</sub>)<sub>3</sub> solution.

## **2.3 Data Evaluation**

In order to avoid repetition all the symbols used in this section are reported at the end.

## 2.3.1 Conversion and yield

The activity of the catalyst for the HNCO hydrolysis can be expressed in terms of HNCO conversion (2.3) or in terms of NH<sub>3</sub> yield (2.4):

$$HNCO\ Conversion\ [\%]\ = \frac{[HNCO]_{in} - [HNCO]_{out}}{[HNCO]_{in}} \cdot 100$$
(2.3)

$$NH_3 \text{ yield } [\%] = \frac{\left[HNCO\right]_{in} - \left[NH_3\right]_{out}}{\left[HNCO\right]_{in}} \cdot 100 \tag{2.4}$$

As mentioned in Paragraph 2.1.2, the HNCO generator produced a small amount of  $NH_3$  as a by-product which was introduced in the inlet flow together with HNCO. This amount of  $NH_3$ present in the inlet gas was incorporated in the HNCO<sub>in</sub> term. The expression of the catalytic activity in terms of  $NH_3$  yield furnishes a rapid indication about the selectivity of the catalyst toward ammonia (2.5).

Catalyst Selectivity [%] = 
$$\frac{[NH_3]_{out}}{[HNCO]_{in}} \cdot 100$$
 (2.5)

However, in some cases the activity was expressed in terms of HNCO hydrolysis to enable easier comparison with previous results [*Kleemann et al.* (2000)]. In this case the selectivity to NH<sub>3</sub> was always mentioned.

The activity of the catalysts for the reduction of NOx can be expressed in terms NOx conversion (DeNOx) (2.6):

$$DeNOx [\%] = \frac{\left[NO_{X}\right]_{in} - \left[NO_{X}\right]_{out}}{\left[NO_{X}\right]_{in}} \cdot 100$$
(2.6)

## 2.3.2 GHSV

The Gas Hourly Space Velocity (GHSV) is a very important parameter for the design of an air pollution control system because it determines the time available to treat the gas stream. The GHSV is the inverse of treatment time or residence time and is calculated via equation (2.7).

$$GHSV = \frac{V_N^*}{V_c}$$
(2.7)

A GHSV representative of typical conditions in automotive diesel exhaust is 40000-60000  $h^{-1}$ .

## 2.3.3 Mole and mass balances in adsorption/desorption experiments

The amounts of  $NO_2$  and  $NH_3$  adsorbed stored on  $TiO_2$  during the adsorption were calculated according to equation (2.8).

$$X (NO_2 \text{ or } NH_3) \text{ adsorbed} = \frac{V_N^*}{V_N \cdot W} \int_{t_0}^t ([X]_{in} - [X]_{out}) dt$$
(2.8)

The amounts of  $NO_2$  and  $NH_3$  desorbed during temperature programmed desorption (TPD) experiments were calculated using equation (2.9).

$$X(NO_2 \text{ or } NH_3) \text{ desorbed} = = \frac{V_N^*}{V_N \cdot W} \int_{t_0}^t [X]_{out} dt$$
(2.9)

## 2.3.4 Symbols

[HNCO] <sub>in</sub>	= HNCO concentration at the reactor inlet [ppm]
[HNCO] <sub>out</sub>	= HNCO concentration at the reactor inlet [ppm]
$[NH_3]_{out}$	= NH <sub>3</sub> concentration at the reactor inlet [ppm]
$[NO_X]_{in}$	= $NO_x$ (NO+NO <sub>2</sub> ) concentration at the reactor inlet [ppm]
$[NO_X]_{out}$	= $NO_x$ (NO+NO <sub>2</sub> ) concentration at the reactor inlet [ppm]
$V_N^*$	= volumetric gas flow rate at standard conditions [ $cm_N^3/h$ ]
$V_{C}$	= catalyst volume [cm <sup>3</sup> ]
$V_{_N}$	= molar gas volume at standard conditions [ $cm_N^3$ ]
W	= weight of catalyst [g]
$[X]_{in}$	= concentration of X entering the reactor $[cm_N^3 / m_N^3]$
$[X]_{out}$	= concentration of X entering the reactor [ $cm_N^3 / m_N^3$ ]
X	= NO <sub>2</sub> or NH <sub>3</sub>

## **3** Catalyst Screening

## **3.1 Introduction**

Only one publication dealing with the catalytic hydrolysis of HNCO in typical diesel exhaust environment exists in the literature [*Kleemann et al. (2000)*]. However, some valuable information was available from studies which are not related to urea-SCR [*Dumpelmann et al. (1996); Cant et al. (1997); Chambers et al. (2001)*] and from research on other gas phase catalytic hydrolysis reactions [*Bachelier et al. (1993); Hess et al. (1997); Peter Williams et al. (1999)*]. The analysis of these works suggested the selection of several metal oxides as possible candidates for the development of a specialized hydrolysis catalyst.

From the literature it also clearly emerges that Fe-ZSM5, beside V<sub>2</sub>O<sub>5</sub>/WO<sub>3</sub>-TiO<sub>2</sub>, is receiving much attention as SCR catalyst [*Ma et al. (1999); Long et al. (1999); Ramachandran et al. (2000); Delahay et al. (2005); Qi et al. (2005); Sullivan et al. (2005)*]. This interest is motivated

by the catalytic activity of this material and its outstanding resistance to  $SO_2$  and  $H_2O$ , which are inevitable components of diesel exhaust gas [*Feng et al. (1997); Chen et al. (1998)*]. However, despite the gain in interest for Fe-ZSM5 as active catalyst for the development of compact urea-SCR systems, not much information is available on its hydrolysis properties [*Jones et al. (2004)*]. Therefore the activity of Fe-ZSM5 for the HNCO hydrolysis has been investigated with the purpose to develop an alternative SCR-hydrolysis catalyst. The DeNOx properties of the Fe-ZSM5 samples used for this investigation have been extensively published as result of previous work [*Devadas et al. (2005); Kröcher et al. (2006); Devadas et al. (2006a); Devadas et al. (2006b)*]. Part of these published results is repeated here for comparison purposes and for a better understanding of these materials (section 3.4.2).

## **3.2 Experimental**

## 3.2.1 Specialized Hydrolysis Catalyst

Several commercial metal oxides were used for the catalyst screening. The specifications are given in Table 3.1.  $ZrO_2$  was prepared by calcinations of  $Zr(OH)_4$  (Wacker) at 600 °C for 4 h. Sulfated zirconium oxide was obtained by stirring  $Zr(OH)_4$  (Wacker) with 0.5 M H<sub>2</sub>SO<sub>4</sub> (15 ml g<sup>-1</sup>) at room temperature for 1 h, followed by centrifuging, drying (at 110 °C for 20 h) and calcination at 600 °C in air for 4 h.

Catalyst	BET [m <sup>2</sup> /g]	Supplier	
TiO <sub>2</sub> anatase	57.2	Wacker	
TiO <sub>2</sub> rutile	89.5	Wacker	
Al <sub>2</sub> O <sub>3</sub>	104.5	Wacker	
SiO <sub>2</sub>	350	Grace	
ZrO <sub>2</sub>	67.4	Zr(OH) <sub>4</sub> from Wacker	
Sulfated ZrO <sub>2</sub>	-	Zr(OH) <sub>4</sub> from Wacker	
SiO <sub>2</sub> /Al <sub>2</sub> O <sub>3</sub> (1): 15 % Al <sub>2</sub> O <sub>3</sub> – 85% SiO <sub>2</sub>	573	Grace	
SiO <sub>2</sub> /Al <sub>2</sub> O <sub>3</sub> (2): 24 % Al <sub>2</sub> O <sub>3</sub> – 76% SiO <sub>2</sub>	552	Grace	

 Table 3.1: Specification of the tested oxide catalysts.

The catalysts were tested in form of powder using the glass micro-reactor described in Chapter 2 (section 2.1.3.2). The powder samples were pressed, crushed and sieved in order to achieve the desired particle size (160-200  $\mu$ m). About 150 mg of catalyst was used for the experiments (volume ~ 0.1 ml). The flow rate was typically 200 L<sub>N</sub>/h (GHSV ~ 2·10<sup>6</sup> h<sup>-1</sup>). Prior to testing, the samples were activated for 1 hour at 450 °C under a flow of HNCO and O<sub>2</sub> in N<sub>2</sub>. The catalytic activity was then investigated in the temperature range 150-450 °C by using a gas mixture composed of ~ 1000 ppm of HNCO, 10% O<sub>2</sub> and 5% H<sub>2</sub>O with N<sub>2</sub> balance. H<sub>2</sub>O and O<sub>2</sub> were also added since they are inevitable compounds of the diesel exhaust gas.

The effect of SO<sub>2</sub> on the ZrO<sub>2</sub> sample was analyzed by treating the catalyst with 200 ppm of SO<sub>2</sub> in the presence of 1000 ppm of HNCO and N<sub>2</sub> balance at 350 °C for 90 minutes. Then the catalytic activity was investigated in the temperature range 150-450 °C by using gas mixtures with 200 ppm of SO<sub>2</sub>, ~ 1000 ppm of HNCO, 10% O<sub>2</sub> and 5% H<sub>2</sub>O with N<sub>2</sub> balance.

## 3.2.2 SCR-Hydrolysis Catalyst

Two Fe-ZSM5 samples were prepared by solid state ion exchange, starting from H-ZSM5 with Si/Al = 28, using different ion exchange methods. The first was performed in the typical way with FeCl<sub>2</sub> in a ball mill (Fe-ZSM5<sub>1</sub>) [*Liu et al. (1999)*], the second was prepared using FeCl<sub>3</sub> in a mortar, called the "mechanochemical" route (Fe-ZSM52) [*Heinrich et al. (2001)*]. In both methods the zeolite to iron chloride weight ratio was 2:1. Fe-ZSM5<sub>1</sub> was prepared by mixing H-ZSM5 and FeCl<sub>2</sub> in a ball mill for 1 h. The resulting powder was calcined at 550 °C for 5 h, washed with deionised water to remove the anions (AgNO<sub>3</sub> test) and then dried at 100 °C for 10 h. Fe-ZSM5<sub>2</sub> was prepared by mixing H-ZSM5 and FeCl<sub>3</sub> in a mortar for 1 h. The excess FeCl<sub>3</sub> was washed out with water. Table 3.2 resumes the characteristics of the zeolite catalysts.

 Table 3.2: Specifications of the tested zeolite catalysts.

Catalyst	BET [m <sup>2</sup> /g]	Pore volume [cm <sup>3</sup> /g]	Si/Al (ICP-AES)	wt% Fe (ICP-AES)
H-ZSM5	354	0.11	28	0
Fe-ZSM51	259	0.08	28	11.4
Fe-ZSM5 <sub>2</sub>	353	0.11	28	0.3

For comparison pure  $Fe_2O_3$  (Sigma Aldrich) was also investigated. The activity of the catalysts was tested in form of coated cordierite monoliths (volume 7.5 cm<sup>3</sup>, active mass ~ 0.8 g) in a glass tubular reactor. The monoliths were coated by immersion in a slurry made of 0.5 g of catalyst in 2 cm<sup>3</sup> of a 0.5 M Al(NO<sub>3</sub>)<sub>3</sub>·9H<sub>2</sub>O solution. The samples were then dried at room temperature for 2 h and, finally, calcined at 500 °C for 5 h.

Prior to the experiments the samples were treated at 450 °C for 1 h in a flow of N<sub>2</sub>/O<sub>2</sub>. The HNCO hydrolysis activity was studied between 150-450 °C at a flow rate of 400  $l_N/h$  (GHSV ~ 52,000 h<sup>-1</sup>). The inlet flow was composed of  $\approx$  1000 ppm HNCO, 5% H<sub>2</sub>O, 10% O<sub>2</sub> and balance N<sub>2</sub>. Test were performed also on wet-thermal treated samples: Fe-ZSM5<sub>1</sub> was treated in a nitrogen flow with 5% H<sub>2</sub>O and 10% O<sub>2</sub> at 650 °C for 5 h and H-ZSM5 in air at 700 °C for 5h.

For investigations of the SCR reaction, the composition of diesel exhaust gas was approximated by a model feed gas containing  $10\% O_2$ ,  $5\% H_2O$ , 1000 ppm of  $NO_x$  and balance  $N_2$ . Ammonia was added in the range 100-1000 ppm.

NH<sub>3</sub> TPD was performed with 50 mg of catalyst. The sample was degassed at 550 ° C for 1 h in a He flow and then cooled down to 100 °C. At this temperature adsorption of NH<sub>3</sub> took place until saturation. Afterwards, the catalyst was flushed with He for 30 min. TPD measurements were performed from 100 °C to 650 °C with a heating rate of 20 °C/min, with He as carrier gas. To obtain NMR spectra as quantitatively as possible in the presence of a heterogeneous distribution of quadrupolar coupling constants, the <sup>27</sup>Al nuclei were excited with a single 20° pulse of 1  $\mu$ s. Excitation pulses longer than 3  $\mu$ s were seen to overemphasize the extra-framework aluminum signal intensity relative to the framework aluminum signal. The relaxation delay between the scans was set to 1 s. No saturation effects were observed in the spectrum for relaxation delays longer than 0.5 s.

In addition, in order to compare the hydrolysis activity of Fe-ZSM5 with results previously obtained in our lab for conventional  $V_2O_5/WO_3$ -TiO<sub>2</sub> catalysts [*Kleemann (2000)*], Fe-ZSM5<sub>1</sub> was tested in powder form using the steel micro-reactor (section 2.1.3.3). About 120 mg of catalysts (180-200 µm) and flow rate of 200  $l_N/h$  (GHSV ~  $10^{-6} h^{-1}$ ) were used. The test was performed between 150- 450 °C with an inlet flow composed of ~ 1000 ppm HNCO, 5% H<sub>2</sub>O, 10% O<sub>2</sub> and balance N<sub>2</sub>.

## 3.3 Results: Specialized Hydrolysis Catalyst

## **3.3.1 Hydrolysis Properties**

The results of the catalyst screening performed for the selection of a specialized hydrolysis catalyst are shown in Figure 3.1. For all catalysts the ammonia yield increased with increasing reaction temperature. The highest activity was found for  $ZrO_2$  with a NH<sub>3</sub> yield of 100% at T > 175 °C and with a yield of > 85% at 125 °C. TiO<sub>2</sub> showed a NH<sub>3</sub> yield > 100% for T > 200 °C, and > 85% at T = 175 °C. At lower temperature the NH<sub>3</sub> yield decreased drastically. When modified with sulfur,  $ZrO_2$  showed lower activity, with a resulting NH<sub>3</sub> yield < 100% already at 350 °C. However, the decrease was not drastic since the yield was still 60% at T = 150 °C. Al<sub>2</sub>O<sub>3</sub> also showed a good performance at high temperatures, however, the NH<sub>3</sub> yield decreased drastically for T < 250 °C. SiO<sub>2</sub> showed the lowest performance with maximum NH<sub>3</sub> yield of 38% at 450 °C. SiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub> mixed oxides showed intermediate activity compared to that of the pure oxides, with better performance for the catalyst with higher percentage of Al<sub>2</sub>O<sub>3</sub>.



**Figure 3.1:** Ammonia yield as a function of temperature. 150 mg of catalysts, flow rate =  $200 l_N/h$ , inlet flow composition: ~1000 ppm HNCO, 5% H<sub>2</sub>O, 10% O<sub>2</sub> and N<sub>2</sub> balance. (•) Al<sub>2</sub>O<sub>3</sub>, (□) SiO<sub>2</sub>, (Δ) Al<sub>2</sub>O<sub>3</sub>/SiO<sub>2</sub>(1), (x) Al<sub>2</sub>O<sub>3</sub>/SiO<sub>2</sub>(2), (**■**) TiO<sub>2</sub> anatase, (•) TiO<sub>2</sub> rutile, (**▲**) ZrO<sub>2</sub>, (○) sulfated ZrO<sub>2</sub>.

Since  $ZrO_2$  is known to change its properties in the presence of sulfur [*Ziolek et al. (1996); Bensitel et al. (1987)*] and SO<sub>2</sub> is always a component of the diesel exhaust gases, tests to analyze the effect of SO<sub>2</sub> were also carried out. The results are shown in Figure 3.2. In the presence of 200 ppm SO<sub>2</sub> in the inlet feed the catalytic activity of  $ZrO_2$  (pre-treated with SO<sub>2</sub> at 350 °C) decreased substantially for T < 200 °C and became comparable to the activity of TiO<sub>2</sub>.



**Figure 3.2:** Influence of SO<sub>2</sub> on the activity of ZrO<sub>2</sub>. 150 mg of catalysts, flow rate =  $200 l_N/h$ . ( $\blacktriangle$ ) Fresh sample, inlet flow composition: ~1000 ppm HNCO, 5% H<sub>2</sub>O, 10% O<sub>2</sub> and N<sub>2</sub> balance. ( $\triangle$ ) SO<sub>2</sub> pretreated sample (at 350 °C in a flow of 200 ppm of SO<sub>2</sub>, 1000 ppm HNCO and N<sub>2</sub> balance), inlet flow composition: 1000 ppm HNCO, 200 ppm SO<sub>2</sub>, 5% H<sub>2</sub>O, 10% O<sub>2</sub> and N<sub>2</sub> balance.

TiO<sub>2</sub> was additionally tested in form of a coated cordierite monolith (~ 1.3 g of catalyst). The results showed ~ 100 % NH<sub>3</sub> yield over the entire temperature range (100-450 °C). Pretreatment of the catalyst at 450°C in a flow of 200 ppm SO<sub>2</sub>, 10% O<sub>2</sub> and balance nitrogen did not influence the catalyst performance confirming the known resistance of TiO<sub>2</sub> to SO<sub>2</sub> [*Heck et al.* (2002)].

## 3.3.2 Correlation between acidity and activity

Zirconia, titania anatase and alumina are all considered as amphoteric oxides with both Brønsted and Lewis properties [*Hair (1967); Martin et al. (1997); Parmaliana et al. (1998)*]. The surface of  $\gamma$ -alumina for instance, contains several hydroxyls, the linear ones being Brønsted bases (H<sup>+</sup> acceptors), and the bridged ones Brønsted acids (H<sup>+</sup> donor). After dehydroxylation, the surface develops Lewis acidity (electron acceptor) on the uncoordinated Al<sup>δ+</sup> sites [*Chorkendorff et al. (2003)*].

When zirconia is modified with sulfate, "super-acidity" is developed, mainly due to the increase of the number or the strength of some Lewis acid sites [*Bensitel et al. (1987); Morterra et al. (1994); Martin et al. (1997)*]. Titania rutile was observed to have Lewis acidity only [*Bezrodna et al. (2003); Hadjiivanov (1998)*]. Alumina has medium Brønsted acidity, but Lewis acidity is also important [*Martin et al. (1997)*]. However, impurities in alumina can substantially change his behavior; for instance, chlorinated alumina shows stronger acidity, alumina modified with ceria or alkaline ions is less acidic than the starting oxide [*Martin et al. (1997)*]. When alumina is mixed with silica, "super-acidity" is developed [*Martin et al. (1997); Dines et al. (2003)*]. Silica alumina samples exhibit a higher number of Brønsted acid sites with respect to alumina, while the extent of the Lewis acidity is markedly reduced mainly at the expense of the strong sites [*Auroux et al. (2001)*]. Silica alone has only Brønsted acid sites [*Martin et al. (1997); Parmaliana et al. (1998)*].

The catalyst screening revealed that amphoteric oxides exhibit the highest catalytic activity for the HNCO hydrolysis, with  $ZrO_2$  and  $TiO_2$  being the best materials. Moreover, the results suggest a positive influence of the Lewis acidity of the samples, since  $TiO_2$  and  $ZrO_2$  are known to have pronounced Lewis properties. The activities observed for  $SiO_2/Al_2O_3$  mixed oxides support this hypothesis, since they were intermediate between those of pure  $SiO_2$  (only Brønsted acidity) and pure  $Al_2O_3$  (moderate Lewis acidity). As concluded from this hypothesis, an increase in the Al/Si ratio resulted in a higher activity of the catalyst. Nevertheless,  $ZrO_2$  and  $TiO_2$  remained the most active catalysts.  $TiO_2$  rutile and sulfated  $ZrO_2$  showed a lower activity compared to  $TiO_2$  anatase and pure  $ZrO_2$ , which disagrees with the hypothesis of a positive influence of Lewis acidity since, as above mentioned,  $TiO_2$  rutile is known to have only Lewis acidity and sulfated zirconia is known to be a superacid with a high concentration of Lewis acid sites and a low concentration of Brønsted acid sites [*Martin et al. (1997); Morterra et al. (1994)*]. This indicates that a too high Lewis acidity has an inverse effect on catalytic activity. Morterra et al. [Morterra et al. (1994)] showed that the introduction of water at 150 °C during the isomerization of light paraffins over a sulfated zirconia decreases the activity of the catalyst. They attributed this decrease to surface hydration that would convert the strongest fraction of Lewis acid sites into Brønsted acid sites. Arata and Hino [Arata et al. (1990)] concluded from pyridine adsorption experiments that conversion of Lewis acid sites into Brønsted acid sites easily occurs by adsorption of water molecules. Other authors postulated similar Lewis-Brønsted changes [Parera (1992); Babou et al. (1995)]. Since the HNCO hydrolysis is carried out with excess of water, a similar effect of permanent hydration could occur on sulfated zirconia and TiO<sub>2</sub> rutile surfaces.

