Neopentane conversion over $Pd/\gamma\text{-}Al_2O_3$

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X-ray diffraction showed that during high temperature reduction at 600°C, chlorine-free $Pd/\gamma\text{-}Al_2O_3$ undergoes partial transformation to a Pd–Al alloy, which confirms results of other studies [9]. This evolution appears to have a large effect on the catalytic behaviour in the reaction of neopentane with hydrogen: the selectivity towards isomerization increases from <20 up to $\sim$ 80%. At the same time, the activation energy drops from $\sim$ 60 to $\sim$ 22 kcal/mol. These changes can be reversed by oxidation at 500°C followed by reduction at 300°C. The presence of residual chlorine (ex-$PdCl_2$ precursor) appears to inhibit the Pd induced reduction of Al_2O_3 leading to Pd–Al alloy formation.

Keywords: $Pd/\gamma\text{-}Al_2O_3$; neopentane conversion; X-ray diffraction; Pd–Al formation; isomerization selectivity; effect of residual chlorine

1. Introduction

In our earlier work it was found that $Pd/\gamma\text{-}Al_2O_3$ is much more active than Pd/SiO_2 in the reaction of neopentane with hydrogen [1]. Interestingly enough, after reduction and purging at 600°C, the catalyst exhibited even higher activity leading exclusively to hydrogenolysis at temperatures well below 200°C. Various additional indications, such as IR spectra of adsorbed CO [1] and ESR spectra for variously pretreated $Pd/\gamma\text{-}Al_2O_3$ [2] as well as a reported ability of neopentane activation by Pd^+ ions in a gas phase [3] suggested that Pd^+ ions located in γ-alumina might be sites of very high cracking activity.

In principle, our previous work [1] was aimed towards checking whether a high temperature reduction (HTR) leads to strong $Pd-Al_2O_3$ interactions. We had been inspired by reports showing that Pt/Al_2O_3 catalysts reduced at 500–700°C experienced transformation to Pt–Al alloys [4–6]. Alteration of adsorptive and catalytic properties accompanied such an evolution, e.g. in the reaction of *n*-hexane with hydrogen, the selectivity for isomerization sharply increased [4]. As mentioned, we

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did not observe analogous changes with Pd/γ-Al_2O_3 (only a drastic increase in hydrogenolysis, attributed to a superactivity of Pd^+ species [1]). At that time, such a result did not appear unreasonable, because no conclusive indication had been reported for the formation of Pd–Al alloys from Pd/alumina systems reduced up to 700°C [7,8]. The situation changed, however, when Kępiński et al. provided convincing evidence (by XRD) for the formation of Pd_xAl_{1-x} alloy from a commercial 10 wt% Pd/Al_2O_3 catalyst subjected to HTR [9]. It was shown that the reduction in hydrogen at 700 and 800°C for 40 h causes an incorporation of reduced aluminum into the palladium lattice ($x = 0.06$ at 700°C and 0.10 at 800°C).

Formation of a Pd–Al alloy would not explain our catalytic observations. A possible solution of this apparent conflict came from other works showing that in the case of metal/TiO_2 systems, the SMSI effect may be inhibited by the presence of chlorine [10]. Because in our previous work [1] we used Pd/γ-Al_2O_3 prepared from $PdCl_2$, significant amounts of chlorine were retained in the catalyst, even after HTR at 600°C [11–13]. Therefore, we used a new Pd/γ-Al_2O_3 catalyst, using the same γ-Al_2O_3 and a chlorine-free metal precursor ($Pd(acac)_2$). After subjecting it to various pretreatments (analogous to those used in ref. [1]), the catalyst was investigated in neopentane conversion and X-ray diffraction studies.

2. Experimental

1.45 wt% Pd/γ-Al_2O_3 was prepared by impregnation of γ-alumina (American Cyanamid PHF, 99.99% purity, 75–120 mesh, acid washed) with palladium acetylacetonate (99.8%, Alfa Produkte, Karlsruhe) diluted in a benzene (analytical grade, POCh, Gliwice, Poland) solution according to Boitiaux et al. [14]. After subsequent drying in air oven at 80°C for 2 h, the solid was transferred to a glass-stoppered bottle and kept in a desiccator.

