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Tuning the support adsorption properties of Pd/SiO_2 by silylation to improve the selective hydrogenation of aromatic ketones

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ABSTRACT

Silylation of Pd/SiO_2 catalysts increases the selectivity toward alcohols in the reduction of aromatic ketones. This work demonstrates that the selectivity is directly related to the adsorption strength of the alcohol on the surface of the support relative to the adsorption strength of the ketone. This observation can be explained by interaction of the support coverage with the metal coverage. Silylation yields a more hydrophobic support, on which the aromatic alcohol adsorbs more weakly relative to the ketone, in turn decreasing the amount of the alcohol adsorbed on the metal and thus suppressing the consecutive reduction of the alcohol. Silylation was carried out by using di-alkyl (dichlorodimethylsilane) and tri-alkyl (hexamethyldisilazane and hexamethyldisilane) silylating agents. Hexamethyldisilazane provided to be the most effective agent in terms of incorporation of methyl groups, catalyst hydrophobicity, and stability. Selective hydrogenation of 4-isobutyl acetophenone (4-IBAP) to 4-isobutylphenyl ethanol (4-IBPE) revealed that not only was the fresh hexamethyldisilazane-silylated Pd/SiO_2 catalyst more selective than the untreated catalyst, but also the silylated catalyst was much more selective after a deactivation–regeneration cycle than the untreated Pd/SiO_2 catalyst. The change in selectivity can be explained by a change in the relative adsorption strength of 4-IBPE over 4-IBAP on silylation.

1. Introduction

An appropriate modification of the hydrophobic–hydrophilic properties of a catalyst can optimize the relative adsorption strengths of the reactant and products on a support, and thus the reaction selectivity as well. The most common strategy for increasing hydrophobicity is silylation of the catalyst by alkyl- and chloroalkylsilanes in the gas or liquid phase [1–9]. Silylation reduces the silanol groups of the support, thereby decreasing the adsorption of water and other polar products on the catalyst surface. Hexamethyldisilazane (HMDS) is the most widely used silylating agent due to its high reactivity with silica [7,10].

Silylation has been performed mainly with mesoporous materials, typically Ti-MCM-41 and 48, because of their instability in presence of water. The reactions in which silylated catalysts were tested were mainly selective oxidations, including epoxidation [1–3,8–11], hydroxylation of benzene [11], and oxidative desulfurization of diesel [12], in which the oxidized product had a strong affinity to the catalyst. These catalysts also have been used in the synthesis of alkylamines [13], isomerization reactions with HZMS-5 [6] and Fischer–Tropsch synthesis [7].

Previous studies have reported higher activity, selectivity, and stability of the silylated catalysts compared with their untreated counterparts. Corma et al. [1] correlated selectivity with the percentage of the surface coverage by the methyl groups incorporated on the catalyst. The improved performance is attributed to the hydrophobic properties of the catalyst surface, which particularly affects (i.e., weakens) the adsorption of the oxygenated products; however, the control experiments, in which the relative adsorption strength of the various reactant and products were compared, were not reported.

In the present work, we focused on selective hydrogenation of aromatic ketones to aromatic alcohols [14]. We investigated the industrially important hydrogenation of 4-isobutyl acetophenone (4-IBAP) to 4-isobutylphenyl ethanol (4-IBPE) using supported metal catalysts. This reaction is an intermediate step in the catalytic route developed for ibuprofen, a well-known analgesic [15]. Pd/SiO_2 catalysts are particularly active and selective when hydrogenation of 4-IBAP is carried out in a nonpolar solvent, such as n-decane [16]. The hydrogenation route is shown in Fig. 1 [17]. The following kinetic mechanism has been proposed for this reaction [18]:

$$\mathrm{IBAP} + {}^{*} \leftrightarrow \mathrm{IBAP}^{*} \tag{1}$$

$$\mathrm{H_2} + {}^{*} \leftrightarrow 2\mathrm{H}^{*} \tag{2}$$

$$\mathrm{IBAP}^{*} + \mathrm{H}^{*} \leftrightarrow \mathrm{IBAP{-}H}^{*} + {}^{*} \tag{3}$$

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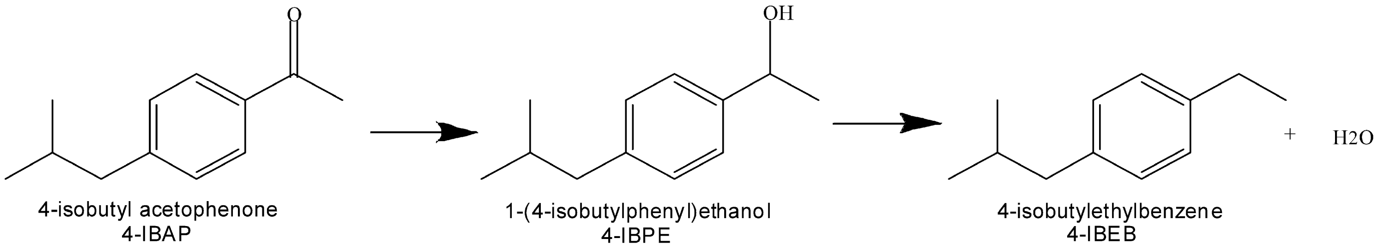

Fig. 1. Reaction scheme for 4-IBAP hydrogenation with Pd/SiO_2.

$$\text{IBAP–H}^* + \text{H}^* \rightarrow \text{IBPE}^* + {}^* \tag{4}$$

$$\text{IBPE}^* \leftrightarrow \text{IBPE} + {}^* \tag{5}$$

$$\text{IBPE}^* + \text{H}^* \leftrightarrow \text{IBPE} - \text{H}^* + {}^* \tag{6}$$

$$\text{IBPE–H}^* + \text{H}^* \rightarrow \text{IBEB} + \text{H}_2\text{O}^* + {}^* \tag{7}$$

$$\text{H}_2\text{O}^* \leftrightarrow \text{H}_2\text{O} + {}^* \tag{8}$$

Here, Eqs. (4) and (7) are the rate-determining steps, and the others are adsorption equilibria on the palladium sites, indicated by *. In this work, we also are interested in the support–metal interaction of adsorbed species. Denoting a physisorption site on the support by #, for IBAP, we write

$$\text{IBAP} + \# \leftrightarrow \text{IBAP}\# \tag{9}$$

$$\text{IBAP}\# + {}^* \leftrightarrow \text{IBAP}^* + \# \tag{10}$$

where Eq. (9) represents physisorption on the support and Eq. (10) demonstrates how strong adsorption on the support enhances the amount adsorbed on the metal by, for example, surface diffusion [19]. Analogous to these equations for IBAP, similar expressions can be written for IBPE, IBEB, and H_2O.

Continuous flow operation of this reaction currently is not possible, because the catalyst deactivates with loss of selectivity. Regeneration of the catalyst after reaction, involving heat treatment in a static air oven at 623 K for 4 h, is required. This treatment allows recovery of the activity and, more importantly, makes the catalyst no longer selective toward alcohol.