Treatment of the  $ZrO_2$  sample with  $SO_2$  showed a decrease of the activity at low temperatures. Ziolek et al. [*Ziolek et al. (1996)*] proposed that  $SO_2$  can be coordinatively adsorbed on Lewis acid sites, acting then as an electron donor. It was stated that the generation of Brønsted acid sites is due to the formation of hydrogenosulfite species. On the basis of a positive influence of the Lewis acidity, this could explain the decrease of the activity with respect to pure  $ZrO_2$ .

## **3.4 SCR-Hydrolysis Catalyst**

### 3.4.1 Hydrolysis properties

The catalytic properties of the tested samples are shown in (Figure 3.3). The results are expressed in terms of NH<sub>3</sub> yield. For T < 300 °C the iron containing samples (Fe-ZSM5<sub>1</sub> and Fe-ZSM5<sub>2</sub>) had higher catalytic activity than the base material (H-ZSM5). 100% NH<sub>3</sub> yield was observed at T  $\geq$  200 °C for both Fe-ZSM5<sub>1</sub> and Fe-ZSM5<sub>2</sub>, suggesting that even higher space velocities may be applied Fe-ZSM5<sub>1</sub> was so active, that even at 150 °C a yield of ~ 70% was reached. At this temperature, Fe-ZSM5<sub>2</sub> exhibited a yield of 47% and H-ZSM5 of 28%. No formation of by-products (NO, NO<sub>2</sub>, N<sub>2</sub>O) was observed for all three catalysts over the entire temperature range, i.e. 100% selectivity to NH<sub>3</sub> was reached.



**Figure 3.3:** NH<sub>3</sub> yield as a function of temperature over (**■**) Fe-ZSM5<sub>1</sub>, (**▲**) Fe-ZSM5<sub>2</sub>, (**●**) H-ZSM5, (x) Fe<sub>2</sub>O<sub>3</sub>, (**□**) thermal/wet-treated Fe-ZSM5<sub>1</sub>, and (**○**) thermal/wet-treated H-ZSM5. Active mass ~ 0.8, flow rate = 400 l<sub>N</sub>/h, inlet flow composition: ~1000 ppm HNCO, 5% H<sub>2</sub>O, 10% O<sub>2</sub> and N<sub>2</sub> balance.

Performance tests showed that the activity of the iron zeolites for HNCO hydrolysis follows the order of their iron content, i.e. Fe-ZSM5<sub>1</sub> with the higher iron loading was more active than sample Fe-ZSM5<sub>2</sub>. However, the iron concentration itself is not the only parameter that determines the hydrolysis activity, since pure Fe<sub>2</sub>O<sub>3</sub> proved to be much less active than the iron zeolites, showing a decrease of the NH<sub>3</sub> yield below 250 °C. This indicates that the zeolite support is essential for good hydrolysis properties. Wet treatment at high temperature of the zeolite samples resulted in an increase of their catalytic activity. Treated Fe-ZSM5<sub>1</sub> reached 100% NH<sub>3</sub> yield already at 175 °C, while treated H-ZSM5 showed more than 90% yield at this temperature. Unfortunately, the reaction could not be tested at higher space velocities due to the limited dosing range of the mass flow controllers.

## 3.4.2 DeNOx properties

The DeNOx performance of the catalysts was measured at 10 ppm ammonia slip through the catalyst, which is regarded to be an acceptable emission level for the practical application. The results are shown in Figure 3.4, expressed in terms of  $NO_x$  reduction efficiency (DeNOx).



**Figure 3.4:** DeNOx at 10 ppm NH<sub>3</sub> slip as a function of temperature. [NOx]inlet = 1000 ppm NO: (**■**) Fe-ZSM5<sub>1</sub>, (**▲**) Fe-ZSM5<sub>2</sub> and (**●**) H-ZSM5. [NOx]<sub>inlet</sub> = 500 ppm NO + 500 ppm NO<sub>2</sub>: (**□**) Fe-ZSM5<sub>1</sub>, (**△**) Fe-ZSM5<sub>2</sub> and (**o**) H-ZSM5.

Fe-ZSM5<sub>1</sub> performed much better than the other catalysts with DeNOx values > 75% at  $T \ge 350$  °C. Fe-ZSM5<sub>2</sub> exhibited a DeNOx of 60% for  $T \ge 400$  °C, whereas H-ZSM5 showed almost no activity over the entire temperature range. Again, no formation of unwanted products was observed for all the three catalysts. These results parallel those observed for the HNCO hydrolysis, where the catalyst activity showed the same order (Fe-ZSM5<sub>1</sub> > Fe-ZSM5<sub>2</sub> > H-ZSM5). With NO<sub>2</sub> in the feed, very high SCR activities were found for Fe-ZSM5<sub>1</sub> and Fe-ZSM5<sub>2</sub>, indicating that NO<sub>2</sub> is required for the SCR reaction [*Long et al. (2001)*]. If NO<sub>2</sub> is absent in the feed,

it must first be produced from NO over the iron centers in the zeolite, which reduces the observed DeNOx values. The role of iron to oxidize NO to NO<sub>2</sub> is also the reason for the inactivity of the base material H-ZSM5 for the SCR reaction with NO, as it has no oxidizing functionality, and its strongly enhanced SCR activity in the presence of NO<sub>2</sub> in the feed. In the further course of the SCR reaction, the NO<sub>2</sub> is believed to react with the NH<sub>3</sub> stored on both Lewis and Brønsted acid sites present on the surface [*Went et al. (1992)*]. More details about the DeNOx properties of this material are reported in [*Devadas et al. (2005); Devadas et al. (2006a); Devadas et al. (2006b); Kröcher et al. (2006)*]

## 3.4.3 Correlation between acidity and activity

The acidity of the samples was characterized by  $NH_3$  TPD (Figure 3.5) and <sup>27</sup>Al MAS NMR (Figure 3.6) spectroscopy.



Figure 3.5: NH<sub>3</sub> TPD profiles of (a) H-ZSM5, (b) Fe-ZSM5<sub>2</sub>, and (c) Fe-ZSM5<sub>1</sub>.



Figure 3.6: <sup>27</sup>Al MAS NMR spectra of (a) H-ZSM5, (b) Fe-ZSM5<sub>2</sub>, and (c) Fe-ZSM5<sub>1</sub>.

With increasing iron content, the number of Brønsted acid sites present on the catalyst surface is decreased. This was evinced by NH<sub>3</sub> TPD experiments which resulted in a low temperature peak at 200-220 °C attributed to physisorbed ammonia [*Topsøe et al. (1981)*] or ammonia from a non-zeolitic impurity [*Chao et al. (1984)*] and a high temperature peak at 420-440 °C attributed to ammonia adsorbed on Brønsted acid sites [*Topsøe et al. (1981)*]. The high temperature peak showed a decrease in Brønsted acidity in the order H-ZSM5 > Fe-ZSM5<sub>2</sub> > Fe-ZSM5<sub>1</sub>. The same order was found by <sup>27</sup>Al MAS NMR spectroscopy, where the area of the signal at 55-60 ppm attributed to tetrahedrally coordinated alumina Al(OSiO)<sub>4</sub> in the framework lattice [*Engelhardt et al. (1987)*] was used to quantify the Brønsted acidity of the sample. The signal at 0 ppm is due to aluminum in octahedral AlO<sub>6</sub> groups [*van Bokhoven et al. (2000)*]. The resonance around 55 ppm, which was very sharp for H-ZSM5, changed into a broad signal after Fe loading. This effect was more evident for Fe-ZSM5<sub>1</sub> since the amount of Fe loaded was higher. Apart from dealumination of the zeolite, the broadening of the resonance signals at 0 ppm might also be due to dislodgement of framework iron, which dampens the Al signal because of its paramagnetic effect [*Perez-Ramirez et al. (2005*]].

The comparison of the Brønsted acidity scale with the HNCO hydrolysis activity scale suggests that Brønsted acidity does not favor the HNCO hydrolysis, supported by the finding that HNCO adsorbs mainly on Lewis acid sites of metal oxides [*Solymosi et al.* (1995)]. This suggests that the hydrolysis activity is correlated with the Lewis acidity of the catalysts.

## 3.4.4 Comparison with conventional V<sub>2</sub>O<sub>5</sub>/WO<sub>3</sub>-TiO<sub>2</sub> SCR catalysts

In Figure 3.7 the catalytic activity of the Fe-ZSM5<sub>1</sub> sample for the HNCO hydrolysis is compared with two V<sub>2</sub>O<sub>5</sub>/WO<sub>3</sub>-TiO<sub>2</sub> catalysts containing 1% and 3% V<sub>2</sub>O<sub>5</sub>, respectively. The results are expressed in terms of HNCO conversion so as to respect the data reported in [*Kleemann et al.* (2000)]. At high temperatures all samples exhibited 100% HNCO conversion, but began to diverge below ~350 °C. Fe-ZSM5<sub>1</sub> showed a higher hydrolysis activity than 3% V<sub>2</sub>O<sub>5</sub>/WO<sub>3</sub>-TiO<sub>2</sub>, but was slightly less active than 1% V<sub>2</sub>O<sub>5</sub>/WO<sub>3</sub>-TiO<sub>2</sub>. It is interesting to note that the hydrolysis activity of V<sub>2</sub>O<sub>5</sub>/WO<sub>3</sub>-TiO<sub>2</sub> decreased with increasing V<sub>2</sub>O<sub>5</sub> content [*Kleemann et al.* (2000)]. This activity order shows once more that Brønsted acidity does not favor the HNCO hydrolysis, since the Brønsted acidity of V<sub>2</sub>O<sub>5</sub>/WO<sub>3</sub>-TiO<sub>2</sub> is known to increase with the V<sub>2</sub>O<sub>5</sub> loading [*Topsøe* (1991); Lin et al. (2003)].



Figure 3.7 HNCO hydrolysis over (**■**) Fe-ZSM51, ( $\Delta$ ) 1% V<sub>2</sub>O<sub>5</sub>/WO<sub>3</sub>-TiO<sub>2</sub>, and (X) 3% V<sub>2</sub>O<sub>5</sub>/WO<sub>3</sub>-TiO<sub>2</sub> powder samples. S<sub>NH3</sub> = 100%.

## **3.5 Conclusions**

The catalyst screening was performed in order to select catalyst for further investigations. Transition metal oxide showed to be very good hydrolysis catalyst even at extremely high space velocities. In view of its catalytic properties,  $TiO_2$  anatase (Wacker, BET= 57.2 m<sup>2</sup>/g) was chosen as the preferred candidate for a dedicated hydrolysis catalyst. The hydrolysis properties of Fezeolite were investigated since this material proved to have interesting SCR properties. Among the catalysts tested, the sample prepared by ion exchange with FeCl<sub>2</sub> in a ball mill (Fe-ZSM5<sub>1</sub>) was selected due to its higher activity for both the SCR and the hydrolysis reaction. In the following chapters more details about these two materials will be presented.

# 4

## **HNCO** Adsorption on TiO<sub>2</sub>

## **4.1 Introduction**

In contrast to the growing interest for the development of mobile urea-SCR systems not much is known about the mechanism of the HNCO catalytic hydrolysis. For clearing up the reaction mechanism of a catalytic process it is important to establish the reaction intermediates. However, this is not an easy task, since most reaction intermediates are only short-lived and, therefore, exist in a very low concentration on the catalyst. This problem is pronounced for the HNCO hydrolysis on TiO<sub>2</sub>, which proceeds extremely fast, i.e. 100% HNCO conversion is found for  $T \ge 200$  °C at a GHSV of about 10<sup>6</sup> h<sup>-1</sup> (Section 3.3.1). Therefore, the first step of this research was to study the species formed on TiO<sub>2</sub> after HNCO adsorption in the absence of water. Some valuable information is available from studies of the HNCO adsorption on metal oxides, which are not related to urea-SCR. Solymosi and co-workers studied the HNCO adsorption on platinum supported by different metal oxides (TiO<sub>2</sub>, SiO<sub>2</sub>, Al<sub>2</sub>O<sub>3</sub>, MgO) [*Solymosi et al. (1979); Bánsági et al. (1983)*] on pure SiO<sub>2</sub> [*Bánsági et al. (1983)*], on H-ZSM-5 and Cu-ZSM-5 [*Solymosi et al.* (*1995)*] and on rhodium supported by W<sup>6+</sup> doped TiO<sub>2</sub> [*Solymosi et al. (2001)*]. Acke and coworkers investigated the HNCO adsorption on  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> [*Acke et al. (1998)*]. These works are related to the reaction between NO and CO over supported metal catalysts, where HNCO is assumed to be a reaction intermediate. For a better interpretation of the surface species formed upon HNCO adsorption, a careful characterization of TiO<sub>2</sub> base material was also carried out.

## 4.2 TiO<sub>2</sub> anatase, background

 $TiO_2$  anatase is a widely used and extensively studied metal oxide [*Diebold (2003)*]. Figure 4.1 shows the building cell (a) and building unit (b) of  $TiO_2$  anatase.



**Figure 4.1:** (a) building cell and (b) building unit of  $TiO_2$  anatase. Yellow = Ti atoms, Blue = oxygen atoms [*Czekaj et al.*].

Titanium atoms in the bulk structure of  $TiO_2$  anatase are six-fold coordinated (Ti(VI)), while bulk oxygen atoms are three-fold coordinated (O(III)), which means that they share three octahedrals.

The atoms present on the top layers of the  $TiO_2$  structure have different coordination than those situated in the bulk due to "neutral" truncation of the crystals, in which an even number of electrical charges remain on each side and from which the surface termination of the solid originates. In the uppermost layer this truncation generates anions and cations that are coordinatively unsaturated. The type of unsaturated ions on the uppermost layer of the crystal structure depends on the surface crystal structure of the sample.

Polycrystalline  $TiO_2$  anatase is known to have a highly heterogeneous surface and a variety of hydroxyl groups and Lewis acid sites have been observed:

#### Hydroxyl groups

The degree of hydroxylation of TiO<sub>2</sub> is a function of the temperature and decreases with increasing temperature. However, even after evacuation at 700 °C, residual hydroxyl groups have been reported to be present on the anatase surface. They were observed in the 3800-3600 cm<sup>-1</sup> region of IR spectra. A good review on this topic is given by Hadjiivanov and coworkers who noticed that two types of residual hydroxyl groups with absorption band at 3715 and 3675 cm<sup>-1</sup> are most often reported [*Hadjiivanov et al. (1996)*]. Different surface hydroxyls are observed on TiO<sub>2</sub> because the oxygen atoms may be bound to a different number of lattice metal atoms [*Tsyganenko et al. (1972)*]:

$$\begin{array}{ccc} H & & H \\ I & & I \\ O & (I) & & O \\ M & & M \\ \end{array}$$

The formation of these bonds results in the lowering of the stretching vibration frequency [*Tsyganenko et al. (1972)*], therefore the absorption bands of type I will have a higher vibration frequency than type II. Additional bands in the OH stretching region can be present due to hydrogen-bonding interaction between adjacent OH groups:

### Lewis acid sites

Lewis acid sites on TiO<sub>2</sub> anatase are coordinatively unsaturated Ti<sup>4+</sup> cations. Some authors reported also the existence of Ti<sup>3+</sup> ions [*Ramis et al. (1987); Fernandez et al. (1988); Ramis et al. (1990a)*], but only after treatment of TiO<sub>2</sub> in vacuum. The Ti<sup>4+</sup> ions at the surface have one or two

coordinative insaturations with respect to the octahedral overall coordination sphere of  $Ti^{4+}$  in the bulk [*Ramis et al. (1987); Busca et al. (1985)*]. These surface titanium cations are situated on different faces (edges, corners, steps) of the oxide crystallites. The acid strength of these sites is dependent on their positioning and their coordination.

A very informative experimental approach towards the characterization of complex polycrystalline metal oxide surfaces is the use of adsorbed surface probe molecules (e.g. CO and NH<sub>3</sub>) and their spectroscopic investigation.

## 4.3 Experimental

Due to its catalytic activity,  $TiO_2$  in the anatase modification with a surface area of 57 m<sup>2</sup>/g was used for the HNCO adsorption experiments. The catalyst was characterized by means of XRD, NH<sub>3</sub>-TPD and DRIFT investigations of the fresh sample and after NH<sub>3</sub> as well as CO adsorption. NH<sub>3</sub>-TPD was performed by saturating 1 g of the sample with NH<sub>3</sub> at 100 °C. After saturation the temperature was maintained at 100 °C for 30 min in order to desorb all physisorbed species. Then, the temperature was increased to 450 °C at a ramp of 15 °C/min. Before saturation at 100 °C, the sample was treated in situ at 450 °C for 1 h in flowing O<sub>2</sub>/He to remove water vapor and impurities. DRIFT investigations of the pure sample were carried starting from room temperature up to  $450^{\circ}$  (pre-treatment temperature for activity measurements). Background spectra were collected at the tested temperatures with KBr in the cell. DRIFT investigations of CO and NH<sub>3</sub> adsorption were carried out pre-treating the sample in situ for 1 h at 450 °C with a flow of N<sub>2</sub> before collecting the backgrounds. The backgrounds were taken at each of the tested temperatures with the sample in place and therefore the final spectra show the adsorbed species only. Ammonia adsorption was performed at 100 and 150 °C by treatment of the sample with 500 ppm NH<sub>3</sub> in N<sub>2</sub> for 15 min. Carbon monoxide adsorption was carried out at RT by treating the sample with 500 ppm of CO in  $N_2$  for 15 min.

Isocyanic acid adsorption was studied by means of DRIFT experiments from RT to 450 °C. The sample was treated with ~ 70 ppm of HNCO in  $N_2$  for 15 min. Then the catalyst was degassed in a  $N_2$  flow for 15 min.

## 4.4 Catalyst characterization

## 4.4.1 NH<sub>3</sub>-TPD

The result of the  $NH_3$ -TPD experiment in Figure 4.2 shows that ammonia starts to desorb immediately when the temperature is increased, reaching a maximum at T = 220 °C. As the desorption temperature is associated with the strength of the acid sites where  $NH_3$  is adsorbed, we can conclude that a major part of the acid sites present on the surface are of rather low acid strength. However, some species are still adsorbed on the surface at high temperatures, which indicates that strong acid sites are also present.



**Figure 4.2:** NH<sub>3</sub>-TPD. 1 g of TiO<sub>2</sub>. NH<sub>3</sub> adsorption at 100 °C, desorption rate = 15 °C/min.

## 4.4.2 DRIFT investigation of the fresh sample

Figure 4.3 shows the change occurring on the  $TiO_2$  sample while increasing the temperature from 50 to 450 °C. The DRIFT spectrum of the pure  $TiO_2$  at 50 °C showed a broad band in the range 2500-3740 cm<sup>-1</sup>, an isolated peak at 1629 cm<sup>-1</sup> and peaks at 3691, 3670 and 3630 cm<sup>-1</sup>. The

band at 1629 cm<sup>-1</sup> is due to the H-O-H vibration of undissociated adsorbed water [*Nakamoto* (1986)]. The bands at 3691, 3670 and 3630 cm<sup>-1</sup> and the broad band at 2500- 3740 cm<sup>-1</sup> are due to the OH vibration of hydroxyl groups (the broad band is due to H-bonded hydroxyl groups [*Hadjivanov et al.* (1994)]).

Below ~ 1000 cm<sup>-1</sup> the bands associated to the skeletal absorption bands of  $TiO_2$  appear. Due to the ionic character of the Ti-O interaction, these bands are very intense and broad, which will prevent the study of this region. In this lower wave number region Raman spectroscopy would be better suited than IR spectroscopy.



**Figure 4.3:** DRIFT spectra of fresh TiO<sub>2</sub> at different temperatures. a) 50 °C, b) 100 °C, c) 200 °C, d) 300 °C, e) 400 °C, f) 450 °C.

