C$_6$-alkane conversion over γ-alumina supported palladium and platinum catalysts

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Abstract

A comparable study of *n*-hexane and 2,2-dimethylbutane reactions in excess hydrogen carried out on differently loaded Pd/Al$_2$O$_3$ and Pt/Al$_2$O$_3$ catalysts at ≤290 °C furnished information which is useful in assessing the role of activated alumina in catalyzing C$_6$-alkane conversion. In particular, it was confirmed that in effect of high temperature reduction (at 600 °C) Al$_2$O$_3$ gains a considerable acidity which must play an important role in transformation of C$_6$-alkanes. This effect is more clearly seen for palladium than for platinum catalysts, the role of palladium is even overshadowed by the action of activated alumina. Platinum exhibits higher intrinsic activity than palladium, so the respective changes associated with the presence of activated alumina are not so pronounced for Pt/Al$_2$O$_3$. Highly reduced catalysts showed completely different performance than lowly reduced samples. In the case of palladium, the high temperature reduction leads to a big enhancement of the catalytic activity and also vastly increases the isomerization selectivity. These variations accompanied by a big decrease of activation energy (from ∼50 to 20 kcal/mol) manifest an important modification of the reaction mechanism which changes from "metallic" to "acidic" one. The 2-methylpentane/3-methylpentane product ratio in *n*-hexane conversion represents another useful diagnostic parameter in assessing the role of activated alumina. "Regeneration" of highly reduced catalysts realized by oxidation of highly reduced samples with subsequent low temperature reduction (at 3000 °C) brings about a partial recovery of metal functioning. Temperature-programmed desorption of pyridine from variously pretreated catalysts appeared a promising method in diagnosing changes in surface acidity and metal state. A drastic decrease of chemisorption capability of palladium upon high temperature reduction of Pd/Al$_2$O$_3$, in combination with a positive correlation of catalytic activity with the amount of alumina in the sample, suggests that a dominant part of C$_6$-alkane isomerization takes place on acid sites of alumina, whereas the role of palladium is largely limited to supplying active hydrogen via spillover.
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Keywords: C$_6$-alkane conversion; 2,3-Dimethylbutane isomerization; Pd/Al$_2$O$_3$; Pt/A1$_2$O$_3$; Role of activated alumina; TPD of pyridine; Support acidity

1. Introduction

Catalytic behavior of supported metals in the conversion of saturated hydrocarbons can be influenced by both components, metal and support. The relative contribution of the support to the overall reactivity is generally attributed to its surface acidity. Our earlier work [1] indicated that γ-Al$_2$O$_3$, which appears to be quite inert catalyst component in alkane conversions (at least for reaction temperatures <350 °C, [2]), may enhance its (Lewis) acidity by thermal pretreatment [3–5], and greatly contribute to the catalytic behavior of Pd/Al$_2$O$_3$ systems. Further studies confirmed that the isomerization capability of Pd/A1$_2$O$_3$ catalysts is markedly improved upon high temperature reduction at 600 °C [6].

However, it is still conceivable that different catalyst pretreatments would positively influence not only the support

but also modify, in a favorable fashion, the state of supported metal component. Therefore, one can always argue that in such cases modification of the state of metal is more important for catalysis than a direct involvement of support in reaction The aim of this study was an attempt to separate these two variables. Such task seems difficult because both components of Pd/Al$_2$O$_3$ catalyst would affect each other. However, this issue seems important in light of common practice of using alkanes as test molecules for probing the state of metal in supported catalysts [7]. We decided to compare catalytic behaviors of chlorine-free platinum and palladium catalysts supported on the same alumina carrier. It was hoped that large differences in intrinsic activities towards alkane rearrangements between these two metals (Pt is generally more active than Pd [8–15]) would allow us to extract important information as to the catalytic contribution of activated alumina. Changes in acidity of differently pretreated catalysts were monitored by temperature-programmed desorption (TPD) of pyridine.

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2. Experimental

2.1. Catalyst preparation, pretreatment and characterization of supported palladium and platinum

The catalyst support was γ-Al_2O_3, Alumina Shell S618 (chemical composition: Al_2O_3, 98.5 wt.%, H_2O, 1.5 wt.%), 240 $m^2 g^{-1}$, pore volume 0.8 $cm^3 g^{-1}$, 75–120 mesh, acid washed. Pd/Al_2O_3 catalysts with the metal loading of 0.3 and 2.77 wt.% Pd were prepared by impregnation 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. [16]. Two Pt/Al_2O_3 catalysts were prepared from platinum acetylacetonate (purity 98%, from Strem) according to Kobayashi et al. [17] and had 0.3 and 0.6 wt.% metal loadings.

