Catalysis Letters 5 (1990) 197–202

ESR STUDY OF ALUMINA-SUPPORTED PALLADIUM CATALYST

Z. KARPIŃSKI [1], W. JUSZCZYK [1], J. HERBICH [1] and J. MICHALIK [2]

[1] *Institute of Physical Chemistry of the Polish Academy of Sciences, ul.Kasprzaka 44/52, 01-224 Warszawa, Poland*

[2] *Institute of Nuclear Chemistry and Technology, ul.Dorodna 16, 03-195 Warszawa, Poland*

Received 8 January 1990; accepted 30 March 1990

ESR of Pd/Al_2O_3, Pd^+ ions, effect of catalyst pretreatment

The ESR spectra of differently pretreated 0.97 wt% Pd/Al_2O_3 catalyst showed very broad signal at $g \approx 2.10$ assigned to Pd^+ ions. The intensity of this signal is stronger after pretreatments at higher temperatures (500-600 ° C). This result appears to support our earlier idea (ref. [2]) as to an important role of electron-deficient palladium as an active centre in catalyzing the reaction of neopentane hydrogenolysis.

1. Introduction

In our previous paper [1], where the catalytic conversion of neopentane was used as a virtually noncoking probe, it was found that, after reduction at moderate temperatures (300–500 ° C), Pd/Al_2O_3 is roughly two orders of magnitude more active than Pd/SiO_2. Our further work revealed that an even higher, although transient, catalytic activity is obtained after reducing Pd/Al_2O_3 at 600 ° C and extensively purging it in helium at this temperature [2]. Because the IR spectra of adsorbed CO revealed the presence of palladium ions in superactive Pd/Al_2O_3, it was proposed that Pd^{n+} ions ($n = 1$ or 2) might be sites of high catalytic activity [2].

It is known that the presence of paramagnetic Pd species (Pd^+ and Pd^{3+} ions) in supported Pd catalysts should be proved by electron spin resonance technique (ESR) [3–7]. Especially, in the case of palladium-loaded zeolite X and Y the presence of ionic Pd species in mildly reduced samples has been confirmed [8–12]. However, in the case of alumina-supported Pd the ESR investigations are complicated by the fact that alumina may give quite a strong broad ESR signal which coincides with the signal characteristic of Pd^+ [13]. The intensity of this broad signal is due to various paramagnetic impurities (mainly iron [13,14]) and depends on a thermal treatment (with evacuation) of alumina [13]. Nevertheless, the presence of Pd^+ species were postulated in a number of cases involving Pd/Al_2O_3 catalysts [3–7]. From the majority of works concerning both alumina-and zeolite-supported palladium, an anisotropic signal with $g_{\perp} \approx 2.10$–2.15 and $g_{\parallel} \approx 2.3$–$3.1$ should be due to Pd^+ [3,5,7,8–12]. Pd^{3+} produces an isotropic signal with $g \approx 2.23$ [7–12].

Here we present an ESR study of 0.97 wt% Pd/Al_2O_3 catalyst pretreated in the same way as the samples prior to the kinetic measurements [2]. We have shown [2] that a variety of catalyst pretreatments lead to large changes in catalytic activity in the neopentane conversion. Our idea as to the essential role of Pd^+ ions in forming superactive sites could be substantiated by a possible detection of Pd^+ species after those pretreatments which produced most active samples of the Pd/Al_2O_3 catalyst.

2. Experimental

The preparation and pretreatment of the 0.97 wt% Pd/Al_2O_3 catalyst have been described in earlier papers [1,2]. Briefly, a 99.99% pure American Cyanamid PHF γ-alumina (80–100 mesh, acid washed) was impregnated by an incipient wetness technique with an aqueous solution of $PdCl_2$. After drying, the catalyst precursor was precalcined and prereduced at temperatures up to 390 ° C, and then stored in a glass-stoppered bottle.

