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Vibrational Spectra of Adsorbates from DFT I. Czekaj, ENE

Hydrolysis of Isocyanic Acid

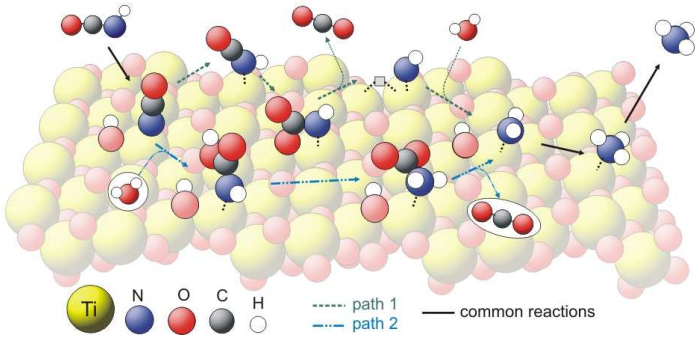
$$\mathbf{HNCO} + H_2O \rightarrow \mathbf{NH_3} + CO_2$$

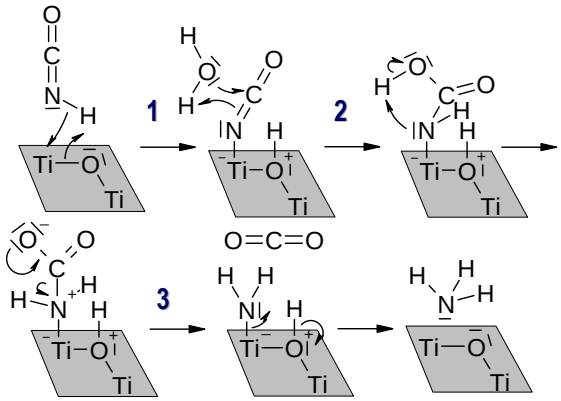
Catalysts:

Transition metal oxides

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

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

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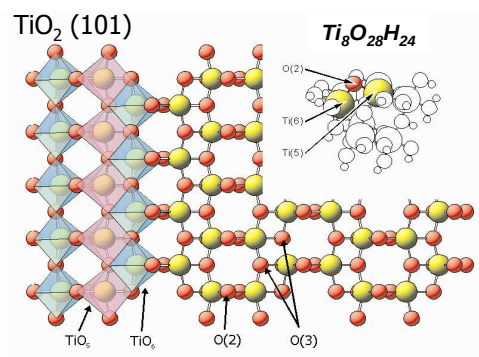
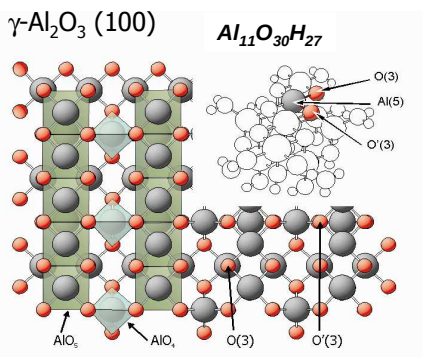
Methodology of studies

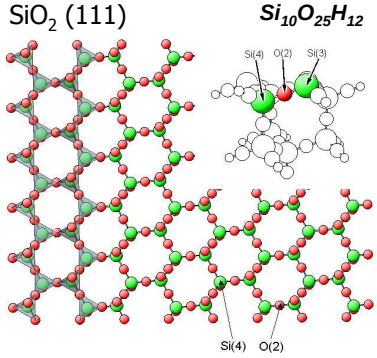
Theory: Density Functional Theory
- catalyst model - cluster
- 3D optimization of adsorbate / cluster
- vibrational analysis

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

"Virtual" Screening of different catalysts







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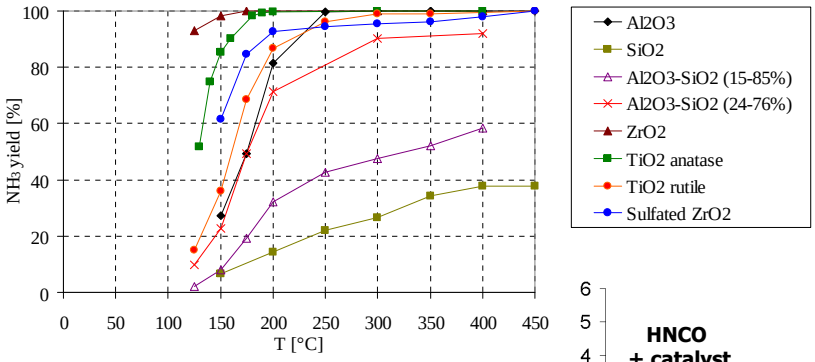
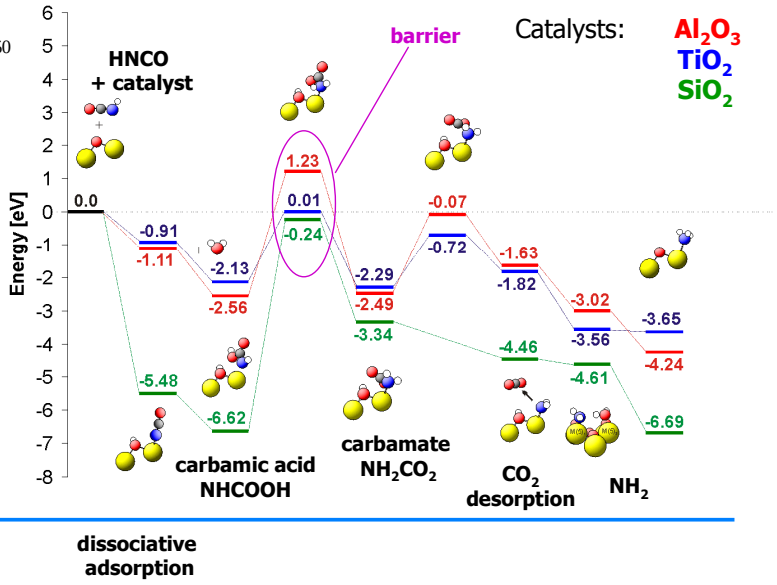
Screening of Metal Oxides



