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Characterization of Supported Palladium Catalysts[1]

III. Pd/Al_2O_3

W. JUSZCZYK, Z. KARPIŃSKI,[2] I. RATAJCZYKOWA, Z. STANASIUK, J. ZIELIŃSKI,
L.-L. SHEU,* AND W. M. H. SACHTLER*

*Institute of Physical Chemistry of the Polish Academy of Sciences, ul.Kasprzaka 44/52, 01-224 Warszawa, Poland, and *V. N. Ipatieff Laboratory, Center for Catalysis and Surface Science, Northwestern University, Evanston, Illinois 60208*

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In Part I of this series [W. Juszczyk *et al.*, *in* "Proceedings, 9th International Congress on Catalysis, Calgary, 1988" (M. J. Phillips and M. Ternan, Eds.), Vol. 3, p. 1238. The Chemical Institute of Canada, Ottawa, 1988] using the catalytic conversion of neopentane as a virtually noncoking probe, we found that after reduction at moderate temperatures (573–773 K), Pd/Al_2O_3 is roughly two orders of magnitude more active than Pd/SiO_2. An even higher, though transient, catalytic activity is now reported after reducing Pd/Al_2O_3 at 873 K and extensively purging it in He at this temperature. The IR spectra of adsorbed CO reveal the presence of Pd^{n+} ions in superactive Pd/Al_2O_3; their concentration positively correlates with catalytic activity. Since other potential causes such as strong acid sites are excluded, it is proposed that Pd^{n+} ions are sites of high catalytic activity. A possible mechanism of their formation and a model of neopentane hydrogenolysis are briefly discussed. Completely reduced Pd appears necessary for neopentane isomerization. © 1989 Academic Press, Inc.

INTRODUCTION

In previous papers of this series (*1, 2*) we reported results on the characterization of the supported Pd catalysts. Our approach was based mainly on studies of chemisorption and reaction kinetics. The reaction of neopentane with hydrogen appeared to probe the nature of palladium catalysts, in particular in the case of Pd/SiO_2 (*1, 2*). Upon high-temperature reduction (HTR) palladium was found to interact with silica, and palladium silicide phase(s) were identified by XRD. At the same time, isomerization selectivity increased from ca. 15% up to 70–80%. For Pd/TiO_2 and Pd/CeO_2 some differences in isomerization selectivity were observed between the SMSI and the non-SMSI state.

Less importance was attached to catalytic changes in the case of the Pd/Al_2O_3 system because preliminary experiments showed rather minor changes in isomerization selectivity (HTR at 773 K vs low-temperature reduction, LTR, at 523 K) (*1*). At that time we did not emphasize that the overall activity level exhibited by Pd/SiO_2 catalyst is achieved by Pd/Al_2O_3 catalyst at temperatures lower by ca. 30 K. Simple calculation, assuming an activation energy of 60 kcal/mole (*3*), indicates that Pd/Al_2O_3 is more active than Pd/SiO_2 by roughly two orders of magnitude. Obviously, such a large difference in catalytic activity called for an explanation. Because blank experiments with pure Al_2O_3 showed its negligible activity, two major causes could be suspected: dual function character of Pd/Al_2O_3 (especially reinforced by the presence of chlorine); and/or modification of Pd by alumina. Both these questions are considered in this paper.

Neopentane, unlike other alkanes, is unable to form olefins or carbenium ions without changing its carbon skeleton; therefore,

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[1] Ref. (*1*) is regarded as Part I of this series.

[2] To whom correspondence should be addressed.

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the catalyst deactivation is negligible with this probe molecule. This fact allows us to attribute the observed variations in catalytic behavior to changes in the catalyst morphology.

EXPERIMENTAL METHODS

The preparation and pretreatment of the 0.97 wt% Pd/Al_2O_3 catalyst have been described in an earlier paper (*1*). Briefly, 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 663 K, and then stored in a glass-stoppered bottle. A few experiments were also carried out with Pd powder (Alfa Ventron product, 99.95%, fraction 0.25–0.55 μm) mixed with γ-alumina. Fractions exposed after various pretreatments were determined from chemisorption of H_2 (at 343 K) and CO (at 293 K) using a pulse technique in the manner described earlier (*1, 2*).

Temperature-programmed reduction (TPR) of the 0.97 wt% Pd/Al_2O_3 catalyst was performed by passing a 5% H_2/Ar mixture through the catalyst bed at a flow rate of 25 ml/min. The heating rate was 8 K/min. Two samples were run: first, the fresh catalyst after pretreatment in flowing oxygen at 573 K for 0.5 h, and second, another which underwent a high-temperature reduction (at 773 K) and subsequent calcination in O_2 at 573 K for 0.5 h.

