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RHEED AND TPD STUDIES OF THE EFFECT OF PARTICLE SIZE ON CO DESORPTION FROM Al_2O_3 SUPPORTED Pd AND Rh MODEL CATALYSTS

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Transition metals in form of small supported particles are frequently used in heterogeneous catalytic reactions. One point of actual interest concerns the reactivity of low co-ordination sites characteristic for particle surface. The non continuous epitaxial layers of Pd and Rh were grown on insulator substrates (Al_2O_3) by molecular beam epitaxy. The reflection high energy electron diffraction (RHEED) offered a readily applicable method for in-situ observation of epitaxial layer growth. As a model reaction CO adsorption was studied by means of the temperature programmed desorption (TPD) using a differentially pumped mass spectrometer with a molecular beam doser. It was shown that the activation energy of CO desorption decreases with decreasing particle size.

1. Introduction

Metal catalysts are used in many industrial processes. They consist of small metal particles ranging in size from 1 to 50 nm supported on porous oxide supports. The surface morphology, namely the surface irregularities, such as step sites with low co-ordination number, can determine the mechanism of catalytic processes, especially in the case of so-called “structure-sensitive” reactions.

Great complexity of most industrial catalysts leads the scientists to investigate the size effect in catalytic reactions. Simple and well–defined, so–called model catalysts (exhibiting metal particles well defined in size, structure, and morphology, deposited on flat supports – alumina, MgO, etc.) are studied under well-defined low pressure conditions. That is possible only in the case of reactions where the bridging of the high/low pressure gap does not introduce changes in reaction mechanisms. Fortunately, a lot of reactions satisfy this condition. The CO oxidation is considered as an example of this reaction [1].

In the field of thin film growth, it is well known that molecular beam epitaxy can produce homogeneous populations of particles having the same orientation and shape. Therefore, it is attractive to use the method to obtain small particles for use as model catalysts [2-9]. The particle shape and crystallographic orientation depend on numerous factors: conditions of particle growth (deposition rate, substrate temperature), particle size, particle/substrate interaction, and interaction with adsorbed molecules. Investigation of these effects needs a simultaneous study of the particle structure and reactivity.

The most reliable method commonly used to characterize the morphological parameters of supported particles is transmission electron microscopy (TEM). A relative shortcoming of this technique for a catalyst study results from the difficulties of in-situ examination that is due to the complexity of this technique given by the necessity of special particle supports and preparation [10].

Reflection high energy electron diffraction (RHEED) is attractive as a technique for surface structural determination. Because of a favourable geometry (grazing angles of incidence and exit) it makes possible to investigate in-situ epitaxial thin film growth in real time. The diffraction pattern analysis permits to distinguish between different modes of overlayer formation [11-13].

The reactivity of Rh and Pd particles was investigated via a model reaction of CO adsorption using the temperature programmed desorption (TPD) and molecular beam (MB) scattering method. MB and TPD techniques are well adapted to the investigation of adsorption/desorption kinetics and they allow the direct determination of the activation energy of adsorption, sticking probabilities of gas molecules and their coverage [4,5,9].

2. *Experimental*

The studies of reactivity of small particles were performed in a specially designed UHV systems. The Pd and Rh particles were grown by vapour deposition. The metal source was a micro electron bombardment evaporation source. The usual flux employed for the deposition was 1×10^{13} atoms cm^{-2} s^{-1}. The RHEED instrument was equipped with a CCD camera and a computer data acquisition system which permits both image processing and real time analysis of intensity profiles of diffracted beams. The particle size and epitaxial orientation depended on substrate temperature and on the deposition rate.

The experimental details of TPD and MB experiments have been described previously [9]. TPD and MB measurements were made with the sample oriented in line-of-sight to the quadrupole mass spectrometer (QMS) which was differentially pumped and fitted with a nozzle. This system permits achieving a high resolution TPD data, necessary for the analysis of different adsorption states on particle surface. A linear heating rate of 2.8 K/s was obtained with a termoelectric programmer.

3. *RHEED study of the particle structure*

RHEED permits to obtain 3 types of information on deposited layers:
(i) crystallographic structure and epitaxial orientation,
(ii) lattice parameter,
(iii) estimation of particle size and morphology.