After impregnation and drying in air oven at 80 °C for 12 h, the catalysts were precalcined in air flow 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 $\sim$8°C min^{-1}. Prior to reaction and adsorption studies, the samples underwent three special pretreatments. First, they were subjected to low temperature reduction (LTR) treatment which was realized by precalcination under O_2 flow (25 $cm^3 min^{-1}$) from room temperature (RT) to 400 °C at 4° min^{-1} ramp, then cooling to RT in O_2 flow and reduction in a 10% H_2/He stream (25 $cm^3 min^{-1}$) with a temperature ramp of 8°C min to 300 °C, and finally cooled to reaction temperature (290 °C). Second pretreatment was the high temperature reduction (HTR) which consisted in oxidizing the LTR sample under O_2 flow at 300 °C for 0.5 h, and, after a short purge in He at 300 °C, reduction in H_2 flow at 600 °C for 17 h. After reduction the sample was purged in He at 600 °C for 1 h, and cooled to the reaction temperature. Third pretreatment called "Regeneration" denotes: sample investigated after HTR was oxidized under O_2 flow at 500 °C for 1 h, then after a short purge in He at 500 °C, reduced in H_2 at 300 °C for 1 h, and finally cooled to the reaction temperature. The same sample pretreatments were applied prior to metal dispersion measurements by hydrogen pulse chemisorption, as described elsewhere [18]. Table 1 presents data of metal dispersion in variously pretreated palladium and platinum catalysts.

2.2. Catalytic conversions of n-hexane (nH) and 2,2-dimethylbutane (22DMB) over differently pretreated γ-Al_2O_3 supported palladium and platinum catalysts

The catalytic conversions of *n*-hexane (purity >99.9% from Chemipan, Poland) and 2,2-dimethylbutane (puriss, >99.5%, from Fluka AG) in excess hydrogen (purified by passing over a MnO/SiO_2 bed) were conducted in a continuous flow system under atmospheric pressure [1,6]. A tubular fused silica reactor was loaded with different amounts of Pd

Table 1

Metal dispersions in investigated Pd/Al_2O_3 and Pt/Al_2O_3 catalysts after different pretreatments used before catalytic screening experiments

Catalyst	Metal dispersion after different pretreatments (H/metal)[a]		
	LTR[b]	HTR[c]	Regeneration[d]
0.3 wt.% Pd/Al_2O_3	0.23	0.002	0.01
2.77 wt.% Pd/Al_2O_3	0.30	0.19	0.12
0.3 wt.% Pt/Al_2O_3	0.76	0.18	0.40
0.6 wt.% Pt/Al_2O_3	0.85	0.32	0.43

[a] From hydrogen chemisorption studied in pulse system.

[b] LTR denotes: precalcination under O_2 flow (25 $cm^3 min^{-1}$) from room temperature (RT) to 400 °C at 4°C min^{-1} ramp, then cooling to RT in O_2 flow and reduction in a 10% H_2/He stream (25 $cm^3 min^{-1}$) with a temperature ramp of 8°C min^{-1} to 300 °C, and finally cooled to reaction temperature (290 °C).

[c] HTR denotes: oxidizing the LTR sample under O_2 flow at 300 °C for 0.5 h, and after a short purge in He at 300 °C, reduction in H_2 flow at 600 °C for 17 h. After reduction the sample was purged in He at 600 °C for 1 h, and cooled to the reaction temperature.

[d] "Regeneration" denotes: sample investigated after HTR was oxidized under O_2 flow at 500 °C for 1 h, then after a short purge in He at 500 °C, reduced in H_2 at 300 °C for 1 h, and finally cooled to the reaction temperature.

(or Pt)/Al_2O_3 samples: $\sim$0.15 g of 0.6 and 2.77 wt.% metal loading and $\sim$0.25 g for remaining catalysts.

After a specific pretreatment (LTR or HTR or "Regeneration", preceeding subsection) the catalysts were contacted with the reaction mixture (flow of hydrogen at 8.0 $cm^3 min^{-1}$ and C_6-alkane, provided from a saturator kept at constant temperature) at the highest reaction temperature, i.e. 290 °C. The partial pressures of hydrocarbon reactants were: 45 Torr (nH) and 51.5 Torr (22DMB) (1 Torr = 133.32 N m^{-2}). The reactions were followed by gas chromatography (HP 5890 series II with FID, a 50 m PONA, #19091S-001-HP, capillary column). With a few exceptions, the activities of most catalysts declined with time-on-stream. Steady-state conversions were achieved after $\sim$2–2.5 h of time on stream (Fig. 1). Then, a usual catalyst screening was continued, i.e. collection of experimental points at lower temperatures, gradually decreased at $\sim$10 °C intervals.

It was established that there was no effect of external diffusion by examining the effect of variable contact time. Experiments with a more crushed catalyst showed no effect of the catalyst grain size on the percent conversion, which is suggestive of the lack of the effect of an internal diffusion process.

Turnover frequencies (TOFs) were calculated on the basis of the Pd dispersion values (H/Pd). Selectivities (product distributions) were calculated as the carbon percentage of nH (or 22DMB) consumed in the formation of a designated product.