The reaction of neopentane (Merck) with hydrogen (palladium-diffused) was studied in a static–circulation system in the manner described previously (*1, 2*). The reaction mixture (H_2/neopentane = 60/6 Torr, 1 Torr = 133.3 Pa) was admitted to the evacuated reactor (after a given catalyst pretreatment) kept at the lowest reaction temperature, e.g., at 488 K for the catalyst reduced at 523 K. After the first 50–60 min of the reaction (5–6 "injections" to the glc system), the temperature of the furnace was raised as quickly as possible to study the course of the reaction at higher temperatures. The degree of conversion was never higher than 3% for the lowest reaction temperature. Also, at the lowest temperatures the course of the reaction always exhibited good linear relation between concentration of neopentane (and products) and time, as exemplified in Fig. 1. Turnover frequencies (N_t's) were calculated on the basis of the dispersion data shown in Table 1. Only in the case of severely pretreated Pd/Al_2O_3 (at 873 K) was the fraction exposed assumed to be ~0.3. Nearly twofold loss of metal dispersion of Pd/Al_2O_3 catalysts after prolonged reduction at ca. 800–900 K was reported by others (*4, 5*). Initial product distributions (= selectivities) were calculated as the carbon percentage of neopentane consumed in the formation of a designated product, e.g., mole percent of methane from neopentane would be divided by 5 and normalized in deriving the product distribution.

Blank kinetic experiments were done with the alumina after pretreating it in the same manner as 0.97 wt% Pd/Al_2O_3 catalyst. The Al_2O_3 was impregnated with the same amount of chlorine as was used to

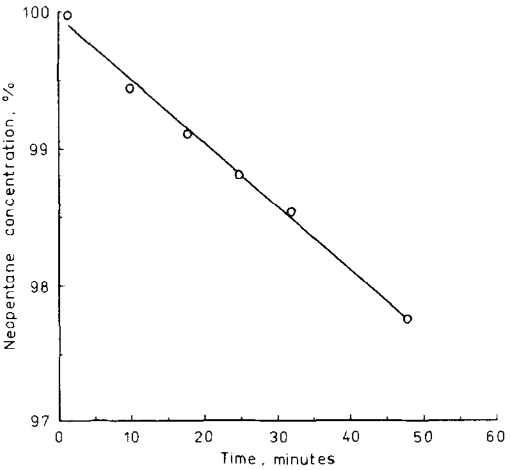


FIG. 1. A typical kinetic run at 452.7 K; H_2: neopentane = 60 : 6 Torr; 0.3 g of 0.97 wt% Pd/Al_2O_3 catalyst after O_2, 573, 0.5; H_2, 873, 17; He, 873, 17 (for the pretreatment code, see Table 1).

TABLE 1

Metal Dispersion Changes in 0.97 wt% Pd/Al_2O_3 Catalyst after Various Pretreatments

Pretreatment[a]	H/Pd_t[b]	CO/Pd_t[c]
O_2, 573, 0.5; H_2, 523, 1; Ar, 723, 1	0.57	0.44
O_2, 573, 0.5; H_2, 573, 1; Ar, 723, 1	0.58	0.42
O_2, 573, 0.5; H_2, 773, 3; Ar, 773, 1	0.45	0.39
O_2, 573, 0.5; H_2, 523, 1; Ar, 723, 1[d]	0.51	0.41

[a] In the pretreatment code O_2, 573, 0.5; H_2, 523, 1; Ar, 723, 1 means that the catalyst was exposed to flowing O_2 at 573 K for 0.5 h, then to H_2 at 523 K for 1 h, and finally to Ar at 723 K for 1 h.

[b] Fraction exposed measured by H_2 chemisorption at 343 K.

[c] Fraction exposed measured by CO chemisorption at 293 K.

[d] This pretreatment was applied to the catalyst prereduced at 773 K for 3 h and flushed out with Ar at 773 K for 1 h.

deposit the Pd. An aqueous solution of $CuCl_2$ was employed as a source of chlorine: Cu is much less active than Pd in the neopentane reaction (*6*). We have rejected the use of HCl because it is known from the literature that it should be much more difficult to remove the chlorine from alumina in the absence of metals (e.g., Ru, Ref. (*7*)).

