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Structure, Dynamics and Reactivity of Molecules, Clusters, and Solids

Catalysts speed up chemical reactions and direct them to desired products. The production of almost all the materials of our modern life such as polymers and synthetic fibres rely on catalysts. The fuel we burn in the engines of our cars is the product of catalytic processes and the exhaust gas is converted by a catalyst into environmentally less harmful gases. The food we eat is grown with the help of fertilisers with ammonia as a key component. Since 1914 the famous Haber-Bosch process catalytically synthesises ammonia from nitrogen and hydrogen. Enzymes which regulate chemical processes in living organisms are nothing else than highly active and highly selective catalysts.

A large share of industrial catalysts are solid materials composed of different chemical substances and organised into a complex atomic structure. Our research is driven by the need to understand the reactivity and selectivity of catalytically active materials as a function of the chemical composition, the atomic structure and the aggregation level. This understanding is prerequisite to the design of new or modified catalysts and more efficient catalytic processes. In contrast to research groups that prepare catalysts by solid state chemical synthesis or study their function in-situ using most sophisticated spectroscopic techniques, we employ the methods of quantum chemistry and computer simulation to examine the structure of catalysts and to reveal the elementary steps of catalytic processes.

The advantage of the computational approach is that simulations can be made on model catalysts and for conditions which are not, not yet or not easily accessible by experiments. This helps to understand what has been observed in experiments. Often spectroscopic signals can only be assigned to atomic structures and elementary processes when comparison is made with theoretical predictions.

Here, we present our work on acidic zeolites and vanadium oxide catalysts, while other projects such as transition metal ions as active sites in zeolites [1–3] and their role in NO decomposition [4, 5] and the search for active species on sulfated zirconia surfaces

Fig. 1
»Divide and Conquer«-Strategy: Integrated high-level/low-level methods that use existing methods and computer codes [8].

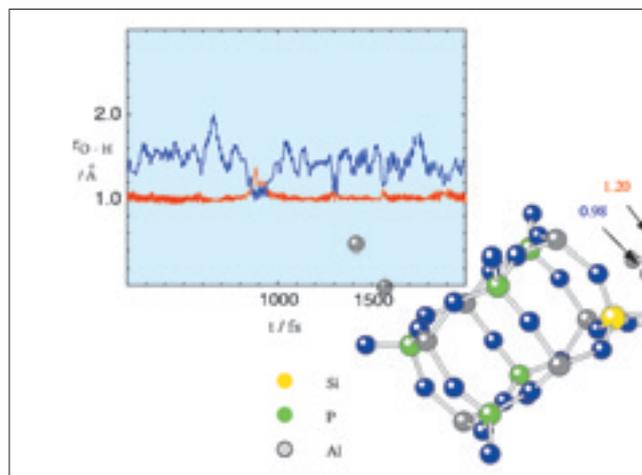
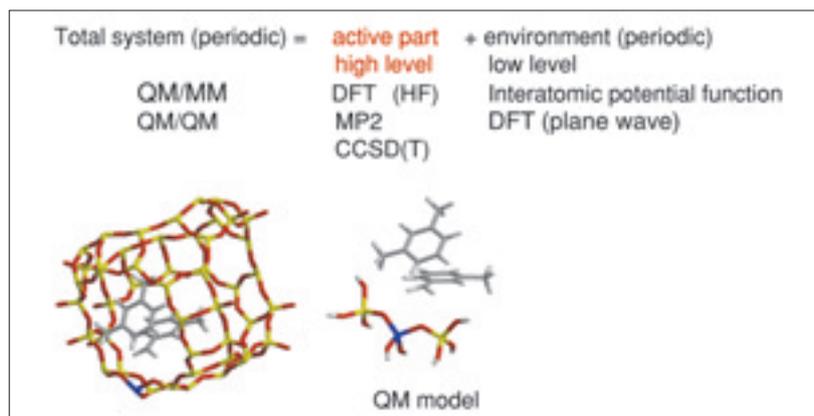


Fig. 2
Molecular dynamics simulation of water molecules in H-SAPO-34. The diagram shows two O-H distances. Equal distances mean that a proton transfer has happened and a protonated dimer $(H_2O)_2H^+$ is formed. It is seen that these are rare events, i.e. the $(H_2O)_2H^+$ species is not stable [12].