2.3. Acidic evaluation

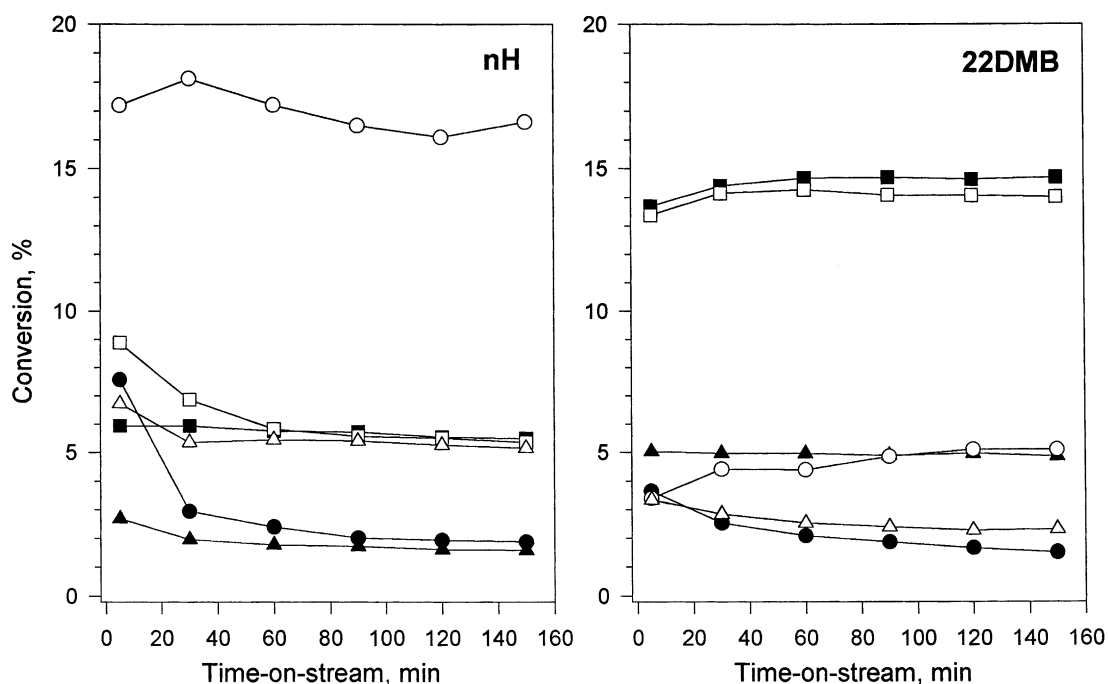The TPD of pyridine (analytical purity from POCh, Gliwice, Poland) was employed for the determination of

Fig. 1. Catalytic conversion of *n*-hexane (a) and 2,2-dimethylbutane (b) at 290 °C. The effect of time-on-stream on overall conversion over 0.3 wt.% Pd/Al$_2$O$_3$ (black symbols) and 0.3 wt.% Pd/Al$_2$O$_3$ (white symbols) catalysts subjected to different pretreatments: LTR (circles), HTR (squares) and "regeneration" (triangles). For pretreatment code, see Table 1.

acidic sites. The base was introduced to a stream of helium (25 cm^3 min^{-1}) from a saturator kept at 0 °C. Before entering the reactor with a 0.26 g catalyst sample, the pyridine/He mixture was dried by passing it through a 3 Å molecular sieves trap. Only Pd-containing catalysts were selected for this study. For comparison, samples of differently pretreated γ-Al$_2$O$_3$ were also investigated. All stages of this experiment, i.e. saturation with pyridine, release of a weakly bound base at 100 °C and TPD of the base and products of its decomposition were monitored by mass spectrometry (M200 from Dycor-Ametek, Pittsburgh, PA). After saturating the pretreated samples with pyridine at 100 °C, the flow of base was stopped and after 0.5 h purge in helium at 100 °C, when the mass signal from the base returned to a negligible level, the temperature was increased in a programmable fashion (at ∼10 °C min) up to 600 °C.

3. Results and discussion

3.1. Catalytic conversions of n-hexane (nH) and 2,2-dimethylbutane (22DMB) on differently pretreated alumina supported Pd and Pt catalysts

Prior to showing catalytic results a comment concerning the metal dispersions (from H$_2$ chemisorption) presented in Table 1 seems appropriate. First, one can see very severe decrease of Pd dispersion in the 0.3 wt.% loaded catalyst after HTR. For 2.77 wt.% Pd/Al$_2$O$_3$, the H/Pd ratio (after HTR)

is also decreased (compared to LTR values), but to a lesser degree. Because it is highly unlikely that more Pd-loaded catalyst would suffer a lesser metal sintering than the samples of lower metal loading, we think that in HTR catalysts some part of the metallic material is undetectable for hydrogen chemisorption. If we assume that the amount of such fraction is comparable in both HTR samples of Pd/Al$_2$O$_3$ catalysts, then it becomes clear that its presence would be more distinctly manifested in suppressing hydrogen uptake for the low Pd loaded catalyst. "Regeneration" of HTR samples by oxidation and mild reduction restores to some extent the dispersion level.