Most infrared (IR) experiments were performed in a static metal cell described elsewhere (*8*). IR spectra were recorded using a computerized Perkin–Elmer Model 325 IR spectrometer at a spectral resolution of 4 cm^{-1} and scanning speed of 1.5 s/cm^{-1}. Spectra were recorded after catalyst pretreatment and evacuation (background) and with CO in the gas phase (2 Torr, at room temperature).

Adsorption of CO on extensively reduced (at 873 K) Pd/Al_2O_3 was studied by FTIR spectroscopy in a flow-type fused silica cell, in the manner described in (*9*). After each pretreatment the samples were cooled in argon (UHP, 99.995%, Matheson, IL) and IR spectra were recorded using a Nicolet 60SX single-beam FTIR spectrometer at a resolution of 4 cm^{-1} (scan number of 200). After recording the background spectrum, CO (99.9%, Matheson, IL, further purified over alumina, molecular sieve, and MnO/SiO_2) was introduced onto the catalyst wafer. Then the cell was purged with Ar at room temperature. FTIR spectra were recorded after a 50-min purging time.

RESULTS

Table 1 shows the metal dispersions measured by chemisorption of H_2 and CO after various pretreatments.

TPR results are shown in Fig. 2. The fresh sample of 0.97 wt% Pd/Al_2O_3 (after calcination at 573 K for 0.5 h) shows a very broad TPR peak with a maximum at 465 K (Fig. 2a). However, the same catalyst after HTR (at 773 K) and subsequent calcination at 573 K for 0.5 h seems to be fully reduced at rather low temperatures (Fig. 2b). In both cases the amount of H_2 consumed during TPR corresponds to complete reduction of Pd^{2+} to Pd^0. The results are in agreement

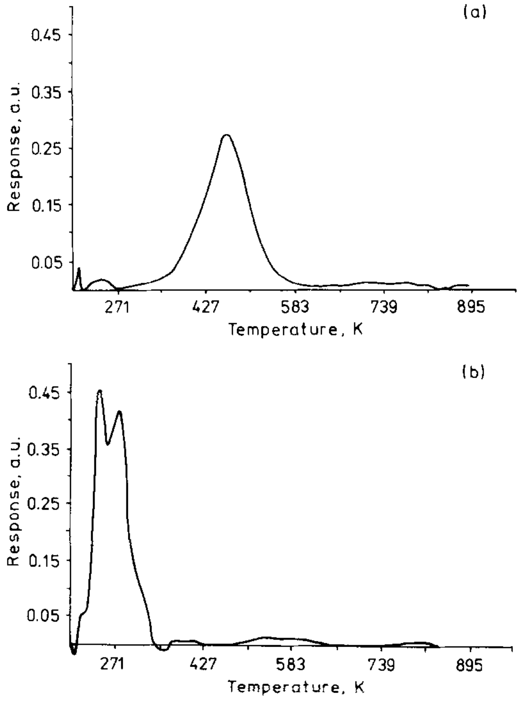


FIG. 2. TPR of 0.97 wt% Pd/Al_2O_3 catalyst: (a) fresh catalyst after calcination at 573 K for 0.5 h; (b) after HTR and subsequent calcination at 573 K for 0.5 h.

TABLE 2

Reaction of Neopentane on 0.97 wt% Pd/Al_2O_3 Catalyst Reduced at Temperatures between 523 and 773 K