Catalyst activity

Reaction mechanism and energy diagram



- TiO_2 – the best catalyst

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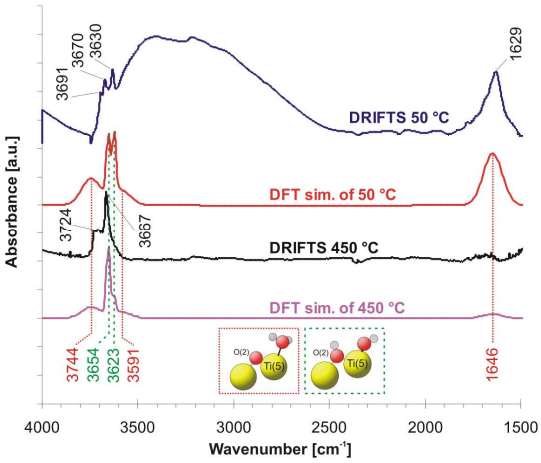
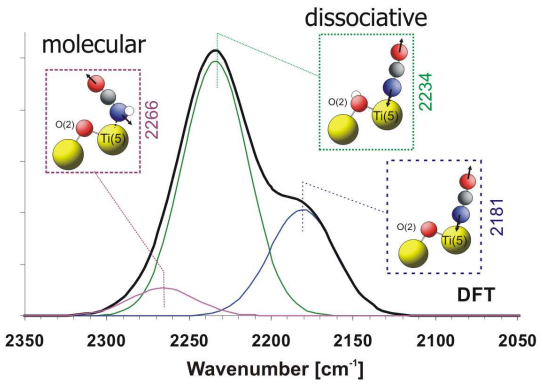
Simulation of theoretical DRIFT spectra

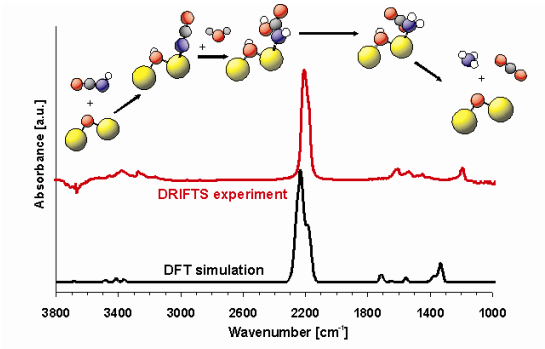
Water adsorption at TiO_2 (101)





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. HNCO in both molecular and dissociative form, NCO radicals



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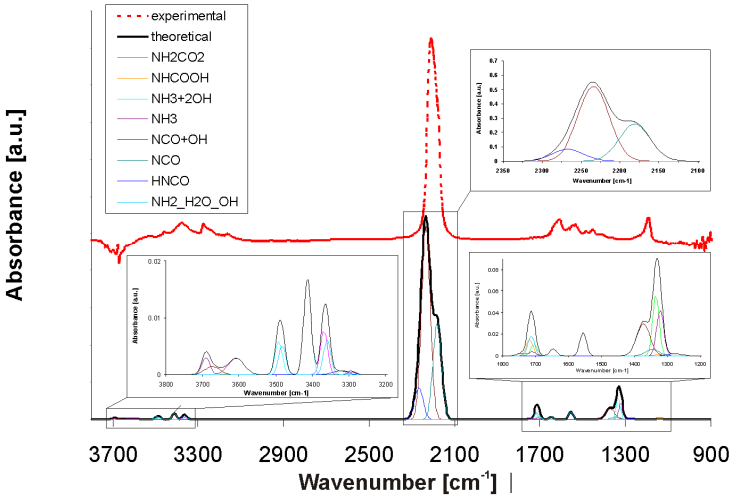
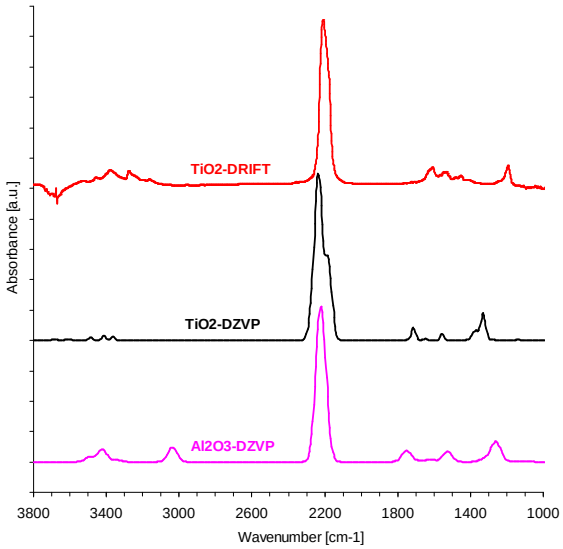
DRIFT vs. DFT: how are theoretical spectra composed?

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:
TiO_2 (TiO_2-DZVP; black)
Al_2O_3 (Al_2O_3-DZVP; magenta)
with experimental DRIFT for TiO_2 (TiO_2-DRIFT; red)



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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