Because we disregard palladium sintering as a principal reason of the vast decrease of H$_2$ chemisorption in the case of 0.3 wt.% Pd/Al$_2$O$_3$ catalyst subjected to HTR, it is possible that during HTR some part of palladium particles is influenced by the support, e.g. some alumina species may be located on the surface of palladium particles. Such a speculation is supported by backscattering studies of model Pt/Al$_2$O$_3$ systems [19,20], where high temperature reduction resulted in the formation of Pt–Al alloy islands having a diminished activity for hydrogen chemisorption. This phenomenon rather than a severe metal sintering seems to better account for the seriously reduced H/metal ratio and is much more strongly pronounced for palladium than platinum catalysts. Furthermore, because this effect is better marked for a low metal loaded sample, we speculate that alumina decorates more efficiently the surface of smaller Pd particles. Inability of HTR sample of the low Pd loaded catalyst to

Table 2

n-Hexane reaction on variously pretreated Pd/Al$_2$O$_3$ and Pt/Al$_2$O$_3$ catalysts: activities per gram of catalyst, turnover frequencies (TOFs), product selectivities (at 290 °C) and activation energies (E_a)

Catalyst pretreatment	Overall catalytic activity (mol s^{-1} g$_{catalyst}^{-1}$)	TOF (s^{-1})	Selectivity (%)[a]			2MP/3MP in products	E_a (kcal/mol)
			$S_{c<6}$	S_{is}	S_{MCP}		
0.3 wt.% Pd/Al$_2$O$_3$							
LTR[b]	2.69×10^{-8}	4.07E−3	78.5	10.1	10.1	3.2	48.2 ± 2.5
HTR[c]	7.87×10^{-8}	1.37E	5.4	90.4	3.9	1.3	25.7 ± 1.7
Regeneration[d]	2.28×10^{-8}	7.93E−2	32.8	62.3	4.3	1.2	31.7 ± 2.4
2.77 wt.% Pd/Al$_2$O$_3$							
LTR[b]	1.25×10^{-8}	1.55E−4	58.8	14.9	23.4	2.7	55.5 ± 3.2
HTR[c]	8.51×10^{-8}	1.68E−3	6.5	89.0	4.2	1.4	29.0 ± 2.0
Regeneration[d]	5.45×10^{-9}	1.70E−4	32.4	23.6	38.0	2.3	58.5 ± 3.7
0.3 wt.% Pt/Al$_2$O$_3$							
LTR[b]	2.39×10^{-7}	2.22E−2	83.7	10.0	4.9	1.7	25.3 ± 0.3
HTR[c]	7.72×10^{-8}	3.00E−2	29.2	51.9	16.1	1.5	27.4 ± 0.4
Regeneration[d]	7.42×10^{-8}	1.32E−2	29.1	43.3	22.7	2.4	30.5 ± 0.4
0.6 wt.% Pt/Al$_2$O$_3$							
LTR[b]	4.49×10^{-7}	2.08E−2	81.4	12.3	4.7	1.7	24.1 ± 0.3
HTR[c]	1.04×10^{-7}	2.04E−2	37.7	39.4	19.5	1.8	33.9 ± 0.5
Regeneration[d]	1.87×10^{-7}	1.53E−2	57.5	27.1	12.6	2.2	28.1 ± 0.4

[a] Product selectivity: $S_{c<6}$, to hydrogenolysis products; S_{is}, to methylpentanes; S_{MCP}, to methylcyclopentane. Other minor products were benzene and cyclohexane ($\Sigma < 5\%$).

[b] LTR denotes: precalcination under O$_2$ flow (25 cm^3 min^{-1}) from room temperature (RT) to 400 °C at 4 °C min^{-1} ramp, then cooling to RT in O$_2$ flow and reduction in a 10% H$_2$/He stream (25 cm^3 min^{-1}) with a temperature ramp of 8 °C min to 300 °C, and finally cooled to reaction temperature (290 °C).

[c] HTR denotes: oxidizing the LTR sample under O$_2$ flow at 300 °C for 0.5 h, and, after a short purge in He at 300 °C, reduction in H$_2$ flow at 600 °C for 17 h. After reduction the sample was purged in He at 600 °C for 1 h, and cooled to the reaction temperature.

[d] "Regeneration" denotes: sample investigated after HTR was oxidized under O$_2$ flow at 500 °C for 1 h, then after a short purge in He at 500 °C, reduced in H$_2$ at 300 °C for 1 h, and finally cooled to the reaction temperature.

recover (in the "regeneration" step), to a considerable degree, its initial chemisorption potential suggests that a large part of palladium surface is irreversibly blocked by alumina.

Tables 2 and 3 show the results of catalytic screening at steady state at 290 °C for nH and 22DMB reaction, respectively. Blank experiments with differently pretreated γ-Al$_2$O$_3$ showed negligible activity in the temperature range used for screening Pd(Pt)/Al$_2$O$_3$ catalysts, i.e. ≤290 °C.