The aim of this work was to demonstrate that silylation of Pd/SiO_2 catalyst also can increase selectivity in hydrogenation. We also found that, more remarkably, the selectivity was maintained after regeneration. We studied the silylation of Pd/SiO_2 catalyst using silylating agents with different functional groups: hexamethyldisilazane [$(H_3C)_6Si_2NH$, HMDS], dichlorodimethylsilane [$(H_3C)_2Si(Cl)_2$, DDMS], and hexamethyldisilane [$(H_3C)_6Si_2$, HMS]. HMDS and DDMS have been reported to be effective surface modification agents for increasing the hydrophobicity of SiO_2 [20,21]. HMS has been successfully used in the silylation of allylic acetates in the presence of Pd catalysts [22]. We compared the activity, selectivity, and stability of the different Pd/SiO_2 catalysts and correlated improvements in selectivity with the relative adsorption strength of 4-IBPE to 4-IBAP.

2. Experimental

2.1. Catalyst preparation

We prepared 2.5 wt% Pd/SiO_2 catalysts through the wet impregnation method, using Pd acetate trimer (Alfa Aesar) as the palladium precursor and Davisil 643 (35–74 µm) as the SiO_2 support [16]. To prepare the catalyst, the required amount of precursor solution was dissolved in an excess of toluene and added to the required amount SiO_2 support suspended in toluene. The mixing was carried out overnight under continuous stirring. The catalyst was filtered under vacuum, dried at 373 K for 16 h, and then heated to 673 K at a rate of 1 K/min and calcined in static air at 673 K for 4 h.

2.1.1. Silylation

Silylation reactions were carried out in the liquid phase with the catalyst. Only in the case of DDMS was silylation carried out with the silica support before Pd application, to avoid leaching of Pd induced by the presence of chloride. In all cases, the concentration of the silylating agent was 5% by volume, which was sufficiently high according to the study of Cagnoli et al. [3], in which five different concentrations of HMDS in toluene, ranging from 0.8% to 16% in volume, were tested. The operating conditions and the chemical reactions for each silylating agent are depicted in Fig. 2. The silylated catalysts were filtered, washed with ethanol, and dried at 383 K in air for 4 h. Hydrophobic silica also was prepared by silylation with HMDS, to study the interaction of the support only with the reactants and products.

2.2. Catalyst characterization

Fresh catalysts “as prepared” and spent catalysts after washing with ethanol and dried at 383 K for 2 h at a heating rate of 0.5 K/min were analyzed by several techniques. Transmission electron microscopy (TEM) was performed using a Philips CM30UT electron microscope with a FEG as a source of electrons operated at 300 kV. Samples were mounted on Quantifoil microgrid carbon polymer supported on a copper grid by placing a few droplets of a suspension of ground sample in ethanol on the grid, followed by drying at ambient conditions.

The catalysts were analyzed by inductively coupled plasma optical emission spectroscopy (ICP-OES) performed in a Perkin–Elmer Plasma 2000 apparatus to determine the palladium content. For the analysis, ca. 35 mg of the sample was digested in 50 mL of an acid mixture (0.7% HCl, 1% HF, and 1.25% H_2SO_4).

Thermogravimetric analysis (TGA) of the catalysts was carried out on a Mettler–Toledo TGA/SDTA851^e thermobalance. The sample powders were heated in air from 298 to 1173 K at heating rate of 10 K/min.

Diffuse reflectance infrared Fourier transform (DRIFT) spectra were recorded with a single beam Nicolet Magna 550 FTIR spectrometer in a Spectratech DRIFTS accessory, against a background recorded for a sample cup filled with KBr. The DRIFTS chamber was flushed with N_2. The spectra were obtained by collecting 256 scans at 8 cm^{-1} resolution and displayed in absorption reflectance units.

Temperature-programmed oxidation–mass spectrometry (TPO-MS) measurements were performed in a conventional flow apparatus using a quartz microreactor, with 0.1 g of the sample heated at a rate of 10 K/min from 298 to 1173 K in 20% O_2 in He (flow rate of 50 cm^3/min). The gaseous species from the sample were monitored by a quadrupole mass spectrometer (Balzers, PRISMA) connected online with the reactor. Mass spectra were recorded in multiple-ion detection (MID) mode using a Channeltron detector.

The porous structure of the catalysts was characterized from the 77 K N_2 adsorption/desorption isotherms using a Quantachrome