Samples of the Pd/γ-Al_2O_3 precursor (~ 0.1 g) were placed on a sintered disc of a tubular reactor, attached to the system by using $\frac{1}{4}''$ Cajun Ultra-Torr fittings. Precalcination of samples was carried out in a flow system in an oxygen stream (40 cm^3/min) at 390°C for 1 h. After short purging in helium at 390°C, the catalysts were reduced in H_2 flow (25 cm^3/min) at 300°C for 1 h (low temperature reduction, LTR) or 600°C for 17 h (high temperature reduction, HTR). The reaction of neopentane (Merck) with hydrogen was conducted in a glass flow system under atmospheric pressure in the temperature range of 150–290°C. Feed partial pressures were 6 and 60 Torr (1 Torr = 133.3 N m^{-2}), neopentane and hydrogen, respectively, in a helium carrier. The overall flow rate of the reacting gas mixture was 68.4 cm^3/min, flows of H_2, neo-C_5H_{12} and He being stabilized by mass flow controllers (Bronkhorst HI-TEC, The Netherlands). Neopentane was purified by passing it through a 5A molecular sieve trap for removing any *n*-butane impurity from the reactant stream. The reaction was followed by gas chromatography (HP 5890 series II with FID, 6 m squalane/Chromosorb P column, with a HP 3396 ser-

ies II integrator). Turnover frequencies (TOF's) were calculated on the basis of the dispersion measured by H_2 chemisorption (H/Pd). Initial product distributions (= selectivities) were calculated as carbon percentage of neopentane consumed in the formation of a designated product, for instance, mol% of methane from neopentane would be divided by 5 and normalized in deriving the product distribution.

Differently pretreated samples of 1.45 wt% Pd/γ-Al_2O_3 catalyst were investigated by X-ray diffraction (Rigaku-Denki, Cu K_α radiation with a Ni filter). Samples were scanned in the 2θ range of 29° to 72° and the data were collected by a step-by-step technique with $\Delta(2\theta) = 0.05°$. Unfortunately, difficulties with separation of broad peaks of Pd from peaks of γ-Al_2O_3 [15], precluded also in our case determination of positions and widths of peaks originating from the metal phase. Therefore, another γ-alumina-supported palladium catalyst, with much higher metal loading (10 wt%, as in ref. [9]) was prepared by incipient wetness technique, using $PdCl_2$ (analytical grade, POCh, Gliwice, Poland), the same γ-Al_2O_3 and some small amounts of HCl for dissolving the metal chloride. This catalyst was subjected to similar pretreatments as the 1.45 wt% metal-loaded sample and investigated by XRD.

Metal dispersion measurements after reduction and flushing out hydrogen with argon at 500 (after LTR) or 600°C (after HTR) for 1 h, were conducted by chemisorbing pulses of hydrogen in argon stream at 70°C.

3. Results

Table 1 shows results of kinetic studies and metal dispersions measured by chemisorption of H_2 after various pretreatments of 1.45 wt% Pd/γ-Al_2O_3 catalyst. In the pretreatment code, O_2, 300, 0.5; H_2, 300, 1; Ar, 500, 1 means that the catalyst was exposed to flowing oxygen at 300°C for 0.5 h, subsequently to hydrogen at 300°C for 1 h and, finally, to argon at 500°C for 1 h. The reduction temperature was varied between 300 and 600°C. The reduction at the highest temperature (600°C) was always followed by 1 h purging in helium at the same temperature. It must be stressed that in order to limit secondary reactions and self-poisoning, the level of the overall conversion was kept very low, usually $<1\%$ at highest reaction temperatures ($\leqslant 290$°C). With such a precaution, self-poisoning was negligible in all cases, as seen from check runs at the same temperature at various points in the sequence.

Fig. 1 shows results of the XRD study of pretreated 10 wt% Pd/γ-Al_2O_3 sample. Spectrum (a) displays the XRD profile after LTR (at 300°C). Respective reflections originating from γ-Al_2O_3 and palladium are marked. Spectra (b) and (c) show profiles for the sample reduced at 600°C for 17 and 33 h, respectively. Apart from some narrowing of the Pd reflections no change is found in comparison to the previous spectrum. Spectrum (d) displays an analogous XRD profile. However, for the sample which after LTR was washed with large quantities of boiled doubly distilled water (1.5 ℓ/g of catalyst, to eliminate chloride ions from the sam-

Table 1
Neopentane conversion over 1.45 wt% Pd/γ-Al_2O_3 ex-Pd(acac)$_2$: initial product distributions and turnover frequencies