Reduction condition:[a] temp., time	Reaction temp. (K)	N_t (s^{-1})	Initial product distribution (%)				
			CH_4	C_2H_6	C_3H_8	iC_4H_{10}	iC_5H_{12}
523 K, 1 h[b]	488	2.3×10^{-5}	31.7	1.2	20.0	45.6	1.5
	498	6.1×10^{-5}	40.3	3.6	34.6	21.4	—
523 K, 1 h[b]	487.5	2.1×10^{-5}	25.2	0.9	17.0	56.9	—
	498	5.2×10^{-5}	36.7	4.0	38.5	20.8	—
573 K, 1 h[b]	484.5	8.4×10^{-6}	20.2	1.1	7.8	60.0	10.9
	494	2.5×10^{-5}	28.7	1.3	19.7	50.4	—
	504	7.4×10^{-5}	35.7	3.8	35.5	24.1	0.8
573 K, 1 h[b]	488	1.3×10^{-5}	32.3	1.3	10.7	55.7	—
	498	4.0×10^{-5}	37.5	2.2	25.3	35.0	—
	524	5.2×10^{-4}	51.9	9.4	35.8	3.0	—
773 K, 3 h[b]	477	3.1×10^{-5}	49.1	0.2	0.1	50.7	—
	487.5	2.9×10^{-5}	31.8	—	—	68.2	—
	497.5	4.1×10^{-5}	24.7	0.1	0.2	71.5	3.4
773 K, 3 h[b]	498	5.7×10^{-5}	28.3	trace	—	67.8	3.9
	508	6.5×10^{-5}	18.8	0.4	1.7	64.3	14.7
	517	1.2×10^{-4}	26.3	0.9	8.5	55.7	8.6
773 K, 3 h[b]	480	3.3×10^{-6}	47.7	—	—	52.3	—
	490	3.0×10^{-6}	29.2	—	—	70.8	—
523 K, 1 h[c]	487.5	8.2×10^{-6}	25.1	0.7	9.0	52.6	12.6
	497.5	2.3×10^{-5}	30.2	1.4	18.4	43.1	6.9
573 K, 1 h[c]	489	5.4×10^{-6}	12.9	0.5	2.9	40.7	42.9
	499	1.7×10^{-5}	23.4	1.7	8.3	50.7	15.9
573 K, 1 h[c]	488	5.2×10^{-6}	8.9	0.2	2.1	30.0	58.8
	498	1.1×10^{-5}	20.0	1.2	3.5	44.2	31.1
		0.76 wt% Pd/SiO_2[b,d]					
573 K, 1 h	521	9.6×10^{-6}	42.4	—	3.7	43.0	11.0
	531	2.7×10^{-5}	36.4	0.4	12.9	50.3	—

[a] All samples were treated with O_2 at 573 K prior to reduction.

[b] Fresh samples.

[c] Samples previously reduced at 773 K for 3 h and run in the reaction.

[d] Most active sample of silica-supported Pd catalyst after "standard" pretreatment (taken from Ref. (*2*)).

with Lieske *et al.* (*10*). Therefore, in order to achieve full reduction before our catalytic experiments we reduced our samples at $T \geq 523$ K.

Table 2 shows the results of kinetic studies collected for 0.97 wt% Pd/Al_2O_3 after various pretreatments. The reduction temperature was varied between 523 and 773 K. For comparison, the results obtained earlier for 0.76 wt% Pd/SiO_2 catalyst are also shown (Part II, Ref. (*2*)). For Pd/Al_2O_3 reduced at 873 K, and for a physical mixture of Pd powder with alumina reduced at 573 and 873 K, the results are presented in Table 3. The reduction at the highest temperature studied was always followed by a prolonged purging (17 h) with an inert gas (Ar or He) at the same temperature. Much shorter purging times would leave unanswered questions about the role of hydrogen left on the catalyst after HTR. A serious poisoning effect of residual hydrogen

TABLE 3

Reaction of Neopentane on 0.97 wt% Pd/Al_2O_3 and Pd + Al_2O_3 Physical Mixture Reduced at Temperatures above 850 K

Sample pretreatment[a]	Reaction		Initial product distribution (%)				
	Temp. (K)	Rate[b]	CH_4	C_2H_6	C_3H_8	iC_4H_{10}	iC_5H_{12}
Pd/Al_2O_3							
H_2, 873, 17; He, 873, 17	452.7	6.0×10^{-5}	32.9	—	—	67.1	—
	463	6.5×10^{-5}	31.9	—	—	68.1	—
	472	6.7×10^{-5}	24.7	—	—	75.3	—
Pd + Al_2O_3							
H_2, 573, 1	527	1.7×10^{-9}	20.8	2.7	4.9	49.0	22.6
	538	6.1×10^{-9}	19.3	1.3	4.0	53.5	21.9
	548	2.1×10^{-8}	24.7	4.0	15.7	50.6	5.0
H_2, 873, 17; He, 873, 17	494	1.8×10^{-9}	80.4	—	—	19.6	—
	503.5	1.9×10^{-9}	45.6	—	—	54.4	—
	523	5.3×10^{-9}	32.0	—	—	68.0	—

[a] All samples were treated with O_2 at 573 K for 0.5 h prior to reduction.

[b] Turnover frequency (s^{-1}) in case of Pd/Al_2O_3 (metal dispersion assumed 0.3, see text); mole · g_{Pd}^{-1} · s^{-1} for Pd powder.