3.1. *Crystallographic structure*

The reflection diffraction pattern of (0001) sapphire surfaces used in our studies consists of spots lying along arcs, showing a smooth surface without defects. After the growth of 3-D rhodium particles at the substrate temperature of 800 K, the reflection diffraction pattern changed to the transmission one formed by spots lying along lines (see Fig. 1).

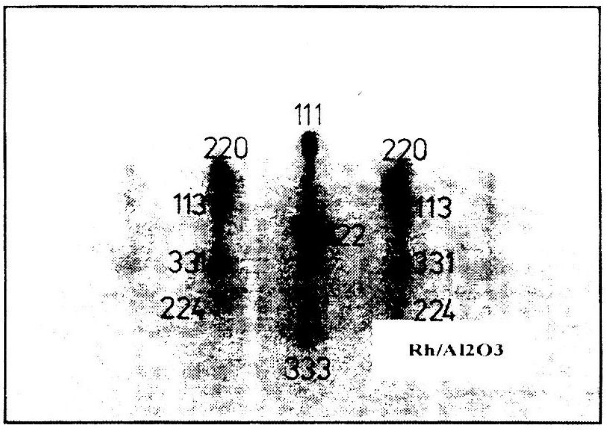


Fig. 1. RHEED pattern of Rh *particles grown on (0001) sapphire,* $E_p = 40$ keV. *The incident electron beam is parallel to the crystallographical direction [110] of* Rh.

Since the main reflections on the middle line correspond to the reciprocal lattice points 111–222 and 333, the particles must be oriented so that their (111) planes are parallel to the substrate. These diffraction spots are a part of two sets of diffraction spots constituting two reciprocal planes (110) given by two sets of particles in "double positioning" (rotated to 180°). An identical diffraction pattern is obtained after rotation of the sample by 60°, the incoming beam being parallel to the sapphire surface. More details about the Rh epitaxial growth on sapphire will be published in the near future [15].

3.2. *Lattice parameter*

Investigation of variations of the lattice parameter at an early stage of overlayer formation demands very precise measurements of distances between diffraction spots. The accuracy of these measurements is limited by several factors: camera spatial distortion, high noise/intensity ratio (especially in the case of low intensity spots) and spot broadening which complicates the determination of spot centre and consequently of lattice parameters.

In order to resolve this problem, an original detection method of the virtual camera subpixel detector [16] is proposed. In order to approximate the camera grey level signal in the neighbourhood of a characteristic spot, a precise contour detection method is necessary. This problem is resolved by adopting an analytical exponential–type function which has a shape very close to the RHEED spot diffraction profiles.

We have observed that the lattice parameter of very small crystallites often differs from the bulk due to the accommodation of particles lattice to the substrate one. Generally, the lattice expansion up to 6% was found for palladium, depending on the choice of the substrate and on the particle size. In the case of the Rh the lattice compression up to 2% was observed. More details concerning these studies will be given in Ref. 15.

3.3. *Particle size*

The degree of spot broadening and their form reflect the shape of growing surface asperities.

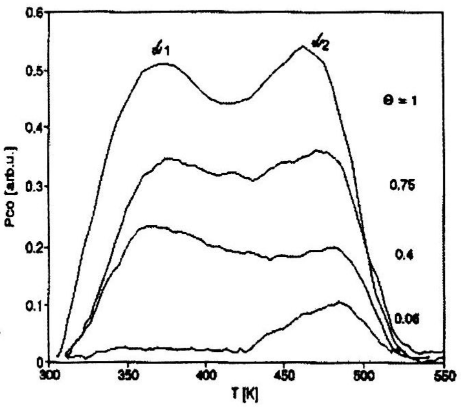
In the case of TEM, the Scherrer equation $L = K\lambda/\beta$ can be used to provide an estimate of the average crystallite diameter L [17]. In this formula β stands for the angular breadth of the electron diffraction ring measured at the FWHM (full width at half maximum) of its intensity profile, λ stands for the electron wavelength and K is the apparatus constant. We have used this equation for RHEED investigation of epitaxial Au/KCl cluster size by controlling the crystallite average diameter by TEM [18]. A relatively good agreement between both methods has been found, showing that the average diameter of supported particles can be determined in-situ by RHEED.

