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The effect of Pd/Al_2O_3 pretreatment on catalytic activity in cyclopentane/deuterium exchange

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Big variations in overall activity and product selectivity in the cyclopentane/deuterium exchange reaction were found in effect of various pretreatments of two chlorine-free Pd/γ-Al_2O_3 catalysts. The most important changes are observed when severely prereduced (at 600 °C) Pd/Al_2O_3 catalysts have been reoxidised and mildly rereduced: the multiple type of exchange, typical of mildly pretreated Pd catalysts, is replaced by a stepwise mode, and a big increase in catalytic activity occurs. At this state, the Pd/γ-Al_2O_3 catalysts retain some water (as surface hydroxyls) generated by reoxidation and mild reduction. Deuterium spillover from Pd onto alumina and changes in acidity of alumina are invoked to rationalize the kinetic results. Changes in the state of Pd after various pretreatments, as probed by temperature-programmed hydride decomposition, can hardly be correlated with changes in the catalytic behaviour in the exchange reaction.

Keywords: Pd/Al_2O_3 catalysts, cyclopentane/D_2 exchange, activated Al_2O_3, hydrogen spillover

1. Introduction

Catalytic activity of metals supported on acidic or basic carriers is invariably a problem of great interest. During the last decade a number of fundamental works was directed towards elucidation of electronic structure of small metal clusters located in zeolites. Although different ideas were proposed for rationalization of catalytic action of such systems, one is always intrigued by enormous catalytic activity enhancement produced by an intimate contact of small metal particles and acidic/basic supports [1]. One of earlier explanations offered on this occasion is bifunctionality of a metal/support system which gives rise to considerable synergistic effects [2]. Frequently, such synergistic effects result from an intimate contact of metal and support and are not obtained by mechanical mixing of these two components [3].

The reaction of H/D exchange in saturated hydrocarbons on supported and unsupported metal catalysts was exhaustively investigated in the past [4–10]. For typical metal oxide supports, such as alumina, the reaction was less studied. A relative inactivity of alumina towards saturated hydrocarbons at temperatures when metals usually exhibit high activity (<100 °C) certainly rationalizes all opinions which consider variations in catalytic activity with the state and structure of supported metal particles [9]. However, it should be recalled that activation at higher temperatures (600–800 °C, typically) which leads to enhancement of Lewis acidity [11–15] renders γ-Al_2O_3 active in D/H exchange of methane [16] and propane [17].

The aim of this work was to investigate whether or not a high-temperature treatment of Pd/Al_2O_3 catalysts would lead to considerable changes in the cyclopentane/D_2 exchange. Previous work [18] showed that alkane conversions are greatly intensified in effect of such a catalyst pretreatment. Those processes were conducted at rather high temperatures ($\sim$300 °C), when hydrogen spillover from Pd onto Al_2O_3 is expected to be substantial [19,20]. Accordingly, this active hydrogen species would play a significant role in the rearrangement of alkane molecules attached to Lewis acid sites on alumina, greatly increasing the overall activity [1]. In the case of the cyclopentane/D_2 exchange when the reaction occurs at much lower temperatures (<100 °C) hydrogen spillover may not operate. Another question remained if cyclopentane can be activated by acid sites of alumina at such low temperatures. Incidentally, recent work [21] showed that hydrogen spillover may play a role in catalyzing D_2/ethylbenzene exchange over PtNaA/H-USY mixed systems.

2. Experimental

Two chlorine-free Pd/Al_2O_3 catalysts were studied, 0.39 and 1.45 wt% Pd/Al_2O_3. They were previously tested and characterized after different pretreatments [18]. Briefly, the low-loaded catalyst was prepared by ion exchange using $Pd(NH_3)_4(NO_3)_2$ and the other by anchoring $Pd(acac)_2$. The support was a PHF γ-alumina (American Cyanamid), acid washed and sieved (75–120 mesh). Metal dispersions measured by H_2 chemisorption are shown in table 1.

The reaction of cyclopentane (c-C_5H_{10}, Fluka, puriss) with deuterium (from CEA-CEN Saclay, France, isotopic

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Table 1
Metal dispersions in 0.39 and 1.45 wt% Pd/Al_2O_3 catalysts after different pretreatments used before catalytic screening runs (taken from [18]).

