

Model studies on heterogeneous catalysts at the atomic level

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Abstract

Model studies carried out on ultrahigh vacuum (UHV) prepared nanoparticles grown on well-ordered oxide surfaces allow insight into structure and reactivity of such systems at the atomic level. We review work on hydrogenation reactions of hydrocarbons on Pd metal particles addressing in particular the question of structure sensitivity and in a second example the preparation and characterization of supported vanadia monolayer catalysts for oxidation reactions. In the latter case we address the vibrational properties of vanadia “monolayer model catalysts” on alumina and on silica.

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1. Introduction

Given the complexity of real heterogeneous catalysts [1] it is mandatory to simplify the problem in a way that an essential part of the complexity is included in a model system but it is still possible to apply methods that allow one to investigate the system at the atomic level [2–11]. A possible approach is to combine scanning probe microscopies with spectroscopic and temperature programmed desorption techniques. Typically applied to single crystal surfaces under ultrahigh vacuum (UHV) conditions, model systems, based on thin well-ordered oxide films, can be studied with such techniques under the same but also ambient conditions. Nanoparticles of the desired chemical composition are then grown on top of such films in order to simulate the situation found in real catalytic samples where often small metal particles or oxide particles represent the active part of the catalyst.

Here we review results on deposited Pd nanoparticles in connection with hydrocarbon hydrogenation reactions [12–15] as well as vanadia particles grown on alumina and silica where we have been interested in understanding the growth and vibrational properties of the supported vanadia material which are interesting oxidation catalysts [16].

2. Experimental

The experiments have been performed in a number of different ultrahigh vacuum apparatuses as well as reactor systems attached to those. Details on Pd particles on alumina can be found in [6], while experimental procedures and detail for the vanadia materials are reported in [16].

3. Results and discussion

We report and discuss first the individual results for the two systems under consideration and then generalize at the end with respect to the investigation of model systems per se.

Hydrogenation of unsaturated hydrocarbons occurs efficiently on noble-metal catalysts, such as platinum, rhodium, and palladium [17]. The reaction mechanism first proposed by Horiuti and Polanyi [18] in 1934 proceeds by: (a) hydrogen dissociation on the metal surface; (b) alkene adsorption; (c) subsequent hydrogen addition to alkene; and finally (d) desorption of the product (alkane). Real hydrogenation catalysts represent very complex systems for studying reaction mechanisms at the molecular level. Therefore, model systems have been invoked ranging from single crystals to metal particles deposited on oxide films [2–11].

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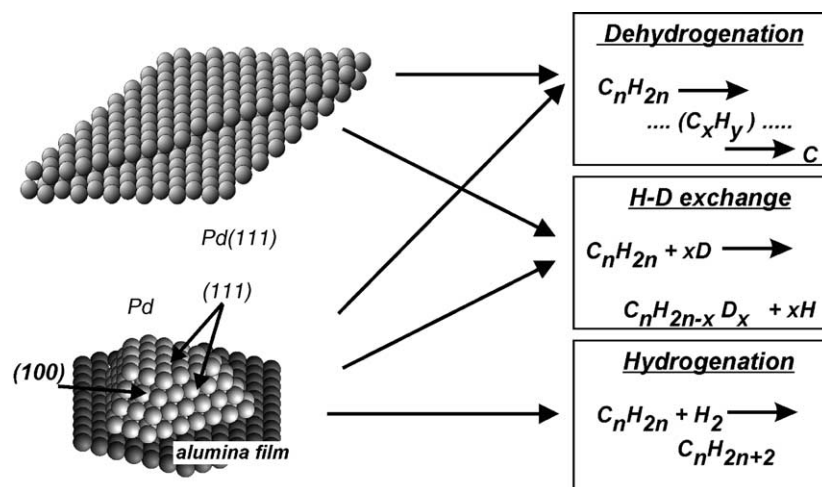


Fig. 1. Schematic representation of the alkene reactions observed on Pd(1 1 1) single crystal and well-faceted Pd particles supported on a thin alumina film.