Increasing the temperature to 200 °C resulted in a remarkable decrease of the bands at 1629, 3691, 3630 and 2500-3700 cm<sup>-1</sup>. The first three bands disappear already at 300 °C while the broad band is stable up to 400 °C. This indicates that a large amount of H<sub>2</sub>O was desorbed and that undissociated adsorbed water (band at 1629 cm<sup>-1</sup>) was no more present at this tempera-

ture. At 450 °C, only the band at 3671 cm<sup>-1</sup> appears at high intensity (moreover this band subsequently shifted towards 3667 cm<sup>-1</sup>), while a band with lower intensity appears at 3724 cm<sup>-1</sup>. The bands at 3667 and 3724 cm<sup>-1</sup> are attributed to free surface hydroxyl groups of type II and I, respectively [*Tsyganenko et al. (1972); Hadjivanov et al. (1994); Busca (1996)*]. It has been observed that, for a given metal oxide, the deprotonation energy varies with the OH stretching vibration: the more acidic the site, the lower the v(OH) wavenumber [*Payen et al. (2002)*]. Acidity also decreases when the number of cations coordinated with OH increases [*Payen et al. (2002)*]. Therefore the hydroxyl at 3667 cm<sup>-1</sup> (type II) is more acidic than the hydroxyl at 3724 cm<sup>-1</sup> (type I). Pre-treatment of TiO<sub>2</sub> at 450 °C with and without 10% O<sub>2</sub> in the feed, did not significantly change the aforementioned results.

## 4.4.3 DRIFT investigation of NH<sub>3</sub> adsorption

When TiO<sub>2</sub> was exposed to ammonia bands at 1170, 1213, 1604, 3155, 3195, 3261, 3351 and 3382 cm<sup>-1</sup> appeared (Figure 4.4). These peaks arise from the NH<sub>3</sub> coordinatively bound to Lewis acid sites and correspond in detail to the splitting of the symmetric deformation band  $\delta_s$ (1213 cm<sup>-1</sup> and 1170 cm<sup>-1</sup>), the asymmetric bending  $\delta_{as}$  (1604 cm<sup>-1</sup>), the splitting of the symmetric stretching v<sub>s</sub> in a Fermi resonance with the asymmetric deformation band  $\delta_{as}$  (3261, 3155 and 3195 cm<sup>-1</sup>) and the splitting of the asymmetric stretching vibrations v<sub>as</sub> (3382 and 3351 cm<sup>-1</sup>) [*Primet et al.* (1971b); *Tsyganenko et al.* (1975); *Busca et al.* (1985); *Busca* (1986); *Ramis et al.* (1990b); *Topsøe* (1991); *Hadjiivanov et al.* (1997); *Centeno et al.* (2001)]. The splitting of  $\delta_s$ , v<sub>s</sub> and v<sub>as</sub> indicate the presence of two types of Lewis acid sites on the surface. Only the asymmetric bending  $\delta_{as}$  is unsplit, probably due to a much lower sensitivity to the strength of the coordination bond than  $\delta_s$  [*Ramis et al.* (1990b)].

Some weak bands associated to ammonia adsorbed on Brønsted acid sites were observed at 1662 and 1430 cm<sup>-1</sup> in the NH<sub>3</sub> bending region. These bands are due to the deformation vibration mode of NH<sub>4</sub><sup>+</sup> ions adsorbed on Brønsted acid sites [ $\delta_s$ (H-N-H) and  $\delta_{as}$ (H-N-H)] [*Busca (1986)*; *Lercher et al. (1996); Hadjiivanov et al. (1997); Centeno et al. (2001)*]. The low intensity of these bands indicated that the surface Brønsted acidity of the sample is weak, which is in line with results reported by other authors [*Primet et al. (1971b*); *Tsyganenko et al. (1975); Busca et al. (1985); Ramis et al. (1990b); Hadjiivanov et al. (1997)*]. However, the strong negative peaks in the OH bending region around 3700 cm<sup>-1</sup> suggest some interaction between NH<sub>3</sub> and OH

groups, probably hydrogen bonding between  $NH_3$  and surface Ti-OH [*Tsyganenko et al. (1975)*]. Spectra which were recorded at 50 °C intervals starting at 150 °C indicated that adsorbed ammonia species were no more detectable after purging with nitrogen for 30 min at 400 °C.



**Figure 4.4:** DRIFT spectra of TiO<sub>2</sub> after NH<sub>3</sub> adsorption (500 ppm) for 15 min at 100 °C (—) and 150 °C (…).

Ammonia adsorption was also performed in the presence of 200 ppm  $H_2O$  and 10%  $O_2$ , but the results did not differ significantly. Bands attributed to molecularly adsorbed  $NH_3$  were detected, while no protonation of ammonia was observed, in agreement with Tsyganenko et al. [*Tsyganenko et al. (1975)*].

## 4.4.4 DRIFT investigation of CO adsorption

Adsorption of CO at room temperature resulted in two sharp peaks at 2208 and 2188  $\text{cm}^{-1}$  and a broader band at 2115  $\text{cm}^{-1}$  (Figure 4.5).



Figure 4.5: DRIFT spectrum of TiO<sub>2</sub> after CO adsorption (500 ppm) at room temperature for 15 min.

The latter is attributed to gaseous CO, while the former two bands are assigned to CO adsorbed on different Lewis acid sites [*Yates (1961); Busca et al. (1985); Hadjiivanov et al. (1996); Hadjiivanov et al. (1997)*]. The Lewis acid sites detected by adsorption of CO on anatase are coordinatively unsaturated Ti<sup>4+</sup> cations. In fact, carbon monoxide coordinates with a  $\sigma$ -bond to metal cations which have no d-electrons like Ti<sup>4+</sup>. Hence, CO adsorption revealed the existence of two kinds of Ti<sup>4+</sup> Lewis acid sites on the sample. Lower coordination leads to stronger interaction with CO [*Lercher et al. (1996)*], which in turn causes a higher IR stretching frequency [*Yates* (*1961)*]. Therefore, the band at 2208 cm<sup>-1</sup> is attributed to stronger acid sites with a lower coordination number, while the band at 2188 cm<sup>-1</sup> is attributed to weaker acid sites with a higher coordination number. This is in agreement with previous studies of CO adsorption on TiO<sub>2</sub> at room temperature, where these sites were mentioned as  $\alpha$  and  $\beta$  sites, respectively [*Yates (1961); Busca et al. (1985); Hadjiivanov et al. (1996); Hadjiivanov et al. (1997)*]. Both adsorption forms are weak and were destroyed within 10 min in a flow of nitrogen. Adsorption performed in the presence of 10% O<sub>2</sub> did not show any difference.

## 4.4.5 XRD pattern

XRD was used in order to determine the most prominent surface structures in the  $TiO_2$  anatase sample used for this study. This information gives a better picture of the surface sites present on the sample. The XRD pattern obtained is shown in Figure 4.6.



Figure 4.6: XRD pattern of TiO<sub>2</sub> anatase.

Crystalline surfaces were identified by comparison with reference data (TiO<sub>2</sub> synthetic anatase) [*ICDD*]. The most prominent surface was the (101) surface. The upper layer of the ideal TiO<sub>2</sub> (101) surface is formed by five and sixfold coordinated titanium ions and two and threefold coordinated oxygen atoms respectively. An idealized representation of the (101) surface is shown in (Figure 4.7).



Figure 4.7: (101) surface of TiO<sub>2</sub> anatase. Yellow = Ti atoms, Blue = oxygen atoms [*Czekaj et al.*].

The XRD spectrum obtained indicated the existence of some reflections of the (001) and (100) surface, in particular (004) and (200), respectively. This surface distribution agrees with other studies on  $TiO_2$  polycrystalline anatase samples [*Vittadini et al. (1998)*].

## 4.5 Adsorption of HNCO

## 4.5.1 DRIFT investigation of HNCO adsorption

Feeding HNCO to the titania sample in the DRIFT cell at 150 °C resulted in the evolution of a strong band at 2209 cm<sup>-1</sup> together with less intense bands at 3524, 3453, 3376, 3273, 3163, 1619, 1602, 1544, 1537, 1480, 1453 and 1190 cm<sup>-1</sup> (Figure 4.8). All bands intensified with increasing adsorption time. In particular, the band at 2209 cm<sup>-1</sup> grew rapidly along with a shoulder at 2174 cm<sup>-1</sup> (Figure 4.9).



**Figure 4.8:** DRIFT spectra of TiO<sub>2</sub> after HNCO adsorption (70 ppm) at 150 °C for 5, 10, and 15 min followed by purging with nitrogen for 15 min. Entire spectrum.



Figure 4.9. Enlargement of Figure 4.8, region of the isocyanate species adsorption band.
The IR spectrum of isocyanic acid has been extensively studied and six fundamental vibrations have been reported [*Reid (1950); Herzberg et al. (1950); Nakamoto (1986)*].



However, only the asymmetric stretching mode  $v_2$  (2274 cm<sup>-1</sup>) exhibits very strong infrared absorption and has been used to identify molecularly adsorbed HNCO on the surface [*Bánsági et al.* (1983)]. The  $v_1$  vibration at 3531 cm<sup>-1</sup> was also observed in some studies, but it was very weak and only visible at low temperatures [*Bánsági et al.* (1983); Solymosi et al. (1995)]. Nevertheless, it has been proposed that HNCO adsorbs mainly dissociatively on metal oxides forming –NCO (isocyanate) species bound to Lewis acid sites [Solymosi et al. (1980); Bánsági et al. (1983); Satsuma et al. (1999)]. The position of the band associated to the –NCO groups strongly depends on the oxide. For TiO<sub>2</sub> the adsorption bands found in previous works are summarized in Table 4.1. In all investigations the band for the –NCO species bound to Ti<sup>4+</sup> sites appeared in the range 2210-2235 cm<sup>-1</sup>. Therefore, we assign the band at 2209 cm<sup>-1</sup>and the shoulder at 2174 cm<sup>-1</sup> to the asymmetric stretching vibration of –NCO species adsorbed on Ti<sup>4+</sup> sites. The shoulder hints at the degeneration of the stretching vibration due to the adsorption on different types of Ti<sup>4+</sup> sites. Along with the HNCO adsorption time, the –NCO band grows, and peaks at 3524 and 3453 cm<sup>-1</sup> evolve. The band at 3524 cm<sup>-1</sup> falls in the region of the  $v_1$  vibration mode of weakly adsorbed HNCO. However, the high adsorption temperature of 150 °C and the observed band stability upon purging with nitrogen is opposed to this band being attributed to HNCO being molecularly adsorbed on the surface. The bands at 3524 and 3453 cm<sup>-1</sup> are more likely caused by the formation of OH groups from the dissociative adsorption of HNCO on the surface [*Bezrodna et al.* (2004)].

Frequency [cm <sup>-1</sup> ]	Catalyst	Reference
2212	TiO <sub>2</sub>	[Solymosi et al. (1979)]
2215-2235	Rh/TiO <sub>2</sub> doped with $W^{6+}$	[Kondarides et al. (2001)]
2215	Rh/TiO <sub>2</sub> doped with $W^{6+}$	[Solymosi et al. (2001)]
2215	TiO <sub>2</sub>	[Solymosi et al. (1978)]
2210	Pt/TiO <sub>2</sub>	[Solymosi et al. (1978);
		Bansagi et al. (1983)]
2210	Ru/TiO <sub>2</sub>	[Bánsági et al. (1983)]
2210	Ir/TiO <sub>2</sub>	[Bánsági et al. (1983)]
2210	Rh/TiO <sub>2</sub>	[Bánsági et al. (1983)]

**Table 4.1:** Absorption frequency of –NCO species adsorbed on Ti<sup>4+</sup> sites reported in the literature.

According to the results of the NH<sub>3</sub> adsorption experiments, the bands at 3376, 3273, 3163, 1602, and 1190 cm<sup>-1</sup> are assigned to NH<sub>3</sub> bound to Lewis acid sites. The detection of NH<sub>3</sub> is explained by the hydrolysis of HNCO on the surface OH groups of TiO<sub>2</sub> or by the adsorption of the NH<sub>3</sub> traces in the inlet flow. As observed in section 4.4.2, some residual OH groups are present on TiO<sub>2</sub> even when treated at 450 °C, in line with the works reviewed in [*Hadjiivanov et al.* (1996)].

Following HNCO adsorption some other small bands were formed in the range 1700-1300 cm<sup>-1</sup> at 1619, 1544, 1537, 1480 and 1453 cm<sup>-1</sup> (Figure 4.8). All these peaks were stable at 150 °C and did not decrease within 15 min of purging with nitrogen. These bands are tentatively attributed to the formation of cyanuric acid by polymerization of isocyanic acid and/or to the formation of s-triazine by reaction of HNCO with the small amount of NH<sub>3</sub> adsorbed on the surface [*Padgett et al. (1958); Wang et al. (1997)*]. Melamine is made commercially by the vapor

phase reaction of HNCO and NH<sub>3</sub> in the presence of an oxide or phosphate catalyst with ammeline and ammelide as possible impurities [*Schmidt* (1966)].

HNCO adsorption was performed also at room temperature and at 100 °C, but the spectra did not change significantly compared with the results obtained at 150 °C. However, when lowering the temperature the stability of adsorbed species increased in a flow on nitrogen and more of the unwanted products were formed. On the contrary, increasing the adsorption temperature further to 150 °C resulted in very unstable species that were removed after short purging with nitrogen. No unwanted products were formed for temperatures higher than 150 °C.

# 4.6 Discussion

NH<sub>3</sub>-TPD and the DRIFT investigation with CO and NH<sub>3</sub> adsorption clearly showed that two different types of Lewis acid sites are present on the TiO<sub>2</sub> anatase. Five coordinated Ti<sup>4+</sup> cations are less acidic, called  $\beta$  sites, whereas four coordinated Ti<sup>4+</sup> cations are more acidic, called  $\alpha$  sites. The XRD pattern of the TiO<sub>2</sub> sample revealed that the (101) surface is the most prominent crystal surface in the sample. This surface exhibits five coordinated Ti<sup>4+</sup> ions on the upper layer. However, when  $TiO_2$  is exposed to the atmosphere these unsaturated atoms favor the adsorption of water (in molecular form as H<sub>2</sub>O and in dissociated form as hydroxyls). Primet et al. proposed that the removal of adsorbed water can generate Ti<sup>4+</sup> sites with higher insaturation [*Primet et al.* (1971a)]. They suggested that sites with higher coordination ( $\beta$ ) are formed by removal of molecular adsorbed water or hydrogen-bonded OH groups, while sites with lower coordination ( $\alpha$ ) are formed by removal of isolated OH groups on the TiO<sub>2</sub> surface. The presence of vacancies and defects on the surface might also be the origin of the  $\alpha$  sites. The intensity of the peaks obtained upon CO adsorption and the shape of the curve obtained from NH<sub>3</sub>-TPD suggest that the concentration of the weaker  $\beta$  sites is higher than the concentration of  $\alpha$  sites, in agreement with a statement of Hadjiivanov et al. [Hadjiivanov et al. (1996)]. Besides, NH<sub>3</sub> adsorption evidenced that almost no Brønsted acidity is present on the surface.

Adsorption of HNCO at room temperature, 100 °C and 150 °C showed that HNCO adsorbs dissociatively on  $TiO_2$  forming –NCO species, bound to  $Ti^{4+}$  cations and hydroxyl groups. The NCO band of the infrared spectrum exhibit a shoulder, indicating that this species is adsorbed on the different  $Ti^{4+}$  sites present on the surface. Peak deconvolution of the isocyanate band (Figure

4.10) shows that the isocyanate species with the higher vibration frequency are more abundant on the surface.



Figure 4.10: Peak deconvolution of the –NCO band in Figure 4.9.

Since CO adsorption experiments showed that more  $\beta$  sites are present on the surface, it is reasonable to assume that the higher –NCO peak is assigned to isocyanates bound to  $\beta$  sites and that the lower peak stems from isocyanates bound to  $\alpha$  sites. However, this would imply that there is no direct correlation between vibration frequency and bond strength between the adsorbed species and the surface. Therefore, additional theoretical calculations on the mode of adsorption and the resulting infrared vibrations are being carried out [*Czekaj et al.*].

# **4.7 Conclusions**

Two types of  $Ti^{4+}$  Lewis acid sites were identified on  $TiO_2$  in the anatase modification and no Brønsted acidity was detected. Performing  $NH_3$  adsorption experiments in the presence of wa-

ter did not result in the formation of ammonium ions indicating that even under hydrated conditions  $TiO_2$  anatase does not exhibit Brønsted acidity. HNCO adsorbed on the surface by forming isocyanate species (–NCO) on  $Ti^{4+}$  sites and hydroxyl groups. The stability of isocyanate species increased with lowering the temperature. On the contrary, increasing the adsorption temperature to 150 °C resulted in very unstable species that were removed after briefly purging with nitrogen. Adsorption of HNCO at low temperatures (< 150 °C) also resulted in the formation of small amounts of byproduct (cyanuric acid and/or s-triazine). However, no unwanted by-products were formed for adsorption temperatures higher than 150 °C.

# 5

# HNCO Adsorption on Fe-ZSM5

### **5.1 Introduction**

For clearing up the catalyst characteristics that positively influence the HNCO catalytic hydrolysis, investigation of the HNCO adsorption on Fe-ZSM5 was also investigated. The experiments were performed on both Fe-ZSM<sub>1</sub> and Fe-ZSM<sub>2</sub> samples. Though Solymosi et al. investigated the HNCO adsorption on Cu-ZSM5 [*Solymosi et al. (1995)*], no such study was performed for Fe-ZSM5. In order to facilitate the interpretation of the spectroscopic results, the base material H-ZSM5 and its constituents SiO<sub>2</sub> and Al<sub>2</sub>O<sub>3</sub> as well as the iron containing samples Fe<sub>2</sub>O<sub>3</sub>, Fe/SiO<sub>2</sub> and Fe/Al<sub>2</sub>O<sub>3</sub> have also been investigated.

# 5.2 Fe-ZSM5 zeolite background

Zeolites are the aluminosilicate within the family of molecular sieves. They are microporous crystalline solids with well-defined structures, consisting of SiO<sub>4</sub> and AlO<sub>4</sub> tetrahedra with additional cations and water within their pores. The SiO<sub>4</sub> and AlO<sub>4</sub> tetrahedra are connected via sharing O atoms in a broad variety of different structures. The tetrahedra can be arranged in several units, called secondary building blocks. Zeolite structures are built up by joining these building blocks into periodic structures. When an Al<sup>3+</sup> replaces a Si<sup>4+</sup> ion atom in the thetrahedra, the units have a net charge of -1, and hence cations are needed to neutralize the charge. The number of cations present in a zeolite structure depends on the number of alumina tetrahedra in the framework.

ZSM5 is a zeolite having a particularly complex structure with straight and sinusoidal channels that are perpendicular to each other (Figure 5.1).



Figure 5.1: Schematic of ZSM5 structure channels.

The catalytic activity of ZSM5 is related to its acidity and to the size and shape of the channels within the zeolite structure.

# **5.3 Experimental**

The following base materials were used: H-ZSM5 with a Si/Al ratio of 28, SiO<sub>2</sub> (Grace),  $Al_2O_3$  (Wacker) and  $Fe_2O_3$  (Sigma Aldrich). The preparation of the Fe-ZSM5 samples is described in section 3.2.2. Iron supported on SiO<sub>2</sub> and  $Al_2O_3$  was prepared by impregnation of 0.5 g of each oxide with a 0.1 M Fe(NO<sub>3</sub>)<sub>3</sub>\*9H<sub>2</sub>O solution and subsequent drying overnight in air at

100 °C. The iron species formed on the surface of the samples were investigated at 20 and -133 °C by ESR spectroscopy.

The adsorption of HNCO on the catalyst surfaces was investigated by means of DRIFT spectroscopy. Before adsorption the samples were pre-treated at 450 °C with N<sub>2</sub> for 1 h and the background spectra were collected, which were subtracted in order to analyze only the surface species in the adsorption experiments. Adsorption of ~ 70 ppm of isocyanic acid was performed for 30 min at 150 °C, followed by a flow of pure N<sub>2</sub> for 30 min and a final temperature ramp.

# **5.4 Results**

#### 5.4.1 Characterization of iron exchanged catalysts

The iron loaded on the samples is present in the form of different species. ESR investigation of Fe-ZSM5<sub>1</sub> revealed signals at  $g \sim 8.5$ ,  $g \sim 5.6$   $g \sim 4.3$ ,  $g \sim 2.3$  (broad), and  $g \sim 2$  Figure 5.2A.



Figure 5.2: EPR spectra of A) Fe-ZSM5<sub>1</sub> and B) Fe-ZSM5<sub>2</sub> at 20 °C and -133 °C, respectively.

