

C₆-Alkane Reactions over γ -Alumina Supported Palladium Catalysts

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A series of Pd/Al₂O₃ catalysts of different Pd loading were tested in C₆-alkane reactions. Different catalyst pretreatment was used to change both the acidity of alumina and the state of palladium. A parallel study with the use of n-hexane and 2,2-dimethylbutane showed several similarities in the catalytic behaviour of the Pd/Al₂O₃ catalysts. Highly reduced catalysts showed completely different performance than samples reduced at lower temperatures. High temperature reduction leads to a big enhancement of catalytic activity and also vastly increases the isomerization selectivity. Considerable changes were also noticed in the activation energy. Oxidation and subsequent mild reduction of highly reduced samples brings about, however, different results for isomerization selectivity: a partial recovery in the case of n-hexane and only a very small change for the 2,2-dimethylbutane reaction. The results confirm the major contribution of acidic sites present in activated alumina to the overall catalytic behaviour of Pd/Al₂O₃ samples.

Key words: catalysis, C₆ alkane conversion, palladium catalysts, role of activated alumina

Recently we have reported considerable variations in the catalytic behaviour of two alumina-supported palladium catalysts which experienced different catalyst pretreatment [1–3]. It has been concluded that a large increase of the activity caused by high temperature reduction (at 600°C) would indicate that the role of alumina is not merely limited to maintaining palladium in the state of high dispersion. It was suggested that as the result of high temperature reduction (HTR), γ -Al₂O₃ gains a considerable Lewis acidity which plays an important role in transformation of C₆-alkanes. It seems that in such a case the role of the metal is even overshadowed by the action of activated alumina.

This work is an extension of the previous study which involved investigation of only two catalysts [1,2]. It appeared interesting to verify earlier results by testing a series of Pd/Al₂O₃ catalysts of different metal loading. It was also important to use only one, chlorine-free, palladium precursor (Pd(acac)₂) for preparation of all our catalysts. Such a situation was not met in our previous study [1,2], so one can raise unanswered questions, as to a possible effect of the metal precursor on the catalyst morphology and, in effect, on the catalytic behaviour [4].

EXPERIMENTAL

The catalyst support was alumina, Alumina Shell S618, 240 m²/g, pore volume 0.8 cm³/g, 75–120 mesh, acid washed. A series of differently metal-loaded Pd/Al₂O₃ catalysts were prepared by impregnation of alumina with palladium acetylacetonate (99.8%, Alfa Produkte, Karlsruhe, Germany) diluted in a benzene (analytical grade from POCh, Gliwice, Poland) solution according to Boitiaux *et al.* [5]. After impregnation and drying in air oven at 80°C for 12 h, the catalysts were precalcined under a flow of air at 350°C, reduced at 200°C for 0.25 h, at fluidized bed conditions, and, finally, after cooling in helium, transferred to glass-stoppered bottles and stored in a desiccator. Both the calcination and reduction steps were preceded by ramping the temperature at ~8°C/min. Prior to reaction or chemisorption studies, the samples underwent special pretreatments, as indicated in Table 1.

Table 1. Characteristics of investigated Pd/Al₂O₃ catalysts.

| Catalyst (metal loading) | Pretreatment | Metal dispersion ^a |
|---|-----------------------------|-------------------------------|
| 0.3 wt.% Pd/Al ₂ O ₃ | LTR ^b | 0.23 |
| | HTR ^c | 0.002 |
| | “Regeneration” ^d | 0.01 |
| 0.6 wt.% Pd/Al ₂ O ₃ | LTR | 0.39 |
| | HTR | 0.017 |
| | “Regeneration” | 0.13 |
| 1.46 wt.% Pd/Al ₂ O ₃ | LTR | 0.29 |
| | HTR | 0.095 |
| | “Regeneration” | 0.15 |

^aFrom hydrogen chemisorption, as H/Pd.

^bLTR (low temperature reduction): O₂, 400°C, 1 h; H₂, 300°C, 1 h.

^cHTR (high temperature reduction), LTR sample was mildly reoxidized and highly rereduced: O₂, 300°C, 0.5 h; H₂, 600°C, 17 h.

^d“Regeneration” denotes: sample investigated after HTR was oxidized in O₂ and mildly rereduced: O₂, 500°C, 1 h; H₂, 300°C, 1 h.

The Pd/Al₂O₃ catalysts were investigated in the reactions of n-hexane (nH) and 2,2-dimethylbutane (22DMB) with dihydrogen. The reactions were conducted in a flow system under atmospheric pressure described previously [1]. In order to avoid secondary reactions and limit self-poisoning, overall conversion was kept low, *i.e.* usually below 10%. After a specified sample pretreatment (LTR, HTR or “Regeneration”, see Table 1), the catalyst was contacted with a reaction mixture (flow of hydrocarbon and hydrogen) at 290°C, *i.e.* at the highest reaction temperature. In order to adequately establish changes in a catalytic behaviour, a typical reaction run lasted ~3 h. After reaching a stable activity at 290°C, the reaction temperature was gradually decreased in 10–20°C intervals and next experimental points were collected, required for calculation of activation energy.