Catalyst	Pretreatment	H/Pd[d]
0.39 wt% Pd/Al_2O_3	LTR[a]	0.91
	HTR[b]	0.38
	OX-LTR[c]	0.28
1.45 wt% Pd/Al_2O_3	LTR[a]	0.62
	HTR[b]	0.28
	OX-LTR[c]	0.31

[a] LTR (low-temperature reduction) denotes: precalcination under O_2 flow from 25 to 400 °C at 4 °C/min ramp, then cooling to 25 °C in O_2 and reduction (TPR) in 6% H_2/He stream with a ramp of 8 °C/min to 300 °C and keeping 300 °C for 1 h.

[b] HTR (high-temperature reduction) denotes: sample investigated after LTR was oxidized in O_2 flow at 300 °C for 0.5 h, then after short purge in He was reduced in H_2 flow at 600 °C for 17 h; then it was purged in He at 600 °C for 1 h.

[c] OX-LTR (oxidation–low-temperature reduction) denotes: sample investigated after HTR was oxidized in O_2 flow at 500 °C for 1 h, then after short purge in He was reduced in H_2 flow at 300 °C for 1 h.

[d] From H_2 chemisorption, considered as palladium dispersion.

purity 99.75%) was carried out in a glass flow system under atmospheric pressure. After a given pretreatment, the reaction mixture ($\sim$30 ml/min) consisting of deuterium, helium (99.99%, additionally purified by passing through a MnO/SiO_2 trap) and cyclopentane from a saturator maintained at -45.2 °C was directed onto a reactor with a catalyst sample. The partial pressures of the reactants were 8.05 Torr ($c\text{-}C_5H_{10}$) and 75.2 Torr (D_2). Helium was the balance gas. Charges of Pd/Al_2O_3 catalysts (0.0563 g for 0.39 wt% and 0.0150 g for 1.45 wt% Pd loadings) reflect comparable amounts of palladium in both samples. The course of H/D exchange was followed by mass spectrometry (M200 from Dycor-Ametek, Pittsburgh, PA). Usual corrections for fragmentation and isotopic abundance of ^{13}C and D in cyclopentane were applied. In sum, both Pd/Al_2O_3 catalysts, the alumina support and a physical mixture of 1.45 wt% Pd/Al_2O_3 and alumina (in such a proportion as to simulate the composition of 0.39 wt% Pd/Al_2O_3) after different pretreatments, were screened.

In separate experiments, a few alumina samples after different pretreatments were exposed to a similar reaction mixture as in the case of the exchange experiments. The only difference was that hydrogen (purified by passing through a MnO/SiO_2 trap) was used instead of deuterium. After 1.5 h of such a treatment, the reactor was cooled down from 80 °C (the highest temperature in H/D exchange runs) to 25 °C. Then, the sample was purged in He for 20 min. This period was sufficient to reduce the mass signal from desorbing cyclopentane (monitored masses 42, 55 and 70) to a very low value. Then, the rest of retained cyclopentane was desorbed in a temperature-programmed regime (10 °C/min ramp) from 25 to 550 °C and monitored by mass spectrometry.

It appeared interesting to check if different catalyst pretreatments generate changes in the state of palladium induced by its interaction with alumina. Changes in a palladium-based phase composition caused by high-temperature reduction would be recognized by testing variations in the propensity of Pd towards forming a Pd hydride phase (H/Pd ratio, [22]). Interestingly enough, the shape of the equilibrium isothermal hysteresis loop of the reaction $Pd + H_2 \rightleftharpoons \beta\text{-}PdH$ depends very much on the support, suggesting its interaction with palladium [23]. The temperature-programmed (palladium) hydride decomposition (TPHD) method permits determination of the stability of a PdH phase [24,25]. The TPHD runs were performed using a 10% H_2/Ar mixture in a manner described previously [25].