These signals were attributed to isolated  $Fe^{3+}$  sites in strong rhombic or axial distortion, which are incorporated in tetrahedral or octahedral positions (g ~ 4.3 and g > 6), isolated  $Fe^{3+}$  species in higher coordination numbers (g ~ 5.6), isolated  $Fe^{3+}$  ions in positions of high symmetry or bulk  $Fe_xO_y$  (g ~2) and  $Fe_2O_3$  particles in the few nanometer range (broad line at g ~ 2.3). The detailed peak assignment can be found in [*Devadas et al. (2006a)*]. The ESR spectrum of Fe-ZSM5<sub>2</sub> showed similar features (Figure 5.2B) at reduced signal intensity, indicating that less Fe was loaded on the catalyst.

The iron species formed on Fe-SiO<sub>2</sub>, Fe-Al<sub>2</sub>O<sub>3</sub> and Fe<sub>2</sub>O<sub>3</sub> were also investigated by means of ESR and the results are shown in Figure 5.3.



Figure 5.3: EPR spectra of A) Fe<sub>2</sub>O<sub>3</sub>, B) Fe-SiO<sub>2</sub> and C) Fe-Al<sub>2</sub>O<sub>3</sub> at 20 °C and -133 °C, respectively.

For pure iron oxide a signal at  $g \sim 2.3$  was observed that vanished at very low temperatures. This signal is typical for Fe<sup>3+</sup> in bulk Fe<sub>2</sub>O<sub>3</sub>. In the ESR spectrum of Fe/SiO<sub>2</sub> three main signals are visible at  $g \sim 8.3$ ,  $g \sim 4.3$ , and  $g \ge 2.3$  (broad). The intensity of the transitions at  $g \sim 8.3$  and  $g \sim 4.3$  increased at lower temperatures, which is typical for paramagnetic species. These signals are suggestive for the presence of isolated Fe<sup>3+</sup> ions with distorted tetrahedral or octahedral coordination [*Kobayashi et al. (1996); Parmaliana et al. (2002); Zhilinskaya et al. (2003)*]. The broad signal at  $g \ge 2.3$  decreased in intensity and was shifted to lower magnetic fields at -150 °C. This signal did not follow Curie's law and can be attributed to small oxidic iron clusters. The analog ESR spectrum obtained for Fe/Al<sub>2</sub>O<sub>3</sub> indicates that the same species were formed on this material. However, the different signal intensities refer to a different species concentration.

#### 5.4.2 HNCO adsorption on Fe-ZSM51 and Fe-ZSM52

Dosing of HNCO for 30 min over Fe-ZSM5<sub>1</sub> at 150°C (Figure 5.4A) resulted in the formation of bands at 2278 and 2212 cm<sup>-1</sup> and a small band at 2139 cm<sup>-1</sup>.



**Figure 5.4:** DRIFT spectra of A) Fe-ZSM5<sub>1</sub> and B) Fe-ZSM5<sub>2</sub> after a) HNCO adsorption at 150 °C for 30 min followed by b) degassing at 150 °C in N<sub>2</sub> for 30 min and increasing the temperature to c) 200 °C, d) 300 °C and e) 400 °C.

The peak at 2212 cm<sup>-1</sup> grew much stronger upon HNCO dosing than the peak at 2139 cm<sup>-1</sup>. After degassing with nitrogen for 30 min at 150 °C the band at 2278 cm<sup>-1</sup> attenuated significantly and disappeared completely at 200 °C. Also the other two bands decreased in intensity, but they required a temperature of 300 °C to disappear.

In Figure 5.4 only the spectral range from 2100 to 2350/2400 cm<sup>-1</sup> is depicted for better resolution of the peaks. However, it should be noted that additional bands at 3370, 3274, 1654 and 1465 cm<sup>-1</sup> and strong negative peaks in the OH region indicate the adsorption of NH<sub>3</sub> on the surface [*Qi et al.* (2004)]. The adsorption experiments were repeated at 300 °C and the same bands were formed as observed at 150°C (Figure 5.5). However, the peak intensities were drastically lowered (in particular the peaks at 2278 and 2139 cm<sup>-1</sup>) and they were completely removed after short purging with nitrogen.



**Figure 5.5:** Comparison of HNCO adsorption experiments performed at different temperatures. Spectra collected after 30 min HNCO adsorption on Fe-ZSM5<sub>1</sub>.

When HNCO was dosed over Fe-ZSM5<sub>2</sub> at 150 °C the same results were obtained, except that the intensity of all bands was significantly reduced (Figure 5.4B).

In order to assign the peaks observed in the 2100-2400 cm<sup>-1</sup> region, additional adsorption experiments were performed with the zeolite base material H-ZSM5, its constituents SiO<sub>2</sub> and Al<sub>2</sub>O<sub>3</sub>, and with the iron containing samples Fe<sub>2</sub>O<sub>3</sub>, Fe/SiO<sub>2</sub>, and Fe/Al<sub>2</sub>O<sub>3</sub>.

#### 5.4.3 Adsorption of HNCO on H-ZSM5 and its constituents

A single peak at 2260 cm<sup>-1</sup> was observed in the DRIFT spectrum upon dosing of isocyanic acid over  $Al_2O_3$  (Figure 5.6A).



**Figure 5.6:** DRIFT spectra of A)  $Al_2O_3$  and B)  $SiO_2$  after a) HNCO adsorption at 150 °C for 30 min followed by b) degassing at 150 C in  $N_2$  for 30 min, increasing the temperature to c) 200 °C, d) 300 °C, e) 400 °C, f) 450 °C and g) degassing at 450 °C for 60 min.

Degassing in a nitrogen flow at 150 °C followed by a temperature ramp resulted in a strong decrease of the peak intensity and a shift to lower wavenumbers. This band, which was completely removed after short purging at 400 °C, is assigned to the asymmetric vibration frequency of isocyanate species adsorbed on Al sites in agreement with ref. [*Solymosi et al. (1978); Solymosi et al. (1975); Acke et al. (1998); Cowan et al. (1998); Bion et al. (2001)*]. It has to be pointed out that Al<sub>2</sub>O<sub>3</sub> and the other oxides studied in the present paper ex-

hibit strong bulk absorption at low frequencies, whereas the symmetric stretch band of the –NCO species cannot be observed. Moreover, the symmetric stretch vibration is known to be much less intense than the asymmetric stretch vibration and it is only discernible at high surface concentrations of –NCO [*Bánsági et al. (1983)*].

During adsorption of isocyanic acid on SiO<sub>2</sub> three infrared adsorption bands evolved (Figure 5.6B). Initially, only bands at 2250 and 2186 cm<sup>-1</sup> appeared, but after a few minutes a band at 2300 cm<sup>-1</sup> began to develop and rapidly became the most intense one. This band was not influenced by purging with nitrogen at 150 °C. Moreover, higher purging temperatures only moderately decreased its intensity and a residual peak was still present after 60 minutes of purging at 450 °C. The bands at 2250 and 2186 cm<sup>-1</sup> were less stable and were already completely eliminated after purging with nitrogen at 150 °C and 300 °C, respectively. In previous works on the HNCO adsorption on SiO<sub>2</sub> the formation of a band at 2300-2313 cm<sup>-1</sup> was reported [Solymosi et al. (1978); Solymosi et al. (1979); Bánsági et al. (1983); Solymosi et al. (1995)]. This band was not observed when adsorption was carried out at T < 25 °C, but became more intense at higher adsorption temperatures and could only be removed by extended purging at high temperature. Considering these results in the literature, the peak at 2300 cm<sup>-1</sup> can be attributed to Si-NCO groups. The band at 2250 cm<sup>-1</sup> might be ascribed to the asymmetric  $v_a$  vibration of molecularly adsorbed HNCO due to its position and its poor stability. The  $v_2$  vibration of HNCO is 2274 cm<sup>-1</sup> in the gas phase and 2246 cm<sup>-1</sup> in the solid phase [*Reid (1950)*]. Bánsági et al. also found evidence for molecularly adsorbed HNCO on SiO<sub>2</sub> at room temperature [Bánsági et al. (1983)]. The above mentioned studies evidenced only one or two bands arising after adsorption of HNCO on SiO<sub>2</sub>. However, in our spectrum an additional band at 2186 cm<sup>-1</sup> appeared (Figure 5.6B), which might be attributed to Si-O-NCO in accordance with Ferullo et al. who calculated the IR bands of -NCO groups adsorbed on silica [Ferullo et al. (2004)].

When isocyanic acid was adsorbed on H-ZSM5 an intense band appeared at 2279 cm<sup>-1</sup> and a small band at 2124 cm<sup>-1</sup> (Figure 5.7). Purging in a nitrogen flow at 150 °C for 30 min attenuated the first band, but temperatures up to 400 °C were required to completely eliminate the band. The adsorption at 2124 cm<sup>-1</sup> disappeared already at 300 °C. Repeating the measurements at 250 °C gave the same peaks in the DRIFT spectra but at lower intensity. The vibration frequency and the temperature stability characteristics of the band at 2279 cm<sup>-1</sup> are in close agreement with those observed for the Al-NCO band in pure Al<sub>2</sub>O<sub>3</sub>. This assignment is in accordance with the results reported by Solymosi et al. [*Solymosi et al. (1995)*]. The band at 2124 cm<sup>-1</sup> might be attributed to the formation of cyanate ions (NCO<sup>-</sup>) [*Solymosi et al. (1978); Matyshak et al. (1995)*] or cyanide groups (CN) [*Matyshak et al. (1995)*].



Figure 5.7: DRIFT spectra of H-ZSM5 after a) HNCO adsorption at 150 °C for 30 min followed by b) degassing at 150 °C in N<sub>2</sub> for 30 min and increasing the temperature to c) 200 °C, d) 300 °C and e) 400 °C.

#### 5.4.4 Adsorption of HNCO on Fe<sub>2</sub>O<sub>3</sub>, Fe/Al<sub>2</sub>O<sub>3</sub>, and Fe/SiO<sub>2</sub>

The adsorption of HNCO on Fe<sub>2</sub>O<sub>3</sub> resulted in the formation of a band at 2206 cm<sup>-1</sup> that grew and shifted to 2212 cm<sup>-1</sup> over the course of the experiment (Figure 5.8A). The band decreased after 30 min of degassing with N<sub>2</sub> at 150 °C and disappeared when the temperature was increased to 300 °C. Various studies showed that HNCO adsorbs mainly dissociatively on transition metal oxides forming isocyanate species bound to Lewis acid sites [*Solymosi et al. (1979); Solymosi et al. (1980); Matyshak et al. (1995); Solymosi et al. (2001)*]. These isocyanate groups showed vibrational bands in the range 2200-2300 cm<sup>-1</sup>. Therefore, it seems plausible to attribute the band at 2212 cm<sup>-1</sup> to Fe-NCO groups.

Adsorption of HNCO on Fe/Al<sub>2</sub>O<sub>3</sub> produced bands at 2256 and 2200 cm<sup>-1</sup> (Figure 5.8B). The former band showed lower intensity and less thermal stability than the second one and was removed already at 300 °C. The band at 2200 cm<sup>-1</sup> was still present at 400 °C, but with very low intensity, and it completely disappeared after a few minutes of purging at this temperature. From a comparison of these result with those obtained for Fe<sub>2</sub>O<sub>3</sub> and Al<sub>2</sub>O<sub>3</sub> these two bands can be assigned to Al-NCO and Fe-NCO species, respectively.

When HNCO was dosed over Fe/SiO<sub>2</sub> a band at 2202 cm<sup>-1</sup> was formed that became very intense and shifted to 2213 cm<sup>-1</sup> at the end of the adsorption (Figure 5.8C). Purging with nitrogen at 150 °C for 30 min decreased the intensity of the band and shifted it back to 2202 cm<sup>-1</sup>. The intensity of this band further decreased at higher temperatures and disappeared at 400 °C. In agreement with the previous observations this band is ascribed to –NCO species adsorbed on iron sites.



**Figure 5.8:** DRIFT spectra of A)  $Fe_2O_3$ , B)  $Fe/Al_2O_3$  and C)  $Fe/SiO_2$  after a) HNCO adsorption at 150 °C for 30 min followed by b) degassing at 150 °C in N<sub>2</sub> for 30 min and increasing the temperature to c) 200 °C, d) 300 °C and e) 400 °C.

# **5.5 Discussion**

ESR measurements showed that the types of iron species present in the samples depend only slightly on the preparation method. The ESR signals were observed at the same positions for both zeolite samples, but with different intensities due to the different amounts of iron loading. The low amount of iron loaded by the mechanochemical method did not change the micropore volume of Fe-ZSM5<sub>2</sub> compared to the base material, whereas the high amount of iron loaded by solid-state ion exchange caused a considerable reduction of the micropore volume. Small iron oxide particles in the range 20-50 nm have been identified on Fe-ZSM5<sub>1</sub> using TEM investigations, which might block the pores of the catalyst [*Devadas et al. (2006a)*].

The DRIFT spectroscopy investigation of the HNCO adsorption on H-ZSM5 showed the formation of a strong Al-NCO band at 2279 cm<sup>-1</sup> and a smaller [NCO]<sup>-</sup> band at 2124 cm<sup>-1</sup>. The adsorption of isocyanic acid on both Fe-ZSM5 samples gave rise to the formation of three similar bands in the 2000-2400 cm<sup>-1</sup> region, but having different intensities. This congruity of the band positions proves that both preparation methods yielded equally coordinated iron, aluminum and silicon species on the catalyst surface. This conclusion is also valid for the iron in the bulk as shown by the EPR results. By comparison of position and stability of these peaks with those obtained for H-ZSM5 the peak at ~2278 cm<sup>-1</sup> can be attributed to the formation of Al-NCO groups and the band at  $\sim 2139 \text{ cm}^{-1}$  to the formation of [NCO]<sup>-</sup> species. In addition, the comparison of the spectra for Fe-ZSM5, Fe/SiO<sub>2</sub> and Fe/Al<sub>2</sub>O<sub>3</sub> suggests that the band at 2212 cm<sup>-1</sup> was caused by the formation of Fe-NCO groups. This conclusion can be drawn despite the different nature of these materials, since ESR spectroscopy confirms the formation of similar iron species in Fe/Al<sub>2</sub>O<sub>3</sub>, Fe/SiO<sub>2</sub>, and in Fe-ZSM5. The broad variety of iron species found by ESR spectroscopy in Fe-ZSM5 suggests that also different Fe-NCO groups are present on the surface. From the literature it is known that -NCO species adsorbed on transition metals are distinguishable by IR spectroscopy if adsorbed on metal sites with different oxidation states [Solymosi et al. (1995); Matyshak et al. (1995)]. However, the fact that only one IR peak was found proves that iron exists only in the oxidation state (+III) at the catalyst surface. It is important to note that the Fe-NCO band was the strongest in the HNCO adsorption region for both Fe-ZSM5 samples. However, Fe-ZSM5<sub>1</sub> caused a stronger Fe-NCO band than Fe-ZSM5<sub>2</sub> due to the higher iron content. Moreover, the intensity of the Al-NCO band decreased compared to the bands obtained for the

base material and no Si-NCO band was observed, even when adsorption was performed at  $300 \,^{\circ}C$  and higher. Interestingly enough, Solymosi et al. investigated the HNCO adsorption on Pt/SiO<sub>2</sub> by infrared spectroscopy and found a migration of –NCO species from the metal centers to silica at room temperature [*Solymosi et al. (1979)*]. The same effect was observed for Cu-ZSM5, where –NCO species moved from copper to the silicon in the ZSM5 framework, however at elevated temperatures [*Solymosi et al. (1995)*]. Therefore, the temperature at which migration starts qualitatively shows the difference in stability of the –NCO species on the metal sites compared to the silicon sites. Considering these results, the absence of the Si-NCO species on Fe-ZSM5 even at 300 °C indicates that Fe sites are highly favored for the formation of isocyanate species.

The adsorption of HNCO on Fe-ZSM5 at  $150^{\circ}$ C also gave rise to the formation of bands indicating the presence of adsorbed NH<sub>3</sub> and by-products. Adsorbed ammonia species might arise from traces of ammonia present in the inlet flow or, more probably, from the reaction of adsorbed HNCO with surface -OH groups.

# **5.6 Conclusions**

DRIFT investigations revealed that at 150 °C HNCO adsorbs dissociatively on Fe-ZSM5 forming isocyanate species, in analogy with  $TiO_2$  (Chapter 4). However, due to the complexity of Fe-ZSM5 composition –NCO groups are bond to different surface sites giving rise to the formation of Fe-NCO and Al-NCO species. Moreover, the formation of [NCO]<sup>-</sup> ions was noticed. No interaction of HNCO with silica sites was observed.

# 6

# **Reaction Mechanism**

# **6.1 Introduction**

In order to better understand the catalytic HNCO hydrolysis, the reactivity of the isocyanate species formed on both  $TiO_2$  anatase and on Fe-ZSM5 toward water investigated in DRIFT experiments. These spectroscopic results were correlated with the hydrolysis activity of the materials in order to examine possible correlations between microscopic properties and the macroscopic catalytic activity. *In-situ* investigation of the HNCO hydrolysis with  $TiO_2$  was also performed. Additional DRIFT investigations on the adsorption modes of the reactants (i.e.,  $H_2O$ ) and products (i.e.,  $CO_2$ ) on  $TiO_2$  anatase were also carried out to ease the interpretation of the spectra.

# **6.2** Experimental

The stability of the –NCO species in the presence of water was studied by means of DRIFT experiments from RT to 450 °C. To analyze the stability of –NCO species on TiO<sub>2</sub>, the sample was treated with ~ 70 ppm of HNCO in N<sub>2</sub> for 15 min. The catalyst was then degassed in a N<sub>2</sub> flow for 15 min before water was introduced in small pulses. For Fe-ZSM5 and Fe<sub>2</sub>O<sub>3</sub> the stability of the adsorbed species to water was studied at 150 °C by dosing a humid N<sub>2</sub> flow (4l<sub>N</sub>/h, saturated at RT) for 10 min, which was started after 15 min of HNCO adsorption.

*In-situ* DRIFT investigation of the HNCO hydrolysis on  $TiO_2$  was carried out by treating the catalyst with ~ 70 ppm HNCO, 200 ppm H<sub>2</sub>O (added by dosing a humid N<sub>2</sub> flow) and 10% O<sub>2</sub> in N<sub>2</sub> for 15 min.

The adsorption of pure water on  $TiO_2$  was also investigated by DRIFT experiments. The sample was treated with ~ 200 ppm of water at 150 °C for 10 minutes before measuring the spectrum.

Adsorption of  $CO_2$  on TiO<sub>2</sub> was performed at 150 °C by dosing 1000 ppm of  $CO_2$  for 25 minutes after which the spectrum was measured.

The sample was pre-treated at 450 °C in  $N_2$  for 1 h prior to each adsorption experiment. In order to analyze only the surface species obtained after adsorption, the background spectrum was always measured and then subsequently subtracted from the final spectrum.

# 6.3 Hydrolysis with TiO<sub>2</sub> anatase

#### 6.3.1 Reactivity of –NCO species in the presence of water

The stability of –NCO species was studied by adding water at room temperature, 100 °C, and 150 °C (Figure 6.1). Temperatures above 150 °C were also tested, however, the isocyanate species vanished immediately after addition of water and therefore results are not shown. At 150 °C, the isocyanate groups rapidly reacted with water, but the reaction slowed at lower temperatures. At room temperature, only a small decrease of the –NCO band intensity was observed, indicating that isocyanate species are almost totally non-reactive at this temperature.

This spectroscopic result is in excellent agreement with the HNCO hydrolysis activity of  $TiO_2$  anatase reported in Chapter 3 (section 3.3.1). Titania revealed a NH<sub>3</sub> yield of more than

85% at T > 150 °C, even at high space velocities and a yield of 100% was always measured for T > 200 °C. Contrary, the NH<sub>3</sub> yield drastically decreased for T < 150 °C.



**Figure 6.1:** Stability of the isocyanate species after addition of water pulses at (A) 150 °C, (B) 100 °C and (C) room temperature.

#### 6.3.2 Adsorption of H<sub>2</sub>O on TiO<sub>2</sub>

Adsorption of water on  $TiO_2$  anatase is known to take place in two ways: part of the water molecules are dissociatively adsorbed forming hydroxyl groups, while part are adsorbed molecularly [*Bezrodna et al. (2004)*]. Water molecules can be bound to the surface either by hydrogen bonds with anions, by weak coordination bonds with metal cations, or by bonds of both types simultaneously.



Figure 6.2: Adsorption of water on TiO<sub>2</sub>. a) Molecular, b) dissociative adsorption.

The spectrum obtained after adsorption of water at 150 °C on  $TiO_2$  anatase (Figure 6.1) is characterized by a broad band at 2700-3700 cm<sup>-1</sup> and two narrow bands at 1185 and 1621 cm<sup>-1</sup>.