Reaction products were analyzed by an on-line gas chromatograph (HP 5890) with a 50 m PONA capillary column (from Hewlett Packard) and a FID detector. The partial pressures of hydrocarbons were: nH - 45 Torr and 22DMB - 51.5 Torr, with hydrogen as a balance gas. This means that the H₂-to-alkane ratio was ~16:1 for nH and ~15:1 for 22DMB reaction, respectively. Turnover frequencies (TOFs) were calculated on the basis of the dispersion measured by H₂ chemisorption (Table 1). Selectivities (product distributions) were calculated as the carbon percentage of nH (or 22DMB) consumed in the formation of a designated product. Blank experiments with differently pretreated γ-Al₂O₃ were also performed. They showed negligible activity of Al₂O₃ in both reactions.

RESULTS AND DISCUSSION

All tested Pd/Al₂O₃ samples after LTR possessed a comparable, medium metal dispersion (Table 1). This fact suggests that we dealt with metal particles of similar size in all, differently metal loaded catalysts, so the main difference between the catalysts consisted in a different concentration of similar in size Pd particles on the surface of alumina.

The results of catalytic screening are presented in graphic form (Figures 1–4). Each figure is composed of two parts. The left part of each figure shows the behaviour of differently pretreated Pd/Al₂O₃ catalysts in the n-hexane conversion, whereas the right sides display analogous data obtained in the 2,2-dimethylbutane reaction.

Figure 1 shows the relation between the overall activity (expressed as TOF at 290°C) and Pd loading. It must be recalled here that the TOF values were calculated per one “hydrogen-titrated” surface palladium atom. Metal dispersion data in Table 1 suggest that in the case of highly pretreated (*i.e.* after HTR and “regeneration”) Pd/Al₂O₃ catalysts, hydrogen chemisorption is suppressed. This effect is best visible for the sample of the smallest loading, *i.e.* for 0.30 wt.% Pd/Al₂O₃. In fact, the very low H/Pd values obtained after HTR do not reflect probably a real metal particle size, because a subsequent regeneration step would not increase palladium dispersion as much as by an order of magnitude (Table 1). We believe that high temperature reduction generates pronounced metal-support interactions, consisting in blocking of palladium surface by the support species or Pd–Al interactions [6,7]. Although the reactivity of n-hexane is higher than that of neohexane, one can see very similar

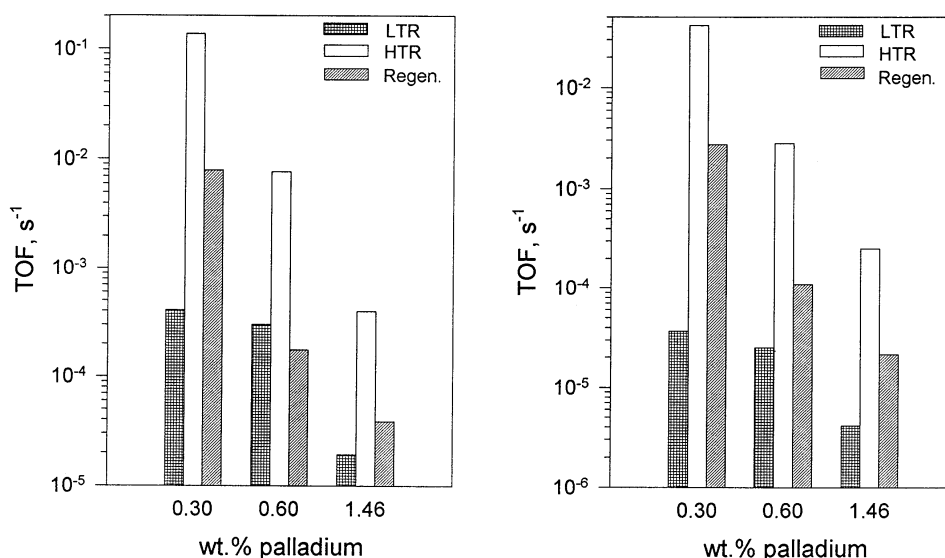


Figure 1. The effect of palladium loading and catalyst pretreatment on catalytic activity of Pd/Al₂O₃ in n-hexane (left section) and 2,2-dimethylbutane (right section) conversions. Reaction temperature: 290°C. For catalyst pretreatment (LTR, HTR, Regen. = “regeneration”) see text and Table 1.

changes in the activity after different pretreatments. In each case, HTR brings about a big increase of the turnover frequencies.