Tables 2 and 3 show changes in isomerization selectivity (S_{is}). LTR samples of alumina-supported Pd and Pt show the catalytic behaviour typically observed for these metals [7–15]. Very low values of S_{is} shown by LTR samples of platinum catalysts in 22DMB conversion are not surprising, because in this reaction hydrogenolysis predominates on small platinum particles [21]. It is recalled that LTR samples of our Pt catalysts were characterized by high metal dispersion (Table 1).

Far more interesting are changes in the catalytic behavior produced by HTR. It is seen that HTR generates very high isomerization selectivity, confirming our earlier results [1,6]. In the case of 22DMB reaction, S_{is} is increased up to 90%, for all tested catalysts. In the case of nH, such a high selectivity level is only reached by palladium catalysts. We conclude, as in our previous paper [1] that such a drastic increase of S_{is} is caused by increase of acidity of γ-alumina, in effect of high temperature reduction pretreatment.

Table 3 reveals a marked decrease in the activation energy for 22DMB reaction upon HTR, suggesting significant mechanistic variations. Clearly, the mechanism of 22DMB reaction changes from "metallic" (characterized by higher activation energy observed earlier, 40–50 kcal/mol, [1,6,22]) to "acidic" one, with a much lower E_a (~20 kcal/mol), [1]. Further evidence for the acidic character of 22DMB isomerization on HTR samples comes from the selectivity pattern. A vast majority of isomerization results in the formation of 2,3-dimethylbutane (23DMB, ~70% of all C$_6$ isomers, Fig. 2). This can be attributed to acidic character of isomerization [7]: the formation of 23DMB involving the reaction of secondary to, a more stable, tertiary carbenium ion is favored. Interestingly, "regeneration" of HTR samples of 0.3 wt.% Pd/Al$_2$O$_3$ brings about even higher selectivities towards 23DMB. This would suggest further increase in acidity caused by "regeneration". However, it must be said that HTR of all samples greatly increased the activity of all catalysts, i.e. conversion level of a few percent for LTR samples was usually increased to 13–15% upon HTR. Available data [23–25] indicate that the formation of 23DMB would be thermodynamically limited (inset in Fig. 2). At lower reaction temperatures (270 and 280 °C), when the overall conversion is much less than 10%, the percentage of 23DMB in C$_6$ isomeric products was found higher than at 290 °C (85% versus ~70%). "Regeneration" restores to a

Table 3

2,2-Dimethylbutane reaction on variously pretreated Pd/Al$_2$O$_3$ and Pt/Al$_2$O$_3$ catalysts: activities per gram of catalyst, turnover frequencies (TOFs), product selectivities (at 290 °C) and activation energies (E_a)

Catalyst pretreatment	Overall catalytic activity (mol s^{-1} g$_{catalyst}^{-1}$)	TOF (s^{-1})	Selectivity (%)[a]			E_a (kcal mol^{-1})
			$S_{c<6}$	S_{is}	S_{MCP}	
0.3 wt.% Pd/Al$_2$O$_3$						
LTR[b]	2.45×10^{-8}	3.69E−3	74.2	25.8	–	55.1 ± 2.7
HTR[c]	2.38×10^{-7}	4.13E	5.7	94.3	0.2	18.5 ± 1.2
Regeneration[d]	7.87×10^{-8}	2.74E−1	5.7	94.0	–	25.0 ± 1.8
2.77 wt.% Pd/Al$_2$O$_3$						
LTR[b]	2.84×10^{-8}	3.53E−4	51.2	48.8	–	51.9 ± 2.8
HTR[c]	3.52×10^{-7}	6.96E−3	6.4	93.4	–	20.2 ± 1.2
Regeneration[d]	3.46×10^{-8}	1.09E−3	21.6	78.4	0.3	42.4 ± 2.7
0.3 wt.% Pt/Al$_2$O$_3$						
LTR[b]	8.20×10^{-8}	3.76E−3	98.6	1.4	–	48.7 ± 0.5
HTR[c]	2.25×10^{-7}	4.37E−2	9.4	90.5	–	19.7 ± 0.3
Regeneration[d]	3.74×10^{-3}	3.27E−3	56.0	44.0	–	36.3 ± 0.5
0.6 wt.% Pt/Al$_2$O$_3$						
LTR[b]	1.49×10^{-7}	5.72E−3	98.9	1.2	–	49.6 ± 0.5
HTR[c]	3.32×10^{-7}	3.38E−2	12.8	87.2	–	20.4 ± 0.3
Regeneration[d]	4.88×10^{-8}	3.60E−3	76.2	23.8	–	41.3 ± 0.6

[a] Product selectivity: $S_{c<6}$, to hydrogenolysis products; S_{is}, to C$_6$-isomers (mostly to 2,3 dimethylbutane); S_{MCP}, to methylcyclopentane.