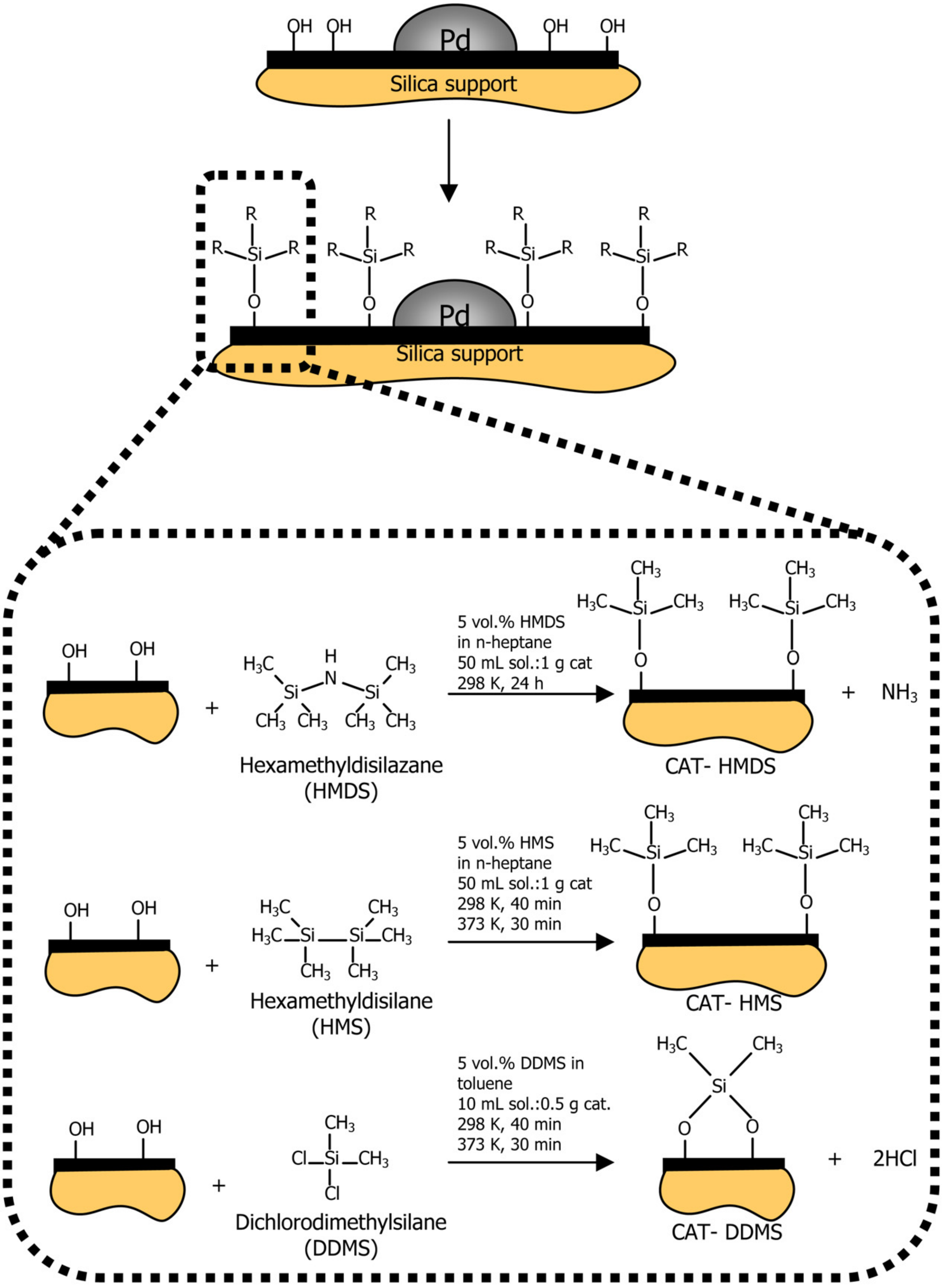

Fig. 2. Operating conditions of the silylation reactions of Pd/SiO_2 catalyst with different silylating agents.

Autosorb-6B apparatus. The samples were first pretreated *in situ* by drying in vacuum at 403 K to remove moisture and other volatile compounds. The isotherms provided information on the specific surface area (S_{BET}), pore volume (V_{P}), and pore diameter (d_{Pore}).

2.3. Selective hydrogenation

Hydrogenation reactions were performed in a stainless steel reactor equipped with a gas-induced stirrer (Premex Reactor

CH-2543). In a typical experiment, after *in situ* reduction of catalyst at 373 K and 10 bar of H_2 for 1 h, the desired amount of reactant (4-IBAP) and solvent (*n*-decane, containing 0.43 wt% of water, measured by Karl Fischer titration) were charged to the reactor from an external injection vessel. The contents (ca. 200 cm^3) were heated up to the reaction temperature and then pressurized with hydrogen to the required pressure. The progress of the reaction was determined by monitoring the hydrogen supply rate as a function of time. All semibatch experiments were carried out under standard conditions of $C_{IBAP} = 0.27$ mol/L, $T = 373$ K, $p_{H_2} = 20$ bar, 0.1 g of catalyst, and a stirring speed of 1500 rpm (see [16]). After 5 h of reaction, the reactor was cooled to room temperature and depressurized. Then one of the following reuse experiments was conducted: addition of 50 mmol of 4-IBAP to the reaction mixture through the storage vessel, to avoid exposure of the catalyst to air, or separation of the catalyst from the reaction mixture followed by regeneration of the catalyst in static air oven at 623 K for 4 h, to remove the surface carbonaceous deposits. In the latter case, the second run was performed as the fresh run, including reduction of the regenerated catalyst.

Experiments with HMDS-silylated silica were performed under the same operating conditions as for the fresh catalysts, to study the interaction of the reactants and products with this material under reaction conditions and to discriminate the interaction with both Pd and the SiO_2 support. For this purpose, two different feeds were introduced to the reactor loaded with 0.1 g of HMDS-silylated silica: ca. 200 cm^3 of a solution of 0.27 mol/L of 4-IBAP in *n*-decane, and ca. 200 cm^3 of a reaction mixture containing 0.06 mol/L of 4-IBAP, 0.12 mol/L of 4-IBPE, and 0.12 mol/L of 4-IBEB, obtained from a previous hydrogenation experiment that had been stopped at an appropriate point. The HMDS-silylated silica turned out to be catalytically inactive in both experiments.

During the hydrogenation experiments, liquid samples were obtained at different times and analyzed with a Chrompack gas chromatograph (CP9001 autosampler), equipped with a CP Sil 8 CB column (50 m × 0.25 mm), under the following conditions: FID temperature, 523 K; injector temperature, 523 K; and column temperature ramped uniformly from 423 to 523 K at 6.7 K/min.

2.4. Adsorption experiments

Adsorption studies were performed by suspending 0.05 g of catalyst in 1.1 mL of reaction mixture in a closed 25-mL flask under stirring. The reaction mixture was obtained from a hydrogenation experiment that had been stopped at the appropriate point to achieve approximately the same concentration for 4-IBAP, 4-IBPE, and 4-IBEB. An additional amount of 4-IBAP had to be added to the reaction mixture to achieve ca. 0.12 mol/L of 4-IBAP, 4-IBPE, and 4-IBEB. The adsorption experiments were carried out at constant temperature of 293 K in a shaker (MS1 Minishaker, IKA) at 800 rpm. Samples were obtained after sufficient equilibration time (4 h) and analyzed by GC as described above, to measure the liquid-phase equilibrium concentrations. The amounts of the competitively adsorbed components were calculated from the mass balance.

3. Results

3.1. Characterization of the catalysts

Table 1 gives the Pd loading (determined by ICP) and the average metal crystal size (determined by TEM) of all catalysts prepared. Pd was well dispersed in all of the fresh catalysts, with particle sizes of 2–4 nm. TEM analyses were performed for Pd/SiO_2 catalyst in each stage (fresh, reduced, used, and regenerated catalyst) to study the size evolution during a complete use cycle. Table 1 also reports textural properties.

Table 1
Metal loading, average Pd crystal size and textural properties of the solids

Catalyst	Pd loading (%)	Average Pd crystal size (nm)	S_{BET} (m^2/g)	V_P (cm^3/g)	d_{Pore} (nm)
Pd/SiO_2					
Fresh	2.5	2–4	389	0.81	7.2
In situ reduction		5–8	NM[a]	NM	NM
Spent		5–7	377	0.83	7
Regenerated		5–8	326	0.62	7
CAT-HMDS					
Fresh	2.5	2–4	355	0.69	7
Spent		2–5	340	0.64	7
Regenerated		3–7	359	0.70	7.2
CAT-HMDS520					
Fresh	2.5	2–4	386	0.76	7
Spent		5–10	348	0.68	7.2
Regenerated		4–10	362	0.71	7
CAT-DDMS					
Fresh	1.54	2–4	389	0.75	7
Spent		3–5	393	0.73	7
Regenerated		3–6	396	0.75	7
CAT-HMS					
Fresh	2.1	2–4	384	0.74	7
Spent		5–8	NM	NM	NM
Regenerated		4–7	390	0.74	7

[a] NM—not measured.