We have studied the surface chemistry of ethene and different pentene isomers on both Pd(1 1 1) single crystal and Pd particles deposited on a thin alumina film (Fig. 1).

The particles studied are approximately 1–5 nm in diameter and consist primarily (~90%) of (1 1 1) facets [6] (~10% are (1 0 0) facets). The experiments were performed in ultrahigh vacuum on clean and well-defined systems. Using the temperature-programmed desorption (TPD) technique, we have observed that a number of hydrocarbon transformations, such as dehydrogenation and H-D exchange, occur on both palladium systems. However, the hydrogenation to alkane only occurs on small particles.

Adsorption of light alkenes, such as ethene, on palladium has been the subject of extensive studies on single-crystal surfaces and supported catalysts. [19,20] There is considerably less data on the interaction of higher hydrocarbons [21–24].

Madix and co-workers studied the adsorption of various alkenes and dienes on the clean and hydrogen (deuterium) precovered Pd(1 1 1) and Pd(1 0 0) surfaces by TPD [21,22]. They observed an H-D exchange reaction, which was assumed to proceed via a half-hydrogenated intermediate species. However, formation of the alkane was not observed on both surfaces.

We have examined the reactions of ethene, 1-pentene, *trans*- and *cis*-2-pentene on Pd(1 1 1) single crystals and supported Pd particles [25–27].

In the first part we review our own studies of hydrogenation of ethene in order to investigate the size-reactivity relationship on Pd nanoparticles. It is useful to recall and summarize the adsorption and dehydrogenation behavior of ethene without the presence of hydrogen.

Combining the results from thermal desorption spectroscopy (TDS) and IRAS [28–30], a general scheme for ethene thermal transformations on Pd particles has been proposed, as depicted schematically in Fig. 2. On small Pd particles, ethene is mainly π -bonded at low temperatures and desorbs intact upon heating. On the larger Pd particles, however, a

fraction of the ethene molecules are di- σ bonded. Again, weakly bonded ethene desorbs intact (its conversion to di- σ species on heating cannot be excluded, however), while di- σ ethene can either desorb near room temperature or dehydrogenate, producing surface species such as ethyldiyne and atomic hydrogen. Dehydrogenation proceeds further on heating until a hydrogen-deficient carbonaceous deposit and hydrogen are formed at elevated temperatures. Hydrogen atoms recombine and desorb as hydrogen molecules. Finally, the surface remains covered by carbon deposits at elevated temperatures.

Accordingly, particle size and roughness strongly influence the distribution of π - and di- σ -bonded ethene molecules. Due to the development of more extended facets on the large particles, which favor ethene di- σ bonding, the reaction pathway shifts toward dehydrogenation and hence to the formation of carbon deposits upon heating.

For pure hydrogen adsorption two adsorption states can be distinguished. One state, leading to desorption around 330 K, is very likely due to hydrogen atoms on the surface of the particles, while a second one desorbing at lower temperatures (β_1 at ~280 K) is tentatively assigned to subsurface hydrogen [31,32]. As a function of particle size, β_2 shifts to lower temperature with increasing particle size d , ranging from 1 nm < d < 5 nm. The formation of the β_1 state is decreased on the smallest particles, its desorption temperature being less influenced by the size of the particles. This can be a result of the decreasing number of subsurface sites available or due to the presence of the support.

Fig. 2 summarizes data for both ethane, pentene and hydrogen adsorption, as well as the corresponding hydrogenation reactions.

The top and bottom panel contain TDS data for ethane (bottom) and pentene (top) for a given average particle size, and the middle panel summarizes turn-over-numbers for hydrogenation of both pentene and ethane under ultrahigh vacuum conditions including a comparative study of ethene hydrogenation on the model system under ambient, higher

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