[b] LTR denotes: precalcination under O$_2$ flow (25 cm^3 min^{-1}) from room temperature (RT) to 400 °C at 4 °C min^{-1} ramp, then cooling to RT in O$_2$ flow and reduction in a 10% H$_2$/He stream (25 cm^3 min^{-1}) with a temperature ramp of 8 °C min^{-1} to 300 °C, and finally cooled to reaction temperature (290 °C).

[c] HTR denotes: oxidizing the LTR sample under O$_2$ flow at 300 °C for 0.5 h, and, after a short purge in He at 300 °C, reduction in H$_2$ flow at 600 °C for 17 h. After reduction the sample was purged in He at 600 °C for 1 h, and cooled to the reaction temperature.

[d] "Regeneration" denotes: sample investigated after HTR was oxidized under O$_2$ flow at 500 °C for 1 h, then after a short purge in He at 500 °C, reduced in H$_2$ at 300 °C for 1 h, and finally cooled to the reaction temperature.
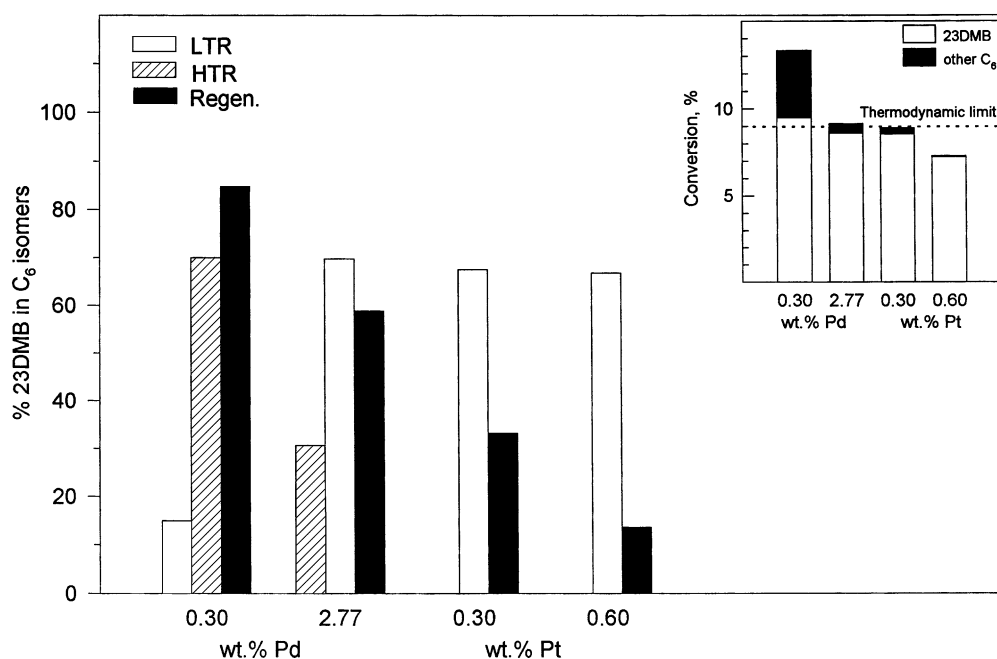

Fig. 2. Variations in the percentage of 2,3-dimethylbutane (23DMB) in C$_6$-isomers produced in 2,2-dimethylbutane (22DMB) conversion on Pd/Al$_2$O$_3$ and Pd/Al$_2$O$_3$ catalysts. Reaction temperature: 290 °C. For catalyst pretreatment (LTR, HTR, Regen. = "regeneration") see text and Table 1. Inset: conversion (%) of 22DMB into C$_6$ isomeric products. Thermodynamic limit for 23DMB formation (at 300 °C) is indicated.

certain extent the "metallic" character of 22DMB reaction, as judged from changes in TOF and E_a values (Table 3). In addition, the recovery is more complete for higher metal loadings (Fig. 2 and Table 3).

HTR samples of Pt-containing catalysts differ from the respective samples of Pd catalysts. It seems that the metal functioning in Pt/Al$_2$O$_3$ is not so drastically masked by the action of activated alumina as in the case of Pd/Al$_2$O$_3$ samples. This is, of course, not surprising because platinum is known as unique among the catalytic metals for its superior propensity in alkane rearrangements. Nevertheless, in case of 22DMB reaction, both the overall activity as well as isomerization selectivity and activation energy experience large changes, similar to those seen for palladium catalysts (Table 3). But in the case of nH reaction, changes in TOF and activation energy caused by HTR are rather small (Table 2). It must be noticed that the activation energy in nH reaction is usually lower than that for 22DMB reaction. The E_a value of 26 kca1/mol was reported for nH conversion on EUROPT-1 [26]. Therefore, a possible change of the reaction mechanism from "metallic" to "acidic" (for which a level of E_a of 20 kca1/mol seems acceptable) cannot be easily reflected by change of E_a. Therefore, it is rather difficult to assess if these small variations in the behavior of Pt catalysts in nH reaction can be attributed to the effect of support acidity or structure sensitivity associated with changes in metal particle size [11,14,15,21], which are inevitable during our catalyst pretreatments.