Reduction condition: temp., time	Reaction temp. (°C)	Initial product distribution [a] (%)							TOF (s^{-1})	Activation energy (kcal/mol)
		Me	Et	Pr	*i*B	*n*B	*i*P	*n*P		
300°C, 1 h	240	19.5	–	–	59.3	9.3	11.9	–	2.01×10^{-5}	58.0 ± 0.7
(H/Pd = 0.62)	250	21.0	–	2.6	62.9	3.0	10.4	–	5.17×10^{-5}	
	260	22.7	0.6	6.9	60.0	3.7	6.0	–	1.58×10^{-4}	
	270	27.2	1.4	15.1	50.0	3.5	2.8	–	4.42×10^{-4}	
600°C, 17 h [b]	181	28.5	–	–	71.5	–	–	–	1.69×10^{-5}	22.0 ± 0.4
(H/Pd = 0.28)	200	23.0	–	–	72.6	–	4.4	–	4.81×10^{-5}	
	220	13.2	–	–	55.2	–	31.6	–	1.17×10^{-4}	
	240	5.7	–	–	20.9	–	73.4	–	2.84×10^{-4}	
	254	4.4	–	–	16.6	0.5	78.5	–	5.02×10^{-4}	
	268	5.4	–	0.3	18.5	1.4	72.7	1.7	8.99×10^{-4}	
300°C, 1 h [c]	241	30.6	–	–	35.7	–	33.6	–	8.57×10^{-5}	65.4 ± 2.0
(H/Pd = 0.30)	260	17.5	–	–	44.0	–	38.5	–	6.61×10^{-4}	
	278	17.2	0.5	1.0	50.3	2.5	28.4	–	5.08×10^{-3}	
	288	18.4	0.8	2.9	52.0	6.3	19.1	0.4	1.49×10^{-2}	
300°C, 1 h [d]	240	27.5	–	–	72.5	–	–	–	9.83×10^{-5}	58.4 ± 1.7
(H/Pd = 0.31)	248	29.9	–	–	70.1	–	–	–	2.32×10^{-4}	
	270	22.0	2.8	5.7	51.9	–	17.7	–	2.29×10^{-3}	

[a] Me = methane, Et = ethane, Pr = propane, *i*B = isobutane, *i*P = isopentane and *n*P = *n*-pentane.
[b] Kinetic run on a sample reduced at 600°C for 17 h and purged in He at 600°C for 1 h.
[c] Kinetic run on a sample previously studied in run [b], after regeneration in O_2, 300°C, 0.5 h and reduction at 300°C for 1 h.
[d] Kinetic run on a sample previously studied in run [c], after regeneration in O_2, 500°C, 1 h and reduction at 300°C for 1 h.

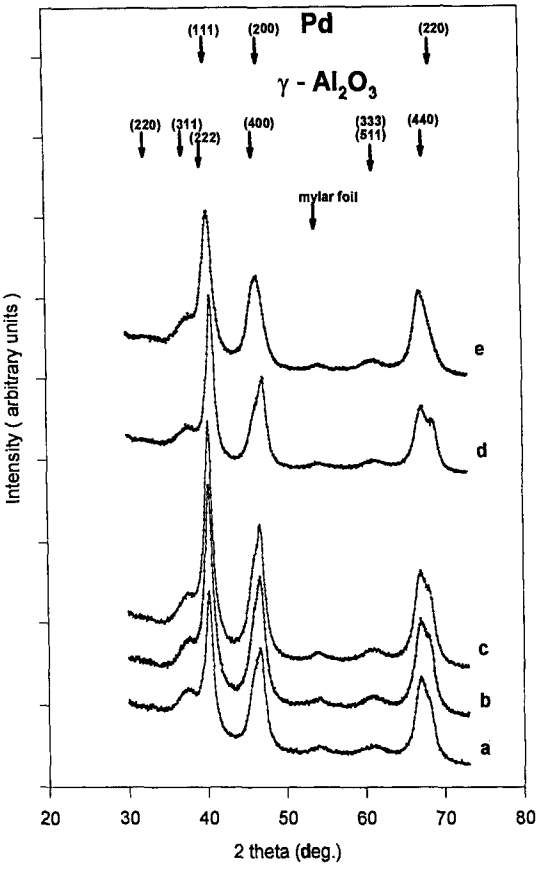

Fig. 1. X-ray diffraction profiles from 10 wt% Pd/γ-Al_2O_3 after various pretreatments: (a) fresh sample + O_2, 390, 1; H_2, 300, 1; Ar, 500, 1; (b) after (a) + O_2, 300, 0.5; H_2, 600, 17; Ar, 600, 1; (c) after (b) + H_2, 600, 16; Ar, 600, 1; (d) fresh sample after reduction at 300°C and washing with boiling H_2O + O_2, 300, 0.5; H_2, 600, 33; (e) after (d) + O_2, 500, 1; H_2, 300, 1, Ar, 500, 1 (for pretreatment code see text). Basic reflections from Pd, γ-Al_2O_3 and mylar (sample holding material) are marked by arrows.