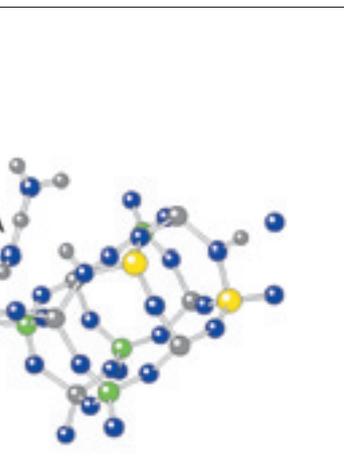
and their role in hydrocarbon activation [6, 7] cannot be mentioned.

Methods for large chemical systems

A reliable quantum mechanical description of solid catalysts is still a challenge for quantum mechanical methods. Even when periodic boundary conditions are applied the pseudo-unit cells of these complex structures may contain several hundred atoms. Density functional theory (DFT) renders such calculations feasible, but they are still computationally very demanding and, for some specific applications, may not be accurate enough.

We attack this problem by a »divide and conquer« strategy and apply an integrated high-level/low-level method [8]. The system studied is divided in an active part, which includes the catalytically active site at which chemical bonds are broken or made, and the environment which imposes geometric constraints on the atoms of the active site and influences their electronic structure. The high-level method is applied to the active part, while the environment is treated by the low-level method. This strategy – also known as QM/MM and QM/QM hybrid method – reduces the computational effort significantly and makes the problem tractable (QM – quantum mechanics, MM – molecular mechanics).

Fig. 1 illustrates the hybrid approach for a hydrocarbon reaction in a zeolite catalyst. The DFT treatment is limited to the zeolite active site and the reacting hydrocarbon (shown on the right), while the periodic zeolite environment including the hydrocarbon-zeolite wall interactions is treated using the much faster molecular mechanics force field calculations (left, not the full periodic zeolite structure is shown, but for better viewing only the zeolite cavity surrounding the hydrocarbon). In this case the combined approach has two advantages compared to full DFT calculations. Not only reduces it the computational effort significantly (enabling us to treat much larger systems), it also



yields more reliable adsorption energies. The reason is that functionals currently available for use in DFT calculations fail to properly describe

van der Waals (dispersion) interactions which dominate binding of hydrocarbons to the zeolite wall, while force fields are known to do very well in this respect. The integrated high-level/low-level method can also be used as a QM/QM hybrid approach with the aim to correct for deficiencies of DFT at the reaction site. Then the DFT description of the large periodic system can be combined with a more accurate quantum chemical ab initio method such as CCSD(T) or MP2.

Our implementation of the integrated high-level/low-level method is basically an optimizer for equilibrium and transition structures (minima and saddle points) with interfaces to existing codes for high-level and low-level calculations such as TURBOMOLE [9] and CPMD [10].

A full quantum mechanical description of periodic structures is computationally most efficient if the wavefunction is expanded in plane waves and not in Gaussian orbitals as in quantum mechanical calculations on molecules. This is a limitation because density functionals which include Fock-exchange and proved the most

accurate in many chemical applications cannot be used and calculations beyond DFT are not possible. However, plane waves speed up the calculations and forces needed for structure optimisation and dynamic runs are very rapidly evaluated. We make use of the Car-Parrinello Molecular Dynamics Code (CPMD) [10] for zeolite simulations and of the Vienna Ab initio Simulation Package (VASP) [11] for transition metal oxides.