The 2-methylpentane/3-methylpentane product ratio (2MP/3MP) from nH conversion may also serve as a diagnostic parameter here. In the case of palladium catalysts, this ratio drops from ∼3 (for LTR samples) to 1.3–1.4 (after HTR). This may suggest that the mechanism of isomerization changes from a bond-shift type on palladium sites [7–11] to an "acidic", involving carbenium ions [27,28]. After "regeneration" the 2MP/3MP ratio does not change for 0.3 wt.% sample, but it increases to 2.3 for the 2.77 wt.%, indicating again that the metallic function of the catalyst is better restored in samples of higher metal loading. In the case of platinum catalysts, the 2MP/3MP ratio (Table 2) experiences much milder changes, which can be attributed to different reasons, among which variations in texture and size of metallic particles induced by different pretreatments can be mentioned.

The fact that HTR reduces the action of the metallic component of the system may result from a Pd–Al$_2$O$_3$ interaction, possibly from a Pd–Al alloy formation, as shown in other works [29,30]. The question arises as to whether the reduced chemisorption capability of palladium is helpful in catalyzing such nondestructive reactions of alkanes like isomerization. A positive modification of palladium surface by alumina leading to superactive, bifunctional sites does not seem to explain the observation that, at least in the case of Pd/Al$_2$O$_3$ catalysts, the activity is very weakly correlated with the amount of metal in the sample (Fig. 3): an almost 10-fold increase of Pd loading brings about either only
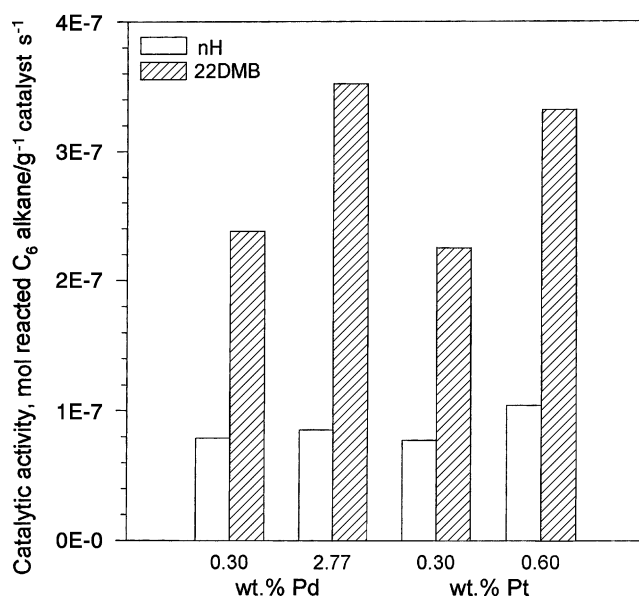

Fig. 3. The effect of metal loading on the catalytic activity (expressed as mol reacted alkane g^{-1}catalyst s^{-1}) of Pd(Pt)/Al$_2$O$_3$ catalysts subjected to HTR. Reaction temperature: 290 °C.

negligible (nH reaction) or very modest changes (22DMB, activity increase by factor of ∼1.5). Thus, the activity strongly depends on the amount of (activated) alumina. It looks like a prevailing part of alumina surface participates in reaction. Because the activity of pure alumina subjected to HTR dies off very quickly with time-on-stream (results of blank tests not shown) we believe that active (atomic) hydrogen must be supplied by dissociative chemisorption on Pd followed by H atom spillover onto the support. We speculate that alkane activation is possible on acid sites of Al$_2$O$_3$, in line with [4]. The reaction may proceed via hydride abstraction with a respective carbenium ion formation, due to active hydrogen supply from the metal [31–33]. It may be argued that the classical dualfunction mechanism [34] would also explain present results. However, because no traces of olefinic species were detected among reaction products (at relatively low reaction temperatures ≤290 °C and high excess of hydrogen) we believe that the classical dual-function mechanism does not operate here.

3.2. Catalyst probing by TPD of adsorbed pyridine

TPD study of adsorbed pyridine furnished significant results which can be of value in diagnosing changes in differently pretreated alumina-supported metal catalysts. It will be shown that these changes concern both the state of metal and the alumina support.