ple [13]) and then reduced at 600°C for 33 h, some small shifts of Pd reflections towards higher angles were noticed. These shifts were significant in spite of the overlap of reflections from Pd and γ-Al_2O_3. As a compromise between the intensities of overlapping peaks from the support and the metal, and the possibility of tracing the background level, for analysis the γ-Al_2O_3 (440) and the Pd (220) reflections were chosen. They were separated by fitting two Pearson VII functions to the experimental profile. For lattice constant calculations their centres of gravity were taken. The peak originating from Pd-based phase is at 68.7° (fig. 2). On the other hand, an analogous peak deconvolution (not shown) performed for profiles (a), (b) and (c) from fig. 1 gives $2\theta = 68.2°$, i.e. the expected value for the (220) reflection of pure Pd.

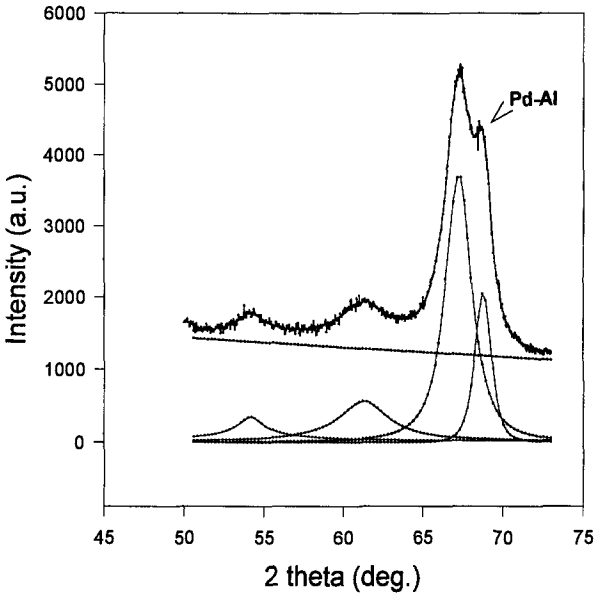

Fig. 2. A part of the XRD spectrum of 10 wt% Pd/γ-Al_2O_3 after pretreatment (d), fig. 1. Separation of (440) reflection from γ-Al_2O_3 shows that (220) reflection originating from Pd-based phase (Pd–Al) is shifted towards higher angles by ~ 0.5° in respect to pure Pd.

4. Discussion

Table 1 shows large changes in the catalytic behaviour of 1.45 wt% Pd/γ-Al_2O_3 catalyst subjected to different pretreatments. Selectivity towards isomerization, regarded as a convenient diagnostic parameter towards determining whether palladium strongly interacts with a support [16,17], is rather low (<20%) resembling the catalytic behaviour of the Pd/γ-Al_2O_3 ex-$PdCl_2$, reported earlier [1]. The fact that the presence of residual chlorine has not much effect on the selectivity is in accordance with some earlier results [18,19]. Menon et al. showed that chloriding of Pt/Al_2O_3 with HCl has a minor effect on the reaction of *n*-pentane with hydrogen [18].

On the other hand, big differences between two catalysts are observed after subjecting them to HTR (600°C for 17 h). The Pd/γ-Al_2O_3 ex-chloride showed high, although transient, activity at low temperatures (150–200°C), giving exclusively methane and isobutane [1]. At higher reaction temperatures (around 250°C) some isomerization also occurred, with a selectivity <25% [20], similar to that exhibited by other supported palladium catalysts [1,16]. In contrast, the Pd/γ-Al_2O_3 ex-$Pd(acac)_2$ shows a considerable increase in isomerization selectivity (up to 78.5% at 254°C, table 1). This selectivity variation caused by HTR resembles very much the catalytic behaviour of silica-supported palladium reduced at 600°C, for what formation of palladium silicide was detected [16,17]. This change in selectivity is

partially reversed by oxidation/reduction at 300°C and more effectively by oxidation at 500°C followed by LTR (table 1). Fig. 3 displays changes in isomerization selectivity after different pretreatments.