(in the supported and unsupported metal catalysts) in the hydrogenolysis of various alkanes was firmly established by Paál, Menon, and others (*11*). Both the alumina-supported Pd and the physical mixture of Pd + Al_2O_3, showed a very high, although "transient," cracking activity after purging at very high temperatures. This "transiency" does not mean that the rate of neopentane conversion decreases with time *at the lowest temperature of the reaction* when the overall conversion is less than 3%. However, after raising the temperature, the rate of reaction does not change very much, suggesting serious deactivation of the catalyst (cf. Table 3). Nevertheless, in the case of higher temperatures we work under much higher conversions, 5–10%, and the metal surface is probably more extensively covered by coke (originated from products more reactive than neopentane, e.g., *i*-butane).

Blank kinetic experiments with Al_2O_3 impregnated with $CuCl_2$ showed no activity up to ca. 673 K after reduction at 523 and 573 K. After the high-temperature reduction and the He purging at 773 and 873 K, the support exhibited some small catalytic activity but only at reaction temperatures well in excess of those employed in the relevant kinetic runs on the Pd/Al_2O_3 catalysts (shown in Tables 2 and 3). After reduction of Al_2O_3 at 773 K (3 h) and He purging at the same temperature for 1 h, some very small hydrocracking activity was detected at 593 K. On the other hand the 0.97 wt% Pd/Al_2O_3 catalyst after the same pretreatment exhibits measurable activity at ca. 100 K lower (Table 2). More drastic reduction and He purging (at 873 K) produces still more active Al_2O_3: here, the hydrogenolysis starts at as low as 500 K. But, again, we can ignore this effect as our Pd/Al_2O_3 catalysts after reduction at 873 K are already active at 450–470 K (Table 3). Therefore, although the problem of the activity enhancement of alumina seems very interesting (for a possible explanation, see Peri (*12*)), for the sake of clarity we shall not treat this problem further.

Figure 3 shows IR data of the adsorbed CO on differently pretreated (at temperatures up to 773 K) 0.97 wt% Pd/Al_2O_3 samples. As only the linearly bound CO species