Changes in acidity of PHF γ-alumina induced by different pretreatments were investigated by temperature-programmed desorption of triethylamine (TEA from Fluka, purum), using a mass spectrometer for identification of all species liberated during the run. After saturating the sample of Al_2O_3 with TEA (diluted in He) at 27 °C, the flow of TEA was stopped and after half an hour purge in helium, the temperature was increased in a programmable fashion (10 °C/min). Special attention was paid to liberation of triethylamine and products of its decomposition (acetonitrile, ethylene and hydrogen).

3. Results and discussion

This section is organized as follows. First, results of screening of Pd/Al_2O_3 in cyclopentane/D_2 exchange will be presented in detail. The effect of catalyst pretreatment will be highlighted as the main result of this work: induced changes in the catalytic behaviour will be compared. More attention will be paid to largest catalytic variations. Next, we present results of characterization studies of differently pretreated Al_2O_3 and Pd/Al_2O_3 samples, in the hope that such results are useful in diagnosing how the surface of Pd/Al_2O_3 is modified in effect of various pretreatments and which active sites participate in the cyclopentane/D_2 exchange. Finally, as we come to the conclusion that D spillover (from Pd to Al_2O_3) must play an important role in the reaction, a separate series of runs with a physical mixture of Pd/Al_2O_3 and Al_2O_3 will be reported.

Figures 1 and 2 show extents of conversion and deuterioisomer product distributions in cyclopentane/D_2 exchange on 0.39 and 1.45 wt% Pd/Al_2O_3 catalysts subjected to the pretreatments described in table 1. After LTR, the samples show the catalytic behaviour typically observed for Pd catalysts [4,6,8,9]. Relative intensities of local maxima at d_1, d_5 and d_{10} deuterioisomers in the initial product distribution depend very much on the reaction temperature, indicating variable contribution of stepwise and multiple modes of exchange [3].

HTR (at 600 °C) of Pd/Al_2O_3 lowers the overall conversion of the parent reactant (sections (b) in figures 1 and 2). Such activity drop (per sample) is partly caused by palladium sintering, as metal dispersion is roughly halved upon HTR (table 1). Interestingly enough, one observes a big increase in activity when the HTR samples are reoxidized