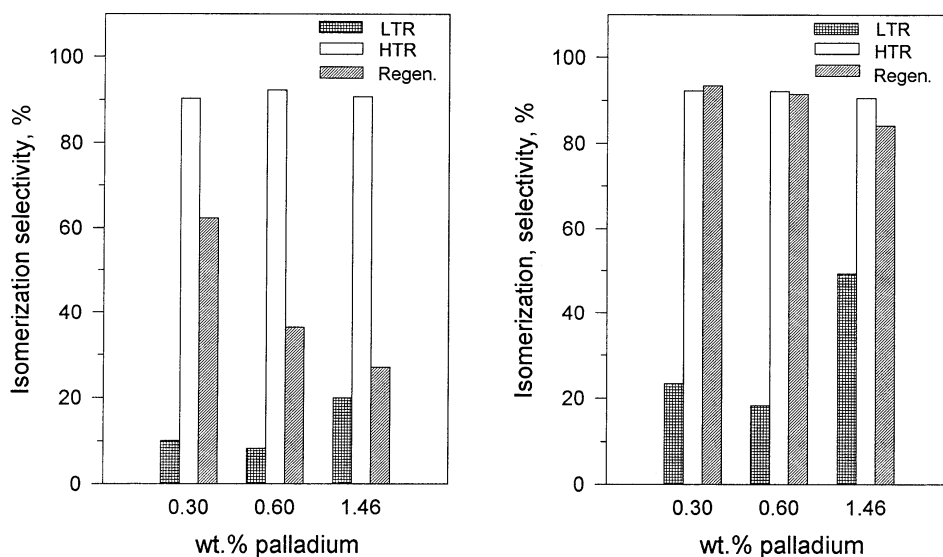


Figure 2. The effect of palladium loading and catalyst pretreatment on isomerization selectivity of Pd/Al₂O₃ in n-hexane (left section) and 2,2-dimethylbutane (right section) conversions. Reaction temperature: 290°C. Designations as in Figure 1.

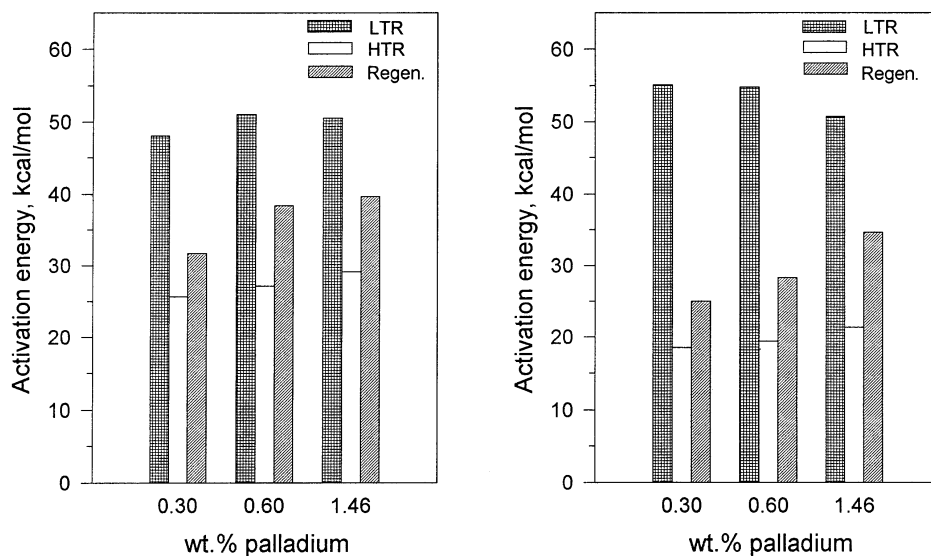


Figure 3. The effect of palladium loading and catalyst pretreatment on apparent activation energy in n-hexane (left section) and 2,2-dimethylbutane (right section) conversions. Designations as in Figure 1.

