MOLECULAR BEAM STUDY OF OXYGEN CHEMISORPTION ON ALUMINA SUPPORTED Pd PARTICLES

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The adsorption of oxygen on γ-alumina supported Pd particles and Pd(111) single crystal has been studied by means of the thermal molecular beam technique at temperatures between 300 and 550 K. The temperature and coverage dependent sticking coefficient has been measured for all samples. In the case of small particles, the initial integral sticking coefficient increased after the first oxygen saturation and its value was found to be abnormally high. These effects can be explained by the diffusion of oxygen across the support surface and/or by the oxygen induced reconstruction of supported palladium particles.

1. Introduction

The study of oxygen chemisorption on platinum group metals like palladium is of fundamental and technological importance, because the interaction of oxygen with metal surfaces is believed to play a key role in catalytic oxidation processes. The majority of oxygen adsorption studies has been performed on well-characterized surfaces, namely single crystals [1-13] showing the dissociative oxygen adsorption on Pd at T > 180 K and a considerable complexity of this effect. In the molecular beam study of O_2 scattering on Pd(111) surface [8] it has been shown that

the initial sticking coefficient of O_2 is about 0.6 at 300 K and decreases linearly with increasing substrate temperature for T < 800 K. The oxygen induced coverage and temperature-dependent reconstruction of Pd(100) surface was reported in several papers [9-11]. The chemisorbed oxygen can diffuse into the subsurface region as was shown in the case of Pd(110) surface [12]. Similarly, the evidence for subsurface diffusion of oxygen has been obtained for a defective surface of polycrystalline palladium [13] and for a defect-rich surface formed by ion sputtering of polycrystalline palladium [14].

Investigation of the size effect in catalysis has led to the exploitation of more realistic model catalysts exhibiting small metal particles of well-defined size, structure and morphology, deposited on flat supports. The surface of small particles contains different low co-ordination adsorption sites which may be responsible for additional size-dependent adsorption and reaction effects. In spite of the extensive study of O adsorption in bulk Pd, the number of oxygen adsorption studies on Pd particles model catalyst remains limited [15,16]. Eriksson et al. [16] have presented the O_2 initial sticking coefficient of 0.8 on SiO_2-supported Pd particles as well as on a polycrystalline Pd film. Unfortunately, the simple and reliable method of temperature programmed desorption (TPD), used in most cases in adsorption studies, cannot be used in the case of small particles due to the relatively high desorption temperature for oxygen (generally above 800 K) and low thermal stability of the samples.

In this paper, we compare the oxygen adsorption data obtained for alumina-supported Pd particles of various sizes and for the Pd(111) single crystal, studied by means of the molecular beam surface scattering technique.

2. Experimental

Molecular beam experiments were carried out in a vacuum system with a base pressure $< 3 \times 10^{-8}$ Pa, equipped with a specially designed spectrometer. Oxygen exposures were made by means of a molecular beam doser directly onto the surface. The intensity of the molecular beam was kept about 5×10^{12} molecules cm^{-2} s^{-1} at the sample surface. The scattered or desorbed molecules were monitored with a differentially-pumped, computer-controlled quadrupole mass spectrometer (QMS). This vacuum system is described in detail in Ref. 17. The temperature of the sample was measured by a very thin Fe-constantan thermocouple which was spot welded to the edge of the Pd single crystal and fastened inside the Pd particle support.

Before the experiments, the Pd(111) single crystal surface was cleaned by cycles of argon ion bombardment (900 eV, 2 μAcm^{-2}) and heating in oxygen (3×10^{-6} Pa) at 900 K during 1 h as has been described in Ref. 18. After each cycle, the saturation CO desorption peak was measured and the cleaning procedure was monitored by the increase of CO desorption peak area versus the number of cleaning cycles. After 6 cycles, the saturation CO desorption peak remained stable and the surface was considered clean.

The alumina layers were obtained by the thermal oxidation method. The 8 mm

$\times$ 8 mm $\times$ 1.5 mm pure (99.999%) Al substrate was kept at 600 °C during 24 hours in order to prepare the 50 – 100 nm thick alumina layer [19]. The structure and morphology of alumina layers were controlled by means of atomic force microscopy (AFM) and transmission electron microscopy (TEM) [20]. It was shown that the layers are formed by the fcc Al_2O_3 crystals of average size of 0.1 μm and lattice parameter a = 0.79 nm, which corresponds to the modification of γ – Al_2O_3 [21].