Nanoporous solid acids, protonated water clusters and shape selective catalysis

Zeolites are nanoporous crystalline aluminosilicates with channels and cavities of molecular dimension. There is a large variety of framework structures with different pore sizes and shapes and also the chemical composition of the framework can vary not only by changes of the Si/Al ratio, but also by substitution of Si by P. The catalytically active site is created by charge compensating cations which can be either transition metal ions or protons. Due to the presence of protons zeolites become solid acids and their catalytic activity is related to the activation of substrates by protonation. While it is a well established fact that ammonia gets protonated in zeolites, for other probe molecules even as simple as water in spite of a large number of experimental and theoretical studies protonation in zeolites remained controversial. Therefore, the first neutron diffraction study of a water loaded zeolite (H-SAPO-34 – a nanoporous aluminiumphosphate) raised great expecta-

Zusammenfassung

Katalysatoren beschleunigen chemische Reaktionen und lenken sie zu gewünschten Produkten. In industriellen chemischen Prozessen werden meist Feststoffe als Katalysatoren verwendet, die aus verschiedenen Verbindungen bestehen und in komplexer Weise aus den einzelnen Atomen aufgebaut sind. Unser Ziel ist, die Funktionsweise katalytisch aktiver Materialien in Abhängigkeit von Zusammensetzung und Struktur auf atomarer Ebene zu verstehen. Im Unterschied zu experimentell tätigen Gruppen verwenden wir dazu Methoden der Quantenchemie und der Computersimulation. Deren Anwendung auf ausgedehnte Festkörper mit lokalen Störungen stellt eine besondere Herausforderung dar, der wir durch eine »Teile und Herrsche«-Strategie begegnen. Die Umgebung des kleinen aktiven Zentrums des Katalysators wird durch weniger aufwendige Methoden beschrieben als das aktive Zentrum selbst.

Dieser Beitrag beschreibt exemplarisch unser Vorgehen für zwei verschiedene Klassen fester Katalysato-

ren: feste Säuren und Oxidationskatalysatoren. Dabei wird deutlich, wieviel man über die Vorgänge an komplexen Oberflächen durch Untersuchung analoger Moleküle und Cluster in der Gasphase lernen kann. Zeolithe sind nanoporöse Festkörper, deren Wirkung als feste Säuren mit der »Gestalt«-Selektivität kombiniert ist. Kontrovers wird diskutiert, welche Moleküle protoniert werden und ob Carbeniumionen (protonierte ungesättigte Kohlenwasserstoffe) als Zwischenstufen in der katalytischen Reaktion auftreten. Eine andere wichtige Klasse von Katalysatoren sind Übergangsmetalloxide. Zum Beispiel katalysiert Vanadiumoxid die Umwandlung von Methanol zu Formaldehyd. Solche Katalysatoren werden nicht in reiner Form verwendet, sondern auf ein anderes Oxid, den Träger, aufgebracht. Wir zeigen anhand einer Testreaktion wie Aggregation (Festkörper – Gasphasen-Cluster) und Träger (Siliziumdioxid, Aluminiumoxid) die Reaktivität von Vanadiumpentoxid beeinflussen.

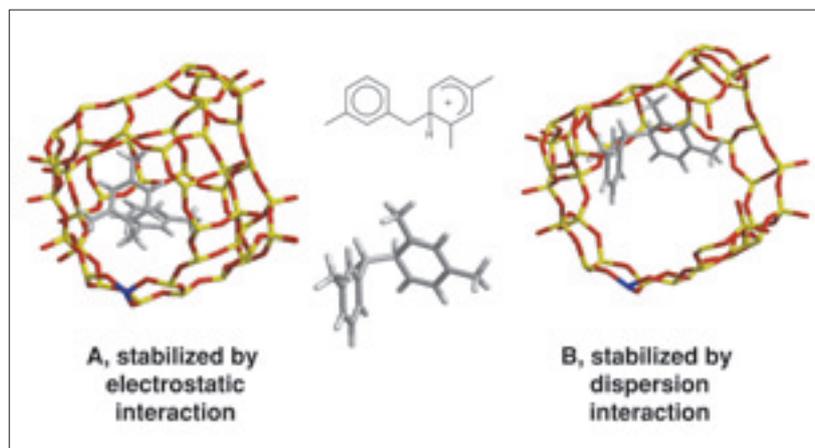


Fig. 3
Benzenium type cation in the cage of zeolite FAU (faujasite). Two different stable positions are shown [17].