Fig. 3 compares the differential thermogravimetric (DTG) profiles of the fresh and spent catalysts and HMDS-silylated silica. It also indicates whether endothermal (i.e., desorption) or exothermal (i.e., combustion) processes occurred, as determined by the single point differential thermal analysis (SDTA) present in the thermobalance. The silylated fresh catalysts and support released adsorbed water at around 330 K. The water peak was strong for the untreated Pd/SiO_2 and HMS and DDMS-silylated catalysts. At around 830 K, the methyl groups grafted on the silica by silylation were burnt off. For the HMDS-silylated SiO_2 without Pd, a second peak appeared at 720 K that also can be attributed to the burning off of methyl groups. This low-temperature peak was not observed for the HMDS-silylated Pd/SiO_2 catalyst, due to the 4-h calcination at 673 K of this catalyst before the silylation step. This calcination removed the most reactive silanol groups (probably the vicinal and geminal ones), leaving mostly isolated silanol groups. As a result, on silylation, these samples formed only those methyl groups that will burn off at 830 K, and the peak at 720 K was absent.

In the spent catalysts, the different peaks can be assigned to (a) molecular water physisorbed on the support ($T < 380$ K; endothermal); (b) hydrocarbons physisorbed on the support ($T =$ 380–530 K; endothermal), mainly 4-IBAP, as can be deduced by comparing the profiles of the SiO_2-HMDS sample exposed only to a solution of 4-IBAP and of the sample SiO_2-HMDS sample exposed mainly to 4-IBPE and 4-IBEB; (c) hydrocarbons chemisorbed on the Pd ($T =$ 510–580 K) (profiles of the SiO_2-HMDS samples did not exhibit this exothermal peak); (d) hydrocarbons chemisorbed on the support ($T =$ 580–680 K; exothermal), mainly 4-IBPE and 4-IBEB; and (e) methyl groups bound to the support ($T =$ 750–850 K; exothermal).

In the spent catalysts, the broad peak at 465 K corresponding to 4-IBAP physisorbed on the silica was almost insignificant for the HMS and DDMS-silylated catalysts and negligible for the most hydrophobic HMDS-silylated catalysts. In the transient TGA experiment, this endothermal desorption cooled the catalyst, which had such a significant effect in the unsilylated catalyst so as to postpone the combustion of the material chemisorbed on the Pd to 580 K. To prove that this shift indeed was due solely to the transient in the TGA, we performed a separate control experiment at a much lower heating rate (2 K/min), and found that the peak for

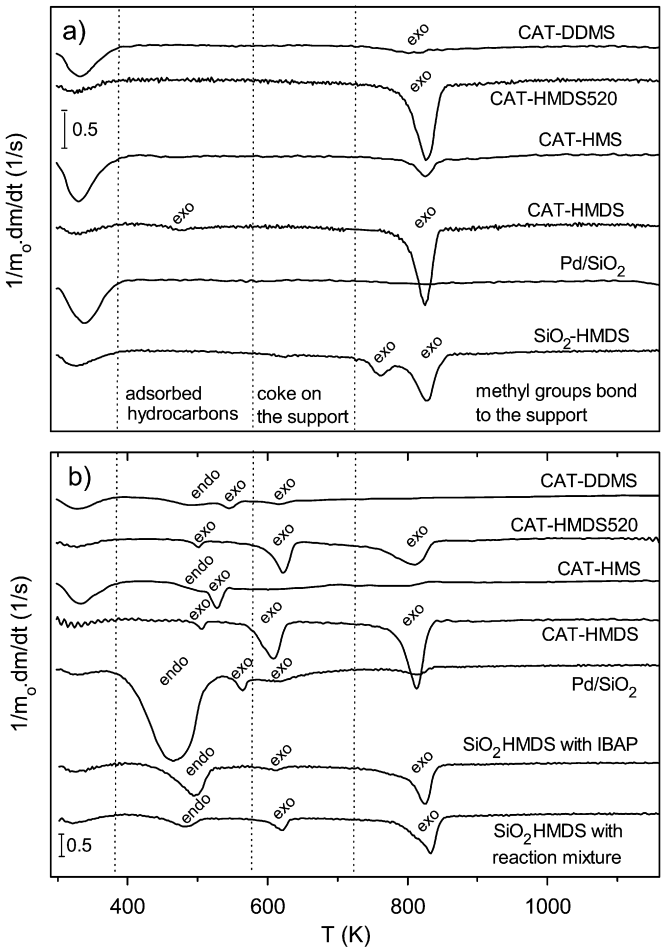

Fig. 3. Differential thermogravimetric profiles in air of the fresh (a) and spent (b) Pd/SiO_2 catalysts as prepared and after different silylation reactions (10 K/min).

material chemisorbed on the Pd occurred at 40 K lower than in the 10 K/min experiment.

The fresh CAT-HMDS exhibited a small exothermal peak at around 470 K, ascribed to material chemisorbed on the Pd, because this peak was not observed in the HMDS-silylated SiO_2 without Pd.

Fig. 4 shows the products that came off of the fresh HMDS-silylated catalysts on heating, as determined by TPO-MS. The five profiles correspond to the evolution of NO, NO_2, CO, CO_2, and H_2O. The figure shows that not only methyl groups, but also nitrogen-containing groups (amines) were incorporated on the Pd during silylation of the samples. Because amines are known to poison Pd sites, leading to loss of activity [23], the CAT-HMDS catalyst was thermally treated at 520 K for 4 h in a static air oven to remove these amines as well as the methyl groups. The resulting catalyst, designated CAT-HMDS520, did not exhibit a peak at 470 K in the DTG profile (Fig. 3), although some remaining methyl and amine groups would be expected to remain, according to the TPO-MS profiles shown in Fig. 4.

To verify that the methyl groups were grafted onto the silica by silylation according to Fig. 2, DRIFT spectra were evaluated (Fig. 5). The presence of CH_3Si was confirmed by the new band at 1260 cm^{-1}. All of the silylated catalysts except CAT-HMS exhibited this band. Moreover, the absorption band at 3740 cm^{-1}, well visible for Pd/SiO_2, which can be attributed to the presence of isolated or geminal silanol groups, disappeared in all of the silylated catalysts (although a weak shoulder remained in CAT-HMS). Although the extent of silylation with HMS was limited, as can be deduced from the absence of methyl silicon bonds (Fig. 5), some methyl groups were bonded to the silica, as indicated by the exothermal peak at 825 K in the DTG profile (Fig. 3) and by the bands at 2963 and 2908 cm^{-1} in the DRIFT spectra (Fig. 5), corresponding to the stretching vibration of C–H bonds in CH_3 and CH_2 groups, respectively. Only with CAT-HMDS were new bands at 3366 and 3277 cm^{-1} detected corresponding to primary and secondary amine groups, respectively, corroborating the TGA and TPO-MS results.