The small supported palladium particles were prepared in-situ by vapour deposition of Pd onto the oxidised aluminium substrates using a micro-electron-beam evaporation source. During the deposition, the support temperature was held at 350 K and the background pressure in the vacuum chamber was lower than 1×10^{-6} Pa. By varying the total amount of deposited Pd, the particles of different sizes were obtained. The freshly deposited Pd particle samples are not stable, and thermal treatments lead to the particle coalescence and rebuilding [22]. It was shown [23,24] that the relatively stable particle populations are obtained after heating in a CO/O_2 atmosphere at a temperature of 550 K. We have stabilised the samples in a 1 : 1 CO/O_2 mixture at a total mixture pressure 1×10^{-5} Pa during one hour. The temperature of 550 K has never been reached during subsequent experiments. At the end of the measurement, the particles were investigated by TEM, using the method of transfer carbon replica. It was found that the thick deposit gave a semi-continuous layer with very large size histogram and average particle size $\oslash = 27$ nm. The thin deposit gave a homogeneous particle distribution with $\oslash = 2.5$ nm and the particle density of 1×10^{12} cm^{-2} [17].

3. Results and discussion

The kinetics of adsorption described in terms of the sticking coefficient $s(\Theta)$ (Θ stands for coverage) can be investigated by the molecular beam technique [25, 26]. At a time $t = 0$, the molecular beam is switched on and a clean surface is exposed to a constant molecular flux. The intensity of scattered gas fluxes is monitored continuously as a function of time during exposure at a given substrate temperature T. As the surface coverage increases, the sticking probability decreases to zero that is reached at the saturation. The absolute value of the sticking coefficient s can be derived from the curves of scattered intensity I according to relationship

$$s(t) = 1 - \frac{I(t)}{I_0},$$

where I_0 is the initial incident beam intensity and $I(t)$ is the intensity of scattered molecules at time t. The time dependence can be easily converted into a variation with relative coverage:

$$\Theta(t) = \frac{\int_0^t (I_0 - I(t))\mathrm{d}t}{\int_0^\infty (I_0 - I(t))\mathrm{d}t}.$$

Figure 1 shows the dependence of the oxygen sticking coefficient on the relative coverage for 2.5 and 27 nm Pd particles and Pd(111) single crystal at different substrate temperatures. The relative coverage $\Theta = 1$ corresponds to the saturation exposure to oxygen at room temperature for each sample. As can be seen in Figs. 1a and b, the curves of $s(\Theta)$ at 300 K for Pd particles lie below the other ones. That is rather surprising. In the case of Pd(111) surface, $s(\Theta)$ decreases "normally" with increasing surface temperature. After each oxygen scattering measurement, the adsorbed oxygen was removed by CO titration and then heated to 500 K in order to desorb chemisorbed CO.
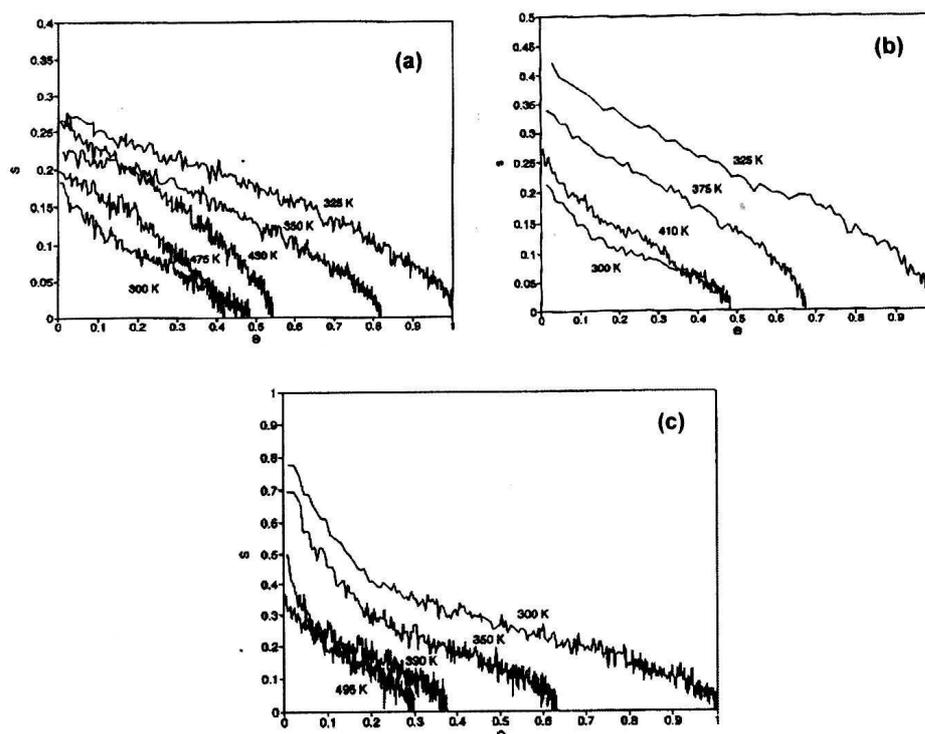

