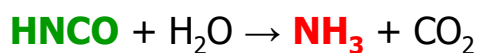
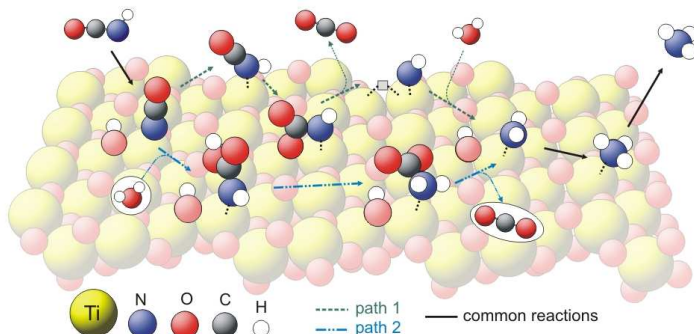


Hydrolysis of Isocyanic Acid



Mechanism of reaction



1. Interaction of HNCO with TiO_2 surface (dissociatively)

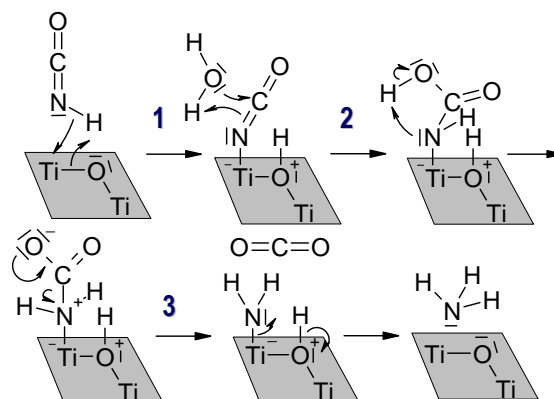
2. H_2O attack & formation of carbamic acid and carbamate complex

3. CO_2 desorption & NH_3 formation

Catalysts:

Transition metal oxides

TiO_2 anatase, Al_2O_3 , SiO_2 ,
 ZrO_2 , Fe-ZSM5



Methodology of studies

Theory: Density Functional Theory

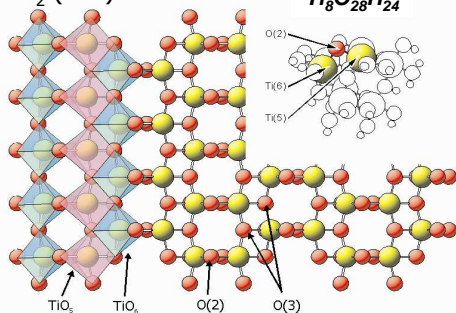
- catalyst model - cluster
- 3D optimization of adsorbate / cluster
- vibrational analysis

Experiment:

- activity of catalyst
- surface analysis of catalyst: XRD, XPS
- infrared spectroscopy: DRIFT

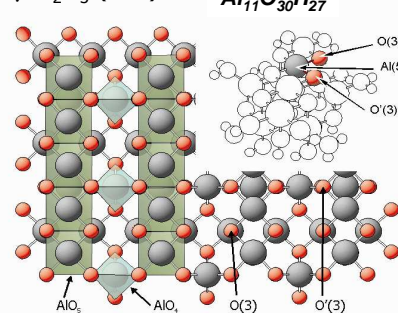
"Virtual" Screening of different catalysts

TiO_2 (101)



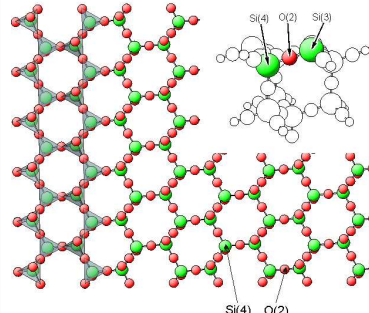
$\text{Ti}_8\text{O}_{28}\text{H}_{24}$

$\gamma\text{-Al}_2\text{O}_3$ (100)

