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Model studies on heterogeneous catalysts at the atomic scale: From supported metal particles to two-dimensional zeolites

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ABSTRACT

After a general introduction to model studies in catalysis, results from different research areas are presented: (a) adsorption and reaction on nanoparticles supported on thin oxide films. It is shown that carbonaceous deposits on specific nanoparticle sites influence hydrogenation reactions through control of hydrogen surface–subsurface diffusion. (b) 2D-3D-morphology, geometric, and electronic structure of supported metal nanoparticles partially in relation to doping of the support. We learn how dopants, as electron sources, even if they are well beneath the active surface influence nanoparticle morphology on surfaces. (c) Strong metal–support interaction (SMSI). Ultrathin oxide films are proven to become chemically active in CO oxidation as they form on deposited nanoparticles dependent on the oxygen chemical potential in the gas phase. (d) Adsorption and reaction on two-dimensional silicates and alumino silicates in ordered and vitreous phases. Bilayer silica films on Ru(0001) are transformed by Al doping into 2D-aluminosilicates and shown to exhibit binding hydroxyl with an acidity close to 3D-zeolites, such as chabazite.

1. Introduction

Heterogeneous catalysts are complex materials consisting of combinations of different components, such as an oxide support and an active disperse metal. The classical model system for these materials, in the past, has been the metal single crystal [1–3]. The reason for this choice can be made transparent by inspecting Fig. 1 [4]. It shows STM images of Pd nanoparticles, which were grown by physical vapor deposition of Pd onto a thin alumina film. The left image showing a larger area reveals the presence of nanoscopic Pd single crystals exposing well-defined facets. The image at atomic resolution supports the idea that the topmost facet, indeed, exhibits (111) morphology and structure. Exactly, those observations, made in the 1960s of the last century, at the time with transmission electron microscopy [1], were the basis for the development of single-crystal model systems of defined orientation within surface science, in order to understand the elementary steps of chemical reactions at surfaces [5,6]. Our understanding of catalysis, and heterogeneous catalysis, in particular, is, to a large extent, based on these investigations of model systems. The enormous impact of metal single-crystal model surface chemistry, pioneered by physical chemists that led to the 2007 Nobel Prize in chemistry for Gerhard Ertl, has been the basis for an outstanding success story [6]. The simplicity of this model approach is particularly appealing, and it is this aspect that has led to some of the groundbreaking ideas influencing our thinking about catalytic reactions. However, it is also very obvious that a full understanding of all factors influencing catalytic reactions requires a considerable increase in complexity in the structure and morphology of the model systems, actually, taking the finite size of the disperse metal particles and the support–metal interface into account [7,8]. The important question is how much complexity is necessary to catch the relevant aspects [9]. It is obvious, however, that the only strategy that will lead to an understanding at the atomic level is to proceed from the simple to the complex and not the other way around!

We have developed concepts to prepare more complex model systems based on single-crystalline oxide films, which are used as supports for metal and oxide nanoparticles [10–13]. Together with the development of novel instrumentation [14], this approach allows us to study the factors influencing catalysis at the atomic level using the tools that have been developed, and so successfully applied, during the last thirty years in surface science, including those based on scanning probe techniques [15,16].

Here, we report on different areas, where such an approach has allowed us to directly establish structure/morphology–reactivity relations previously impossible and thus explain some surprising observations made in real catalysis. Using a model system similar to the one shown in Fig. 1, we investigate the question, why one

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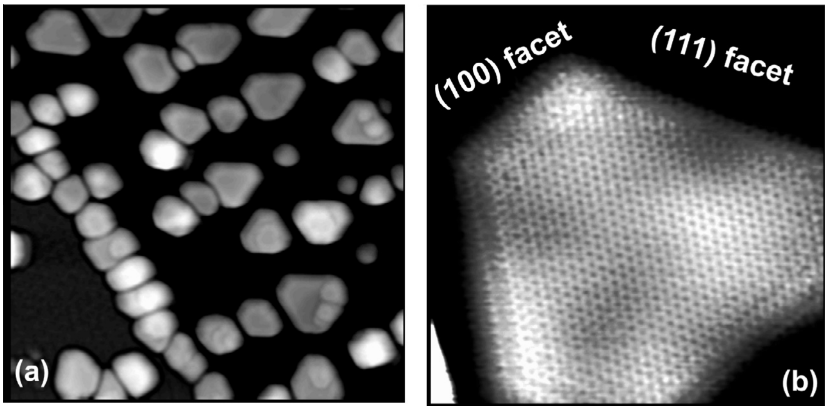

Fig. 1. Scanning tunneling microscopic images of Pd deposited on a thin alumina film at low (left) and high (right) resolution [4].

needs the presence of deposited carbon on nanoparticles to sustain hydrogenation catalysis in the conversion of alkenes to alkanes [17,18], and how does this relate to the higher degree of flexibility of nanoparticles as compared to metal single crystals influencing the adsorption enthalpy of molecules [19,20]. We address in a further case study the morphology and structure of nanoparticulate supported gold occurring as small, flat raft-like aggregates, and the role of the oxide metal interface in relation to its unmatched reactivity in CO oxidation [21–23]. Then, we pursue the study of charge transfer through oxide films as a function of their morphology and thickness to reveal novel mechanisms of molecular activation on oxides in the case of encapsulation of nanoparticles and strong metal–support interaction (SMSI) [24]. In a final case study, we reveal our initial experiments to prepare two-dimensional well-ordered silica and alumino-silica surfaces in an attempt to study the surface science of zeolites [25,26].