tions. The proton positions localised pointed to the presence of protonated water dimers. This was apparently at variance with previous computational studies. However, Car-Parrinello molecular dynamics simulations for the same material as used in experiments showed that protonation of dimers is indeed a rare event (Fig. 2), and neutral hydrogen bonded clusters are stable [12]. During the simulation a cluster of three water molecules was formed which finally became protonated and persisted as a stable protonated trimer [12]. This behaviour is explained by the increasing proton affinity of water clusters with increasing cluster size and the apparent contradiction between computational and experimental findings was due to the limited knowledge about the number of water molecules per acidic proton in the diffraction experiment.

Identification of protonated water dimers in zeolites was so difficult because their vibrational spectrum was not known. In particular, experimental information for the characteristic asymmetric O-H-O stretch vibration was missing. Theoretical predictions are also difficult because the harmonic approximation usually made is not sufficient. Our prediction was based on ab initio (MP2) molecular dynamics (classical treatment of nuclear motions) and a 4-dimensional adiabatic quantum approach [13]. Very recently, a group at Freie Universität Berlin succeeded in recording the experimental spectrum using the free electron laser FELIX [14]. Based on the theoretical predictions, the three strong bands below 1600 cm^{-1} could be assigned to the asymmetric O-H-O stretch and the two O-H-O bending modes. We are currently examining how the spectrum changes when the protonated water dimer is in a zeolite cavity or within another inorganic crystal [15].

The detailed mechanisms by which solid acids catalyse hydrocarbon conversion reactions are still not com-

pletely known. The work of Olah and others demonstrated that liquid super acids protonate hydrocarbons and stabilise carbenium ions, but it is still controversial if zeolites do the same [16]. We have used our hybrid QM/MM method and studied the bimolecular mechanism of the disproportionation of m-xylene into toluene and trimethylbenzene (TMB) [17]. The most important finding from our calculations is that benzenium type carbenium ions (see Fig. 3) are local minima on the potential energy surface and, hence, possible intermediates in the reaction mechanism. Haw et al. [16] have produced NMR evidence for some carbenium ions and concluded that only species with proton affinities (PA) greater than about 874 kJ/mol live long enough in zeolites to be observed on the NMR time scale. The PA of the benzenium ion shown in Fig. 3 is only 821 kJ/mol and it remains to be seen if this is enough to observe it experimentally.

Both the ionic attraction between the negatively charged active AlO_4^- site on the zeolite framework and the positively charged benzenium ion and the van der Waals (dispersion) interaction with the zeolite wall contribute to the stabilisation of the benzenium-type intermediate in the zeolite cavity. While the electrostatic attraction dominates for position A close to the negatively charged active site, in structure B the benzenium ion fits tightly to the zeolite wall far from the active site where it maximises the vdW interaction.

The unique feature of zeolite catalysts is that they combine the activation of molecules with the confinement of the nano-sized pores and cavities. This has led to the concept of transition state shape selectivity. It states that some isomers may not be observed in the product stream, not because they are too bulky to leave the pores, but because the transition state they have to pass to form at the active site may be too bulky to fit into the pore of a given zeolite. An experimental proof is difficult and therefore we have used our hybrid method to study a sterically demanding reaction, the disproportionation of m-xylene into trimethylbenzene and toluene [17]. No indication of transition state shape selectivity has been found and the conclusion is reached that transition state shape selectivity is a seductive concept without real proof.