0.2 g samples of the Pd/Al_2O_3 catalyst for ESR investigations were prepared in a fused silica U-tube reactor with a side-arm (an ESR tube) and two closing stopcocks, in the apparatus used previously for kinetic studies [2]. After a given pretreatment, the reactor was detached and the catalyst sample was in-situ transferred from the U-tube to the side-arm (by turning the reactor upside-down) and the side-arm was sealed off from the rest of the reactor by means of a gas torch. The following catalyst pretreatments were used (see [2]):

A. O_2, 300 ° C, 0.5 h; H_2, 300 ° C, 1 h; He, 300 ° C, 1 h,
B. O_2, 300 ° C, 0.5 h; H_2, 500 ° C, 3 h; He, 500 ° C, 1 h,
C. O_2, 300 ° C, 0.5 h; H_2, 600 ° C, 17 h; He, 600 ° C, 1 h,
D. O_2, 300 ° C, 0.5 h; H_2, 600 ° C, 17 h; He, 600 ° C, 17 h.

ESR spectra of the catalyst samples were compared with those of pure alumina pretreated in the same four ways. ESR spectra were recorded at various temperatures between −160 ° C and 20 ° C with a Jeol Me-3X spectrometer. The experiments indicate an independence of the spectra of temperature.

Palladium dispersion changes in the 0.97 wt% Pd/Al_2O_3 catalyst after various pretreatments were reported in the previous paper [2].

3. Results and discussion

ESR spectra of differently pretreated Pd/Al_2O_3 and Al_2O_3 samples are shown in fig. 1. The spectra show that the signal characteristic of the alumina is not

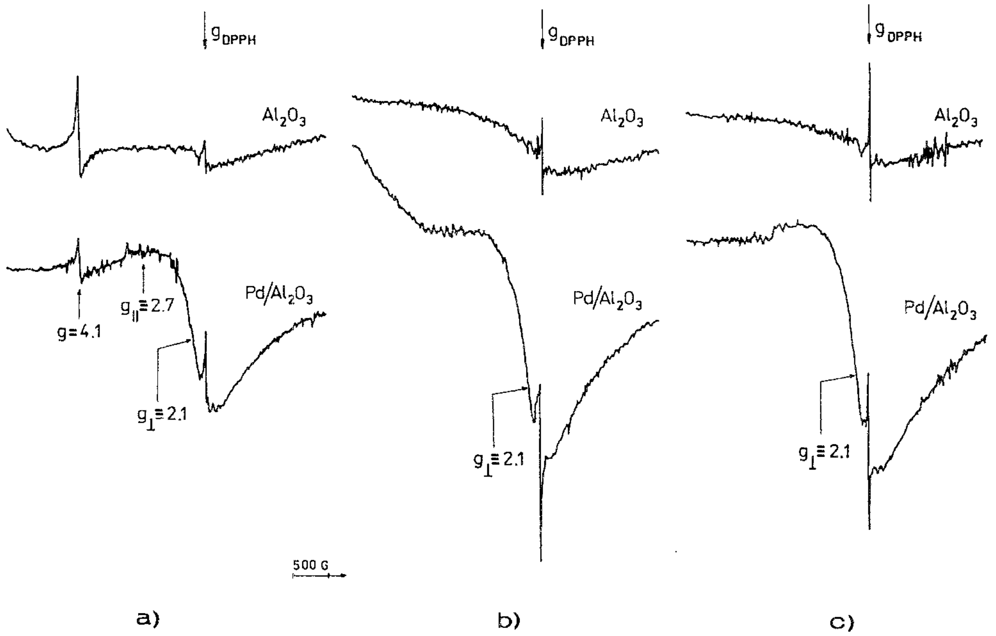

Fig. 1. ESR spectra of 0.97 wt% Pd/Al_2O_3 catalyst and pure γ-alumina (recorded at $-120\,°C$) after various pretreatments:
(a) O_2, 300 °C, 0.5 h; H_2, 500 °C, 3 h; He, 500 °C, 1 h;
(b) O_2, 300 °C, 0.5 h; H_2, 600 °C, 17 h; He, 600 °C, 1 h; and
(c) O_2, 300 °C, 0.5 h; H_2, 600 °C, 17 h; He, 600 °C, 17 h.
All the ESR spectra were recorded with the same amplification.