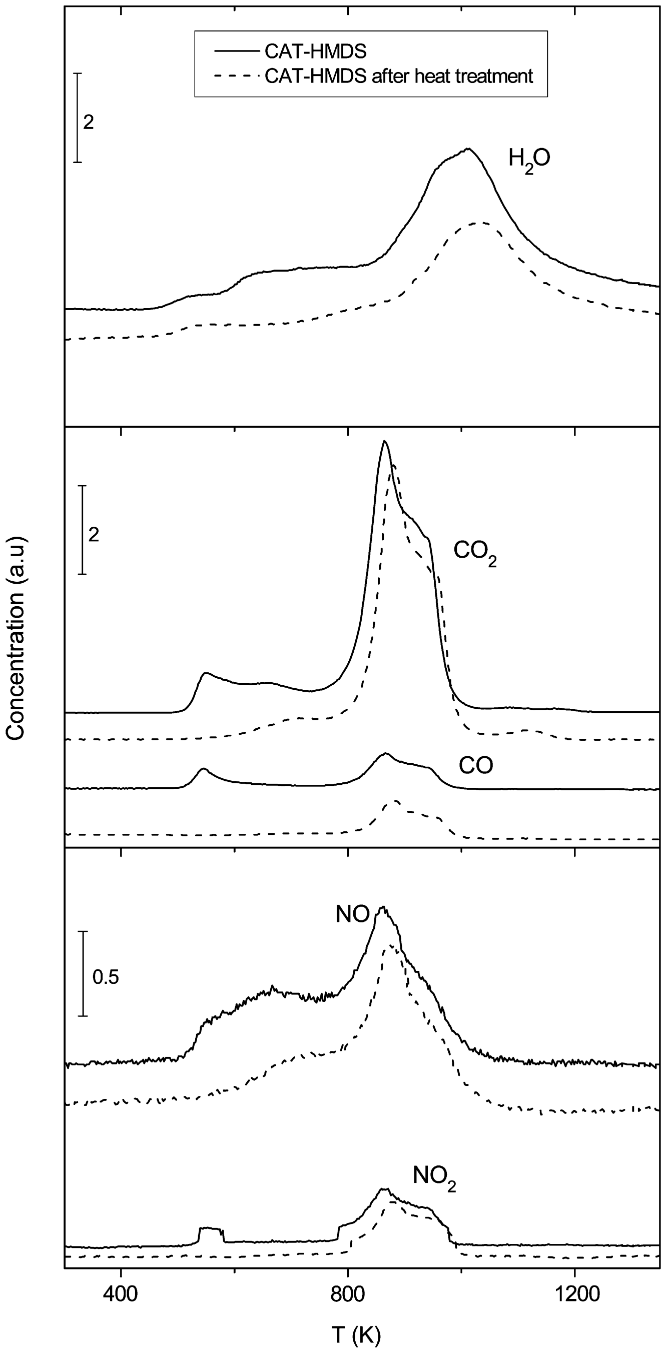

Fig. 4. TPO-MS profiles of the fresh HMDS-silylated catalysts before and after heat treatment at 520 K in a static air.

3.2. Activity, stability, selectivity, and adsorption measurements

Fig. 6a shows a typical concentration–time profile of the various components involved in the hydrogenation of 4-IBAP using a fresh, nonsilylated Pd/SiO_2 catalyst. These results confirm the pro-

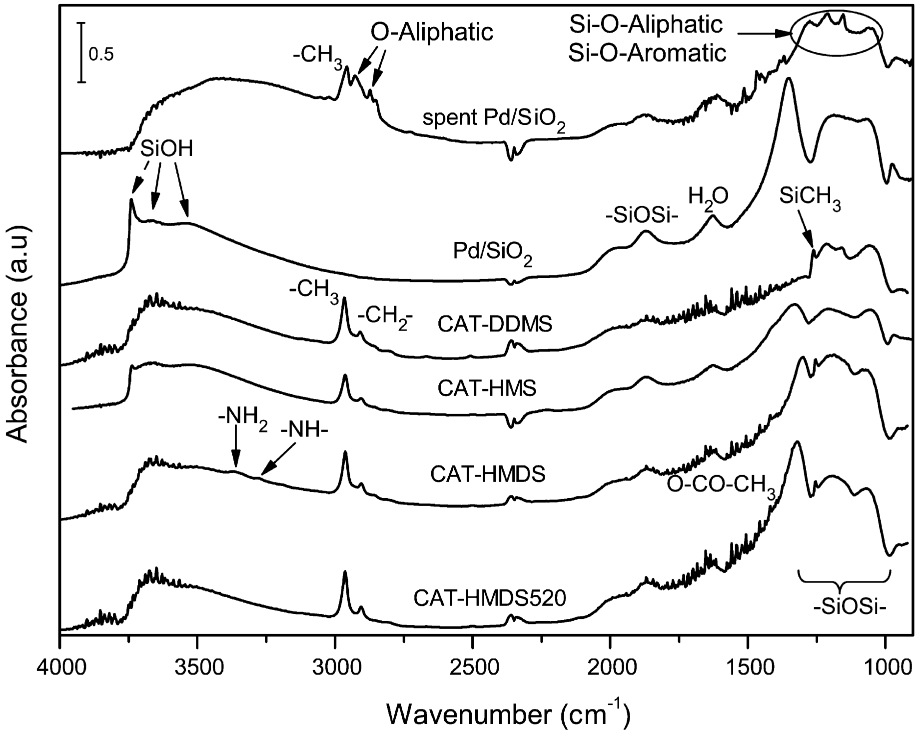

Fig. 5. DRIFT spectra of the fresh untreated and silylated catalysts and spent untreated Pd/SiO$_2$ recorded at 323 K in 20% O$_2$ in He.