The methodology used for these studies is presently further developed and applied to additional reactions within a project that is part of the Deutsche Forschungsgemeinschaft (DFG) priority program 1155 »Molecular modelling and simulation in chemical engineering« [18].

Supported vanadium oxide catalysts

Most industrially used metal oxide catalysts have the active transition metal oxide supported on another oxide such as SiO_2 , Al_2O_3 , TiO_2 or ZrO_2 . One of the key questions in understanding heterogeneous catalysis is the role of the support. Is it an inert substance that provides a high surface area for the active oxide and improves the mechanical stability of the catalyst particle or does the support affect activity and selectivity in a more specific way? In a collaborative effort funded by the DFG 17 research groups in different institutions in Berlin try to answer this question for vanadium oxide based catalysts (Sonderforschungsbereich 546 [19]). A large variety of model catalysts is prepared and characterised ranging from gas phase clusters and single crystal surfaces to deposited clusters and epitactic layers. Their structure and reactivity will be compared with laboratory prepared supported catalysts.

Quantum chemical studies are essential to bridge the gap between different types of aggregates such as gas phase clusters and supported oxide species. As a step towards understanding the relation between structure (type of aggregate/local coordination) and reactivity we design model systems for computational studies (Fig. 4). These include the ideal (001) surface of V_2O_5 single crystals [20], $(\text{V}_2\text{O}_5)_n$ gas phase clusters [21], and two different models for supported catalysts, epitactic layers of V_2O_5 on Al_2O_3 (0001) surfaces terminated by vanadyl groups [22] and V-substituted silsesquioxane cages [23]. As a test reaction which is closely related to the oxidative function of the catalysts we compare energies for removing one vanadyl oxygen atom. A study of the catalytic conversion of methanol into formaldehyde revealed that it is this oxygen atom which takes up the hydrogen atoms of methanol and is left as water molecule on the surface (Fig. 5):

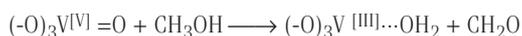
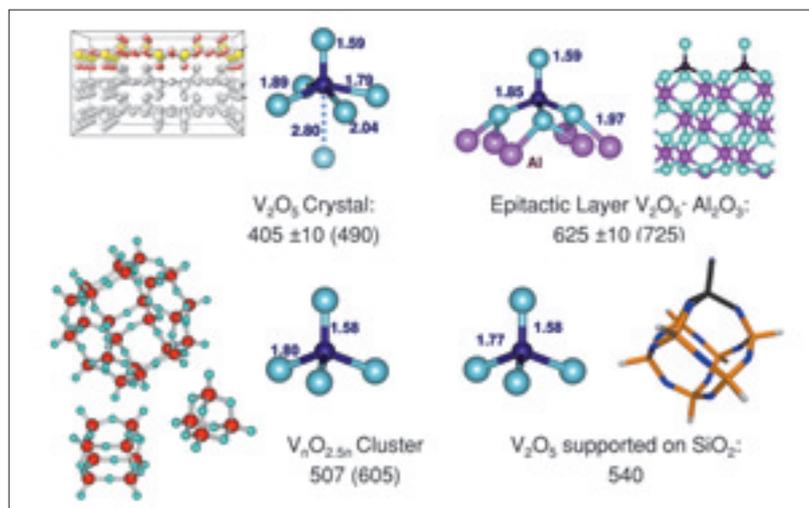


Fig. 4 shows that in the gas phase clusters and in the supported forms the coordination of V is very different from that in the single crystal surface, even if V always has a double bond to O (vanadyl group) and is in the oxidation state +5. In the single crystal surface V is five-fold coordinated and has an additional weak coordination to the vanadyl oxygen atoms of the layer below. This turns out to be very important for the reactivity. In the gas phase the most stable V_2O_5 isomers are polyhedral cages. Vanadium is four-fold coordinated to oxygen atoms and one bond is again a vanadyl bond. On the surface of the supported systems the V coordination is the same, and only the next coordi-