**Figure 6.3**: DRIFT spectra of  $H_2O$  adsorbed on TiO<sub>2</sub>.  $H_2O$  adsorption carried out at 150 °C for 10 minutes with ~ 200 ppm  $H_2O$ .

The band at 1621 cm<sup>-1</sup> results from the deformation vibration  $\delta$ (H-O-H) of H<sub>2</sub>O and evidences undissociated water molecules adsorbed on the TiO<sub>2</sub> surface [*Hadjiivanov et al.* (1996);

*Bezrodna et al. (2004)*]. The broad band at 2500-3700 cm<sup>-1</sup> is due to physisorbed water molecules.

It is known that anatase can reach a high level of surface hydration. To justify this property Bezordna et al [*Bezrodna et al. (2004)*] proposed that once the surface of  $TiO_2$  is filled with water, new adsorption sites are created and water complexes can be formed (Figure 6.4). In fact, the unshared electron pairs from the H<sub>2</sub>O oxygen atom are pulled towards the inner d-orbital of titanium atoms, which weakens the intramolecular bonds inside the water molecules. This protonization results in further strong water adsorption centers.



**Figure 6.4:** H<sub>2</sub>O adsorption complexes on TiO<sub>2</sub> proposed by [*Bezrodna et al. (2004)*].

This high level of anatase hydration is probably responsible for the absorption band at 1185 cm<sup>-1</sup>. It is known that bands in this region resulting from deformation vibration of Ti-O-H bonds can be observed [*Bezrodna et al. (2004)*].

The adsorption of water on  $TiO_2$  anatase has been studied mostly theoretically so far. Calculations predict the dissociative adsorption is more favorable on  $TiO_2$  anatase (001) [*Homann et al.* (2004); Bredow et al. (1995)], while molecular adsorption is more likely on the (101) surface [Selloni et al. (1998); Vittadini et al. (1998)]. Due to the high amount of physisorbed water at 150 °C, a quantitative comparison on the amount of molecularly and dissociatively adsorbed was not possible. However, as most of the surface of this sample was made of anatase (101) (Chapter 4), the theoretical investigations suggest that water adsorbs mostly in molecular form.

#### 6.3.3 Adsorption of CO<sub>2</sub> on TiO<sub>2</sub>

Adsorption of CO<sub>2</sub> on TiO<sub>2</sub> at 150 °C resulted in the appearance of two intense bands at 2355 and 2344 cm<sup>-1</sup> plus a weak band at ~ 1570 cm<sup>-1</sup> and (Figure 6.5).



**Figure 6.5:** DRIFT spectra of CO<sub>2</sub> adsorbed on TiO<sub>2</sub>. H<sub>2</sub>O adsorption carried out for 25 minutes at 150 °C with ~ 1000 ppm CO<sub>2</sub>.

The two peaks at 2355 and 2344 cm<sup>-1</sup> are very close to the symmetric stretching vibration of gaseous  $CO_2$ . Therefore, these bands are attributed to  $CO_2$  molecules being physisorbed on the catalyst surface.

The weak band at 1570 cm<sup>-1</sup> might be attributed to the formation of carbonates via interaction of CO<sub>2</sub> with surface oxygen or CO<sub>2</sub><sup>-</sup> carboxylate species linked to metal cations [*Yates* (1961); Busca et al. (1982); Baraton (1996); Martra (2000)]. Both, adsorbed carbonates and  $CO_2^{-1}$  species are characterized by a splitting of the asymmetric stretching vibration and, therefore, two bands are expected in the 1700-1200 cm<sup>-1</sup> region [*Busca et al. (1982)*]. The magnitude of this splitting is often used to identify the adsorbed species. However, the second component at lower vibration frequency was not visible in the spectra obtained, probably due to the small amount of species formed. This result hinders a more accurate assignment of the band at 1572 cm<sup>-1</sup>. Traces of water might be the reason for the irregular pattern of this peak.

#### 6.3.4 HNCO hydrolysis over TiO<sub>2</sub>

The results obtained performing the HNCO hydrolysis *in-situ* on  $TiO_2$  at 150 °C are shown in Figure 6.6.



**Figure 6.6:** DRIFT spectra of TiO<sub>2</sub> after HNCO adsorption (70 ppm) in the presence of 200 ppm H<sub>2</sub>O at 150 °C for 5, 10, and 15 min.

Figure 6.6 shows that under reacting conditions the amplitude of the -NCO band at 2209 cm<sup>-1</sup> was very small and at the same time the intensity of the NH<sub>3</sub> and CO<sub>2</sub> bands increased substantially. This demonstrates that the HNCO hydrolysis reaction was taking place. The band at

1630 cm<sup>-1</sup> shows the presence of molecularly adsorbed water. Additional bands appeared at 1559, 1380 and 1356 cm<sup>-1</sup> together with smaller bands at 2952, 2864 and 2740 cm<sup>-1</sup>, all of which are tentatively attributed to the formation of formate ions. The bands at 1356 and 1380 cm<sup>-1</sup> are due to the  $v_s(\text{COO}^-)$  and  $\delta(\text{CH})$  vibrations. The small absorption bands around 2740-2950 cm<sup>-1</sup> are due to the C-H stretching vibration mode. The band at 1559 cm<sup>-1</sup> is due to  $v_{as}(\text{COO}^-)$  [*Busca et al. (1982)*]. These bands proved to be stable at 150 °C and did not disappear after treatment with N<sub>2</sub> for 30 min. However, increasing the purging temperature decreased the intensity of these peaks. They completely disappeared at 300 °C, in agreement with the stability observed for formate species [*Munuera (1970)*]. Finally, the peaks did not appear at all when performing the HNCO hydrolysis at 300 °C.

#### 6.3.5 Discussion

The congruity between the reactivity of -NCO species with water (Figure 6.1) and the catalytic properties of TiO<sub>2</sub> for the HNCO hydrolysis (Chapter 3) suggests that the reaction proceeds via -NCO species as intermediates. These isocyanate species proved to be very reactive in the presence of water with a marked temperature dependency.

Water was calculated to adsorb on the (101) surface of anatase mainly in molecular form which suggests that isocyanates species might react with molecularly adsorbed water. Moreover, Primet et al. [*Primet et al. (1971a)*] observed that repetition of hydration and dehydration cycles on TiO<sub>2</sub> anatase leads to a decreasing concentration of the sites for dissociative adsorption of water. They attributed this effect to surface reconstruction. The hydrolysis properties of the TiO<sub>2</sub> sample used in this study proved to remain stable even after several experiments (since several dehydration and hydration cycles were performed in the experiments from 450 °C to 150 °C). This revealed that an eventual disappearance of sites for dissociative adsorption of water does not influence the catalytic activity of the catalyst. Due to the high level of hydration that TiO<sub>2</sub> anatase reaches, reaction of –NCO species with water molecules bounded in water clusters is also possible.

The formation of isocyanate species as intermediates in the HNCO hydrolysis agree with the catalytic activities observed for different oxide catalysts in Chapter 3. The tests indicated that Lewis acidity favors the HNCO catalytic hydrolysis and this is in accordance with the formation of isocyanate groups on Lewis acid sites and their reactivity. However, a too high Lewis acidity

(as for  $TiO_2$  rutile and  $ZrO_2$ ) might result in a stable dissociative adsorption of water, which consequently blocks the sites for HNCO adsorption and, thereby, decreases the catalytic activity.

This role of isocyanate species as intermediates is also supported by the results of Solymosi et al. who found that –NCO species are more stable on  $TiO_2$  doped with W<sup>6+</sup> than on pure  $TiO_2$  [*Solymosi et al.* (2001)]. Similarly, the hydrolysis activity of this catalyst was measured to be lower for TiO<sub>2</sub> doped with W<sup>6+</sup> than for pure TiO<sub>2</sub> [*Kleemann et al.* (2000)].

Performing the HNCO hydrolysis *in-situ* over  $TiO_2$  resulted in the formation a very weak –NCO band and of molecularly adsorbed NH<sub>3</sub> and CO<sub>2</sub>, indicative of the occurrence of the hydrolysis reaction. In addition, bands associated to formate species were observed. These latter species proved to be stable for T < 300 °C. Since the activity of TiO<sub>2</sub> is very high also for temperatures below 300 °C, this suggests that these species are not active reaction intermediates, but most probably only by-products.

### 6.4 Hydrolysis with Fe-ZSM5

The stability of –NCO groups formed after HNCO adsorption on Fe-ZSM5<sub>1</sub>, Fe-ZSM5<sub>2</sub>, was studied (Figure 6.7).



**Figure 6.7:** DRIFT spectra of A) Fe-ZSM5<sub>1</sub> and B) Fe-ZSM5<sub>2</sub> after a) HNCO adsorption at 150 °C for 15 min followed by b) dosing HNCO and water for 10 min.

The addition of water to the inlet flow reduced the intensity of the bands in the DRIFT spectrum associated with the adsorbed HNCO species (in particular the band at ~2200-2212 cm<sup>-1</sup>, attributed to Al-NCO and Fe-NCO species respectively), and increased the intensity of the bands attributed to adsorbed NH<sub>3</sub> (3370, 3274, 1564 and 1465 cm<sup>-1</sup>). Moreover, no formation of new adsorbed species was observed. The same behavior was found for both Fe-ZSM5<sub>1</sub> and Fe-ZSM5<sub>2</sub>, again confirming the congruity of the surface species.

The DRIFT spectra obtained were normalized (Figure 6.8) and the relative decay of the -NCO infrared band in the presence of water was compared with the catalytic activity for the HNCO hydrolysis observed in Chapter 3. Pure Fe<sub>2</sub>O<sub>3</sub> was also investigated. For comparison purposes the hydrolysis properties of the investigated materials are again shown in Figure 6.9. The isocyanate species formed on Fe<sub>2</sub>O<sub>3</sub> reacted slower with water than the -NCO groups on Fe-ZSM5. On the other hand, the rate of hydrolysis of the Fe-NCO species on the two Fe-ZSM5 samples did not vary considerably. These results suggest that the HNCO hydrolysis occurs via the formation of isocyanate species as intermediate, as has been proposed for TiO<sub>2</sub>. Since the amount of iron loaded on Fe-ZSM5<sub>1</sub> is higher than in Fe-ZSM5<sub>2</sub>, it is reasonable that the former sample exhibited higher activity than the latter.



**Figure 6.8:** Normalized DRIFT spectra of A) Fe-ZSM5<sub>1</sub>, B) Fe-ZSM5<sub>2</sub> and C) Fe<sub>2</sub>O<sub>3</sub> after a) HNCO adsorption at 150 °C for 15 min followed by b) dosing HNCO and water for 10 min.



**Figure 6.9:** NH<sub>3</sub> yield as a function of temperature. (**■**) Fe-ZSM5<sub>1</sub>, (**▲**) Fe-ZSM5<sub>2</sub> and (x) Fe<sub>2</sub>O<sub>3</sub>.

# **6.5 Conclusions**

The results presented in this chapter showed that reactivity of -NCO species with water to give NH<sub>3</sub> follows the catalytic activity of TiO<sub>2</sub> and Fe-ZSM5 for the HNCO hydrolysis.

The study of the HNCO hydrolysis with  $TiO_2$  *in situ* at 150 °C revealed that reactants and products are all adsorbed on the catalyst during the reaction. The investigation of the adsorption modes of water on  $TiO_2$  would suggest that –NCO species react with molecularly adsorbed water bonded with Ti sites via oxygen or to the surface oxygen via hydrogen bonding. However, since  $TiO_2$  anatase proved to reach high level of surface hydration by formation of different layers of water molecules, the reaction with water molecules on the top layer is also possible.

# **7** Influence of NO<sub>2</sub>

# 7.1 Introduction

The use of NO<sub>2</sub> to enhance the NO<sub>x</sub> conversion in the SCR process is well known [*Koebel et al.* (2002b); *Rahkamaa-Tolonen et al.* (2005)]. This effect is most pronounced for an equimolar ratio of NO and NO<sub>2</sub> due to the stoichiometry of the "fast SCR" reaction (1.2):

$$2NO + 2NO_2 + 4NH_3 \rightarrow 4N_2 + 6H_2O \tag{1.2}$$

The higher rates of the fast SCR allow obtaining higher  $NO_x$  conversions and this effect is most pronounced at low temperatures. The nitrogen oxides in diesel exhaust gas are mainly composed of NO and in order to make use of the fast SCR reaction the  $NO_2$  content is usually increased by oxidizing part of the NO over an oxidizing catalyst. This catalyst is typically positioned before the urea injection point in order to avoid oxidation of ammonia. As result, the thermo-hydrolysis of urea occurs in the presence of high concentrations of NO<sub>2</sub>. For that reason, the effect of NO<sub>2</sub> on the hydrolysis reaction over both TiO<sub>2</sub> and Fe-ZSM5 was studied.

### 7.2 Experimental

The catalytic performance of TiO<sub>2</sub> was tested in the plug flow glass micro-reactor (Chapter 2, section 2.1.3.2). About 150 mg of catalyst (particle size 160-200  $\mu$ m) were used and the overall gas flow rate was 200 l<sub>N</sub>/h (GHSV ~ 2·10<sup>6</sup> h<sup>-1</sup>). The catalytic activity of Fe-ZSM5<sub>1</sub> was tested using the monolithic catalyst prepared as described in Chapter 3 (section 3.2.2). The overall gas flow rate was 400 l<sub>N</sub>/h (GHSV ~ 52000 h<sup>-1</sup>). Prior to each experiment, the samples were treated for 1 h at 450 °C in a flow of N<sub>2</sub> and 10% O<sub>2</sub>. The experiments were performed in the temperature range 100-400 °C and the catalytic activity was tested with model diesel exhaust gas (10% O<sub>2</sub>, 5% H<sub>2</sub>O, N<sub>2</sub> balance) containing ~1000 ppm HNCO. The influence of NO<sub>2</sub> was studied by addition of 200 ppm NO<sub>2</sub> to the inlet flow.

Temperature programmed desorption (TPD) and transient reaction (TR) experiments were performed in the tubular glass reactor (Chapter 2, section 2.1.3.1). The experiments were carried out with 3 g of TiO<sub>2</sub> (particle size 100-1000  $\mu$ m) in the presence of 10% O<sub>2</sub> with N<sub>2</sub> balance at a gas flow rate of 300 l<sub>N</sub>/h. TPD experiments were performed by saturating the sample at 150 °C in the presence of 10% O<sub>2</sub> and 2.5% H<sub>2</sub>O. For the NH<sub>3</sub>-TPD experiment 500 ppm of NH<sub>3</sub> were used, while for the NO<sub>2</sub>-TPD 370 ppm of NO<sub>2</sub> were dosed. After adsorption weakly bound species were desorbed by purging the sample with 10% O<sub>2</sub> in N<sub>2</sub>. TPD was completed by increasing the temperature up to 450 °C at 17 °C/min. The role of NO<sub>2</sub> was investigated in combined TR and TPD experiments by the following procedure: hydrolysis of ~ 1000 ppm HNCO was carried in the presence of 2.5% H<sub>2</sub>O and 10% O<sub>2</sub> at 150 °C for 25 minutes. Subsequently, 370 ppm of NO<sub>2</sub> were added for 1 h. After 85 min, the NO<sub>2</sub>, HNCO and H<sub>2</sub>O feeds were stopped and the catalyst was purged for 30 min with N<sub>2</sub>. For the TPD, two procedures were tested: a fast heating rate of 28 °C/min under dry conditions and a slow heating rate of 12 °C/min under humid conditions (2.5% H<sub>2</sub>O).

DRIFT investigations were performed collecting all spectra against the background measured from the adsorbate-free TiO<sub>2</sub> at the corresponding temperatures. Therefore, the final spectra show the adsorbed species only. Experiments were carried out by adsorbing 80 ppm of HNCO (and 25 ppm of NH<sub>3</sub> as impurity) in the presence of 200 ppm H<sub>2</sub>O and 10% O<sub>2</sub> at 150 °C. After 25 min of adsorption, 100 ppm of NO<sub>2</sub> was added for 1 h. The sample were pretreated with a flow of N<sub>2</sub> (40 ml/min) for 1 h at 450 °C before the experiments. Spectra were collected every five minutes in order to observe the temporal evolution of adsorbed species.

# 7.3 HNCO hydrolysis with in the presence of NO<sub>2</sub>

#### 7.3.1 TiO<sub>2</sub> anatase

The investigation of the catalytic properties showed that  $NO_2$  considerably reduced the hydrolysis of HNCO for T < 200 °C (Figure 7.1).



**Figure 7.1:** The hydrolysis of HNCO to NH<sub>3</sub> over TiO<sub>2</sub>. 150 mg of catalyst, flow rate =  $200 \text{ l}_{\text{N}}/\text{h}$ , inlet flow composed of ~ 1000 ppm HNCO, 10% O<sub>2</sub>, 5% H<sub>2</sub>O, 0-200 ppm NO<sub>2</sub> and N<sub>2</sub> balance. ( $\Box$ ) In the presence of 200 ppm NO<sub>2</sub>, and ( $\blacksquare$ ) without NO<sub>2</sub>.

This difference became greater with decreasing temperature and conversion reached almost zero at 100 °C. Steady-state conditions were reached only after several minutes of NO<sub>2</sub> addition. However, the catalytic activity was completely recovered by a treatment in  $O_2$  and  $N_2$  at 450 °C.

#### 7.3.2 Fe-ZSM5

Since Fe-ZSM5 exhibits SCR activity besides HNCO hydrolysis properties, the hydrolysis activity of Fe-ZSM5<sub>1</sub> was tested on the presence of equimolar amounts of NO<sub>2</sub> and NO (Figure 7.2). The results are expressed in terms of HNCO conversion because in the presence of NO and NO<sub>2</sub> all NH<sub>3</sub> produced is immediately consumed in the fast SCR reaction and, therefore, showing the NH<sub>3</sub> yield could be misleading.



**Figure 7.2:** Hydrolysis of HNCO over Fe-ZSM5<sub>1</sub>  $\square$ ) without NO and NO<sub>2</sub>, and **\blacksquare**) in the presence of 350 ppm NO + 350 ppm NO<sub>2</sub>.

At high temperatures the HNCO hydrolysis was not affected, but for T < 200 °C the combined addition of NO and NO<sub>2</sub> resulted in a slow decrease of the HNCO conversion from ~ 97% to ~ 75% at 175 °C and from ~ 68% to ~ 42% at 150 °C. In analogy to the TiO<sub>2</sub> sample, steadystate conditions were reached only after several minutes of NO<sub>2</sub> addition. The catalytic activity was completely recovered by a treatment in  $O_2$  and  $N_2$  at 450 °C.

# 7.4 Role of NO<sub>2</sub>

The role of  $NO_2$  was studied in more detail on  $TiO_2$  anatase.

#### 7.4.1 TPD of NH<sub>3</sub> and NO<sub>2</sub>

Since NO<sub>2</sub> in the feed gas and NH<sub>3</sub> formed by HNCO hydrolysis interact with the catalyst, the stability of these species on TiO<sub>2</sub> was studied with TPD experiments of NH<sub>3</sub> and NO<sub>2</sub> (Figure 7.3 and Figure 7.4). After NH<sub>3</sub> adsorption at 150 °C and purging for 30 min, ammonia immediately started to desorb when increasing the temperature. This gave evidence that NH<sub>3</sub> is weakly bound to the catalyst surface, in contrast to NO<sub>2</sub>, which required temperatures above 250 °C to desorb, indicating that NO<sub>2</sub> is much more strongly bound to TiO<sub>2</sub>.



**Figure 7.3:** NH<sub>3</sub> TPD. 3 g of catalyst, flow rate =  $300 l_N/h$ , NH<sub>3</sub> in = 500 ppm. Adsorption performed at 150 °C in the presence of 2.5% H<sub>2</sub>O and 10% O<sub>2</sub>. TPD carried out in the presence of 10% O<sub>2</sub> with a heating ramp of ~ 17 °C/min.



**Figure 7.4:** NO<sub>2</sub> TPD. 3 g of catalyst, flow rate =  $300 l_N/h$ , NO<sub>2</sub> in = 370 ppm. Adsorption performed at 150 °C in the presence of 2.5% H<sub>2</sub>O and 10% O<sub>2</sub>. TPD carried out in the presence of 10% O<sub>2</sub> with a heating ramp of ~ 17 °C/min.

Mole balance calculations showed that the adsorbed  $NH_3$  and  $NO_2$  were quantitatively desorbed during TPD (Table 7.1).

Table 7.1: Mass balance of NH<sub>3</sub> and NO<sub>2</sub> adsorbed and desorbed during the TPD tests.