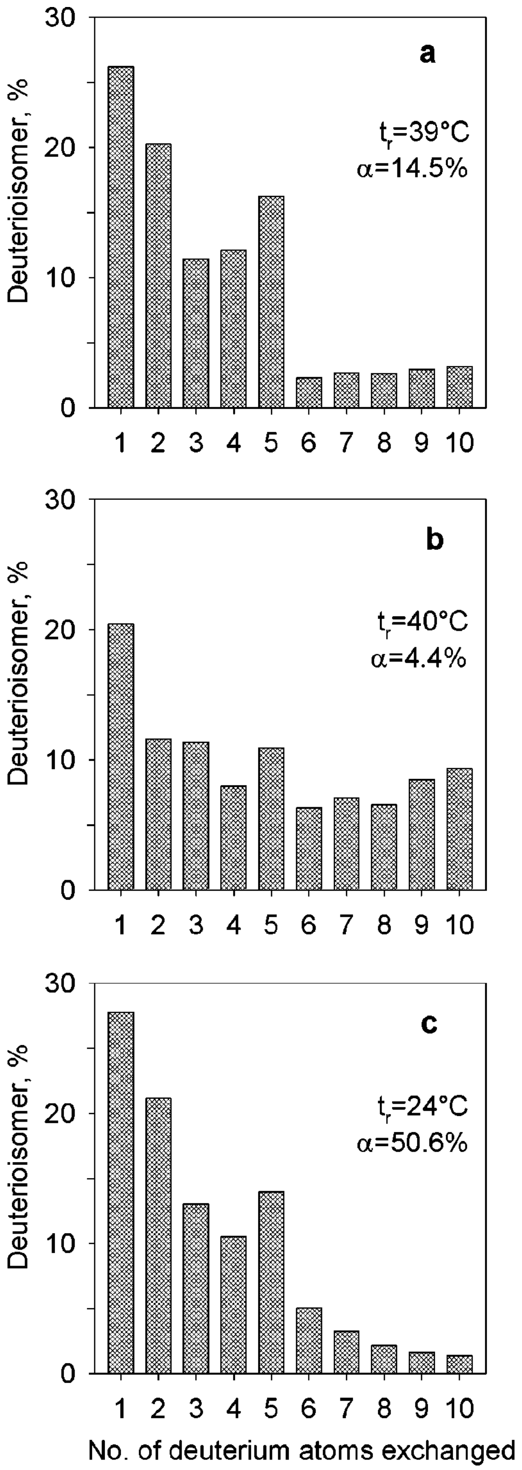

Figure 1. Deuterioisomer product distribution for cyclopentane/D_2 exchange over 0.0563 g of 0.39 wt% Pd/γ-Al_2O_3 subjected to different pretreatments: (a) after LTR, (b) after HTR and (c) after OX-LTR. For pretreatment code, see table 1. Reaction temperatures (t_r) and conversions (α, loss of cyclopentane-d_0) are enclosed.

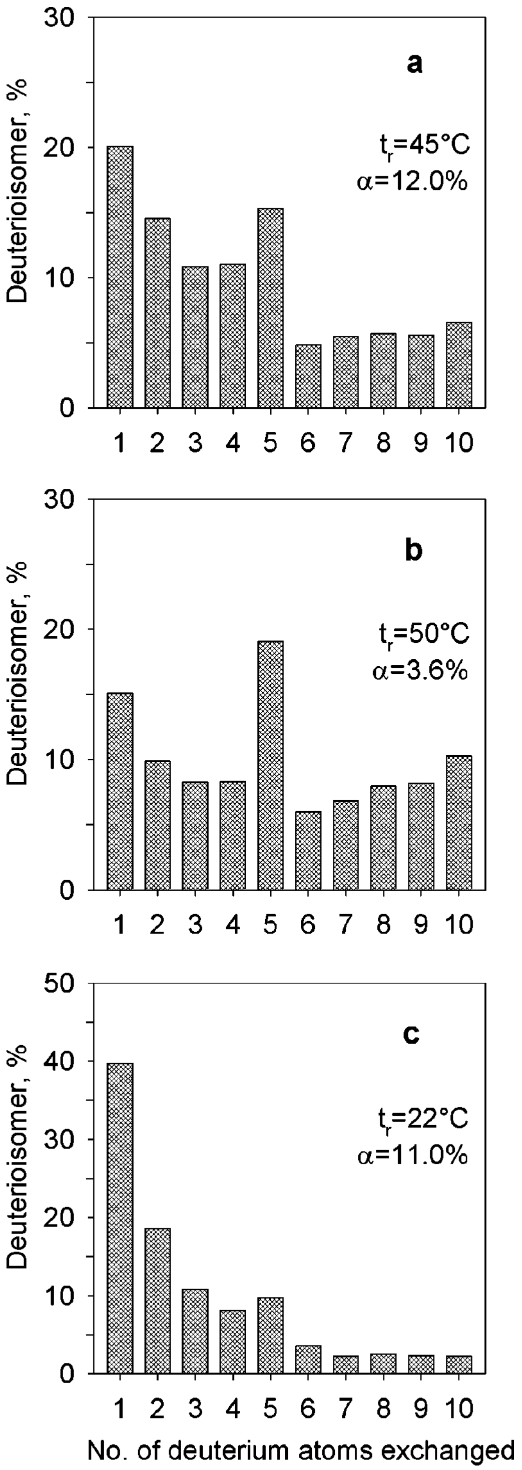

Figure 2. Deuterioisomer product distribution for cyclopentane/D_2 exchange over 0.0151 g of 1.45 wt% Pd/γ-Al_2O_3 subjected to different pretreatments: (a) after LTR, (b) after HTR and (c) after OX-LTR. For pretreatment code, see table 1. Reaction temperatures (t_r) and conversions (α, loss of cyclopentane-d_0) are enclosed.

at 500 °C and mildly reduced at 300 °C (sections (c) in figures 1 and 2). In addition, the deuterioisomer product distribution experiences a considerable change: a huge amount of d_1 product indicates a predominant contribution from stepwise (simple) exchange. Since the metal dispersion was practically not changed in effect of such a pretreatment (i.e., between HTR and OX-LTR), one must consider a catalytic effect of the alumina support.