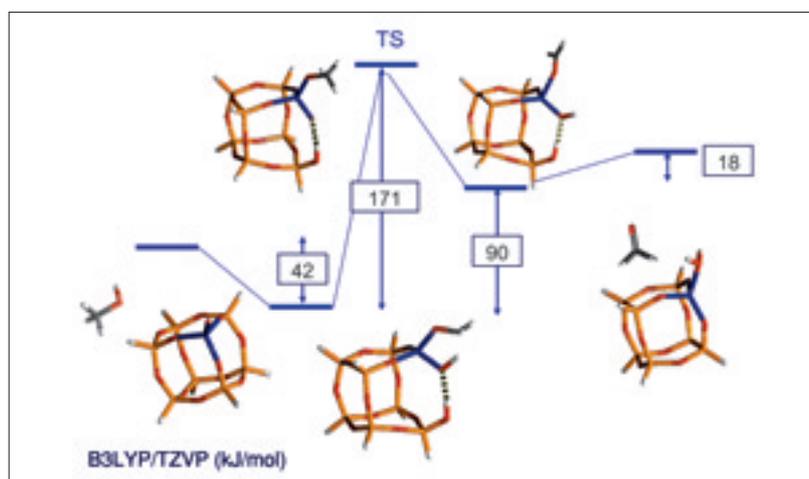


dination sphere is different: 3 Si or 3 Al atoms instead of 3 V atoms in the gas phase clusters.

The energies for removing the vanadyl oxygen from the different materials show large differences. Oxygen can be most easily removed from the single crystal surface. The reason is the possibility of forming a bond with the vanadyl group of the layer below which distributes the two electrons left on the surface V atom when the vanadyl O atom is removed over the two V atoms in the top two layers (Fig. 6). In the other materials, this relaxation is not possible and they all have larger O binding energies. A lower reactivity is sometimes needed to achieve high selectivity. V_2O_5 supported on SiO_2 shows a lower reactivity than V_7O_5 gas phase clusters because in the final state the d electrons cannot delocalise over neighbouring V sites (site isolation). In the supported materials neither structure relaxation (forming a new bond to a neigh-

Fig. 4
Structure and coordination of VO_x in different aggregates: Gas phase clusters, single crystal surfaces and vanadium oxide on SiO_2 and Al_2O_3 supports. Given are also O dissociation energies in kJ/mol (B3LYP functional, in parenthesis: PW91).

Fig. 5
Reaction energy diagram for key steps of the catalytic oxidation of methanol to formaldehyde on supported VO_x catalysts. (yellow – Si, red – O, blue – V, grey – C, white – H) [23].



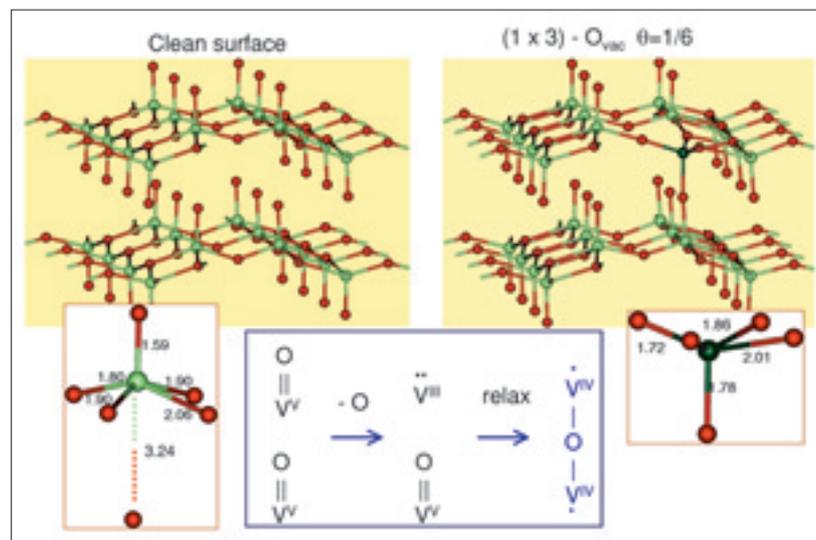


Fig. 6
 $V_2O_5(001)$ single crystal surface: Structure relaxation following removal of a vanadyl O atom from the surface [20].