Fig. 1. Sticking coefficient s as a function of relative coverage for different substrate temperatures and a) 2.5 nm Pd particles, b) 27nm Pd particles, c) Pd(111) single crystal.

The initial sticking probabilities s_0 (i.e. zero coverage sticking coefficient), measured as a function of the substrate temperature T, are presented for all samples in Fig. 2. One can see that for the Pd(111) crystal and larger Pd clusters, the value of s_0 falls linearly with increasing substrate temperature, and in the case of smaller Pd clusters, s_0 is approximately temperature independent. The initial sticking probability of 0.77 on the Pd(111) at 300 K is a little higher than the value presented in [8]. In contrast to Pd(111), the first value of s_0 (at 300 K) for supported palladium particles is lower than the next ones. The increase of s_0 after the

first oxygen scattering experiment (for both supported Pd samples) is accompanied by an important increase of saturation surface concentration of oxygen, as can be seen in Fig. 3.
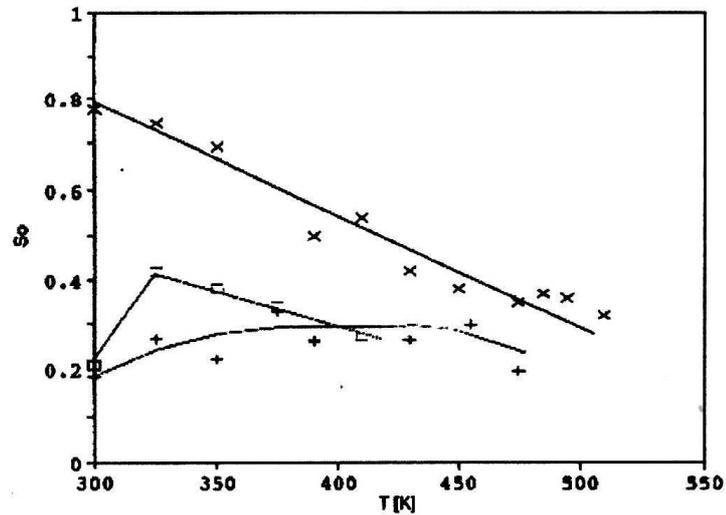

Fig. 2. Initial sticking coefficient s_0 for O_2 as a function of the substrate temperature T, $+$ – Pd(2.5 nm)/ Al_2O_3, $\square$ – Pd(27 nm)/Al_2O_3, $\times$ – Pd(111) single crystal.
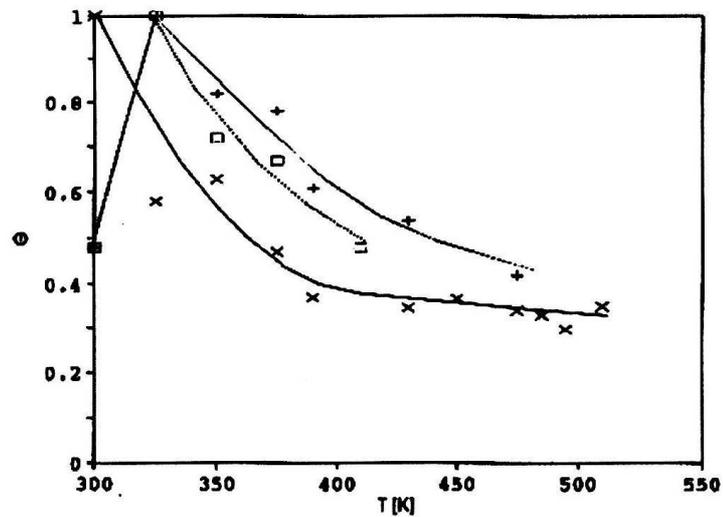
Fig. 3. Dependence of relative oxygen coverage Θ on the substrate temperature T, $+$ – Pd(2.5 nm)/ Al_2O_3, $\square$ – Pd(27 nm)/Al_2O_3, $\times$ – Pd(111) single crystal.