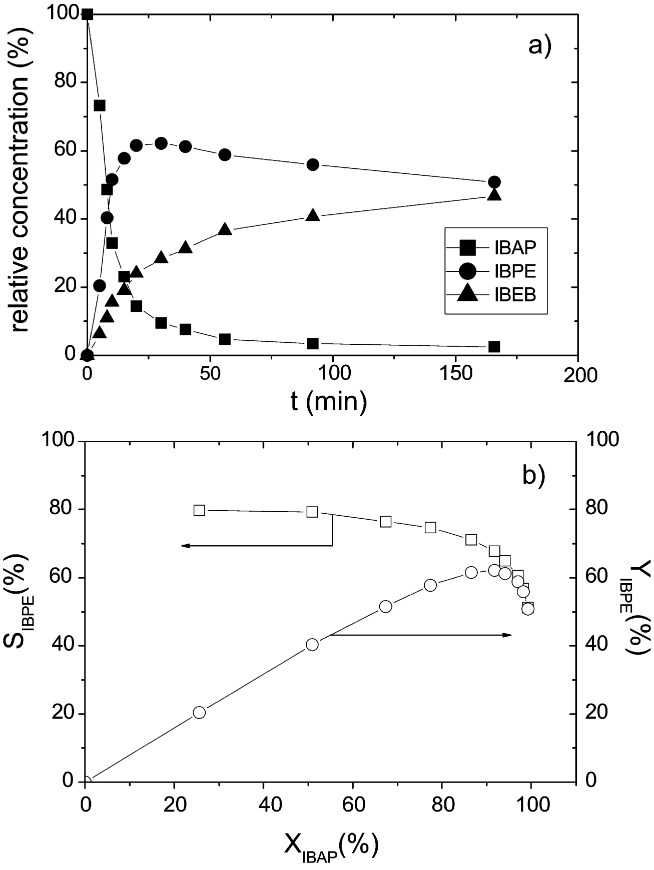

Fig. 6. Relative concentrations as a function of reaction time (a) and overall selectivity and yield of 4-IBPE as a function of 4-IBAP conversion (b) during hydrogenation of 4-IBAP with Pd/SiO$_2$ catalysts under standard reaction conditions: $C_{\text{IBAP}} = 0.27$ mol/L, $T = 373$ K, $p_{\text{H}_2} = 20$ bar, $w_{\text{cat}} = 0.1$ g, solvent n-decane, stirring rate = 1500 rpm

posed reaction pathway shown in Fig. 1. The same three species were always detected in hydrogenation with the different silylated catalysts; no other components were found in the GC analysis.

Fig. 6b shows the overall selectivity (S_{IBPE}) and yield (Y_{IBPE}) for the alcohol as a function of 4-IBAP conversion (X_{IBAP}). These variables were calculated as follows:

$$S_{\text{IBPE}} = \frac{C^{\text{IBPE}}}{C^0_{\text{IBAP}} - C_{\text{IBAP}}} \tag{11}$$

$$Y_{\text{IBPE}} = X_{\text{IBAP}} \cdot S_{\text{IBPE}} \tag{12}$$

$$X_{\text{IBAP}} = \frac{C^0_{\text{IBAP}} - C_{\text{IBAP}}}{C^0_{\text{IBAP}}} \tag{13}$$

According to the results, a selectivity up to 80% and a maximum yield around 60% could be expected at 373 K and 20 atm of hydrogen pressure for the nonsilylated Pd/SiO$_2$ catalyst.

Fig. 7 shows the effect of silylation on initial activity (i.e., the consumption rate of 4-IBAP at minimal conversion levels, per kg of Pd) at various moments in a deactivation–regeneration cycle. Activity is reported for fresh catalysts, for spent catalysts reused in a consecutive run in which fresh reactant is added to the converted reaction mixture from the first run, and for a second run after catalyst regeneration. The reproducibility, indicated by the error bars in Fig. 7, was calculated as the standard deviation from repeated experiments. For the nonsilylated catalysts, wide ranges of selectivity values (40% to 80%) and yield (35% to 60%) were found.

The initial activity and the stability of Pd/SiO$_2$ catalyst were influenced by the silylating agent. Silylation with DDMS resulted in the highest activity and stability; in contrast, the HMS-silylated catalyst was completely deactivated after the first run. The effect of regeneration in terms of activity recovery was excellent for the untreated Pd/SiO$_2$ catalyst (with TGA and DRIFT spectra demonstrating the complete removal of the physisorbed and chemisorbed hydrocarbons and coke); good for CAT-HMDS, CAT-HMDS520 and CAT-DDMS; and detrimental for CAT-HMS.

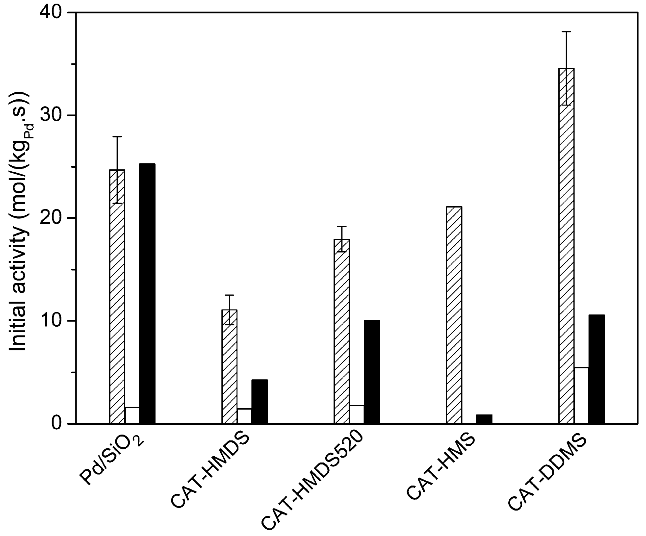

Fig. 7. Effect of silylating agents on the initial activity of Pd/SiO$_2$ catalyst for 4-IBAP hydrogenation under standard conditions: $C_{\text{IBAP}} = 0.27$ mol/L, $T = 373$ K, $p_{\text{H}_2} = 20$ bar, $w_{\text{cat}} = 0.1$ g, solvent *n*-decane, stirring rate = 1500 rpm. Legend: (▨) 1st run; (☐) 2nd run after injection of additional reactant to the mixture of the 1st run; (■) 2nd run after regeneration. Error bars indicate the standard deviation from the repeated experiments.

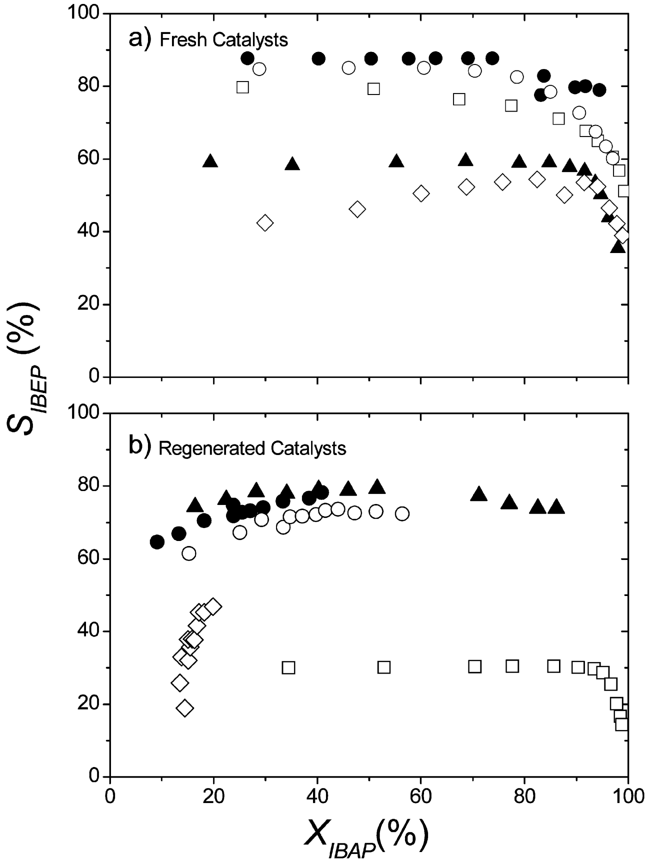

Fig. 8. Effect of silylating agent on the overall selectivity to 4-IBPE as a function of 4-IBAP conversion of fresh (a) and regenerated (b) Pd/SiO$_2$ catalysts; results obtained under standard conditions: $C_{\text{IBAP}} = 0.27$ mol/L, $T = 373$ K, $p_{\text{H}_2} = 20$ bar, $w_{\text{cat}} = 0.1$ g, solvent *n*-decane, stirring rate = 1500 rpm. Legend: (☐) Pd/SiO$_2$ catalyst; (●) CAT-HMDS; (○) CAT-HMDS520; (◇) CAT-HMS; and (▲) CAT-DDMS.