	Adsorbed [mol]	Desorbed [mol]	Error [%]
NH <sub>3</sub>	0.00030	0.00029	4
NO <sub>2</sub>	0.00045	0.00044	2

#### 7.4.2 Combined TPD/TR experiments

Combined TR and TPD experiments were performed in order to elucidate the role of NO<sub>2</sub> in the activity decrease of the HNCO hydrolysis.

Figure 7.5 shows the temporal decrease of the HNCO hydrolysis as soon as  $NO_2$  was introduced into the feed at 150 °C.


**Figure 7.5:** HNCO conversion and NH<sub>3</sub> yield during the addition of NO<sub>2</sub> in TR experiments. 3 g of catalyst, T = 150 °C, flow rate = 300 L<sub>N</sub>/h, inlet flow composed of ~ 1000 ppm HNCO, 10% O<sub>2</sub>, 2.5% H<sub>2</sub>O, 370 ppm NO<sub>2</sub>. (x) NO<sub>2</sub>, (•) HNCO conversion, ( $\Box$ ) NH<sub>3</sub> yield.

At this temperature the hydrolysis of isocyanic acid has 100% selectivity towards NH<sub>3</sub>. However, during the addition of NO<sub>2</sub> the NH<sub>3</sub> yield was lower than the HNCO conversion. Also the amount of NO<sub>2</sub> at the outlet was lower than at the inlet. This suggests that NH<sub>3</sub> and NO<sub>2</sub> were being adsorbed on the surface or a reaction between NH<sub>3</sub> and NO<sub>2</sub> was taking place. During purging with nitrogen, some weakly bound NH<sub>3</sub> was desorbed, but no NO<sub>2</sub> was detected. Then TPD was performed under two different desorption conditions. Fast desorption under dry conditions (Figure 7.6) resulted in the detection of substantial amounts of NH<sub>3</sub>, NO<sub>2</sub> and N<sub>2</sub>O, while slow desorption under humid conditions (Figure 7.7) revealed the formation of NH<sub>3</sub>, NO<sub>2</sub> and HNO<sub>3</sub>.



**Figure 7.6:** Fast TPD under dry conditions (N<sub>2</sub> flow). 3 g of catalyst, flow rate 300  $l_N/h$ , heating ramp ~ 28 °C/min. (x) NO<sub>2</sub>, ( $\Box$ ) NH<sub>3</sub>, ( $\blacktriangle$ ) N<sub>2</sub>O, (solid line) T.



**Figure 7.7:** Slow TPD under humid conditions (2.5% H<sub>2</sub>O in N<sub>2</sub> flow). 3 g of catalyst, flow rate 300  $l_N/h$ , heating ramp ~ 12 °C/min. (x) NO<sub>2</sub>, ( $\Box$ ) NH<sub>3</sub>, (•) HNO<sub>3</sub>, ( $\blacktriangle$ ) N<sub>2</sub>O, (solid line) T.

These results suggest that during HNCO hydrolysis in the presence of NO<sub>2</sub>, part of the NO<sub>2</sub> and NH<sub>3</sub> was stored on the catalyst, while another portion reacted yielding ammonium nitrate by reaction (7.1), as previously reported for V<sub>2</sub>O<sub>5</sub>/WO<sub>3</sub>-TiO<sub>2</sub> SCR catalysts [*Koebel et al. (2002a*); *Koebel et al. (2001); Madia et al. (2002)*].

$$2NH_3 + 2NO_2 \rightarrow NH_4NO_3 + N_2 + H_2O \tag{7.1}$$

Although  $NH_4NO_3$  is stable under at room temperature, it undergoes different decomposition reactions when the temperature is raised. Thereby, the decomposition products depend on the conditions used [*Koebel et al. (2002a); Gerhartz (1985)*].

• Decomposition to N<sub>2</sub>O and H<sub>2</sub>O are expected above 200 °C during fast heating under dry conditions:

$$NH_4NO_3 \to N_2O + 2H_2O \tag{7.2}$$

• Dissociation to HNO<sub>3</sub> and NH<sub>3</sub> above 169 °C during slow heating under wet conditions:

$$NH_4NO_3 \rightarrow HNO_3 + NH_3$$
 (7.3)

The results of the combined TR and TPD experiments support these two decomposition paths. Under dry conditions and a fast heating rate NH<sub>3</sub> desorbed immediately when increasing the temperature, in agreement with the onset of the NH<sub>3</sub> peak in Figure 7.1. At 200 °C the evolution of N<sub>2</sub>O was detected as expected from the decomposition temperature of NH<sub>4</sub>NO<sub>3</sub> by reaction (7.2). At T > 250 °C NO<sub>2</sub> started to desorb in substantial amounts, in agreement with the NO<sub>2</sub> desorption peak in Figure 7.4. Under humid conditions and a slow heating rate the evolution of NH<sub>3</sub> and NO<sub>2</sub> was again observed. However, the amount of N<sub>2</sub>O desorbed was drastically reduced and at T  $\geq$  350 °C the evolution of HNO<sub>3</sub> was detected. Moreover, the amount of NH<sub>3</sub> desorbed was higher than in the case of fast and dry desorption, indicating that ammonium nitrate was decomposed via reaction (7.3). The delayed desorption of HNO<sub>3</sub> compared to NH<sub>3</sub> show that HNO<sub>3</sub> is more strongly bound and requires a higher desorption temperature. Since no accurate calibration spectra for HNO<sub>3</sub> could be acquired, the calculation of mass balances for the formation and decomposition of ammonium nitrate was not possible.

#### 7.4.3 DRIFT experiments

More details about the HNCO hydrolysis in the presence of NO<sub>2</sub> could be revealed by DRIFT experiments. Figure 7.8 shows the IR bands formed during HNCO hydrolysis on TiO<sub>2</sub>. As already observed in Chapter 6, the introduction of HNCO and H<sub>2</sub>O on the sample results in the appearance of bands which are characteristic for ammonia coordinatively bound to Lewis acid sites (3382, 3268, 3158, 1599 and 1177 cm<sup>-1</sup>) and characteristic for adsorbed water (1630 cm<sup>-1</sup> and broad band between 2500 and 3600 cm<sup>-1</sup>). A small –NCO band at 2204 cm<sup>-1</sup> (with a shoulder at 2170 cm<sup>-1</sup>) was also visible. This band was very small due to the reactivity of the –NCO species in the presence of water. Additional small bands due to formation of formate species were also formed (2954, 2863, 1561 and 1357 cm<sup>-1</sup>).



**Figure 7.8:** DRIFT spectra of the adsorbed species during HNCO hydrolysis on  $TiO_2$  at 150 °C. 25 mg of catalyst. Adsorption of 80 ppm of HNCO in the presence of 200 ppm H<sub>2</sub>O and 10% O<sub>2</sub> at 150 °C.

The addition of NO<sub>2</sub> (Figure 7.9) led to the appearance of additional peaks. Bands at 1491 and 1469 cm<sup>-1</sup> were formed together with bands at 1574, 1322 and 1257 cm<sup>-1</sup>. The regions around the bands at 1469 and 1322 cm<sup>-1</sup> suggest the presence of further underlying bands, e.g. at 1430 cm<sup>-1</sup> and a shoulder to the right of the band at 1322 cm<sup>-1</sup>, which are masked by larger signals.



**Figure 7.9:** DRIFT spectra of the adsorbed species arising during HNCO hydrolysis on TiO<sub>2</sub> at 150 °C in the presence of NO<sub>2</sub>. 25 mg of catalyst, adsorption of 80 ppm of HNCO in the presence of 200 ppm H<sub>2</sub>O, 100 ppm NO<sub>2</sub> and 10% O<sub>2</sub> at 150 °C.

According to Hadjiivanov, NO<sub>2</sub> gives rise to an absorption band in the 1642-1605 cm<sup>-1</sup> region when adsorbed molecularly on oxide surfaces [*Hadjiivanov (2000)*]. However, NO<sub>2</sub> is known to interact with the OH groups present on the surface of TiO<sub>2</sub> yielding nitrate species [*Ramis et al. (1990b); Hadjivanov et al. (1994); Hadjiivanov (2000)*], which is easily explained in view of the pronounced hydrophilic properties of the NO<sub>2</sub> molecule that favor reaction (7.4):

$$2(-OH) + 3NO_2 \rightarrow 2(-NO_3) + H_2O + NO \tag{7.4}$$

Therefore, the growth of nitrate bands is usually accompanied by the development of a negative band in the OH stretching region. Nitrates can adsorb in monodentate, bidentate or bridged form on Ti<sup>4+</sup> sites of TiO<sub>2</sub> anatase, because Ti<sup>4+</sup> sites with different coordination numbers (one or two vacancies) are present on the surface (Chapter 4). Surface nitrates have usually  $C_{2y}$ symmetry, whereby the asymmetric stretching mode  $(v_3)$  splits in two bands [*Nakamoto (1986)*]. The position of the two components of the  $v_3$  vibration can be used as a rough guide to determine the type of nitrates present on the surface. In general monodentate nitrates have a high wavenumber component between 1570 and 1460 cm<sup>-1</sup>, bidentate nitrates between 1600 and 1500 cm<sup>-1</sup> and bridged nitrates between 1660 and 1590 cm<sup>-1</sup> The second band associated with the lower wavenumber component should appear in the 1330-1220 cm<sup>-1</sup> region [Busca et al. (1981)]. Coordinated nitrate ions exhibit an additional band near 1000 cm<sup>-1</sup> due to the symmetric stretching mode. However, due to the strong bulk adsorption of TiO<sub>2</sub> below 1000 cm<sup>-1</sup>, this band cannot be detected. Moreover, in view of the fact that adsorbed ammonia, water and nitrate species adsorb in the same region, it was not always possible to observe well-resolved bands. Considering the position, the thermal stability and the frequency difference the bands at 1491 and 1322 cm<sup>-1</sup> are attributed to monodentate nitrates and the bands at  $1574 \text{ cm}^{-1}$  and  $1257 \text{ cm}^{-1}$  to bidentate nitrates. The first two bands showed lower thermal stability and were completely removed at 400 °C, as expected for monodentate nitrate, while the other two bands required a temperature increase up to 450 °C to disappear, as expected for bidentate species. Also the band at 1599 cm<sup>-1</sup> required a treatment at 450 °C to be removed. This is in contrast with ammonia adsorption experiments (Chapter 4) that proved the disappearance of the NH<sub>3</sub> band at 1599 cm<sup>-1</sup> already at 400 °C. This suggests an overlay of the NH<sub>3</sub> band with a nitrate band at the same position, which is stable up to 450 °C. This band is attributed to bridged or bidentate nitrates, whose lower component is covered by the band at 1322 cm<sup>-1</sup>, characteristic for monodentate nitrates. The band at 1469 cm<sup>-1</sup> is assigned to the asymmetric deformation mode of ammonium ions. These ions are formed when ammonia adsorbs on Brønsted acid sites, which might be generated on the catalyst by the presence of nitrate ions according to Ramis et al. [Ramis et al. (1990b)] and Hadjiivanov et al. [Hadjivanov et al. (1994)]. This implies that surface-bound ammonium nitrate was formed on the catalyst. Besides, the shape of the band at 1469 cm<sup>-1</sup> suggests the formation of another weak band around 1430 cm<sup>-1</sup>. This band could be generated by nearly symmetrical nitrate ions [*Ramis et al.*] (1990b)] as would be expected for bulk ammonium nitrate.

#### 7.5 Discussion

At temperatures below 200 °C the activity of TiO<sub>2</sub> and Fe-ZSM5 towards the HNCO hydrolysis is strongly influenced by the presence of NO<sub>2</sub> in the gas feed. A more detailed investigation on TiO<sub>2</sub> demonstrated how this compound affects the catalytic activity. Combined TR and TPD investigations as well as DRIFT experiments demonstrated that NO<sub>2</sub> adsorbs stably on the surface and starts to desorb quantitatively at T > 250 °C. By means of DRIFT investigations it has been observed that the adsorption of nitrogen dioxide proceeds by the formation of nitrate ions coordinated to the catalyst surface. The adsorption of ammonia in the presence of water does not result in the formation of ammonium ions on titania (Chapter 4). However, the presence of  $NO_3^-$  ions on the surface generates sites, on which  $NH_3$  can adsorb in form of  $NH_4^+$  ions. As a consequence, a kind of surface ammonium nitrate is formed, which differs in some spectroscopic features from bulk ammonium nitrate as described in section 7.4.3. The formation of nitrates results from interaction of  $NO_2$  with the hydroxyl groups present on the catalyst surface, as shown in reaction (7.4). This interaction is further promoted both by the water produced via reaction (7.4) and by the water present in the inlet feed. Despite the fact that water is known to adsorb on TiO<sub>2</sub> anatase mainly in molecular form, some dissociative adsorption also occurs, creating hydroxyl groups [Hadjiivanov et al. (1996)].

The surface nitrate ions are coordinated with the Ti ions of TiO<sub>2</sub>. However, isocyanic acid adsorbs on the same sites to form Ti–NCO species. Assuming that the HNCO catalytic hydrolysis occurs via these species as proposed in Chapter 6, the presence of NO<sub>2</sub> in the feed decreases the catalytic activity due to a competitive adsorption of NO<sub>2</sub> and HNCO. In addition, DRIFT investigation proved the formation of small amounts of solid NH<sub>4</sub>NO<sub>3</sub>, which can deposit on the pores of the catalyst physically blocking the active sites and hence decreasing the activity. Ammonium nitrate could be produced by reaction of NO<sub>2</sub> and NH<sub>3</sub> (7.1) as already observed for vanadia based SCR catalysts [*Koebel et al. (2001); Koebel et al. (2002a); Madia et al. (2002)*]. Since vanadia-based SCR catalysts consist mainly of titania, the formation of ammonium nitrate over titania alone is obvious. The NO<sub>2</sub> inhibition effect is most pronounced at low temperatures since NO<sub>2</sub> adsorption and the reaction between NO<sub>2</sub> and NH<sub>3</sub> to give NH<sub>4</sub>NO<sub>3</sub> become more important at low temperatures. Nevertheless, the deactivation is not permanent, since the surface and bulk ammonium nitrate species decompose for T > 200 °C, and NO<sub>2</sub> desorbs completely if the tem-

perature is increased up to 450 °C. An extended treatment of the catalyst at 450 °C completely recovers the catalytic activity.

#### 7.6 Conclusions

The low temperature catalytic activity of TiO<sub>2</sub> and Fe-ZSM5 for the hydrolysis of isocyanic acid decreases considerably in the presence of NO<sub>2</sub> in the gas feed. The NO<sub>2</sub> deactivation increases for lower temperatures, which poses a problem for practical applications since NO<sub>2</sub> is usually produced in a pre-oxidation catalyst upstream of the SCR system in order to enhance the SCR reaction. The decrease in activity is explained by the adsorption of NO<sub>2</sub> on the surface, which creates stable NO<sub>3</sub><sup>-</sup> species decreasing the number of free active sites. The nitrate ions itself create Brønsted acid sites which adsorb ammonia in the form of ammonium ions, thus, creating stable surface ammonium nitrate. Moreover, the formation of small amounts of bulk ammonium nitrate was evident. However, the deactivation is not permanent and a treatment of the catalyst at 450 °C in N<sub>2</sub> and O<sub>2</sub> completely recovered the catalytic activity due to NO<sub>2</sub> desorption and NH<sub>4</sub>NO<sub>3</sub> decomposition.

The experiments to evaluate in detail the role of  $NO_2$  on the catalyst deactivation were performed on TiO<sub>2</sub>. However, the deactivation observed for the Fe-ZSM5<sub>1</sub> sample likely occurs in the same way.

# **8** Influence of NH<sub>3</sub>, NO and SO<sub>2</sub>

#### **8.1 Introduction**

The hydrolysis properties of  $TiO_2$  and Fe-SZM5 were studied in the presence of NH<sub>3</sub>, NO and SO<sub>2</sub>, since these are typical components of diesel exhaust gases.

At low temperatures NH<sub>3</sub> was observed to inhibit the hydrolysis reaction on V<sub>2</sub>O<sub>5</sub>-WO<sub>3</sub>/TiO<sub>2</sub> [*Kleemann et al.* (2000)] and the SCR reaction on H-ZSM5 [*Eng et al.* (1997); *Stevenson et al.* (2000)] and V<sub>2</sub>O<sub>5</sub>-WO<sub>3</sub>/TiO<sub>2</sub> [*Nova et al.* (2000)], due to co-adsorption on the surface. Moreover, at high temperatures NH<sub>3</sub> is known to oxidize on Fe-ZSM5, which might result in a consumption of part of the NH<sub>3</sub> produced by the HNCO hydrolysis [*Huang et al.* (2002)]. On the contrary, NO had a positive effect on the hydrolysis properties of V<sub>2</sub>O<sub>5</sub>-WO<sub>3</sub>/TiO<sub>2</sub> at low temperatures [*Kleemann et al.* (2000)].

The negative effect of SO<sub>2</sub> on SCR catalysts is well known [*Dunn et al.* (1998); Forzatti (2001)]. Sulfur dioxide is formed from the oxidation of sulfur contained in diesel fuels. The catalytic oxidation of SO<sub>2</sub> can generate SO<sub>3</sub>. Ammonia readily combines with sulfur trioxide at temperatures below 250 °C to form ammonium sulfate, which may then be deposited on the catalyst surface at temperatures below 250 °C [*Bosch et al.* (1988)]. A catalyst able to suppress the oxidation of sulfur dioxide to sulfur trioxide would allow lower operating temperatures without the need to worry about this production and deposition of ammonium sulfate. TiO<sub>2</sub> anatase is known to be only weakly and reversibly sulfated in the presence of SO<sub>2</sub> and oxygen [*Forzatti* (2001)] and, as mentioned in Chapter 3 (section 3.3.1), a test on its hydrolysis properties performed in the presence of SO<sub>2</sub> did not show any relevant effect. Therefore, the influence of SO<sub>2</sub> on the catalytic activity was not further investigated.

#### 8.2 Experimental

The influence of NH<sub>3</sub> on the HNCO hydrolysis was investigated by FTIR measurements of the catalyst activity and by DRIFT spectroscopy.

The DRIFT investigation of the influence of  $NH_3$  on the HNCO adsorption on  $TiO_2$  was performed by pre-saturating the sample with 200 ppm  $NH_3$  in  $N_2$  for 30 min at 150 °C. Then ~ 70 ppm of HNCO (in  $N_2$ ) were adsorbed at the same temperature for 15 min before measuring the spectrum.

The catalytic performance of TiO<sub>2</sub> was tested in the plug-flow glass micro-reactor (Chapter 2, section 2.1.3.2). The overall gas flow rate was 200  $l_N/h$  (GHSV ~ 2·10<sup>6</sup> h<sup>-1</sup>) and about 150 mg of catalyst (particle size 160-200 µm) were used. The activity of the Fe-ZSM5<sub>1</sub> sample in the presence of NO and NH<sub>3</sub> was tested in the plug-flow steel micro reactor (Chapter 2, section 2.1.3.3) in order to compare the results with previous investigations on V<sub>2</sub>O<sub>5</sub>-WO<sub>3</sub>/TiO<sub>2</sub> [*Kleemann et al.* (2000)]. About 120 mg of catalyst with a flow rate flow rate of 200  $l_N/h$  (GHSV ~ 10<sup>6</sup> h<sup>-1</sup>) was used. The influence of SO<sub>2</sub> on Fe-ZSM5<sub>1</sub> was investigated on the monolithic catalyst (prepared as described in Chapter 3, section 3.2.2). A flow rate flow rate of 400  $l_N/h$  (GHSV ~ 52000 h<sup>-1</sup>) was used. All experiments were performed with a feed gas containing ~1000 ppm HNCO, 10% O<sub>2</sub>, 2.5% H<sub>2</sub>O and N<sub>2</sub> balance. The influence of NH<sub>3</sub> and NO was tested by dosing 1000 ppm NH<sub>3</sub> or 100 ppm NO to the inlet flow. The experiments were performed in the tem-

perature range 100-450 °C. The influence of SO<sub>2</sub> was investigated by pre-treating the sample for 2 h in a flow of 200 ppm SO<sub>2</sub>, 10% O<sub>2</sub> and balance N<sub>2</sub>. The hydrolysis reaction was then carried out as described above.

#### 8.3 Results: TiO<sub>2</sub> anatase

#### 8.3.1 Influence of NH<sub>3</sub> and NO on the catalytic activity

Figure 8.1 compares the hydrolysis activity of  $TiO_2$  with and without  $NH_3$  in the inlet flow. The presence of NO on the inlet feed did not show a significant effect on the catalytic activity of  $TiO_2$  and is therefore not shown.