The results of TPD of adsorbed pyridine are collectively presented in Fig. 4. It may be seen that for all tested samples, i.e. pure alumina and two Pd/Al$_2$O$_3$ catalysts, more pyridine desorbs after HTR than after LTR (peak maximum at <200 °C). In the case of pure alumina, HTR increases the
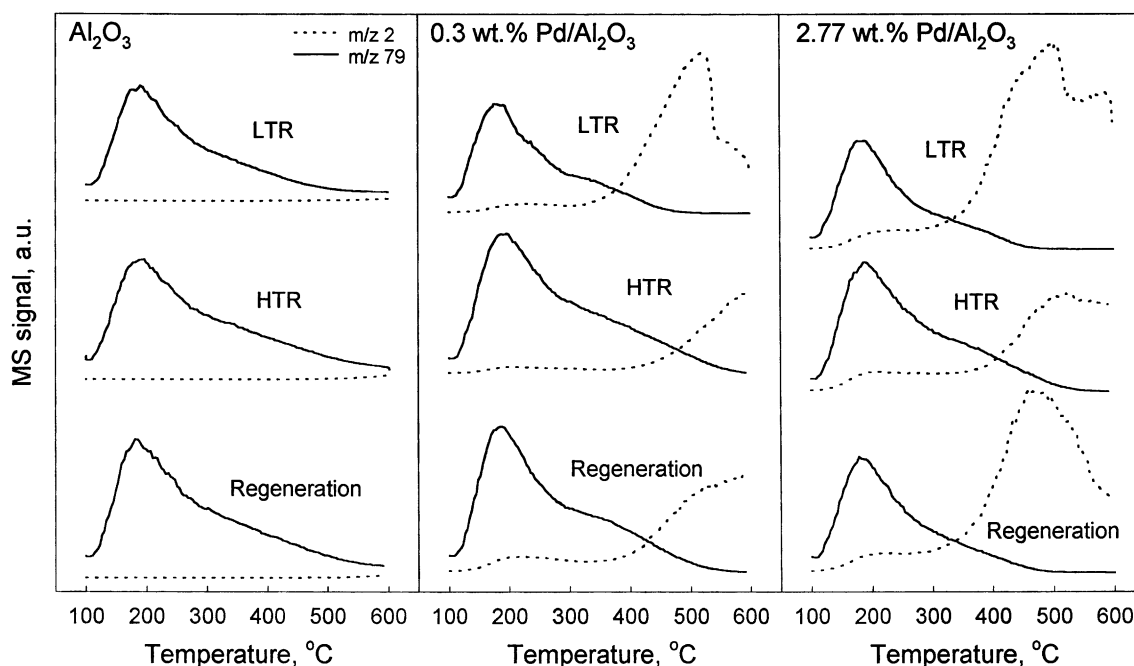
Fig. 4. TPD profiles after pyridine adsorption on Al_2O_3 and two Pd/Al_2O_3 catalysts, subjected to various pretreatments. Evolution of pyridine (mass 79) and hydrogen (mass 2) are shown. For pretreatment code (LTR, HTR, regeneration) see text and Table 1.

amount of desorbed pyridine by 30%, whereas for 0.3 wt.% Pd the analogous change reaches 50%. Because, the basic difference concerns changes in the shape of the right-branch of TPD peak, at the 300–450 °C range, it is considered that HTR generates stronger acid sites in alumina. It is seen that during TPD runs with differently pretreated alumina, only negligible amounts of hydrogen are released. On the other hand, for Pd-containing samples a significant portion of adsorbed pyridine is decomposed leading to a massive release of hydrogen. Decomposition of adsorbed pyridine during TPD runs was found for several metal surfaces [35–41]. A part of pyridine adsorbed at subambient temperatures on Pt(1 1 1) surface desorbs after heating to ~13 °C, however a significant part (50%) of this amine decomposes giving α-pyridyl fragment and hydrogen, which desorbs in a few steps: at ~60, ~240 and ~350 °C [36]. In our case, massive release of hydrogen takes place at >400 °C. Interestingly enough, the amount of hydrogen released during TPD from LTR samples seems to be directly correlated with the amount of metal in the sample. Therefore, we conclude that pyridine dehydrogenation occurs on palladium surface. On the other hand, the Pd/Al_2O_3 samples subjected to HTR liberate much less hydrogen than the LTR ones. It seems that a considerable part of Pd surface is blocked in effect of HTR. Such a conclusion is supported by a drastic decrease of hydrogen chemisorption capability of HTR samples (Table 1). Thus, we suggest that, in addition to testing surface acidity, TPD of pyridine is a sensitive method in probing availability of exposed palladium surface.

4. Conclusions

These comparable study of Pd/Al_2O_3 and Pt/Al_2O_3 catalysts in nH and 22DMB conversions substantiate our earlier speculations as to the important role of activated alumina in alkane transformations at relatively low temperatures ($\leq$290 °C), [1,6]. An increase of Lewis acidity of alumina due to high temperature reduction (at 600 °C), confirmed by TPD of pyridine, changes the overall catalytic behavior: Al_2O_3 becomes an active catalyst component in reaction. Such changes (in overall activity, product selectivity and activation energy) are more pronounced for the catalysts characterized by very low metal loading. In addition, these variations are much more clearly marked for palladium than for platinum catalysts, in case of Pd/Al_2O_3 the role of metal is even overshadowed by the action of activated alumina since the activity does not depend on the amount of metal component in catalyst. Metallic platinum is much more active than palladium in alkane conversions, so the contribution of activated alumina is less seen. "Regeneration" of highly reduced catalysts realized by oxidation of highly reduced samples with subsequent low temperature reduction (at 300 °C) brings about a partial recovery of metal functioning.

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