Whereas Fig. 7 shows only activity data, Fig. 8 shows the evolution of selectivity toward the alcohol during conversion for differently silylated samples and untreated Pd/SiO$_2$. The evolution of

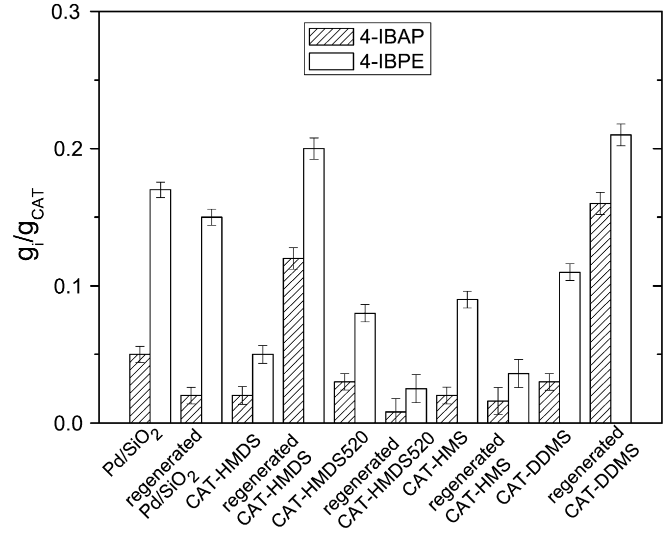

Fig. 9. Amounts adsorbed at room temperature from a mixture of equal amounts of reactants and products. Error bars estimated by the error propagation analysis. Conditions: $C_{\text{IBAP}} \approx 0.12$ mol/L, $C_{\text{IBPE}} \approx 0.12$ mol/L, $C_{\text{IBEB}} \approx 0.12$ mol/L, $T = 293$ K, $p = 1$ bar, $t = 4$ h, $w_{\text{cat}} = 0.05$ g, $V_{\text{L}} = 1.1$ mL, solvent *n*-decane.

selectivity differed between the fresh samples (top plot) and the samples after deactivation and regeneration (bottom plot). Selectivity was clearly affected by the silylating agent. Only the HMDS-silylated catalysts exhibited greater selectivity than the nonsilylated catalysts. The selectivity of the DDMS catalyst dropped to 60%. The hardly active HMS-silylated catalyst exhibited a peculiar behavior, with its (relatively low) selectivity increasing during the conversion of 4-IBAP. After regeneration, the untreated Pd/SiO$_2$ catalyst lost most of its original selectivity, whereas the appropriate silylated catalysts remained selective, in a range of 70%–80%.

The results of the competitive adsorption experiments, collected in Fig. 9, show that in general, 4-IBPE adsorbed more favorably than 4-IBAP on the fresh and used catalysts. The effect of silylation and regeneration in relation to the catalyst selectivity is discussed in the next section.

4. Discussion

4.1. Silylation

The effectiveness of the silylation quantified from the weight loss in the TGA experiments can be ranked as follows: CAT-HMDS = CAT-HMDS520 (10%) > CAT-HMS (8.5%) > CAT-DDMS (6%). This may be related to the stoichiometry of the silylation reactions. With DDMS, for each silanol group, one methyl group was incorporated, compared with three methyl groups with HMDS and HMS (Fig. 2). These values are in the same range as those reported in previous studies using the same HMDS:sample ratio [1,3].

Silylation modified the support and did not lead to significant coverage of the Pd, except for HMDS. Only for HMDS did the characterization techniques (TGA, DRIFT and TPO) indicate the blocking of active sites by amine groups (Figs. 3, 4, and 5) and fouling by carbon groups (Figs. 3 and 5).

The effectiveness of treatment in terms of hydrophobicity, as reflected by the amount of water desorbed below 380 K (Fig. 3), can be ranked as CAT-HMDS > CAT-HMDS520 > CAT-DDMS > CAT-HMS = Pd/SiO$_2$. The HMS silylating agent seemed to have no significant affect on the hydrophobic–hydrophilic properties of the Pd/SiO$_2$; as deduced earlier based on the DRIFT spectra (Fig. 5), the yield of the silylation was quite limited. Based on these findings, we can conclude that silylating agents that contain a functional group or a heteroatom (i.e., amine or halogen) are more effective.

HMDS was the most efficient silylating agent, providing the most hydrophobic Pd/SiO_2 surface. It is also the most stable among those investigated (Fig. 3). Comparing the DTG profiles of the fresh and used silylated catalysts (Fig. 3), we can deduce that the HMDS-silylated catalyst lost only a small fraction of the methyl groups during the hydrogenation reaction.

DDMS did not act as a stable silylating agent for the hydrogenation of aromatic ketones. The DTG results showed a complete absence of methyl groups after the reaction. Moreover, in the DRIFT spectra of the used DDMS-silylated catalyst (not shown), a new band appeared at 3740 cm^{-1}, attributed to terminal or geminal silanol groups. This can be explained by the interaction between Si–CH_3 groups and water produced on the hydrogenation reaction, resulting in hydrolysis of the O–Si bonds. This structure is known to be less stable in the presence of water [24].

During the *in situ* reduction (at 100 °C and 10 atm) of Pd/SiO_2, the dispersion decreased by 50% and it decreased no further during the reaction (Table 1). It is significant that this did not affect the activity; the activity of the Pd/SiO_2 catalyst was fully recovered after regeneration (Fig. 7).

Silylation did not promote Pd sintering. Spent silylated catalysts exhibited a similar decrease in dispersion as the untreated catalysts except when amines and methyl groups were poisoning the Pd sites, as in the HMDS-silylated catalyst, in which case Pd sintering seemed to be suppressed (Table 1). Only silylation with HMDS, with no post-treatment, affected the textural properties of the Pd/SiO_2 catalyst. The HMDS-silylated catalyst had a slightly reduced specific surface area and pore volume, due to the presence of alkylsilane groups at the surface of the pores, in agreement with previous reports [3,7].

Silylation did not provoke Pd leaching under the conditions used here in any of the agents except DDMS. In this case, to avoid strong leaching of Pd (ca. 70%), the silica support was first silylated, followed by Pd application. As a result, the Pd loading was lower than the target value due to the smaller amount of anchoring centers for Pd in the silica surface.