**Figure 8.1:** Hydrolysis of HNCO to NH<sub>3</sub> over TiO<sub>2</sub>. Powder samples (150 mg). Flow rate =  $200 l_N/h$ , inlet flow composed of ~ 1000 ppm HNCO, 10% O<sub>2</sub>, 2.5% H<sub>2</sub>O, 0-1000 ppm NH<sub>3</sub> and N<sub>2</sub> balance. (**■**) Without NH<sub>3</sub> and (**□**) in the presence of 1000 ppm NH<sub>3</sub>.

 $NH_3$  in the inlet flow did not influence the conversion from 175 to 450 °C, but at lower temperatures the ammonia yield was decreased. The effect became more pronounced at low tem-

peratures. This result agrees with that observed by Kleemann et al. for the  $V_2O_5$ -WO<sub>3</sub>/TiO<sub>2</sub> catalyst [*Kleemann et al.* (2000)].

#### 8.3.2 DRIFT investigation of the HNCO/NH<sub>3</sub> competitive adsorption

The adsorption of isocyanic acid on  $TiO_2$  was investigated with and without pre-adsorbed NH<sub>3</sub> (Figure 8.2). The spectra show that the –NCO bands formed after HNCO adsorption (2209 and 2174 cm<sup>-1</sup>) were much higher on the NH<sub>3</sub>-free surface, indicating that HNCO and NH<sub>3</sub> adsorb on the same surface sites. For a clearer representation Figure 8.2 shows only the isocyanate peaks region. However, it is important to mention that the DRIFT spectrum also revealed that no additional by-products were formed.



**Figure 8.2:** DRIFT spectra of TiO<sub>2</sub> after HNCO adsorption (70 ppm) at 150 °C for 15 min on a ( $\cdots$ ) fresh and (–) NH<sub>3</sub> pre-treated sample.

The drastically decreased amount of isocyanate species detected on the NH<sub>3</sub> covered titania sample substantiates the idea that HNCO and NH<sub>3</sub> adsorb on the same sites. Considering that adsorption of ammonia on TiO<sub>2</sub> anatase occurs mainly on Ti<sup>4+</sup> sites (Chapter 4), this result further confirms that the sites for the dissociative adsorption of HNCO are the Ti<sup>4+</sup> cations of titania, as proposed in Chapter 4. Another reason for the lowered HNCO adsorption could be the reaction with pre-adsorbed NH<sub>3</sub>. However, this explanation is unlikely, because no new additional product peaks were observed during adsorption. This spectroscopic result and the deduced picture of the co-adsorption of NH<sub>3</sub> and –NCO species on the same active sites agree with the reduced HNCO conversion over TiO<sub>2</sub> in the presence of NH<sub>3</sub> shown in Figure 8.1. This effect is predominant at low temperatures, when ammonia adsorbs more stably on the surface thus blocking the active sites of TiO<sub>2</sub>. In this respect, the general decrease in conversion for low temperatures might be due also to the slow desorption of the ammonia produced by HNCO hydrolysis.

#### 8.4 Results: Fe-ZSM5<sub>1</sub>

#### 8.4.1 Influence of NH<sub>3</sub> and NO on the catalytic activity

The results of the investigations on the influence of  $NH_3$  and NO on the hydrolysis properties of Fe-ZSM5<sub>1</sub> are combined in Figure 8.3. All results are expressed as HNCO conversion instead of  $NH_3$  yield, because in some experiments the  $NH_3$  produced from HNCO hydrolysis reacts further with NO in the standard SCR reaction (1.1):

$$4NO + 4NH_3 + O_2 \rightarrow 4N_2 + 6H_2O \tag{1.1}$$

In the presence of 1000 ppm of NO in the inlet flow, the HNCO conversion increased at low temperature. On the contrary, 1000 ppm of NH<sub>3</sub> resulted in a reduced HNCO conversion at low temperature, which again supports the conclusion of a competitive adsorption of NH<sub>3</sub> and HNCO. The positive effect of NO is attributed to the occurrence of the SCR reaction (1.1), which reduces the amount of NH<sub>3</sub> adsorbed on the surface. If NH<sub>3</sub> and HNCO adsorb on the same surface sites, a reduction of NH<sub>3</sub> on the surface directly results in an increase of the HNCO conversion, since a higher number of active sites are available for HNCO adsorption. The influence of NO and NH<sub>3</sub> at higher temperatures might have been masked by the higher overall conversion level.



**Figure 8.3:** Hydrolysis of HNCO to NH<sub>3</sub> over Fe-ZSM5<sub>1</sub>. Powder samples (120 mg). Flow rate = 200  $l_N/h$ , inlet flow composed of ~ 1000 ppm HNCO, 10% O<sub>2</sub>, 2.5% H<sub>2</sub>O, 0-1000 ppm NH<sub>3</sub> and N<sub>2</sub> balance. (**■**) Without NH<sub>3</sub> and NO<sub>2</sub>, (**●**) in the presence of 1000 ppm NO and (**▲**) in the presence of 1000 ppm NH<sub>3</sub>.

#### 8.4.2 Influence of SO<sub>2</sub>

Figure 8.4 shows the influence of  $SO_2$  on the hydrolysis properties of Fe-ZSM5<sub>1</sub>. The NH<sub>3</sub> yield varied only slightly after pre-treatment with  $SO_2$ , which is in agreement with the low activity of Fe-ZSM5 for the oxidation of  $SO_2$  to  $SO_3$  [*Long et al.* (1999)].



**Figure 8.4:** Hydrolysis of HNCO to NH<sub>3</sub> over Fe-ZSM5<sub>1</sub>. Test on monolithic sample (active mass ~ 0.8 g). Flow rate =  $200 l_N/h$ , inlet flow composed of ~ 1000 ppm HNCO,  $10\% O_2$ ,  $2.5\% H_2O$ , and N<sub>2</sub> balance. (**■**) Fresh catalyst and ( $\Box$ ) SO<sub>2</sub> treated catalyst.

#### **8.5** Conclusions

 $NH_3$  reduced the activity of  $TiO_2$  anatase and Fe-ZSM5 for the HNCO hydrolysis. This effect is attributed to the competitive adsorption of HNCO and  $NH_3$  on the active sites.

The catalytic activity of Fe-ZSM5 for the HNCO hydrolysis increased in the presence of NO in the inlet feed. This effect is attributed to the partial removal of adsorbed  $NH_3$  from the surface by the standard SCR reaction, thereby freeing the HNCO adsorption sites. No similar effect was observed for TiO<sub>2</sub> in agreement with the negligible SCR properties of this material.

The catalytic properties of both TiO<sub>2</sub> and Fe-ZSM5 were nearly not influenced by SO<sub>2</sub>.

## 9

### Kinetics of the HNCO Hydrolysis

#### 9.1 Introduction

#### 9.1.1 Analysis methods

The reaction rate of the HNCO consumption as a function of reactant concentrations can be expressed simply as a power-law rate equation (9.1) (symbols are listed at the end of the section).

$$r_{HNCO} = -k_a [HNCO]^{\alpha} [H_2 O]^{\beta} [NH_3]^{\delta} [CO_2]^{\gamma}$$
(9.1)

Equation (9.1) can also be written in logarithmic form (9.2):

$$-\ln r_{HNCO} = \ln k_a + \ln[HNCO]^{\alpha} + \ln[H_2O]^{\beta} + \ln[NH_3]^{\delta} + \ln[CO_2]^{\gamma}$$
(9.2)

The reaction orders can be determined by systematically varying the initial concentrations of the reactants. The reaction is run by over-supplying 3 of the components, which being in excess can be considered as constant. Only the remaining component is varied, thus allowing the determination of its reaction order. For instance, to determine the reaction order with the respect of HNCO ( $\alpha$ ) the reaction is carried out with an excess of H<sub>2</sub>O, NH<sub>3</sub> and CO and reaction (9.1) and (9.2) become:

$$r_{HNCO} = -k_{obs} [HNCO]^{\alpha}$$
(9.3)

$$-\ln r_{HNCO} = (\ln k_a + \ln[H_2O]^{\beta} + \ln[NH_3]^{\delta} + \ln[CO_2]^{\gamma}) + \ln[HNCO]^{\alpha} =$$
(9.4)  
$$= \ln k_{obs} + \ln[HNCO]^{\alpha} = \ln k_{obs} + \alpha \ln[HNCO]$$

being  $k_{obs}$  = pseudo rate constant =  $k_a [H_2 O]^{\beta} [NH_3]^{\delta} [CO_2]^{\gamma}$ 

The reaction order can be determined from the slope of the logarithm of the reaction rate plotted as a function of the logarithm of the HNCO concentration Figure 9.1.



Figure 9.1: Plot used for the determination of the reaction order  $\alpha$ .

The reaction rate can be determined experimentally by operating the plug flow reactor in the differential mode. This is the case when the reactant concentration through the bed can be considered essentially constant, i.e. the conversion is small, the reactor is homogeneous and the reaction rate is spatially uniform within the bed. This allows modeling the reactor as a CSTR and to calculate the reaction rate using the design equation of a CSTR reactor (9.5).

being i = HNCO for this study.

The activation energy can be calculated using the reaction orders. If experiments are performed with the plug flow reactor operated in the integral mode, large conversions are permitted and the reaction rate can be expressed using the typical plug-flow reactor design equation (9.6):

$$r_{i} = \frac{dF_{i}}{dW} = -\frac{F_{in}dX}{dW}$$
(9.6)

being i = HNCO for this study.

Combining equation (9.1) and (9.6) it is possible to calculate the rate constant  $k_a$ . The rate constant can also be expressed as a function of temperature using the Arrhenius equation (9.7):

$$k_a = A \exp(-\frac{E_{att}}{RT}) \tag{9.7}$$

which in logarithmic form becomes:

$$\ln k_a = \ln A - \frac{E_{att}}{R} \cdot \frac{1}{T}$$
(9.8)

From the reaction rate constant  $k_a$  at different temperatures the activation energy is determined by plotting the logarithm of the rate constants against the inverse temperature. The slope of this plot (Arrhenius plot) is equal to  $-E_{att}/R$ .

#### 9.1.2 Symbols

 $r_i$  = reaction rate [mol/gs]

- $F_{i_{m}}$  = molar flow rate at the inlet [mol/s]
- $F_{i_{men}}$  = molar flow rate at the outlet [mol/s]

 $[i]_{in}$  = concentration of a component i at the inlet [mol/cm<sup>3</sup>]

 $[i]_{out}$  = concentration of a component i at the outlet [mol/cm<sup>3</sup>]

$$W = \text{catalyst weight } [g]$$

- $V^*$  = volumetric flow rate at actual conditions [cm<sup>3</sup>/s]
- $k_a$  = apparent rate constant
- $\alpha$  = reaction order for HNCO
- $\beta$  = reaction order for H<sub>2</sub>O
- $\delta$  = reaction order for NH<sub>3</sub>
- $\gamma$  = reaction order for CO<sub>2</sub>
- X = HNCO conversion
- *A* = pre-exponential factor
- $E_{att}$  = activation energy [kJ/mol]
- R = gas constant = 8.314 [J/kmol]
- T = temperature [K]

#### 9.1.3 Review of the analysis method

The use of the differential method is the simplest way to provide the order of reaction with respect to reactant and products. However, this method presents some limitations:

- since the conversions are small, large errors in analysis can occur,
- if the catalyst under investigation decays rapidly, the reaction rate parameters at the start of a run will be different from those at the end of the run,

if the catalyst is very active, as in the case of  $TiO_2$ , large dilution is needed in order to reduce the conversion However, the excessive dilution of the catalyst may negatively influence the conversion due to local bypassing of the catalyst [*Berger et al. (2002a); Berger et al. (2002b)*].

The experiments reported in this chapter were repeated several times, showing only a partial reproducibility of the conversion obtained (variation in the order of  $\pm 10\%$ ). However, the trend of the conversion as a function of temperature proved to be very reproducible, thus lending reliability to the reaction orders obtained. The low reproducibility of the conversion can be attributed to differences in the distribution of the mixture catalyst/diluents. Due to the high activity of TiO<sub>2</sub>, small variations of the catalyst distribution inside the bed (with the eventuality of local bypassing of the catalyst) can generate large deviation in the conversion. In order to limit this effect very high dilutions were not tested.

Due to the limited dilution applied and the need for low conversion, high temperatures (175 °C) could not always be tested (depending on the reactants' concentration). The experiments performed resulted in a conversion  $\leq 30\%$ . The conversion might be further lowered by increasing the flow rate or decreasing the reaction temperature. However, flow rates higher than 300 l<sub>N</sub>/h resulted in a unacceptable increase of the pressure drop. The use of very low temperatures also poses some problems, since additional reactions can take place (e.g, reaction between HNCO and NH<sub>3</sub>, HNCO polymerization). For that reason, the investigation of the reaction orders was performed primarily at 150 °C, with only few tests carried out at lower temperatures.

#### 9.2 Determination of the reaction orders

The experiments with the differential reactor were performed diluting the catalyst bed with SiC. This material proved to have no effect on the HNCO hydrolysis. Different concentrations and different temperatures were tested so as to obtain an acceptably low HNCO conversion (< 30%). More details on the procedures used are given in the following paragraphs.

#### 9.2.1 Reaction order for $CO_2(\gamma)$

Several tests performed with  $CO_2$  showed that carbon dioxide had no influence on the reaction rate, indicating that the  $CO_2$  reaction order is 0.

#### 9.2.2 Reaction order for $NH_3(\delta)$

For determining the reaction order with respect to  $NH_3$  ( $\delta$ ), 150 mg of  $TiO_2$  were diluted in 100 mg of SiC (particle size 160-200 µm). The concentration of HNCO and H<sub>2</sub>O were kept constant at 1000 ppm and 2.5 %, respectively, while the concentration of  $NH_3$  was varied from 200 to 1000 ppm. The flow rate was held at 300  $I_N/h$ . CO<sub>2</sub> was not dosed since no influence on the HNCO conversion was observed.

Reaction orders were obtained at different temperatures. The experimental results for the rate of HNCO consumption as a function of the ammonia inlet concentration from 125 to150 °C are presented in Figure 9.2.



**Figure 9.2:** Logarithmic plot of the measured reaction rated as function of the NH<sub>3</sub> inlet concentration. 50 mg of TiO<sub>2</sub>. ( $\Delta$ ) 150 °C, ( $\Box$ ) 135 °C and ( $\circ$ ) 125 °C. Linear regression was performed with EXCEL.

For each data set, the coefficient of determination,  $R^2$ , exhibits a good linear fit between the reaction rate and reactants' concentration. It is interesting to note that the rate of reaction measured at 125 °C and 135 °C decreases slightly for increasing NH<sub>3</sub> concentration, revealing an 'inhibition effect' of ammonia, due to the adsorption of ammonia on the catalyst surface. This inhibition becomes more significant at lower temperatures, where ammonia adsorption is favored. However, for T = 150 °C this effect became very small and the reaction rate remain constant. From the slope of the regression line, activation orders of 0.29, 0.16 and 0.08 were obtained at 125, 135 and 150 °C, respectively.

An additional test performed at 175 °C with 25 mg of catalyst (bed of 150 mg total) showed that the influence of  $NH_3$  on the reaction rate is further reduced at this temperature. This leads to the conclusion that the reaction order of  $NH_3$  can be approximated as 0 for T > 150 °C.

#### **9.2.3 Reaction order for HNCO (α)**

For determining the reaction order with respect to HNCO ( $\alpha$ ), the concentration of H<sub>2</sub>O was held at 2.5%, while the concentration of HNCO was varied from 400 to 1000 ppm. The reaction order was determined at 150-175 °C. In consideration of the results reported in section 9.2.2 (reaction order of ammonia = 0 for T > 150 °C), no ammonia was dosed. This also reduces the risk of by-product formation from the reaction between HNCO and NH<sub>3</sub>. For the tests at 150 °C, 50 mg of TiO<sub>2</sub> were diluted in 100 mg of SiC. For the tests at 175 °C further dilution was needed in order to keep the conversion low. Therefore 25 mg of catalyst were diluted in 100 mg of SiC. The particle size was 160-200 µm and the flow rate was held at 300 l<sub>N</sub>/h. The experimental results of the rate of HNCO consumption as a function of HNCO concentration are graphically presented in Figure 9.3. The coefficient of determination, R<sup>2</sup>, shows an excellent linear fit. From the slope of the regression curves, activation orders of 0.92 and 0.97 were obtained at 175 and 150 °C, respectively.



**Figure 9.3:** Logarithmic plot of the measured reaction rate as function of the HNCO inlet concentration. ( $\Box$ ) 150 °C, 50 mg of TiO<sub>2</sub>( $\Delta$ ) 175 °C, 25 mg of TiO<sub>2</sub>. Linear regression was performed with EXCEL.

#### 9.2.4 Reaction order for $H_2O(\beta)$

For determining the reaction order of water ( $\beta$ ), 150 mg of TiO<sub>2</sub> were diluted in 100 mg of SiC (particle size 160-200 µm). HNCO was held at ~ 1000 ppm, while the concentration of H<sub>2</sub>O was varied from 150 to 1000 ppm. The flow rate was fixed at 300 l<sub>N</sub>/h. The experimental results in the temperature range 150-175 °C are presented in Figure 9.4. The coefficient of determination, R<sup>2</sup>, shows an excellent linear fit. From the slope of the regression lines, activation orders of 1.09 were obtained at 175 and 150 °C.

For typical diesel exhaust conditions, i.e. in the presence of excess of water,  $H_2O$  showed only negligible influence on the reaction. This indicates that in this case the surface of TiO<sub>2</sub> is covered with water and that the reaction order  $\beta$  can be approximated to 0.



**Figure 9.4:** Logarithmic plot of the measured reaction rated as function of the water inlet concentration. 50 mg of TiO<sub>2</sub>. ( $\Delta$ ) 150 °C, ( $\circ$ ) 175 °C. Linear regression was performed with EXCEL.

#### 9.2.5 Reproducibility of the data

In the previous sections only one test is shown, however experiments were repeated several times which always resulted in comparable activation orders. The following list summarizes the average of three measurements of the NH<sub>3</sub> reaction order plus the average of two measurements each for the HNCO and the water reaction orders:

-NH <sub>3</sub> reaction order $(\delta)$ at	125 °C: -0.26 ± 0.03
	135 °C: -0.17 ± 0.03
	150 °C: -0.08 ± 0.01
-HNCO reaction order (a) at	150 °C: 0.93 ± 0.06
	175 °C: 0.95 ± 0.04

-H<sub>2</sub>O reaction order (β) at 150 °C: 1.04 ± 0.07 175 °C: 1.19 ± 0.16

#### 9.3 Activation energy under typical diesel exhaust conditions

Summarizing the results of the previous sections, in the presence of an excess of water the reaction can be considered to be first order with respect to HNCO and zeroth order with respect to H<sub>2</sub>O, NH<sub>3</sub> and CO<sub>2</sub> in the temperature interval 150-175 °C. With these assumptions the reaction equation (9.2) can be written:

$$r_{HNCO} = -k_a [HNCO] \tag{9.8}$$

The activation energy can be determined under typical diesel exhaust conditions by combination of equation (9.8) with the design equation of the ideal plug flow reactor (9.5):

$$k_{mass} = -\frac{F_{HNCO}^0}{\left[HNCO\right]_0 W} \ln(1-X)$$
(9.9)

with  $k_{mass}$  = reaction rate constant [cm<sup>3</sup>/gs]  $F_{HNCO}^{0}$  = molar HNCO feed rate [mol/s] [HNCO]<sub>0</sub> = molar HNCO concentration at the inlet [mol/cm<sup>3</sup>] W = catalyst weight [g] X = HNCO conversion

To calculate the activation energy the HNCO conversion was tested over 50 mg of catalyst diluted in 100 mg of SiC (particle size 160-200  $\mu$ m) in the temperature range 150-200 °C. The flow rate was set to 300 l<sub>N</sub>/h and the inlet feed was composed of 1000 ppm HNCO, 10% O<sub>2</sub>, 2.5 % H<sub>2</sub>O and balance N<sub>2</sub>. The obtained HNCO conversion is plotted versus the temperature in Figure 9.5.



**Figure 9.5:** HNCO conversion over  $TiO_2$  as function of temperature. 50 mg of catalysts diluted in 100 mg SiC, flow rate =  $300 l_N/h$ , inlet flow composition: 1000 ppm HNCO, 2.5% H<sub>2</sub>O, 10% O<sub>2</sub> and N<sub>2</sub> balance.

The Arrhenius plot of the natural logarithm of  $k_{mass}$  as function of the inverse temperature is shown in Figure 9.6. From the slope of this line, and activation energy of ~ 44 kJ/mol was obtained.