In the case of supported metal particles, the sticking coefficient measured in this

way has an integral character. It consists of a sticking coefficient of gas molecules impinging directly on the metal particles and a sticking probability of molecules impinging on the substrate, which is practically zero. So, it depends on a ratio of metal/substrate surface that is known from TEM observation. The results are presented in Table 1. It can be seen that in the case of 2.5 nm Pd clusters, which represent only 10 % of the whole sample surface, the real sticking coefficient of Pd would be 1.8 what is not possible in principle. This behaviour could be explained in terms of the surface diffusion of oxygen on the alumina substrate as was already reported in [27]. This effect is based on the geometric consideration. It depends on the particle size and density. In the case of the diffusion, the molecules physisorbed and diffusing across the alumina surface are captured by Pd clusters where they chemisorb. In this way the sticking coefficient increases virtually and can reach values above unity. A similar effect has been reported for CO diffusion on mica [28] and alumina [29,30].

TABLE 1

Comparison of zero coverage sticking probabilities for oxygen adsorption on Pd.

Sample	Pd surface area	s_0	s_{OT}	s_0/s_{OT}
Pd(111)	1	0.77	0.77	–
Pd(27 nm)/Al$_2$O$_3$	0.34	0.21	0.26	–
Pd(2.5 nm)/Al$_2$O$_3$	0.10	0.18	0.08	2.3

The above presented results obtained for small supported particles, i.e., the initial increase of oxygen sticking coefficient with temperature and its abnormally high value, cannot be unambigously explained without in-situ observation of the catalyst structure. Nevertheless, we hypotesize two causes in order to explain this behaviour: (i) the instabilities of catalyst morphology given by the oxygen induced reconstruction of particle surface and a possible temperature dependent oxygen subsurface diffusion, accompanying the saturation of Pd surface (it should be noted that in previous experimental steps and particle stabilisation, the oxygen coverage remained very low [31]). (ii) the temperature dependent oxygen diffusion on the substrate surface. The increase of diffusion coefficient with the surface temperature can be responsible for virtual increase of oxygen sticking coefficient on Pd particle surface.

The results presented in this paper show that the oxygen adsorption on supported particle surface is a complex problem, probably more complicated than the oxygen interaction with Pd surfaces of bulk samples. In order to elucidate the mechanisms of oxygen adsorption, the simultaneous investigation of particle structure and reactivity would be necessary. The RHEED (reflection high energy electron diffraction) method seems to be a tool which can be used to this purpose [24]. Therefore, we are preparing the study of CO and oxygen induced reconstruction of supported model catalysts using the simultaneous RHEED and TPD experiments.

4. Conclusion

Adsorption of O_2 on the Pd(111) single crystal and on supported Pd particles has been studied by means of molecular beam scattering. The oxygen sticking coefficient has been determined as a function of coverage and substrate temperature. For the Pd(111), the zero coverage sticking probability is 0.77 at room temperature. The initial sticking coefficient for smaller supported Pd particles exhibits a larger value than expected, and increases after the first oxygen saturation of the surface at room temperature.

Two hypotheses that permit explaining these properties are advanced:

(i) the oxygen induced particle rebuilding

(ii) the temperature dependent oxygen diffusion over the particle support surface.

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ISTRAŽIVANJE KEMISORPCIJE KISIKA NA Pd ZRNCIMA NA KORUNDU METODOM MOLEKULSKOG SNOPA

Adsorpcija kisika na Pd zrncima na γ-Al$_2$O$_3$ i Pd (111) monokristalu proučavana je metodom toplinskih molekulskih snopova na temperaturama izmedu 300 i 550 K. Mjeren je faktor zaljepljenja u ovisnosti o temperaturi i prekrivenosti. S malim Pd zrncima se početni ukupni faktor zaljepljenja nakon prvog zasićenja kisikom povećao i postigao nestvarno visoku vrijednost. Ti se učinci tumače difuzijom kisika preko podložne površine i/ili rekonstrukcijom Pd zrnaca kisikom.