From Fig. 1, using this method, the average diameter of Rh particles was found to be 1.9 nm. The possibility of this analysis is particularly useful due to the fact that TEM investigation of size of particles deposited on massive alumina represents a difficult experimental problem (see for example Ref. 19).

4. *Influence of particle size on CO adsorption*

4.1. Palladium

The CO TPD spectra for different initial CO coverages Θ were measured using 27 nm Pd particles deposited on polycrystalline γ–alumina (Fig. 2). For more details see Ref. 9. At low relative coverage, a single peak at 515 K was detected. For a saturation exposure, the peak has its maximum at 475 K. The TPD data for 2.5 nm Pd particles prepared in the same way, are plotted in Fig. 3. A double–peak structure of desorption profiles was obtained on this sample. The peaks, called α_1 and α_2 (see Fig. 3), are clearly resolved indicating two different adsorption states.



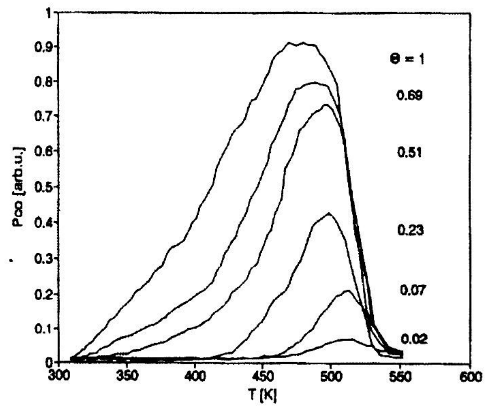


Fig. 2. TPD spectra of CO adsorbed on the 27 nm Pd *particles for various initial relative coverages.*

Fig. 3. TPD spectra of CO adsorbed on the 2.5 nm Pd *particles for various initial relative coverages (right).*

Comparing the 27 nm Pd particles to the Pd (111) data [9] it can be seen that an essentially identical single desorption state at low coverage occurs. However, a shift of 25 K of maximum of the peak was observed. At high CO coverage, 27 nm particles TPD data exhibit the same overall shape and similar peak temperature as does the Pd (111) single crystal. For smaller, 2.5 nm particles, at the saturation CO exposure, the α_1 and α_2 peak maxima are situated 130 and 27 K lower than the peak maximum for the single crystal. At very low coverage only α_2 peak appears and it is shifted by 52 K to 488 K. The comparable intensity of both peaks for all intermediate initial CO coverages shows that the probability of CO occupation of α_1 and α_2 states is approximately the same during the desorption process.

Since the desorption data from our Pd samples are of sufficient quality to warrant a more quantitative treatment, we derive desorption activation energy E_d. A simple Redhead's analysis was used [20], assuming that the desorption order is equal to 1 and the value of preexponential factor is 10^{13} s^{-1}. The results for low and saturation relative coverages are presented in Table 1. In the case of the 27 nm Pd particles, the results are practically the same as for the Pd (111). These data suggest that the 27 nm particles exhibit bulk Pd chemisorption properties. For the 2.5 m particles, the desorption energies are quite different from the other two samples. The values of E_d for low or saturation CO coverages are significantly lower than the Pd (111) and the 27 nm particle values.

TABLE 1.

The desorption activation energies for low and saturation coverages, * calculated for α_1 peak and ** calculated for α_2 peak.

Sample	E_d [kJ/mol] low coverage	E_d [kJ/mol] saturation coverage
Pd(111)	138.3	125.4
27 nm Pd	135.2	124.1
2.5 nm Pd	127.6	93.4*/120.9**
Rh foil	136.5	125.8
5 nm Rh	126.4	122.0
2.5 nm Rh	120.2	111.2

We conclude that variations of desorption activation energy can be explained by the effect of particle size: the activation energy for CO desorption decreases with the decreasing size of palladium particles. The same behaviour was observed for Pd particles on α–alumina (0001) [21]. On the other hand, the opposite tendency in E_d variation with particle size, obtained for Pd particles deposited on (100) MgO, has been published [4,8]. This disagreement can be explained by different morphology of alumina supported (111) particles, exhibiting (111) plane parallel with the support, and MgO (100) particles [9].