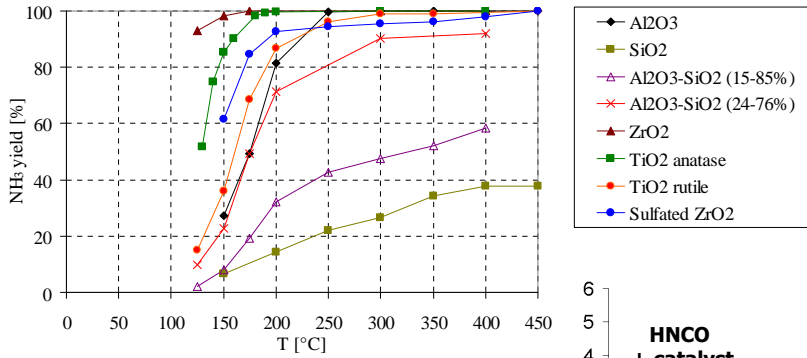


$\text{Al}_{11}\text{O}_{30}\text{H}_{27}$

SiO_2 (111)



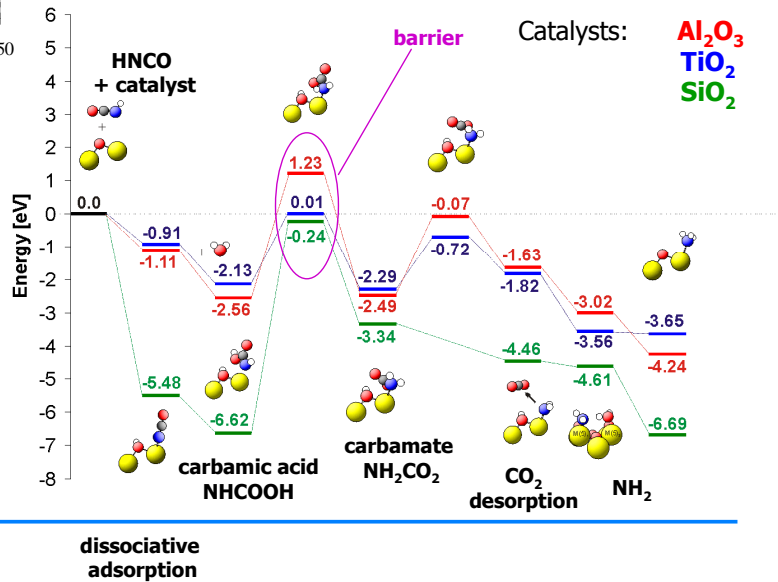
$\text{Si}_{10}\text{O}_{25}\text{H}_{12}$



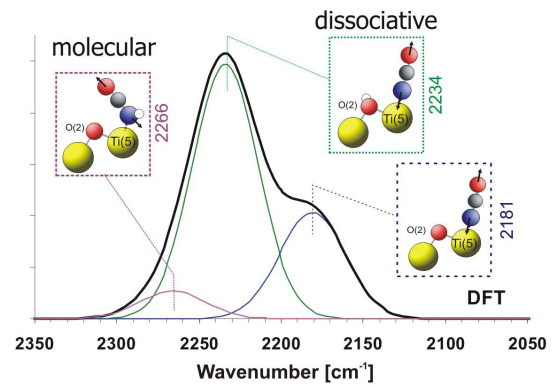
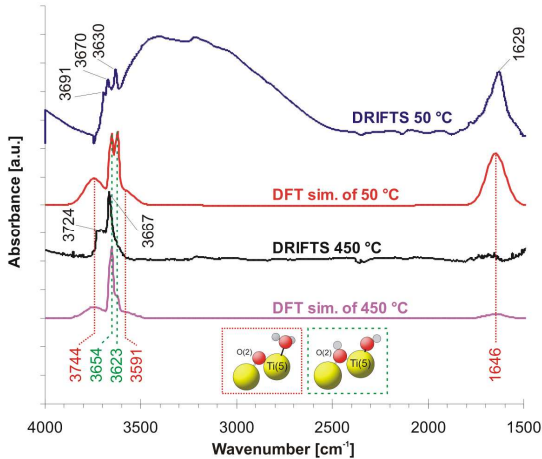
← **Catalyst activity**