Table 1 also shows big changes in activation energy in neopentane conversion. A typical value of E_A = 55–65 kcal/mol characteristic for Pd catalysts [21] drops to 22 kcal/mol after HTR in order to return to the initial level after the oxidation/LTR cycles.

We think that this is the formation of Pd–Al alloys which would account for the observed increase of isomerization selectivity. The serious difference in the catalytic behaviour apparently caused by different levels of chloride impurities is reminiscent of results with Ru/TiO_2 catalyst where a SMSI effect was suppressed by the presence of chlorine [10]. It was proposed that Cl^- can be mobile and able to partition between metal and support [10]. The SMSI effect in the case of TiO_2-supported metals is seen as a migration of TiO_x species onto metal particles [22]. This migration is apparently inhibited by chlorine, perhaps due to limitation of the extent of hydrogen spillover [10]. As HTR did not produce any increase in isomerization selectivity for chlorided Pd/γ-Al_2O_3, we deduce that no Pd–Al formation took place [1]. We suggest that hydrogen spillover is limited by chlorine in the case of alumina-supported metals. As mentioned above, some results point to the formation of Pt–Al alloys during HTR of Pt/alumina catalysts [4–6]. Our X-ray diffraction studies of 10 wt% Pd/γ-Al_2O_3 confirm the formation of Pd–Al during less severe reduction than in ref. [9]. However, such an interaction could only take place after chlorine removal from the catalyst. Reduction of the catalyst prepared from $PdCl_2$ at 600°C still leaves considerable amounts of chlorine [12]. This chlor-

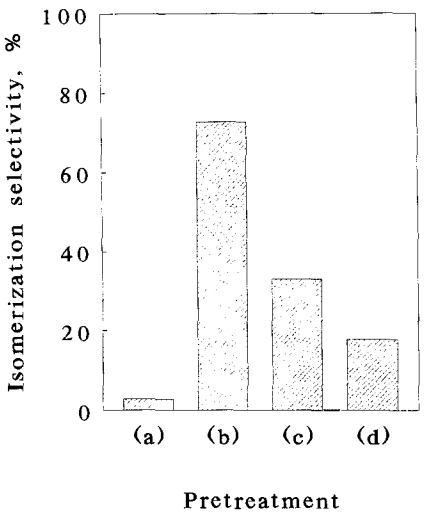

Fig. 3. Isomerization selectivities in neopentane conversion at 270°C over differently pretreated 1.45 wt% Pd/γ-Al_2O_3 catalysts: (a) LTR, at 300°C, (b) after HTR, at 600°C, (c) after HTR followed by oxidation at 300°C and LTR, and (d) after HTR followed by oxidation at 500°C and LTR.

ine apparently inhibits formation of Pd–Al phases because none of such have been detected in the XRD spectrum (for 10 wt% loaded sample) and we did not observe any considerable increase of isomerization selectivity (for 1 wt% loaded sample [1]). With the same 10 wt% loaded catalyst, after very careful removal of chloride ions and reduction at 600°C for 33 h, significant incorporation of aluminum into the Pd lattice (fig. 1, spectrum (d) and fig. 2) is indicated by a shift of the 220 peak of Pd (at $2\theta = 68.2°$) towards higher angles by $\sim 0.5°$. This value is much higher than $\pm 0.03°$ (2θ) being the reproducibility of the peak centre of gravity calculations (expressed as standard deviation). Such a shift is indicative of a contraction of the Pd lattice by almost 0.03 Å. According to Ellner [23], aluminum incorporation into palladium reduces the Pd lattice parameter from 3.8907 to 3.868 Å for $Pd_{82}Al_{18}$. Obviously, one may expect that the higher metal dispersion of 1 wt% Pd/γ-Al_2O_3 should lead to stronger interactions between metal and support than in the case of the 10 wt% Pd-loaded sample (crystallite size of $\sim$ 100 Å as estimated from the integral width of XRD lines).

Some authors suggested that such a strong metal–support interaction can only take place when impurities such as sulfur are present in γ-Al_2O_3 [22]. The PHF γ-Al_2O_3 from American Cyanamid used in this work is 99.99% pure with iron as the major impurity (30 ± 10 ppm). We, therefore, believe that in this case no enhancement of Al_2O_3 reduction by sulfur is prevailing. On the other hand, from the comparative studies of two Pd/Al_2O_3 samples prepared from two different precursors we believe that the presence of Cl inhibits the formation of Pd–Al alloys. This fact has substantial catalytic effect, as the isomerization selectivity of palladium is greatly improved by its dilution with another component (Al – this work, Si or Ag [16]).

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