2. Experimental

The experiments were carried out in a number of custom made ultrahigh vacuum (uhv) systems, including equipment to bring samples to ambient conditions with direct transfer. A broad variety of experimental techniques have been applied [14]. These include scanning tunneling microscopy in uhv and ambient conditions, non-contact atomic force microscopy, elastic and inelastic electron scattering, photon STM, infrared Fourier transform spectroscopy, non-linear optical techniques, electron spin resonance spectroscopy, resonant nuclear reaction analysis, molecular beam techniques, microcalorimetry, and combinations thereof. The materials were prepared by epitaxial growth of oxides by reactive physical vapor deposition in uhv. Surface modifications and exposure to gases were carried out via specifically designed gas-handling systems.

3. Results and discussion

3.1. Carbon deposits on supported Pd nanoparticles and its flexibility

Fig. 2 shows a comparison of hydrogenation rates of trans-2-butene to d_2-butane obtained from a series of pulsed molecular beam experiments, in which Fe_3O_4(1 1 1) supported Pd nanoparticles of 4 nm average diameter (similar to the Pd particles on alumina imaged in Fig. 1) were exposed to a continuous D_2 molecular beam and a modulated cis-2-butene (which was chosen as the model di-methyl substituted ethene) molecular beam at 260 K [17]. The figure shows that the product response curves obtained for hydrogenation under steady-state conditions in comparison with similar results on Pd(1 1 1). The rates were calculated by averaging the reaction rates from the last 30 long pulses of the experiment and were normalized to the number of the surface Pd atoms for quantitative comparison. Shown are the hydrogenation rates plotted as a function of time on Pd(1 1 1) (upper row) and Pd particles (lower row) on the C-free (black curves) and C-containing (gray curves) surfaces. It is noteworthy that on both C-free surfaces, no sustained hydrogenation is observed [17,18,27,28]. Fig. 3 shows the production rate of butane-d_2 resulting from the reaction of cis-2-butene with D_2 over a C-free (Fig. 3a) and C-precovered (Fig. 3b) Pd-supported model catalysts at 260 K, which were pre-saturated with D_2 prior to the olefin exposure. A sequence of cis-2-butene pulses, consisting of 50 short (4 s on, 4 s off) and 30 long (20 s on, 10 s off) ones, was applied using an independent beam source concomitant with the continuous D_2 exposure. The reaction was carried out in a large excess of D_2 with the ratio of D_2:cis-2-butene molecules amounting to 570. On the pristine Pd particles (Fig. 3a), the initial period of high hydrogenation activity on D-saturated catalyst is followed by a decrease in the reaction rate to zero under steady-state conditions. Remarkably, carbon deposition prevents the suppression of the hydrogenation pathway in the steady state and results in persisting hydrogenation activity at the initially high level (Fig. 3b). It should be noted that the reaction rate of the

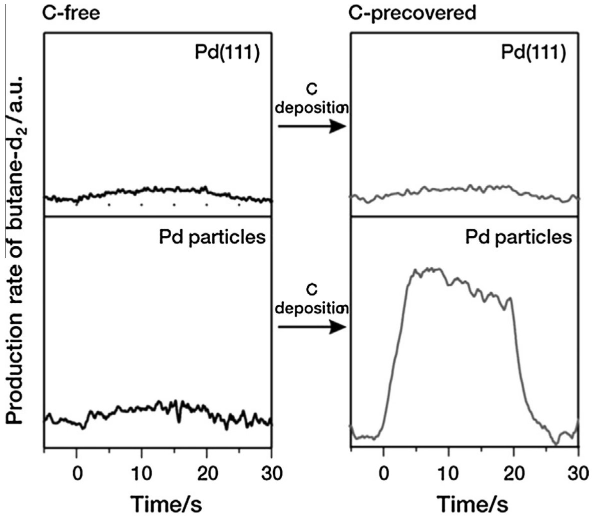

Fig. 2. Average hydrogenation rates on Pd/Fe_3O_4(1 1 1)/Pt(1 1 1) model catalyst, in comparison to a Pd(1 1 1) single crystal. The panel shows the situation for the model catalysts without pre-deposition of carbon on the left and after carbon deposition on the right [17].