Figure 9.6: Arrhenius plot of the natural logarithm of  $k_{mass}$  as function of the inverse temperature. Linear regression was performed with EXCEL.

#### 9.3.1 Considerations on mass transfer and reactor ideality

The calculated activation energy of ~ 44 kJ/mol is between those usually obtained for the kinetic regime and the mass transfer regime. Therefore, the criteria typically used to check the existence of mass transfer limitations and to find deviations of the reactor from the ideal behavior were applied. These criteria are well known in the literature [*Shah et al. (1987); Cussler (1997); Pérez-Ramírez et al. (2000)*] and they are resumed in the following pages. The symbols are listed at the end of section 9.3. The calculations were performed assuming the values in the following list:

- Flow rate =  $300 l_N/h$
- Particle diameter =  $180 \,\mu m$
- Porosity ( $\varepsilon$ ) = 0.5 (suggested value from the literature [*White* (1988)])
- Constriction factor ( $\sigma$ ) = 1 (suggested value from the literature [*White* (1988)])
- Tortuosity ( $\tau$ ) = 5 (suggested value from the literature [*White* (1988)])
- Bulk concentration = 1000 ppm

- Reaction order = 1 (typical diesel exhaust conditions)
- <sup>-</sup> Volume of the catalyst =  $8.9 \times 10^{-8} \text{ m}^3$
- Void fraction of the bed  $\varepsilon_b = 0.5$  (which represent the worst case)

#### 9.3.1.1 <u>Criteria</u>

#### Criterion for extraparticle mass transfer

For the exclusion of extraparticle mass transfer the Carberry number (*Ca*) must satisfy the following expression:

$$Ca = \frac{r_{v,obs}}{a'k_{d}c_{b}} < \frac{0.05}{|n|}$$
(9.10)

#### Criterion for intraparticle mass transfer:

To neglect the intraparticle mass transfer the Wheeler-Weisz modulus ( $\Phi$ ) must satisfy the following equation.

$$\Phi = \eta \phi^2 = \left(\frac{r_{v,obs}L^2}{D_{eff}c_s}\right) \left(\frac{n+1}{2}\right) < 0.15$$
(9.11)

#### Minimum reactor diameter to neglect gas wall effects in gas-solid operation

The difference between the packing density inside the bed and that near the wall and the flat surface of the wall may cause a deviation from the ideal plug flow. This wall effect causes a higher local velocity near the wall, resulting in a non flat radial velocity profile and a possible bypass of gas along the wall. For gases, the wall effect can be neglected if the ratio between bed diameter and particle diameter is larger than 10. This ratio was always guaranteed with the particle range used for the experiments (particle size =160-200  $\mu$ m, reactor diameter = 0.006 m).

#### **Pressure drop**

A rule of thumb is that the pressure drop should be lower than approximately 20% of the total operating pressure in the reactor. This means that the maximum pressure drop should be ~ 0.2-0.26 bar. The observed pressure drop was always below this limit.

#### 9.3.1.2 Calculations

In general, the rate of mass transfer for a single sphere is described by equation (9.12) [*Scott Fogler* (1999)]:

$$Sh = 2 + 0.6 \operatorname{Re}^{1/2} Sc^{1/3}$$
(9.12)

with:

$$Sh = \frac{k_d d_h}{D} \tag{9.13}$$

$$\operatorname{Re} = \frac{\mu \rho d_p}{\mu} \tag{9.14}$$

$$Sc = \frac{\mu}{\rho D} \tag{9.15}$$

A similar power-law behavior is observed for packed beds and this has led to analogous equations for the Sherwood, the Reynolds and the Schmidt numbers. However, important differences in the functionality are caused by the void space found in a packed bed. Several correlations obtained from experimental work are present in the literature. Thoenes and Kramers [*Thoenes et al.* (1958)] proposed equation (9.16) for the calculation of the Sherwood number. This correlation is valid for  $0.25 < \varepsilon_b < 0.5$ , 40 < Re' < 4000, 1 < Sc < 4000.

$$Sh' = (\operatorname{Re'})^{\frac{1}{2}} (Sc)^{\frac{1}{3}} = \frac{k_d d_p}{D}$$
 (9.16)

with:

$$\operatorname{Re}' = \frac{\operatorname{Re}}{(1 - \varepsilon_b)\gamma} \tag{9.17}$$

$$Sh' = \frac{Sh\varepsilon_b}{(1 - \varepsilon_b)} \frac{1}{\gamma}$$
(9.18)

Another correlation that is valid for a larger range of Re and Sc (Re>1, wide range of Sc) is the one proposed using the Colburn factor  $(j_d)$  by Gupta and Thodos [*Gupta et al. (1962)*] for fixed beds of spheres:

$$\varepsilon_b j_d = 0.010 + \frac{0.863}{\text{Re}^{0.58} - 0.483} = \frac{\varepsilon_b k_d}{u} S c^{\frac{2}{3}}$$
(9.19)

Table 9.1 shows the mass transfer coefficients calculated from these correlations. The diffusion coefficient of HNCO in air as function of the temperature has been obtained from [*DHNCO*]. Table 9.2 resumes the rate coefficient and reaction rate observed experimentally.

Table 9.3 shows the obtained values for the Carberry number and the Wheeler-Weisz modulus. Additional calculations excluded Knudsen diffusion and, therefore, the gas phase diffusivity D was used for the calculation of  $D_{eff}$ .

**Table 9.1:** Values used for the calculation of the mass transfer coefficients. (a) Thoenes and Kramers and(b) Gupta and Thodos correlations for the mass transfer coefficient. Dynamic viscosity is given by Sutherland's law.

<i>T</i> [°C]	D [m <sup>2</sup> /s]	$ ho_{N_2}$ [kg/m <sup>3</sup> ]	$\mu_{\scriptscriptstyle N_2}$ [kg/ms]	Re	Re'	Sc	Sh'	k <sub>d</sub> <sup>(a)</sup> [m/s]	jd	k <sub>d</sub> <sup>(b)</sup> [m/s]
150	3.15*10 <sup>-5</sup>	0.80	$2.29*10^{-5}$	28.54	57.09	0.91	7.33	1.28	0.29	0.893
200	$3.86*10^{-5}$	0.71	$2.48*10^{-5}$	26.40	52.80	0.90	7.02	1.50	0.30	0.943

**Table 9.2:** Experimental value of the rate constant and calculated reaction rate.

Т [°С]	k <sub>mass</sub> [m <sup>3</sup> /gs]	Observed rate [mol/sm <sup>3</sup> ]
150	$2.96 * 10^{-3}$	4.72
200	$1.12 * 10^{-3}$	15.99

Т [°С]	Ca <sup>(a)</sup>	Ca <sup>(b)</sup>	Φ
150	0.004	0.006	0.047
200	0.013	0.020	0.147

**Table 9.3:** Calculated values for the Carberry number and the Wheeler-Weisz modulus. (a) Thoenes andKramers and (b) Gupta and Thodos correlations for the mass transfer coefficient.

The values obtained showed that the criteria to exclude extraparticle and intraparticle mass transfer are satisfied and that, therefore, the HNCO hydrolysis reaction is in chemically controlled regime the tested conditions. The strong dependence of the HNCO conversion on temperature in the low temperature range is an additional confirmation of the chemical controlled regime. Moreover, repetition of the tests at different conditions (with different amount of catalysts and different flow rates) always resulted in a comparable value for the activation energy (~  $40 \pm 4 \text{ kJ/mol}$ ).

#### 9.3.2 Symbols

- $k_d$  = mass transfer coefficient [m/s]
- $d_h$  = hydraulic diameter = particle diameter [m]

 $D = \text{gas phase diffusivity } [m^2/s]$ 

- u = superficial gas velocity through the bed [m/s]
- $d_p$  = particle diameter [m]

 $\rho$  =density [kg/m<sup>3</sup>]

 $\mu$  =dynamic viscosity [kg/ms]

 $r_{v,obs}$  = observed reaction rate [mol/sm<sup>3</sup>]

 $k_{mass}$  = observed rate constant per unit mass [cm<sup>3</sup>/gs]

*a*' = specific external surface area of the catalyst particle  $[m^2/m^3]$  (6/d<sub>p</sub> for spherical particles)

- $c_b$  = bulk concentration [mol/m<sup>3</sup>]
- n = reaction order
- $\eta$  = effectiveness factor
- $\phi$  = Thiele modulus ( $\phi = L_{\sqrt{k_v}/D_{eff}}$ , with  $k_v$  = rate constant per unit volume [s<sup>-1</sup>])
- L = characteristic catalyst dimension (L = d<sub>p</sub>/6 for spherical particles) [m]

 $c_s$  = concentration at the external particle surface (= bulk concentration when no extra particle mass transfer) [mol/m<sup>3</sup>]

$$D_{eff}$$
 = effective diffusivity in the particle  $[m^2/s] = \frac{D\varepsilon\sigma}{\tau}$ 

- $\varepsilon$  = porosity of the catalyst
- $\sigma$  = constriction factor
- $\tau$  = tortuosity
- $\boldsymbol{\varepsilon}_b$  = void fraction of the bed
- $\gamma$  = shape factor = 1 for spherical particles

$$j_d$$
 = Colburn factor for mass transfer =  $\frac{k_d}{\mu}Sc^{\frac{2}{3}}$ 

 $\gamma$  = shape factor = 1 for spherical particles

#### 9.4 Conclusions

The analysis method used for the determination of the kinetic parameters has some limitations and therefore allows determination of the reaction orders for only a few temperatures. A complete definition of the kinetic parameters requires experiments with broader variety of experimental conditions. However, the obtained results are fairly reliable and very valuable because no information on the kinetics of the catalytic HNCO hydrolysis can be found in the literature. The results revealed a zeroth reaction order for CO<sub>2</sub>, a first reaction order for HNCO as well as H<sub>2</sub>O and a negative order for NH<sub>3</sub> at low temperatures. The reaction order for ammonia decreased while increasing the temperature, proving an inhibition effect for ammonia. However, for T > 150 °C a zeroth order was calculated for NH<sub>3</sub>, showing that the inhibition effect was negligible. This result is in agreement with those reported in Chapter 8 on the influence of NH<sub>3</sub> on the TiO<sub>2</sub> catalytic activity. The reaction orders obtained for HNCO and water suggest that the reaction follows the stoichiometry. However, for water excess (which is typical for a diesel exhaust) the rate of HNCO conversion became nearly zeroth-order with respect to  $H_2O$ . This result suggests that the catalyst is covered with  $H_2O$  under reacting conditions. The activation energy was calculated to be ~  $40 \pm 4$  kJ/mol for typical diesel exhaust conditions. Investigation of possible mass transfer control revealed that the kinetic parameters were obtained in the kinetically controlled regime.

# 10

### **Conclusions and Outlook**

It is now time that we arrange our key, as far as discovered, in a tabular form, to avoid confusion.

E. A. Poe (Tales of mystery and imagination)

#### **10.1 Conclusions**

The purpose this work was to investigate the catalytic hydrolysis of isocyanic acid (HNCO) which is a reaction involved in the selective catalytic reduction of nitrogen oxides with urea (urea-SCR) in diesel exhaust gases. Two families of catalysts are active in HNCO hydrolysis: metal oxides and SCR catalysts. Extensive analysis of the first group showed high catalytic performance for TiO<sub>2</sub> in the anatase phase, even at high space velocities. In the family of SRC catalysts, over-exchanged Fe-ZSM5 prepared by ion exchange with FeCl<sub>2</sub> exhibited high activity. The catalytic activity of both TiO<sub>2</sub> and Fe-ZSM5 increased with temperature.

Characterization experiments carried out on TiO<sub>2</sub> anatase sample (characterized primarily by the (101) crystal surface) revealed two types of Ti<sup>4+</sup> sites on the surface. These sites are fourand five-coordinated Lewis acid sites exhibiting different acid strengths. Some residual OH groups present on the surface were also observed, even after treatment at 450 °C. However, the acidity of these groups was not strong enough to protonate ammonia. DRIFT investigations of the adsorption of isocyanic acid on TiO<sub>2</sub> revealed that HNCO adsorbed dissociatively, thus forming isocyanate species (-NCO) on Ti<sup>4+</sup> sites and hydroxyl groups. The stability of isocyanate species increased with decreasing temperature. On the contrary, increasing the adsorption temperature to 150 °C caused the removal of –NCO groups even after briefly purging with nitrogen. Adsorption of HNCO at low temperatures also led to the formation of small amounts of by-products (cyanuric acid and/or s-triazine); however these species were removed by heating the catalyst in a nitrogen flow. An in-situ study of the HNCO hydrolysis at 150 °C revealed that both reactants and products adsorbed on the catalyst during the reaction. These results showed the presence of isocyanate species, molecularly chemisorbed water, NH<sub>3</sub> adsorbed on Lewis acid sites, and physisorbed CO<sub>2</sub>. Moreover, cyanuric acid and/or s-triazine did not form in the presence of water, however, stable formate groups were detected. These groups were removed by heating the catalyst at 300 °C. The reactivity of the –NCO species with water (producing NH<sub>3</sub>) follows the same trend as the catalytic activity of TiO<sub>2</sub>, thus leading to the conclusion that they are reaction intermediates. Investigations of the adsorption modes of water on TiO<sub>2</sub> suggest that the -NCO species react with molecularly chemisorbed water bonded to Ti sites via oxygen, or to the surface oxygen via hydrogen bonding. However, TiO<sub>2</sub> anatase reaches a high level of surface hydration by formation of clusters of water molecules; therefore the reaction may also be taking place with water molecules not directly adsorbed on the surface.

Characterization experiments carried out on Fe-ZSM5 revealed a complex structure in which different Fe surface sites exist, i.e.  $Fe^{3+}$  framework sites in tetrahedral or octahedral coordination, bulk  $Fe_xO_y$  and  $Fe_2O_3$  particles. HNCO adsorbed dissociatively on Fe-ZSM5 to form isocyanate species, analogous to the case of TiO<sub>2</sub>. However, due to the complexity of the Fe-ZSM5 structure, –NCO groups bonded to different surface sites, thus giving rise to the formation of Fe-NCO and Al-NCO species. Formation of [NCO]<sup>-</sup> ions was also observed. No interaction of HNCO with silica sites was observed. Experiments performed in the presence of water again showed that isocyanate species readily react with water to form NH<sub>3</sub>. The reactivity of –NCO
species with water to form NH<sub>3</sub> correspond to the catalytic activity of Fe-ZSM5, further proving their key role in the reaction.

Investigations of  $TiO_2$  and Fe-ZSM5 carried out under realistic conditions showed that the presence of  $SO_2$  led to little or no variation in their catalytic activity. On the contrary, when performing the reaction in the presence of  $NH_3$  at low temperatures, deactivation was obsserved. This result is in close agreement with the competitive adsorption of HNCO and ammonia on the same active sites.

In the presence of NO, increase in the catalytic activity of Fe-ZSM5 at low temperature was observed. In view of the assumption of competitive adsorption between  $NH_3$  and HNCO, this effect was attributed to the partial removal of adsorbed  $NH_3$  from the surface during the occurrence of the SCR reaction. As expected, no similar effect was observed for  $TiO_2$ , owing to the negligible SCR properties of this material.

The low temperature catalytic activity of TiO<sub>2</sub> and Fe-ZSM5 for the hydrolysis of isocyanic acid also decreased considerably in the presence of NO<sub>2</sub>. This effect was more pronounced at lower temperature. The decrease in activity can be explained by the adsorption of NO<sub>2</sub> on the surface, which creates stable  $NO_3^-$  species, thus decreasing the number of available active sites. The nitrate ions themselves create sites on which ammonia adsorbs in the form of ammonium ions; thus forming stable ammonium nitrate on the surface. Moreover, the formation of small amounts of bulk ammonium nitrate was observed. However, this did not cause a permanent deactivation: treatment of the catalyst at 450 °C in N<sub>2</sub> and O<sub>2</sub> completely recovered the catalytic activity due to  $NO_2$  desorption and  $NH_4NO_3$  decomposition.

The competitive adsorption of HNCO and  $NH_3$  on the hydrolysis catalyst might be a problem under real-life conditions in diesel exhaust, since  $NH_3$  is always present in the gas feed as a product of the urea thermo-hydrolysis. Similarly, the deactivation effect of  $NO_2$  could also pose a problem for practical applications, since  $NO_2$  is usually produced in the pre-oxidation catalyst upstream of the SCR system in order to enhance the SCR reaction. However, high temperatures reduce these effects because of the desorption of ammonia from the surface and the decomposition of the ammonium nitrate formed on the catalyst. Thus high-load engine operation helps to regenerate the catalyst.

Kinetics investigation of the reaction on  $TiO_2$  revealed a zeroth reaction order for  $CO_2$ , first order reaction for HNCO and H<sub>2</sub>O, and negative order for NH<sub>3</sub>. The reaction order of ammonia

decreased with increasing temperature, proving the inhibition effect of ammonia. However, for T > 150 °C, a zeroth order for NH<sub>3</sub> was calculated, showing that the inhibition effect was negligible. This result is in agreement with the results on the influence of NH<sub>3</sub> on the TiO<sub>2</sub> catalytic activity. The reaction orders obtained for HNCO and water suggest that the reaction is stoichiometric. However, in the presence of large amounts of water (typical in diesel exhaust), the rate of HNCO conversion becomes nearly zeroth order with respect to H<sub>2</sub>O. This result suggests that the catalyst surface is covered by H<sub>2</sub>O under typical reaction conditions. The activation energy in typical diesel exhaust conditions was calculated to be ~ 40 ± 4 kJ/mol. Investigation of possible mass transfer control revealed that the kinetic parameters were obtained under kinetic regime.

### **10.2 Outlook**

The results obtained in this work suggest the –NCO species are reaction intermediates on the catalytic hydrolysis of isocyanic acid. However, in order to obtain deeper insight into how these species react after adsorption on the surface, theoretical investigations are being carried out [*Czekaj et al.*].

An important aspect in the use of a different catalyst dedicated to HNCO hydrolysis is the method used to assemble the catalysts in order to obtain the best performance. Jacob [*Jacob* (1992)] described a system that consists of spraying a urea solution onto a separated ammonia generator and converting it to ammonia and carbon dioxide by means of a separate hydrolysis catalyst. The ammonia obtained is then transferred to the SCR catalyst connected. He also proposed the use of monoliths with special designs that can reduce the space velocity (i.e., increase the contact time) inside the ammonia generator [*Jacob* (2005)]. It would be interesting to investigate these materials along with TiO<sub>2</sub> coating techniques. Moreover, novel materials like foams might be studied as support for both TiO<sub>2</sub> and Fe-ZSM5.

As mentioned in the first chapter, the use of a specialized catalyst for the hydrolysis of HNCO such as TiO<sub>2</sub>, would allow introduction of a section dedicated to the thermo-hydrolysis of urea before the SCR reduction, with possible improvement of the overall performance. However, the drawback of this solution is the more complex and larger catalytic system required. Therefore the use of a SCR catalyst active also for the HNCO hydrolysis, as Fe-ZSM5, remains a competi-

tive option. However, in order to demonstrate the advantage of this solution, the competition between SCR reaction and HNCO hydrolysis on Fe-ZSM5 needs to be investigated further.

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# List of Publications

The following list summarizes the papers, reports, talks and posters which resulted or are related to this study.

#### **Publications**

- G. Piazzesi, M. Elsener, O. Kröcher, A. Wokaun, *Influence of NO*<sub>2</sub> on the hydrolysis of *isocyanic acid over TiO*<sub>2</sub>, Appl. Catal. B 65 (2006) 169-174.
- G. Piazzesi, O. Kröcher, M. Elsener, A. Wokaun, Adsorption and hydrolysis of isocyanic acid on *TiO*<sub>2</sub>, Appl. Catal. B 65 (2006) 55-61.
- G. Piazzesi, M. Devadas, O. Kröcher, M. Elsener, A. Wokaun, *Isocyanic acid hydrolysis* over *Fe-ZSM5 in Urea-SCR*, Cat. Comm. 7 (2006) 600-603.
- G. Piazzesi, M. Devadas, O. Kröcher, M. Elsener, A. Wokaun, *Investigation of the HNCO adsorption and hydrolysis on Fe-ZSM5*, submitted to J. Catal.

#### <u>Reports</u>

- G. Piazzesi, M. Elsener, O. Kröcher, A. Wokaun, *Investigation of the Hydrolysis of Iso-cyanic Acid in Urea SCR: Catalyst Screening and Low-Temperature Kinetics*, PSI Scientific Report 2004, V, (2005), 87.
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<u>Talks</u>

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# Curriculum Vitae

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It only remains for me to add a hope, that this little offering may serve to make new friends to our beautiful and useful science.

> **Justus Liebig** (1803-1873)