Alumina can be activated by high-temperature pretreatment, acquiring a considerable (Lewis) acidity [11–15].

Our experiments with differently pretreated PHF γ-alumina showed its negligible activity in cyclopentane/D_2 exchange. Thus, the big enhancement in the exchange activity can be visualized in a synergistic action of palladium and Al_2O_3. In the light of recent publications, one should consider the possibility that an increased acidity of the carrier (alumina) would influence the chemical (electronic) state of the metal (palladium) [1,26,27]. This possibility seems relevant especially because Fitzsimons et al. [28] have recently shown that electron-deficient Pd active sites in supported catalysts are manifested by a marked shift from multiple to stepwise mode of the cyclopentane/D_2 exchange. To have an insight into the state of supported palladium particles we performed a study of temperature-programmed palladium hydride decomposition (TPHD). It was assumed (see section 3) that conceivable changes in the state of palladium produced on high-temperature reduction of Pd/Al_2O_3 would be reflected in its propensity towards β-PdH formation. Figure 3 shows that indeed some changes take place as the 1.45 wt% Pd/Al_2O_3 sample reduced at 600 °C (profile (b)) behaves differently from that reduced at 300 °C (profile (a)). After HTR, hydrogen evolution (profile (b)) commences at much lower temperature than in profile (a), resulting in a considerably wider shape of the hydride decomposition peak than that obtained after LTR. It appears that the hydride phase of the HTR state is less stable than that of the LTR state. Although this result suggests that some Pd–Al_2O_3 interactions would be induced by HTR, nevertheless, the samples after HTR exhibited only moderate decrease in specific activity, because one should consider changes in palladium dispersion (table 1). Much larger activity variations occur after reoxidation and mild reduction of the HTR state of the Pd/Al_2O_3 catalysts (OX-LTR). Figure 3 shows, however, that reoxidation and mild reduction of highly prereduced catalyst results in TPHD trace (c), which is almost indistinguishable from profile (b). Although the results of TPHD characterization must be confirmed by application of more sophisticated techniques (e.g., EXAFS), our tentative conclusion is that the state of palladium in HTR and OX-LTR states does not differ much. Therefore, although catalytic consequences very similar to ours (change from multiple to stepwise exchange) have recently been attributed to the presence of electron-deficient Pd sites [28], we believe that this is not a likely explanation of the present results. It is important to mention that the shift from multiple to stepwise exchange (after OX-LTR of the HTR samples) was always associated with a huge increase in overall activity, which was not the case for the Pd catalysts tested by Fitzsimons et al. [28]. Therefore, in the following discussion we shall concentrate on the question as to how the activated alumina may catalyze the cyclopentane/D_2 exchange. The first thing is to determine changes in acidity of PHF alumina caused by different pretreatments used in this work.

Figure 4 collects TPD results of adsorbed triethylamine (TEA) from two samples of alumina, differing in their pretreatments. A dominant portion of TEA, monitored as mass 86, is desorbed at ~100 °C; it is ascribed to weakly bound TEA. Further release, observed at higher temperature (~420 °C) is mainly associated with the appearance of species produced by elimination from the amine: acetonitrile (mass 41), ethene and hydrogen (not shown). Since acetonitrile is hardly detectable during desorption of TEA from silica, one assumes that its presence in the case of