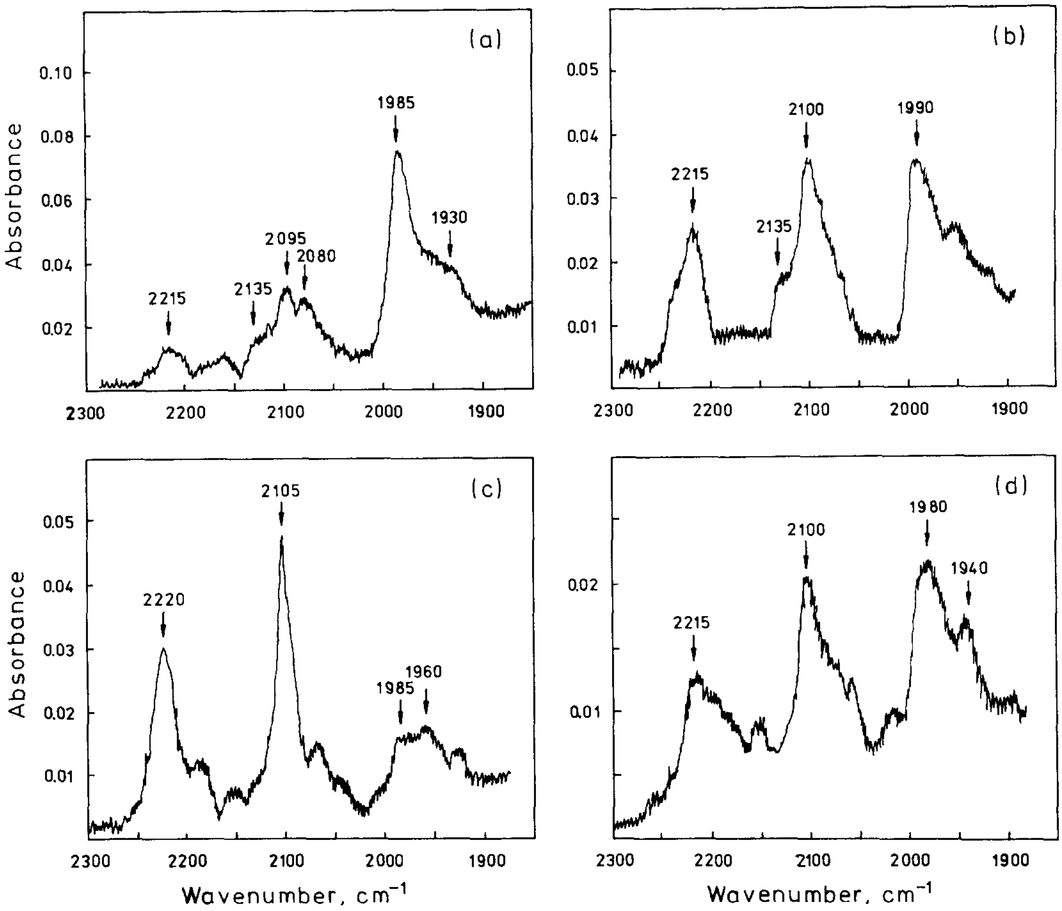


FIG. 3. IR spectra of adsorbed CO (2 Torr) on 0.97 wt% Pd/Al_2O_3 catalyst after various pretreatments: (a) after O_2, 573, 0.5; H_2, 573, 1; (b) after O_2, 573, 0.5; H_2, 673, 1; (c) after O_2, 573, 0.5; H_2, 773, 3; (d) sample (c) after subsequent O_2, 573, 0.5; H_2, 573, 1.

are of interest here, only that part of the spectrum with wavenumbers >1900 cm^{-1} is presented. The IR spectrum on Pd/Al_2O_3 reduced at 573 K (Fig. 3a) shows a shoulder at 2135 cm^{-1} suggesting the presence of Pd^+ ions (*13, 14*) in addition to Pd^0–CO complexes (at 2095–2100 cm^{-1}). This assignment was confirmed by the spectrum of the adsorbed CO on a Pd/Al_2O_3 wafer oxidized at 573 K. Reduction at 673 K seems to reduce the relative ratio of Pd^+/Pd^0 as judged by the intensity ratio of this 2135 cm^{-1} shoulder to the 2100 cm^{-1} peak (Fig. 3b). An increase in the reduction temperature also seems to lower the intensities of all the peaks (due to metal sintering). The only exception is a growth of a peak at 2215 cm^{-1} ascribed to the Al^{3+}–CO linearly bound species (*15*). Reduction at 773 K for 3 h sharply reduces all band intensities (Fig. 3c). However, even such a drastic reduction does not seem to eliminate the bands ascribed to Pd^+ ions (at 2135 cm^{-1}) and Pd^{2+} ions (at 2160 cm^{-1}) (not indicated in Fig. 3c). Recalcination and subsequent reduction (both at 573 K) of the HTR sample appear to eliminate the 2135 cm^{-1} shoulder (Fig. 3d).

Figure 4 shows the FTIR spectra for the adsorbed CO on the catalyst after HTR at 873 K. Spectrum (a) reflects the catalyst after HTR and Ar purge at 873 K for 1 h,

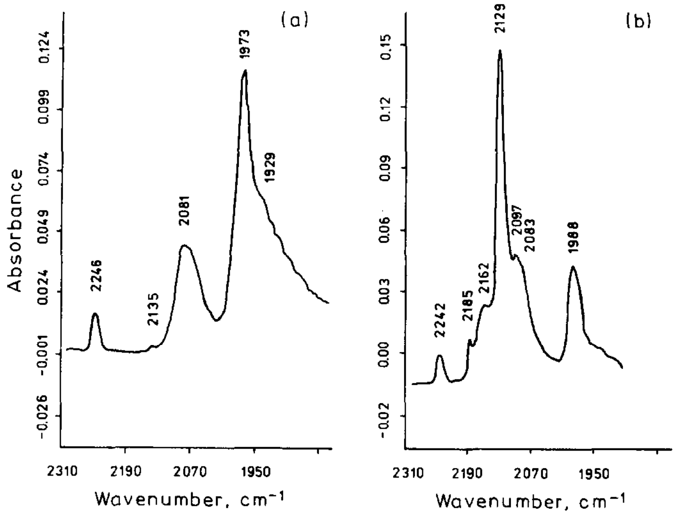


FIG. 4. FTIR spectra of CO adsorbed on 0.97 wt% Pd/Al_2O_3 after reduction at 873 K for 17 h followed by Ar purging at 873 K: (a) 1 h purging; (b) 17 h purging.

whereas spectrum (b) has been recorded after much longer Ar flushing (17 h) at 873 K. In the first case (1-h purge) spectrum (a) shows a low-intensity band due to Pd^+–CO species (2135 cm^{-1}) in addition to the bridged and linearly bonded CO on Pd^0. However, the longer Ar purging at 873 K markedly reduces all bands characteristic of Pd^0 (linear and bridging CO) whereas the band at ca. 2130 cm^{-1} (Pd–CO) is now much better developed. Also a band at 2162 cm^{-1} (Pd^{2+}–CO) is seen.