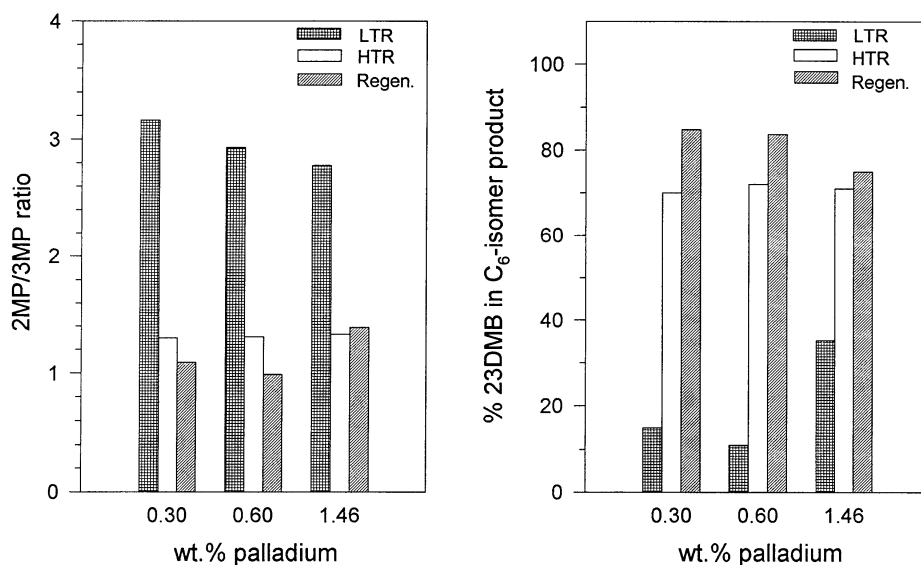


Figure 4. The effect of palladium loading and catalyst pretreatment on some selectivity changes in alkane conversions. The left part shows changes in the ratio of 2-methylpentane-to-3-methylpentane in products of n-hexane conversion. The right part shows changes in the percentage of 2,3-dimethylbutane in C₆-isomers produced in 2,2-dimethylbutane conversion. Designations as in Figure 1.

The remaining figures (2–4) are not affected by uncertainties in estimation of palladium dispersion because they concern various selectivity patterns. Figure 2 deals with isomerization selectivity changes. In agreement with the previous results [1,2], the selectivity to isomerization is vastly enhanced by HTR, from 10–20% to > 90%. Interestingly enough, “regeneration” has a different effect on this selectivity, depending on the hydrocarbon tested. In the case of n-hexane, a lower isomerization selectivity, characteristic of palladium action (and observed for LTR samples) is partly restored. This effect is better seen for high metal loaded samples (*i.e.* 0.6 and 1.46 wt.%). However, in the case of 2,2-dimethylbutane, the very high isomerization selectivity after HTR is hardly changed by the “regeneration” pretreatment. We shall return to this problem later on.

Figure 3 shows analogous changes in the activation energies. Here, the picture is similar for both reactions. Very high activation energy for LTR samples (about 50 kcal/mol) is considerably lowered upon HTR, down to 20–25 kcal/mol. As mentioned earlier [1] such a big change in E_A must reflect changes in the reaction mechanism. We believe that metal-catalyzed conversion on LTR samples is replaced by an acidic mechanism of alkane rearrangement on alumina. “Regeneration” gradually returns the metal-catalyzed behaviour, the extent of this recovery is higher the higher is the metal loading. In addition, the catalytic behaviour is better restored for n-hexane than for the 2,2-dimethylbutane reaction.

Figure 4 combines some selectivity changes which are more specific for each reaction. For n-hexane conversion, the relative ratios of two isohexane products are displayed. Rather high 2-methylpentane/3-methylpentane ratio (~ 3 for LTR samples, suggesting a major contribution of bond-shift vs. C_5 -cyclic mechanism, [1]) is greatly diminished upon high temperature pretreatments. The 2MP/3MP ratio about one is suggestive of an acidic action of the catalysts [1]. Interestingly, after "regeneration" this quantity does not return to the value characteristic for the LTR samples, in fact, it is even slightly lower than after HTR. This may suggest that isomerization proceeds primarily on acid sites of the support, whereas palladium catalyzes mainly hydrogenolysis.

Figure 4 also shows the percentage of 2,3-dimethylbutane (23DMB) in C_6 -isomer products of the 22DMB conversion. LTR samples produce rather modest amounts of 23DMB. Such a behaviour is typical of palladium surfaces [1,8]. On the other hand, the dominant amounts of 23DMB in C_6 -isomer product speak again for an acidic character of this rearrangement (not for a bond-shift mode, characteristic for metal action), involving the reaction of a secondary to, a more stable, tertiary carbenium ion [9]. Further increase of this quantity after "regeneration" is another indication of high residual acidity of γ - Al_2O_3 . It seems possible that oxidation and low temperature reduction of HTR samples, realized in the "regeneration" step generates even stronger acid sites than Lewis acid sites created by dehydroxylation of alumina during HTR. It is recalled that "regeneration" only marginally changes the overall isomerization selectivity (Figure 2). "Regeneration" must produce water (*via* reduction of PdO), which would be strongly bound to certain Lewis acid sites and give rise to some Brønsted acidity [10]. In order to prove this speculation one should determine changes in surface acidity by studying adsorption of appropriate bases by IR spectroscopy and/or thermodesorption techniques. Such studies are under way in our Laboratory.

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