Projects of the DFG-Collaborative Research Centre 546: »Structure, Dynamics and Reactivity of Aggregates of Transition Metal Oxides«

- C. van Wüllen (TU Berlin): Quantum chemical calculations of the electronic structure and reactivity of mono- and bi-centred vanadium oxide clusters
- D. Schröder / H. Schwarz (TU Berlin): Transition metal oxides in the gas phase
- K. Asmis / K. Rademann / L. Wöste (FU Berlin, Humboldt-Universität zu Berlin): Structure, stability and reactivity of transition metal oxide aggregates; $V_mO_n^{-0/+}$ cluster and cluster ions ($m \infty 10$)
- J. Sauer (Humboldt-Universität zu Berlin): Comparison of the structure, dynamics and reactivity of different vanadium oxide aggregates with DFT methods
- M. Bäumer / H.-J. Freund (Fritz-Haber-Institut der MPG, Berlin): Small oxide aggregates on oxide surfaces
- R. Schlögl / J. Urban (Fritz-Haber-Institut der MPG, Berlin): Partial oxidation of small hydrocarbons with microscopic quantities of V_xO_y -catalyst systems
- M. Baerns (Institut für Angewandte Chemie, Berlin-Adlershof): Catalytic activity of VO_x -aggregates in the oxidation of ethane and propane
- E. Kemnitz (Humboldt-Universität zu Berlin): Synthesis of VO_x doped SiO_2 - and ZrO_2 -aerogels and cryogels and oxygen exchange studies using ^{18}O -isotope
- C. Limberg (Humboldt-Universität zu Berlin): Synthesis and reactivity of model molecules for the

bouring oxygen atom) nor delocalisation is possible. The Al_2O_3 support makes removal of vanadyl oxygens most difficult. This explains the observation that V_2O_3 particles supported on Al_2O_3 films easily cover with vanadyl groups.

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active sites of vanadium oxide catalysts (in preparation)

- H. Kuhlenbeck / H.-J. Freund (Fritz-Haber-Institut der MPG, Berlin): Electronic structure and adsorption mechanism of ordered and defective ordered vanadium oxide surfaces
- H. Niehus (Humboldt-Universität zu Berlin): Geometric and electronic structure of oxide surfaces and adsorbed clusters
- K.H. Rieder / W. Theis / F. Moresco (FU Berlin): Atomic beam diffraction and low temperature STM investigations of oxide surfaces and thin oxide films
- P. Schilbe / K. Ploog (FU Berlin, Paul-Drude Institut für Festkörperelektronik, Berlin): Preparation and characterization of single crystalline transition metal oxides
- M. V. Ganduglia-Pirovano / J. Sauer (Humboldt-Universität zu Berlin): DFT calculations with periodic boundary conditions of the structure, dynamics and reactivity of vanadium oxide aggregates
- K. Hermann (Fritz-Haber-Institut der MPG, Berlin): Local and periodic models of the geometric and electronic structure of vanadium oxide surfaces
- W. Widdra (TU Berlin, Max-Born-Institut für Nichtlineare Optik und Kurzzeitspektroskopie, Berlin): Adsorption and reaction of unsaturated hydrocarbons on vanadium oxide surfaces
- D.P. Woodruff / J. Sauer (University of Warwick, Humboldt-Universität zu Berlin): Structure determination of VO_x surfaces, thin films and interfaces using scanned-energy mode photoelectron diffraction

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