4.2. Rhodium

The CO desorption profiles, as a function of temperature for different initial CO coverages, were measured for 3 samples: 2.5 nm, and 5 nm particles and Rh foil. Fig. 4 shows the results obtained for particles of 2.5 nm. The values of E_a were calculated using Redhead's analysis [20]) and are presented in Table 1. It can be easily recognized that E_a generally decreases with the relative CO coverage, this dependence being qualitatively the same for all the samples. The differences are in the values of E_a, the highest are for the Rh plain foil, intermediate for 5 nm particles and the lowest for 2.5 particles. More details about this study can be found in Ref. 22.

The dependence of E_a on particle size exhibits the same general tendency for Pd and Rh alumina supported particles, E_a decreases with decreasing particle size. Unfortunately, it was not possible to compare E_a for larger particles because the Rh particles are always grown of relatively small size. The results of the CO desorption studies were reproducible, showing that there no irreversible particle reconstruction occurs during the desorption experiments.

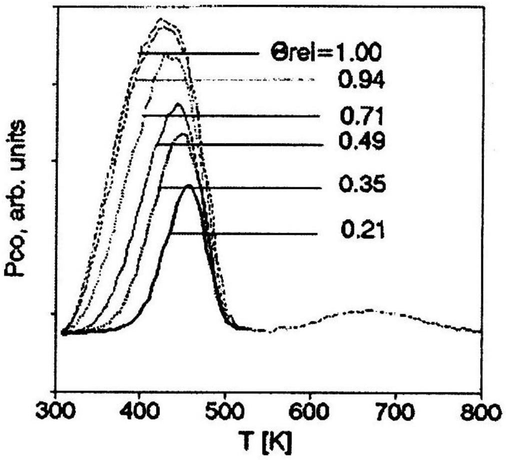


Fig. 4. TPD spectra of CO adsorbed on the 2.5 nm Rh *particles for various initial relative coverages.*

5. Conclusion

The combination of the RHEED and TPD methods represents a powerful tool of in-situ investigation of size effects in catalysis.

The improved experimental set-up of the TPD facility, using the differentially pumped mass spectrometer and the molecular beam doser, allows to obtain well resolved TPD spectra which permit to distinguish between different adsorption sites on particle surface.

The example of study of CO adsorption on Pd and Rh particles is presented in this paper. It is shown that the activation energy of desorption decreases with decreasing particle size. There are large discrepancies between the results reported by various research groups for CO with Pd particles. Most groups have reported stronger adsorption sites on smaller particles. These differences are undoubtedly due to the crystallographic effects, influenced by the choice of substrates and annealing conditions.

Similarly as in the case of E_a, we have observed the important size effect for CO and O sticking coefficient [23,24] and activation energy of CO oxidation [25].

The correlation between particle structure and reactivity presents a serious problem in size effect studies. The possible reconstruction of particles due to their interaction with external atmosphere makes the in–situ investigation obligatory. The RHEED method seems to be a relatively simple means of the particle structure observation. It makes possible to estimate the particle average size, to observe the particle crystallographic structure and epitaxial orientation on their support as well as their possible modifications during different steps of catalytic experiment.

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PROUČAVANJE UČINKA VELIČINE ČESTICA NA DESORPCIJU CO IZ KATALIZATORA Pd I Rh NA Al_2O_3 PODLOZI POMOĆU RHEED I TDP

Sitna zrnca prijelaznih metala često se upotrebljavaju u heterogenim katalitičkim reakcijama. Važan problem je reaktivnost niskih koordinacijskih mjesta na površini zrnaca. Istraživni su necjeloviti epitaksijski slojevi Pd i Rh, izrasli na Al_2O_3 podlozi epitaksijom molekulskim snopom. Opažanje epitaksijskog rasta načinjeno je pomoću RHEED. Adsorpcija CO proučavana je metodom temperaturno programirane desorpcije (TDP), Ustanovljeno je da se aktivacijska energija CO desorpcije smanjuje za manje veličine čestica.