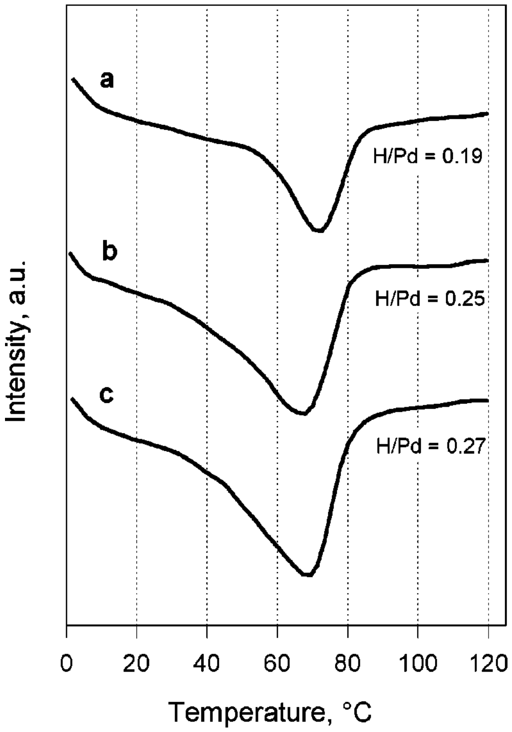

Figure 3. Temperature-programmed hydride decomposition profiles for 0.24 g of 1.45 wt% Pd/Al_2O_3 subjected to different pretreatments: reduction at 300 °C for 1 h (a), reduction at 600 °C for 17 h (b), and reoxidation of the sample (b) and reduction at 300 °C for 1 h (c).

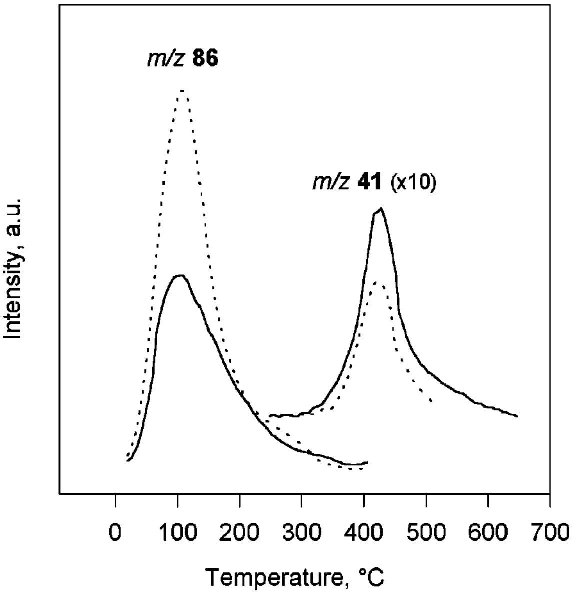

Figure 4. Temperature-programmed desorption of triethylamine (TEA) from γ-Al_2O_3 (0.20 g) subjected to LTR (- - -) and HTR (—). Desorption of TEA (mass 86) and acetylonitrile (mass 41).

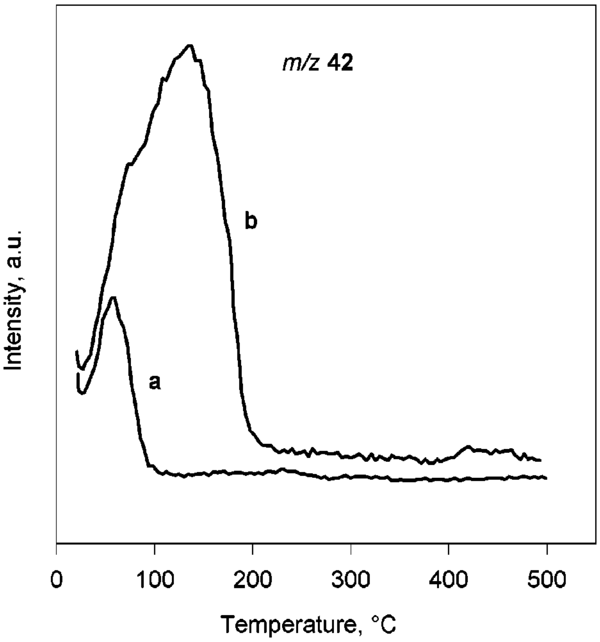

Figure 5. Temperature-programmed desorption of cyclopentane from 0.200 g of PHF γ-alumina subjected to LTR (a) and HTR (b). Adsorption of cyclopentane (from a flowing mixture of c-C_5H_{10}, H_2 and He) was carried out at 80 °C for 1.5 h.