DISCUSSION

The catalytic behavior of Pd/Al_2O_3 was found less sensitive to pretreatments than that of Pd/SiO_2 studied previously (*1*, *2*). The observed changes in selectivity and, in particular, in the overall activity are, however, significant (Tables 2 and 3). As far as isomerization of neopentane is concerned, most of the pretreatments brought very modest selectivity, anywhere from a few to 15%. Only in the case of the catalyst which had been rereduced at 573 K after previous pretreatment at 773 K in H_2 (bottom lines in Table 2), isomerization selectivity was considerably higher. The IR spectrum of the chemisorbed CO on such a catalyst shows virtually no Pd^{n+}–CO species (Fig. 3d).

Remarkably, the overall activity of our Pd/Al_2O_3 catalysts exceeds that of Pd/SiO_2 by approximately two orders of magnitude (Table 2). This estimation follows from the fact that with the Pd/Al_2O_3 the reaction temperature had to be lowered in order to obtain a level of the catalytic activity comparable to that of Pd/SiO_2, $E_A \approx 60$ kcal/mole (*3*). Different metal particle sizes in combination with an assumed structure sensitivity for hydrogenolysis of neopentane over Pd catalysts might be one cause contributing to this striking result. However, such an explanation appears unsatisfactory in view of very similar metal dispersions for Pd/Al_2O_3 (Table 1) and Pd/SiO_2 (relevant data in (*1*, *2*)). Also, our recent work (*3*) shows that neopentane conversion over Pd/SiO_2 catalysts appears almost structure-insensitive (H/Pd_t in the range 0.071–0.856).

A role of acid sites causing the high activity, either as such or in conjunction with the reduced Pd, is ruled out for a number of reasons. The presence of chlorine (ex-$PdCl_2$), which strongly enhances acidity, does not seem to have an effect on the catalytic activity. For Pt/Al_2O_3, prepared from chloroplatinic acid, no dual function catalysis was observed below 623 K (*16, 17*); the present data were collected well below this temperature. Moreover, we observed large changes in the activity which were similar to those reported here for physical mixtures of Pd powder and Al_2O_3 in the absence of chlorine (Table 3). The results of blank kinetic experiments with alumina impregnated with $CuCl_2$ rule out any significant catalytic role of chlorine in our case.

The observed large difference between silica- and alumina-supported Pd, as well as the very high cracking activity of our Pd/Al_2O_3 catalyst after purging at 873 K (Table 3), seem to be well correlated with the occurrence of Pd^{n+} ions in Pd/Al_2O_3, detected by IR (Figs. 3 and 4). The TPR data (Fig. 2) indicate that the reduction of Pd/Al_2O_3 is complete at fairly low temperatures (<523 K) and Fig. 4 shows that Pd^{n+} species are formed during purging with Ar at 873 K. Since after similar pretreatment the catalyst exhibits very high activity for hydrogenolysis (Table 3), these Pd^{n+} species seem to be responsible for this growth in the activity. Our interpretation involving the Pd^{n+} species seems to have rather good support in the earlier findings (*13, 18–28*). Some electron-deficient palladium species in Pd/Al_2O_3 and Pd/zeolite catalysts after reduction at 573 K (and above) were found to be present. Different techniques were used: XPS (*13, 20, 23, 27*), IR spectra of adsorbed CO (*13, 19, 21, 23*), ESR (*19, 21, 24–28*), and extraction with acetylacetone (*29*). Catalytic consequencies were also reported; e.g., interaction of Pd with zeolite Y (*21*) or Al_2O_3 (*26*) led to the formation of some highly active electron-deficient metal species (hydrogenation of benzene (*21*) and styrene (*26*)). The essential role of Pd^{n+} ions in catalyzing the production of methanol from synthesis gas has been demonstrated by Ponec *et al.* (*29*). Similarly, Pd^+ ions (in Pd*X* zeolites) were identified as active species in dimerization of ethylene (*27, 28*). Now we offer evidence that Pd^{n+} species can play a significant role in catalyzing the reaction of neopentane with hydrogen. Very high cracking activity of electron-deficient palladium in Pd/Al_2O_3 catalysts should also be considered in the light of recent results of Tolbert *et al.* (*30*). In the study of activation of alkanes (also neopentane), they found a uniquely high Lewis acidity of Pd^+ ions in the gas phase.

Thus, the present discussion will concentrate on the following three key questions:

(1) What is the mechanism of formation of Pd^{n+} sites during the course of purging at higher temperatures?

(2) Why are these Pd^{n+} formed and/or stabilized on Al_2O_3 but not on SiO_2?