Reaction mechanism and energy diagram

- TiO_2 – the best catalyst

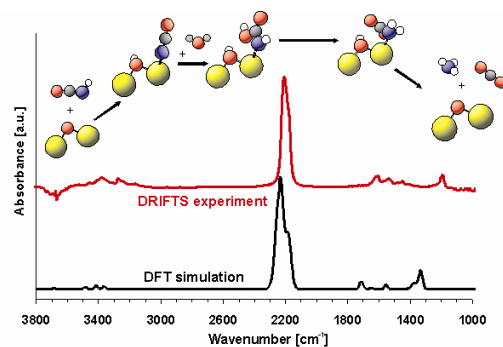


Water adsorption at TiO_2 (101)



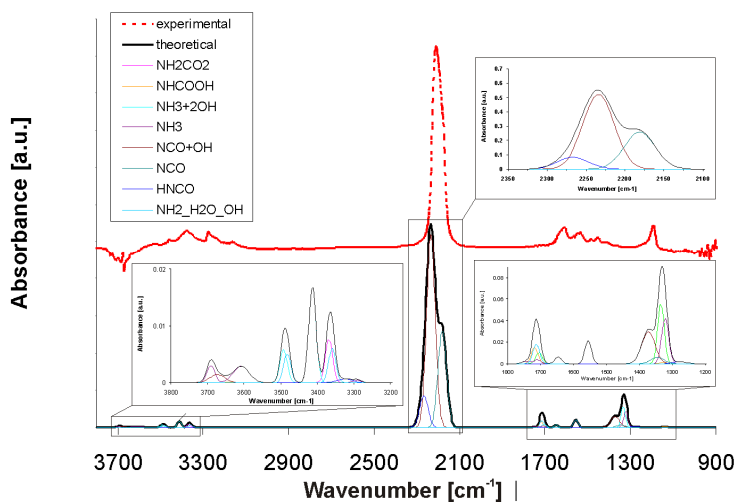
DFT simulations:

- help with better understanding of calcination process and adsorbates remaining at surface (e.g. H_2O , OH groups)
- explain role of different adsorbates present during reactions (e.g. H2CO in both molecular and dissociative form, NCO radicals)



DRIFT vs. DFT: how are theoretical spectra composed?

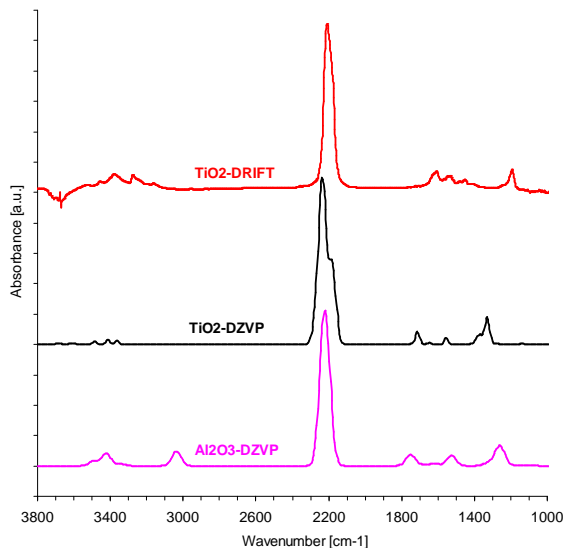
Detailed composition of theoretical DRIFT spectra



- The vibrations of all adsorbates, which appear during the reaction or due to different conditions, have to be considered in all different local environments (e.g. with water adsorbed at adjacent centers) for correct simulation of theoretical DRIFT spectra

Comparison of theoretical DRIFT spectra of two catalysts:

TiO₂ (TiO₂-DZVP; black)
Al₂O₃ (Al₂O₃-DZVP; magenta)
with experimental DRIFT for TiO₂ (TiO₂-DRIFT; red)



Conclusions

- Measured DRIFT spectra could be reproduced by DFT calculations
 - A reaction mechanism could be developed on the basis of DFT calculations, which is consistent with
 - all DRIFT spectra and kinetics of the reaction
 - Reaction mechanism holds also for all catalysts
 - „Virtual“ catalyst screening might be feasible for HNCO hydrolysis catalyst in comparison with experiments on **INDUSTRIAL** catalyst
- ⇒ Presented methodology of DFT modeling can be used for successful combination with different experimental methods available at PSI for variety of questions and complex catalytic systems

DFT ↔ DRIFTS / IR
DFT ↔ UPS
DFT ↔ XPS
DFT ↔ STM
DFT ↔ XAS/NEXAPS