Modelling an amorphous catalyst

First principle study of the local structure and its influence on the reactivity of amorphous ACF

***B. Paulus, A. C. Telorman, C. Becker**, Institut für Chemie und Biochemie - Physikalische und Theoretische Chemie, Freie Universität Berlin*

In Short

- Investigation of the synthesis of the ACF catalyst out of $AlCl_3$
- Investigation of the interaction of $AlCl_3$ and ACF with the fluorinating agent HF
- Influence of the local structure of ACF due to the exchange of bulk fluorine to chlorine atoms
- Determination of transition states of exchange reactions with the „nudged elastic band“ method

Modelling the structure of different active sites in heterogenous catalysts is one of the major fields in theoretical surface science. Especially the structure of amorphous Lewis acidic catalysts aluminiumchlorofluoride, short ACF, and high-surface aluminiumfluoride, short HS-AlF_3, is of high interest for understanding the resulting high activity in several reactions, like C-H bond activation or hydroarylation reactions. [1] In other reactions the experientalists found that HS-AlF_3 and the ACF catalyst catalyse C-F/Cl bond activation and isomerization reactions.[2][3] In selected reactions these catalysts shows equal or even higher activity than SbF_5.[5] But due to their lower cost, lower toxicity and the more easier usage, they are of high interest for industry. One of the differences between the ACF and the HS-AlF_3 catalysts is their synthesis. For the ACF catalysts a one step Cl/F exchange reaction is needed. For this very exothermic reaction $AlCl_3$ suspended in CCl_4 is used as a precursor. As flourination agent $CFCl_3$ is used. The HS-AlF_3 catalyst is synthesised via a two step synthesis, beginning with a flourolytic sol-gel reaction and a followed treatment with flourinating gas. Up to now, in the project bec00148, we have investigated selected reactions by modelling the catalyst as the α-AlF_3 surface with terminal chloride on the surface.[4] The first step is the investigation of the precursor of the ACF catalyst, $AlCl_3$ with the Vienna ab initio package (VASP) [6,7].

Therefore the different surfaces of the precursor will be determined and the interaction with HF, as alternative fluorinating agent, will be investigated to model the fluorination of the precursor to get a possible pathway to the structure of the ACF catalyst. Afterwards we will determine the interaction of ACF

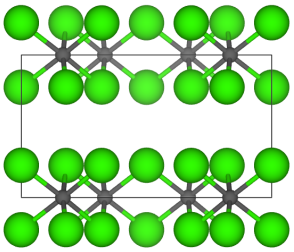

***Figure 1:** Bulk structure of the $AlCl_3$ crystal. grey = aluminium, green = chlorine[8]*

with the fluorinating agend HF and the influence of different bulk positions of chlorine in ACF structures. This project is constructed in strong collaboration with the experimental group of Prof. Braun who try to characterize the local structure of ACF with different methods including NH_3-TPD, FTIR spectroscopy and MAS NMR. [9] We want to compare these experimental data of AG Braun, HU Berlin with our theoretical results to expand the knowledge of $AlF_{3-x}Cl_x$-systems.

WWW

http://userpage.fu-berlin.de/~agpaulus/

More Information

[1] B. Calvo, J. Wuttke, T. Braun, and E. Kemnitz. *ChemCatChem*, **8**, 1945 (2016).

[2] B. Calvo, C. P. Marshall, T. Krahl, J. Kröhnert, A. Trunschke, G. Scholz, T. Braun, and E. Kemnitz. *Dalton Trans.*, **47**, 16461 (2018).

[3] M. Kervarec, C. P. Marshall, T. Braun, and E. Kemnitz. *Journal of Fluorine Chemistry*, **221**, 61 (2019).

[4] R. Pandharkar, C. Becker, J. H. Budau, Z. Kaawar, and B. Paulus. *Inorganics*, **6**, 124 (2018).

[5] B. Calvo, T. Braun, and E. Kemnitz. *ChemCatChem*, **10**, 403 (2018).

[6] Kresse, G.; Furthmüller, J., *Physical Review B* **54**, 11169 (1996).

[7] Kresse, G.; Furthmüller, J., *Computational Materials Science* **6**, 15 (1996).

[8] S.I. Troyanov, *Zhurnal Neorganicheskoi Khimii*, **37**, 266 (1992).

[9] B. Calvo, C. P. Marshall, T. Krahl, J. Kröhnert, A. Trunschke, G. Scholz, T. Braun and E. Kemnitz, *Dalton Trans.*, **47**, 16461 (2018).

Project Partners

AG Braun Humboldt Universität Berlin

Funding

CRC1349 - Fluorine specific interactions