(3) What is the mechanism of neopentane conversion at the superactive site?

The first two questions are dealt with in the following subsection. The mechanism of neopentane hydrogenolysis is briefly discussed in the next subsection.

Mechanism of Formation of the Pd^{n+} Sites

In our experiments the He (or Ar) was purified to eliminate oxygen to less than 0.1 ppm at the reactor inlet. This was checked occasionally by replacing the reactor with a U-tube filled with low-loaded MnO/SiO_2. Therefore the total amount of oxygen which could be picked up by the 0.97 wt% Pd/Al_2O_3 (usual charge of 0.3g ≈ 30 μmoles of Pd) during 17 h purging with He (20 ml/min) was <0.1 μmole. Therefore, O_2 impurity as a possible oxidant is thus excluded.

The most probable agents for oxidation of Pd^0 to Pd^{n+} are the surface hydroxyl groups according to the redox reaction

$$n(OH_s^-) + M^0 \rightarrow (O^{2-})_nM^{n+} + (n/2)H_2(g)$$

This reaction was found for molybdenum (*31*), iron (*32*), and nickel (*33*) on alumina. While this oxidation seems more difficult for even small agglomerates of atoms of noble or near-noble metals (*34, 35*), it has been found that Pt atoms located in sodalite cages in Y zeolite are oxidized by the surface hydroxyls (*34*). Considerable gain in entropy, due to the formation of gaseous H_2, makes this reaction more feasible at very high temperature.

An important question is how these Pd^{n+} species can be stabilized on the support. Alumina, unlike silica, has unoccupied octahedral sites (to meet the requirement of electrical neutrality). 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 (Fig. 5). It is possible that Pd^{n+} ions are stabilized in these vacant octahedral holes. The recent EXAFS study by Lesage-Rosenberg *et al.* (*36*) shows that fixation of the active cation (from Pd acetonate precursor) on alumina involves octahedral aluminum vacant sites of the carrier, forming locally a phase close to an aluminate. On the other hand, silica has only tetrahedral sites which are fully occupied, so the stabilization of Pd^{n+} species is more difficult than in the case of Al_2O_3. It should be mentioned that Pd/SiO_2 is transformed to Pd-silicide(s) upon HTR (*1, 2*).

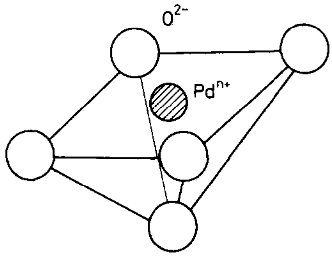
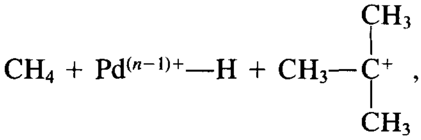


FIG. 5. Model of superactive Pd^{n+} site-stabilized on alumina surface.

Mechanism of Neopentane Conversion on the Superactive Pd^{n+} Site

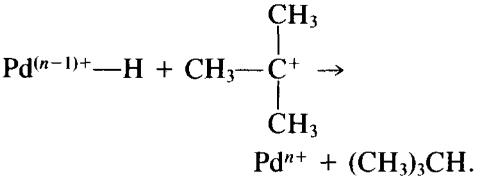
It is tempting to consider hydrogenolysis of neopentane via bonding to one Pd^{n+} site. Two basic steps are proposed:

(1) $Pd^{n+} + C(CH_3)_4 + H_2 \rightarrow$



$$CH_4 + Pd^{(n-1)+}{-}H + CH_3{-}\overset{\displaystyle CH_3}{\underset{\displaystyle CH_3}{\overset{|}{\underset{|}{C^+}}}},$$

where $n = 1$ or 2. This step is favored by the stability of the tertiary carbenium ion and the strong $Pd^{(n-1)+}$–H bond. Tolbert *et al.* (*30*) suggest that the activation of neopentane by Pd^+ ions in the gas phase proceeds via an insertion of Pd^+ between the methyl and tert-butyl fragments of the molecule of neopentane. Pd^+ ions exhibit uniquely high Lewis acidity in the activation of neopentane (*30*). The next step is

(2)


$$Pd^{(n-1)+}{-}H + CH_3{-}\overset{\displaystyle CH_3}{\underset{\displaystyle CH_3}{\overset{|}{\underset{|}{C^+}}}} \rightarrow Pd^{n+} + (CH_3)_3CH.$$

This step is facilitated by C–H bond formation; it regenerates the Pd^{n+} site.

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