4.2. Selective hydrogenation

Silylation affected the hydrophobic character of the catalysts and, consequently, the adsorption of organic reactants and products (Fig. 9) and thus the activity (Fig. 7) and selectivity (Fig. 8). All silylated catalysts would be expected to be less active than the untreated catalyst, because the Pd active sites are exposed to lower local concentrations of 4-IBAP (Fig. 9). Our experiments shown in Fig. 7 confirm this hypothesis, except for the fresh DDMS-silylated catalyst. This higher activity may be due to a promoting effect of chlorides remaining on the support after silylation. The low activity seen in the HMDS-silylated samples can be attributed to poisoning of the Pd sites by amine groups, as confirmed by comparing the activity of CAT-HMDS and the heat-treated sample CAT-HMDS520, in the latter, the fresh catalyst demonstrated greater activity.

The decreased activity in the nonmodified Pd/SiO_2 catalyst from 25 to 1 mol/(kg_{Pd} s) in a consecutive run can be attributed to the large amount of 4-IBAP physisorbed/chemisorbed on the silica surface and chemisorbed on the Pd sites (Fig. 3). In agreement with this, DRIFT spectra (Fig. 5) of the untreated Pd/SiO_2 catalyst confirmed the loss of isolated hydroxyl groups on the silica and the appearance of methyl groups, alkoxy groups, and silyl ether groups. Hydration of the catalyst also occurred, as indicated by the increased band range from 3500 to 3400 cm^{-1}. Thus, Pd/SiO_2 catalyst deactivated during the reaction ([16], Fig. 7) due to surface deposition mainly on the support and also on the Pd.

Although regeneration removed the deposits and allowed the recovery of activity, it changed the adsorption properties of untreated Pd/SiO_2 catalyst (Fig. 9). Fig. 10 shows the effect of the relative adsorption of 4-IBPE/4-IBAP on the initial overall selectivity. The regenerated Pd/SiO_2 catalyst demonstrated a high relative adsorption 4-IBPE/4-IBAP value compared with the fresh catalyst, but with a decrease in selectivity.

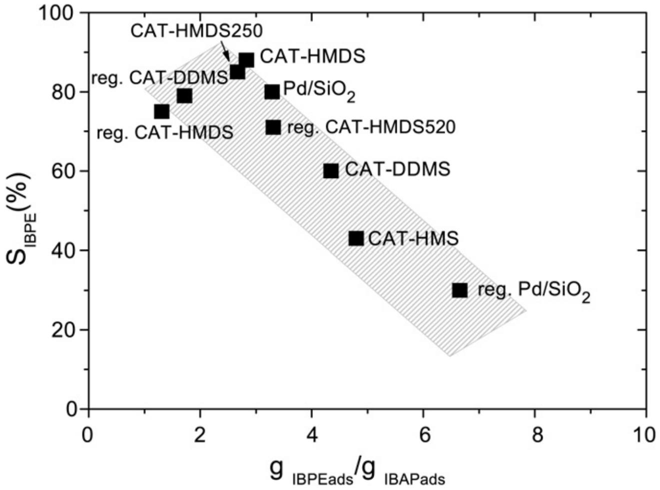

Fig. 10. Correlation of the relative adsorption strength of 4-IBPE to 4-IBAP with the selectivity at 30% of 4-IBAP conversion. Conditions: $C_{IBAP} \approx 0.12$ mol/L, $C_{IBPE} \approx 0.12$ mol/L, $C_{IBEB} \approx 0.12$ mol/L, $T = 293$ K, $p = 1$ bar, $t = 4$ h, $w_{cat} = 0.05$ g, $V_L = 1.1$ mL, solvent *n*-decane.

The silylating agent had a strong impact on the selectivity of fresh and regenerated catalysts. Only HMDS, the most effective silylating agent, improved the selectivity of the untreated catalyst. The most remarkable finding is that the properly silylated catalysts (HMDS and DDMS) remained selective after regeneration (Fig. 8). This can be explained in terms of the adsorption strength of reactants and products on the support, not on the Pd sites (Figs. 3 and 10). In these regenerated silylated catalysts, the adsorption of 4-IBPE relative to 4-IBAP did not change as much (CAT-HMDS) or even decreased (CAT-DDMS) compared with their fresh counterparts. Their behavior on regeneration was even more spectacular, with selectivity remaining at ca. 80% (Fig. 10).

Based on these findings, we can conclude that the competitive adsorption of the reactant and product on the catalyst had an important effect on the selectivity of this hydrogenation reaction, a correlation illustrated in Fig. 10. Silylation reduced the polarity of the surface and thus the adsorption of ketone 4-IBAP and alcohol product 4-IBPE. The likelihood of alcohol forming hydrogen bridges with the surface was reduced significantly, so that the relative composition of the adsorbed phase on the metal changed in favor of the ketone by equilibria such as shown in Eq. (10). This increased the first hydrogenation step [Eq. (4)] relative to the undesired second hydrogenation [Eq. (7)], resulting in a more favorable yield of alcohol. Apparently, silylation also stabilized the relative adsorption of the product 4-IBPE to the reactant 4-IBAP on regeneration of the catalyst, in contrast with the situation for the untreated Pd/SiO_2 catalyst, in which this changed unfavorably on regeneration (Fig. 9), promoting the consecutive reaction and resulting in low selectivity.

Previously, silylation to reduce the surface polarity of catalysts has been applied mainly to selective oxidation reactions, for which the products obviously are more polar than the reactants and are more prone to consecutive conversion or strong adsorption. The present study has demonstrated that this approach can be applied to certain selective hydrogenations as well, when the products formed interact through hydrogen bridges with the surface silanol groups, such as in the hydrogenation of a ketone, aldehyde, or epoxide to an alcohol. Clearly, in such cases, changing the hydrophobic properties of catalyst surfaces can improve reaction selectivity.

5. Conclusion

In this study, the selectivity of Pd/SiO_2 catalysts in the hydrogenation reaction of an aromatic ketone to the corresponding alcohol was significantly improved by silylating the catalyst. A clear correlation between the suppression of adsorption of the desired aromatic alcohol and the suppression of the consecutive reaction of that alcohol was observed. Silylation was found to decrease the relative adsorption strength of the desired alcohol to the ketone reactant, suppressing further hydrogenation of the alcohol and maintaining the selectivity. Silylation was especially effective for the regenerated catalyst in which the untreated Pd/SiO_2 had lost most of its original selectivity.

HMDS proved to be the most effective silylation agent among those investigated in terms of incorporation of methyl groups, catalyst hydrophobicity, and stability. The use of a silylating agent with a functional group or a heteroatom was the most effective approach for obtaining appropriate silylation yields. Because silylation does not cover active Pd, as long as the silylating agent does not cause the metal leaching, silylation of the catalyst is preferred over silylation of the support, which leads to a lower metal loading due to removal of the isolated hydroxyl groups where Pd is anchored.

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