negligible. The presence of an iron impurity in our alumina (30 ± 10 ppm, [15]) cautions us against the danger of misinterpreting the ESR spectra obtained for Pd/Al_2O_3 samples [13], the more so as a narrow line at $g \sim 4.1$ unequivocally indicates the presence of Fe^{3+} cations in samples pretreated at 500 °C (fig. 1a) and 300 °C (not shown). However, if one compares the spectra of Pd/Al_2O_3 and Al_2O_3 pretreated in the same experimental conditions, it seems apparent that the introduction of palladium onto alumina brings about a broad ESR signal with strong anisotropy. We believe that this signal, clearly seen for drastically pretreated samples (at 500 °C (fig. 1a) and 600 °C (fig. 1b and c)), with $g_{\perp} \approx 2.1$ and somewhat less pronounced $g_{\parallel} \approx 2.7$ (fig. 1a), should be ascribed to Pd^+ species [3,5,8–12]. The possibility that the observed ESR spectrum represents the magnetic resonance of conduction electrons in small palladium clusters (with dimensions less than 5 nm) seems less likely. According to the theoretical predictions [16] this type of resonance should be characterized by symmetric Lorentz line. In the samples pretreated at 300 °C, the ESR intensity was only slightly larger than the "background" signal originated from the alumina (not shown).

In the previous paper [2] we suggested that the most probable agents for oxidation of Pd^0 to Pd^{n+} are the surface hydroxyl groups of alumina. At temperatures higher than 300 ° C, alumina begins to lose its hydroxyl groups [2,4] which may oxidize palladium. Obviously, such a redox reaction (with evolution of gaseous H_2) is more feasible when the catalyst is pretreated in an inert gas (He, Ar, or in vacuum) than in H_2.

The intensity of the ESR signal with $g_\perp \approx 2.1$ seems to change with the sample pretreatment in the following order (figs. 1a, b and c): pretreatment D $\approx$ pretreatment C $>$ pretreatment B $\gg$ pretreatment A. This correlation reflects the change of the amount of unpaired spins (i.e. the concentration of Pd^+ ions in the samples) with the pretreatment. It should be recalled here that the catalytic activity in neopentane hydrocracking changes with the sample pretreatment in a similar way [2]. In conclusion, the results of these ESR studies confirm our earlier speculation (based on IR studies of adsorbed CO, ref. [2]) as to an important role of electron-deficient palladium as an active centre in the hydrogenolysis of neopentane.

Ben Taarit et al. [9] reported a similar anisotropic ESR signal ($g_\perp = 2.146$, $g_\parallel = 2.97$) in the case of a mordenite-supported Pd after oxidation and evacuation at 500 ° C. This signal was unambiguously assigned to Pd^+ ions bonded to four lattice oxygen ions in a pseudo-square-planar symmetry. H_2 and CO adsorption led to some decrease in the g values with respect to the initial Pd^+ ions. This decrease was interpreted in terms of the ligand effect, with the CO or the OH adduct in an axial position of a pyramidal square-planar complex, and the equatorial positions occupied by the four O^{2-} ions. Recently we suggested [2] that palladium ions may be stabilized on the surface of γ-alumina by assuming octahedral vacant sites of the carrier. If we assume that on the surface of Al_2O_3 the top O^{2-} ion of the octahedron is missing, the remaining part of the O^{2-} skeleton forms a square pyramid (see fig. 5 in ref. [2]). Thus, although our ESR spectra are somewhat difficult to be interpreted (the signal is very broad), it looks that our model suggested in [2] may be supported be the presented ESR data. A considerably broadening of the ESR signal of Pd^+/Al_2O_3 may result from a superposition of several ESR signals originating from somewhat differently coordinated Pd^+ ions. The presence of different planes (e.g. (110) and (100)) and various defects on the surface of highly dehydroxylated alumina [17,18] may be one of the reasons of "surface heterogeneity" of γ-alumina. In their ESR study of Pd/Al_2O_3 catalyst (oxidized and degassed at 550 ° C) Shubin et al. [6] found the superposition of at least two ESR signals ascribed to Pd^+ ions ($g_\perp^{1,2} \approx 2.13$, $g_\parallel^1 = 2.92$, $g_\parallel^2 = 2.42$). On the other hand in the case of Pd/zeolite catalysts, where the situation of trapped Pd^+ ions is more clearly defined, the respective ESR spectra show relatively narrow signals [8–12].

