

BRINGING TOGETHER IN-SITU SPECTROSCOPY AND ELECTRON MICROSCOPY TO STUDY THE FUNCTION OF COMPLEX OXIDE CATALYSTS

Robert Schlögl¹, Christian Hess, Annette Trunschke, Axel Knop-Gericke, Dangsheng Su, Thomas W. Hansen, Jean P. Tessonnier, Sharifah A. Hamid²

¹ Fritz-Haber- Institut der Max-Planck Gesellschaft, Berlin (Germany)
www.fhi-berlin.mpg.de, *acsek@fhi-berlin.mpg.de

² COMBICAT Center, University of Malaya, Kuala Lumpur (Malaysia)

Introduction

The function of complex high surface area oxides for selective oxidation is still treated at a conceptual level lacking a physical basis as it is available for some metal systems. The main reason for this deficit inhibiting to benefit from the massive improvements possible in this chemistry, is the enormous complexity of working systems and the widespread inability of model systems to perform a catalytic function defined as a cyclic transformation of the reagents. One strategy to improve the situation is to reduce the chemical complexity of technical systems to the minimum constituents necessary. This approach requires a simultaneous adaptation of structural complexity¹ as in many cases constituents in a base material are added to control the structure without being essential *per se* for the desired conversion. This strategy requires well-controlled synthesis procedures for reproducible high surface area model systems. The widely used approach² to circumvent many challenges of producing bulk functional materials by using supported systems is only partly useful as their reactivity is limited and severe challenges arise in characterizing the structure of the model systems

Methods

The present paper describes an approach towards generation of catalytic fully functional model systems with significantly reduced complexity. It uses elements from the approaches described in the literature and combines them in such a way that the top target of full functionality of the system is maintained. The reactions studied are the functionalisation of propane and butane. The option for a novel approach opens by relaxing the rigorous requirements of structural definition introduced by the single crystal approach through the extensive use of in-situ characterization methods and the coupling of spectroscopy and electron microscopy with full functional verification of the reactivity. A combination of in-situ X-ray diffraction, in-situ EXAFS, environmentally controlled thermal analysis and high-pressure photoemission with analytical and high resolution electron microscopy is a powerful methodology. Catalytic reactions are tested with the smallest possible amounts of material to ascertain a representative microscopic description using specially designed³ micro-reactors. Some devices allow additionally the application of in-situ RAMAN, in-situ IR and in-situ UV-VIS spectroscopies, even in combination⁴ with XPS or XRD.

Material systems are high surface area powder systems⁵ or supported model systems. We use mesoporous systems⁶ and carbon nanotubes⁷ as size-controlling supports and prepare also flat thin films.

Results and Discussion

The catalytic chemistry revolves around the cooperative function of molybdenum and vanadium systems. Starting systems are VPP, MoVTe and HPA systems. In a first phase substantial synthetic efforts were necessary to prepare phase-pure and single-phase systems. It turned out that the best catalytic function was obtained from single-phase systems and no evidence was found for phase cooperation or synergy of active phases. A common property of active systems is their structural dynamics transforming the pre-catalyst into an active form usually with reduced oxygen content. The detectable oxygen mobility explains the concept of “bulk lattice oxygen” as being instrumental for catalytic function. Its detection is a sign of the structural dynamics and is (except in the “riser reactor” mode) not required for the substrate conversion.

In a second phase of the study, models are prepared that mimic the matrices of active phases generated during activation from bulk catalyst systems. As a step of complexity reduction, thin layer systems of pure molybdenum and vanadium oxides are synthesized and characterized. A common feature is the concomitant necessity for delocalized electrons, for metal-oxygen terminal doubly bonds and for bridging “surface lattice oxygen” elements in the active state. We confirm that the activation of alkanes requires the presence of vanadium, whereas the transformation of olefins works well with single phase molybdenum systems. The presence of a variety of other elements in the high surface area systems generates and stabilizes the structural dynamics (structural promotion).

In the third phase initial experiments are conducted aiming at quantifying functional properties. This still widely methodical effort aims at detecting and quantifying the “active oxygen”, at a description of acidity and at elucidating the redox properties through analysis of the surface electronic structure under working conditions.

Significance

The approach has generated sufficient results that it can be expected to generate a consistent structure-function relation for these reactions. A substantial progress in synthesis methods has also been made allowing phase purity and surface area to be controlled. This is essential for transferring the obtained knowledge into (technical) design of improved catalysts.

References

- (1) Abd Hamid, S. B.; Othman, D.; Abdullah, N.; Timpe, O.; Knobl, S.; Niemeyer, D.; Wagner, J.; Su, D.; Schlögl, R. *Topics in Catalysis* **2003**, *24*, 87-95.
- (2) Hess, C.; Wild, U.; Schlögl, R. *Microporous and Mesoporous Materials* **2006**, *95*, 339-349.
- (3) Havecker, M.; Pinna, N.; Weiss, K.; Sack-Kongehl, H.; Jentoft, R. E.; Wang, D.; Swoboda, M.; Wild, U.; Niederberger, M.; Urban, J.; Su, D. S.; Schlögl, R. *Journal of Catalysis* **2005**, *236*, 221-232.
- (4) Hess, C.; Schlögl, R. *Chemical Physics Letters* **2006**, *432*, 139-145.
- (5) Knobl, S.; Zenkovets, G. A.; Kryukova, G. N.; Maksimovskaya, R. I.; Larina, T. V.; Vasenin, N. T.; Anufrienko, V. F.; Niemeyer, D.; Schlögl, R. *Physical Chemistry Chemical Physics* **2003**, *5*, 5343-5348.
- (6) Hess, C.; Looi, M. H.; Abd Hamid, S. B.; Schlögl, R. *Chemical Communications* **2006**, 451-453.
- (7) Su, D. S.; Maksimova, N.; Delgado, J. J.; Keller, N.; Mestl, G.; Ledoux, M. J.; Schlögl, R. *Catalysis Today* **2005**, *102*, 110-114.