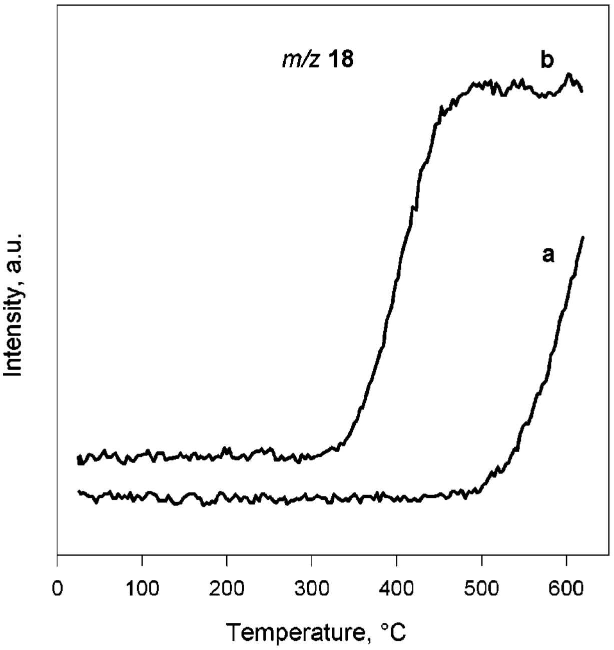

Figure 6. Temperature-programmed desorption of water from 0.3034 g of 0.39 wt% Pd/Al_2O_3 (a) and 0.0816 g of 1.45 wt% Pd/Al_2O_3 (b), after OX-LTR. For pretreatment code, see table 1.

γ-alumina must be associated with an interaction of TEA with (Lewis) acid sites [29]. A more plentiful evolution of acetonitrile is seen for highly reduced alumina (figure 4, solid line, common for HTR and OX-LTR samples of Al_2O_3). However, as mentioned earlier, the HTR pretreatment of Pd/Al_2O_3 which certainly increases the concentration of Lewis acid sites in alumina *lowers* the overall exchange activity (sections (b) versus (a) in figures 1 and 2); the exceptional increase of activity is observed only after OX-LTR (figures 1 and 2, sections (c) versus (a) and (b)).

Nevertheless, it should be noticed that the reported enhancement of Lewis acidity of γ-alumina contributes to a more extensive and stronger adsorption of cyclopentane (figure 5). However, a more extensive binding of cyclopentane by activated alumina can not solely guarantee an enhanced exchange rate on alumina sites as Pd-free Al_2O_3 is inactive in this reaction, at least at temperatures applied in this work. It seems that here another factor plays a significant role: a sufficient transport of active deuterium species to cyclopentane species bound to alumina. Active deuterium species must be formed on palladium and transported (by spillover) to active sites of alumina. Much higher activity of OX-LTR catalysts implies that, for this state, D spillover is more efficient than for the catalyst in HTR state.

Oxidation (at 500 °C) of a prereduced Pd/Al_2O_3 catalyst followed by reduction in hydrogen (OX-LTR) must create water which, at 300 °C (reduction temperature), should reconstitute surface hydroxyls [30,31]. Such a water retention (as hydroxyls) in our Pd/Al_2O_3 catalysts was checked by temperature-programmed desorption. Figure 6 shows that in the case of the 0.39 wt% loaded sample, water is more strongly held as its evolution begins at much higher temperature than for the 1.45 wt% Pd/Al_2O_3. Thus, rehydration leads to different results for two Pd/Al_2O_3 catalysts characterized by so different metal loading. Comparable amounts of water should be formed in effect of reoxidation and reduction of comparable amounts of palladium in samples. However, for the low metal loaded catalyst (0.39 wt%) this amount of water falls to larger amount of alumina than in the case of the 1.45 wt% Pd/Al_2O_3. Therefore, a larger concentration of OH groups is reconstituted in alumina of the 1.45 wt% Pd/Al_2O_3. In addition, heterogeneity of alumina distributes the adsorbed portion of water among sites according to their adsorption strength (strong sites are saturated first). Figure 6 shows that water desorption from 1.45 wt% Pd/Al_2O_3 occurs sooner than in the case of the 0.39 wt% Pd/Al_2O_3. However, the larger concentration of OH groups seen as efficient D spillover carriers is not an exclusive condition for the exchange reaction on the alumina support. It appears that the active alumina should possess two types of active sites: Lewis acid sites for cyclopentane binding and a sufficient number of surface hydroxyls for facilitating D transport by spillover from palladium [32]. Rehydration of the HTR state of the 1.45 wt% Pd/Al_2O_3 in effect of OX-LTR treatment leads to a more efficient elimination of Lewis acid sites in alumina than the same pretreatment applied to 0.39 wt% Pd/Al_2O_3. It appears that some balance in the relative concentration of two types of active sites (Lewis acid centers and hydroxyls) prescribes the exchange activity of alumina in Pd/Al_2O_3 catalysts.