It should be recalled here that the results of IR studies of adsorbed CO on the Pd/Al_2O_3 catalyst after pretreatments C and D showed quite a large effect of He purge time on the concentration of superficial electron-deficient Pd species: a longer purge brought about more reoxidation (figs. 4a and b, in ref. [2]). This appears in a disagreement with the results of our ESR studies (figs. 1b and 1c). Of course, one should remember that ESR is a bulk technique which monitors all (bulk and superficial) Pd^+ species. In fact, we incline to believe that in our case a part of Pd^+ species is situated on the surface, but some of them are in the bulk of Pd crystallites. In this respect, another explanation of the broadening of the ESR signal is a possibility of a fast spin-spin relaxation through interaction of Pd^+ ions with Pd^0 species within small metal crystallites (ref. [19] for Pt/Al_2O_3). In such a case, Pd^+ species should be located close to the $Pd-Al_2O_3$ interface [19].

Our model [2] emphasizes the essential role of Pd^+ ions in neopentane hydrocracking. Their concentration is probably rather low (*although changeable with a catalyst pretreatment*) but, due to their superactivity, they may play a predominant role in catalyzing conversions of alkanes.

Acknowledgement

This work was carried out within Research Projects: CPBR 03.20 and CPBP 01.19.

References

[1] W. Juszczyk, Z. Karpiński, J. Pielaszek, I. Ratajczykowa and Z. Stanasiuk, in: *Proc. 9th ICC* (Calgary 88), eds. M.J. Phillips and M. Ternan, Vol. 3 (1988) 1238.
[2] W. Juszczyk, Z. Karpiński, I. Ratajczykowa, Z. Stanasiuk, J. Zieliński, L.-L. Sheu and W.M.H. Sachtler, J. Catal. 120 (1989) 68.
[3] J. Turkevich, F. Nozaki and D. Stamirez, in: *Proc. 3rd ICC* (Amsterdam 64), eds. W.M.H. Sachtler, G.C.A. Schuit and P. Zwietering, Vol. I (1965) 586.
[4] G.D. Zakumbaeva, V.A. Naidin, T.S. Nadirov, E.N. Litvyakova and L.M. Kurashvili, Kinet. Katal. 23 (1982) 126.
[5] V.E. Shubin, V.A. Shvets, G.A. Savel'eva, N.M. Popova and V.B. Kazanskii, Kinet. Katal. 23 (1982) 1153.
[6] V. Parvulescu, I. Sandulescu, N. Grecu, C. Contescu and I.V. Nicolescu, Rev. Roum. Chim. 33 (1988) 3.
[7] A. Rakai, PhD Dissertation, Université Pierre et Marie Curie, Paris, 1989.
[8] C. Naccache, J.F. Dutel and M. Che, J. Catal. 29 (1973) 179.
[9] Y. Ben Taarit, J.C. Vedrine, J.F. Dutel and C. Naccache, J. Magn. Reson. 31 (1973) 251.
[10] J. Michalik, H. Lee and L. Kevan, J. Phys. Chem. 89 (1985) 4282.
[11] J. Michalik, M. Narayama and L. Kevan, J. Phys. Chem. 89 (1985) 4553.
[12] A.K. Ghosh and L. Kevan, J. Phys. Chem. 93 (1989) 3747.
[13] P.A. Berger and J.F. Roth, J. Catal. 4 (1965) 717.
[14] J.W. Geus, in: *Proc. 3rd ICC* (Amsterdam 64) eds. W.M.H. Sachtler, G.C.A. Schuit and P. Zwietering, Vol. I (1965) 597.
[15] M. Kobayashi, Y. Inoue, N. Takahashi, R.L. Burwell, Jr., J.B. Butt and J.B. Cohen, J. Catal. 64 (1980) 74.
[16] A. Kawabata, J. Phys. Soc. Jpn. 29 (1970) 902.
[17] B.C. Lippens and J.J. Steggerda, in: *Physical and Chemical Aspects of Adsorbents and Catalysts*, eds. B.G. Linsen et al. (Academic Press, London, 1970) Ch. 4.
[18] H. Knözinger and P. Ratnasamy, Catal. Rev.–Sci. Eng. 17 (1978) 31.
[19] T. Huizinga and R. Prins, J. Phys. Chem. 87 (1983) 173.