Since deuterium exchange of alkyl and aromatic hydrogens of ethylbenzene was recently observed on physical

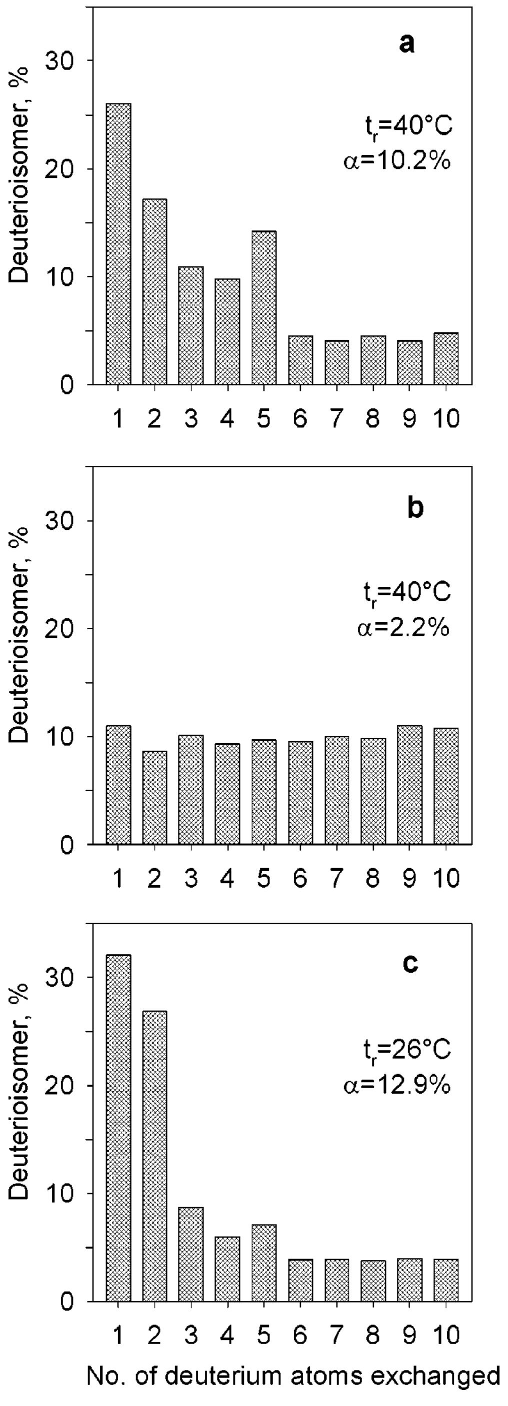

Figure 7. Deuterioisomer product distribution for cyclopentane/D_2 exchange over physical mixture of 1.45 wt% Pd/γ-Al_2O_3 (0.0151 g) and γ-Al_2O_3 (0.0404 g) subjected to different pretreatments: (a) after LTR, (b) after HTR and (c) after OX-LTR. For pretreatment code, see table 1. Reaction temperatures (t_r) and conversions (α, loss of cyclopentane-d_0) are enclosed.

mixtures of Pt/NaA and H-USY zeolite [21], we decided to run a series of experiments with a physical mixture of 1.45 wt% Pd/Al_2O_3 with alumina. The proportion of these two components was adjusted in such a way as to match the composition of the 0.39 wt% Pd/Al_2O_3 catalyst. It is seen (figure 7) that changes in the catalytic behaviour after various pretreatments are much smaller than in the case of 0.39 wt% Pd/Al_2O_3 (figure 1). This result may suggest that deuterium spillover from Pd/Al_2O_3 grains to premixed Al_2O_3 is less effective at low temperatures, because of a loose structure of the physical mixture.

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