

**Aromatic alcohols as model molecules for studying hydrogenolysis
reactions promoted by palladium catalysts**

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Abstract

The hydrogenolysis reaction of aromatic alcohols (benzyl alcohol, 1-phenylethanol and diphenylmethanol), promoted by supported palladium catalysts, such as Pd/TiO₂, Pd/SiO₂ and Pd/Co₃O₄, has been investigated at 0.1 MPa H₂ and 323 K. The catalysts have been characterized by BET, TPR, XRD, TEM and XPS. A different kinetic behaviour was observed: in presence of Pd/TiO₂ and Pd/SiO₂ catalysts, prepared by impregnation, the hydrogenolysis activity follows the order benzyl alcohol > 1-phenylethanol ≥ diphenylmethanol, whereas it is totally reversed on Pd/Co₃O₄, prepared by co-precipitation. All results indicate that the reactivity of supported Pd catalysts, in the hydrogenolysis reaction, depends on the support nature, the preparation method of catalysts and the aromatic alcohols structure. Kinetic experiments carried out at different partial hydrogen pressure allow to elucidate the pathway of the C-OH bond scission, involving a radical substitution of the carbon bonded OH group by a hydrogen atom coming from the metal surface “via” associative and dissociative paths.

Keywords: Hydrogenolysis, Aromatic alcohols; Supported palladium catalysts; Reaction mechanism

1 Introduction

Catalytic hydrogenation of C=O bond and hydrogenolysis of C-OH bond are very important in organic synthesis [1, 2], pharmaceutical production [3] and biomass conversion [4, 5]. Generally, these reactions are carried out under hydrogen, using supported noble metal catalysts. In this context, palladium is largely employed since it offers some interesting peculiarities. For example, conventional catalysts (Pd/C, Pd/SiO₂, Pd/TiO₂) easily hydrogenate aromatic carbonyls to the analogous hydrocarbons, involving aromatic alcohols as intermediates, whereas fail to reduce aliphatic carbonyls [6, 7]. Conversely, Pd/Fe₃O₄ and Pd/Co₃O₄ catalysts, prepared by the co-precipitation technique, are able to reduce both aromatic and aliphatic carbonyls [8]. Therefore the flexibility of palladium systems helps to achieve a chemoselective control in organic synthesis.

Hydrogenolysis of aromatic alcohols, differently than that of analogous aliphatic, is an easy reaction and can be carried out using both hydrogen and a supported metal catalyst or the catalytic transfer hydrogenation technique [9-11]. Takar et al. postulate two possible mechanisms in the hydrogenation of 1-(4-isobutylphenyl) ethanol to 4-isobutylbenzene on Ru/Al₂O₃, Pd/SiO₂ and Pd/C catalysts: a dehydration-hydrogenation route in presence of Pd/C containing adsorbed protons or, otherwise, a direct C-OH bond breaking by an incoming hydrogen atom [12].

One of the most fascinating problems, arising from the modern industrial research, attains to the possible transformation of polyols, mainly glycerol, produced by biomass feedstocks, aiming to obtain high added value chemicals. The catalytic hydrogenolysis of glycerol is the most preferred route to both 1,2- and 1,3-propanediols at high temperature and pressure [13, 14]. Although conventional supported palladium substrates are generally poor in performing polyols reactions, it was discovered that Pd/Fe₃O₄ and Pd/Co₃O₄, prepared by the co-precipitation technique, are very suitable for making hydrogenolysis processes [15-17].

The bond breaking energy of the primary C-OH group in glycerol (C3-polyol) is 79.6 kcal/mol and is strictly comparable with that of benzyl alcohol (~80 kcal/mol) and relatively much lower than that of ethanol (93.5 kcal/mol) [18].

In this context, it is not unsound that the hydroxyl-hydrogen substitution in aromatic alcohols can be considered as a model reaction study for better understanding the polyols hydrogenolysis.

In this paper we report a study concerning the hydrogenolysis reaction of benzyl alcohol, 1-phenylethanol and diphenylmethanol, carried out in ethanol and in presence of impregnated Pd/SiO₂ and Pd/TiO₂ catalysts. Results are compared with those obtained using Pd/Co₃O₄, prepared by co-precipitation, a very suitable catalyst in glycerol hydrogenolysis. The aim of the work is twofold:

- 1) to highlight the influence of the organic molecule structure and the peculiarities of the catalysts on the reactivity;
- 2) to study the hydrogenolysis mechanism.

A characterization of the structural properties of the catalysts by nitrogen adsorption (BET), X-ray diffraction (XRD), temperature-programmed reduction (TPR), transmission electron microscopy (TEM), X-ray photoelectron spectroscopy (XPS) was also performed with the aim to link the observed reactivity to the structure of the catalysts.

2 Experimental

2.1 Catalysts preparation

Chemicals were purchased from Sigma-Aldrich and used without further purification. Nominal 5% palladium catalysts were obtained by incipient wetness impregnation of the commercial support TiO₂ (anatase phase, particle size 325 mesh, purity \geq 99%, S_{BET} = 11.6 m²/g) and SiO₂ (S_{BET} = 500 m²/g, particle size 70-230 mesh) [19] with an acetone solution of palladium (II) acetylacetonate (purity 99%). After impregnation, the sample was dried for 1 day under vacuum at 353 K and reduced at 473 K for 2h under flowing H₂.

5% Pd/Co₃O₄ was prepared, using the co-precipitation technique, from an aqueous solution of the corresponding inorganic precursors, palladium chloride anhydrous (purum, 60% Pd) dissolved in HCl, poured with cobalt (II) nitrate hexahydrate (purity \geq 99%) dissolved in water. The so obtained metal salts solution was added, drop by drop, into an aqueous solution of Na₂CO₃ 1M. After filtration and washing until chloride was removed, the sample was dried for 1 day under vacuum at 353 K and further reduced at 473 K for 2h under flowing hydrogen. During all experiments Pd/Co₃O₄ was handled with care avoiding as much as possible contact with air.

The main characteristics of the catalysts are reported in Table 1.

Table 1 Main characteristics of supported Pd catalysts

Catalyst	Palladium loading (wt %)		S_{BET} (m ² /g)	d_n (nm)*
	Nominal	XRF		
Pd/TiO ₂	5	3.5	15.5	5.2
Pd/SiO ₂	5	5.0	450	3.5
Pd/Co ₃ O ₄	5	3.7	106	10.7

* Mean particles size from TEM

2.2 Catalysts characterization

The content of the metal in all catalysts was determined by X-ray fluorescence (XRF) analysis, carried out using a BRUKER AXS S4 Explorer spectrometer, operating at a power of 1 kW and equipped with a Rh X-ray source, a LiF 220 crystal analyzer and a 0.12° divergence collimator.

BET surface areas were determined by N₂ adsorption-desorption isotherms at the liquid nitrogen temperature by using a Micromeritics Chemisorb 2750 instrument. The composition of the flow gas was N₂:He = 30:70. Samples were outgassed under flowing nitrogen for 1h at 473 K, before measurements.

The metal particles size and the relative morphology of the catalysts were analyzed by transmission electron microscopy (TEM), using a JEOL 2000 FX instrument operating at 200 kV and directly interfaced with a computer for real-time image processing. The specimens were prepared by grinding the powder reduced catalyst in an agate mortar, then suspended in isopropanol. A drop of the suspension, previously dispersed in an ultrasonic bath, was deposited on a copper grid coated by a holey carbon film. After evaporation of the solvent, the specimens were introduced into the microscope column. Particles size distributions were obtained by counting several hundred particles visible on the micrographs of each sample. From the size distribution the average diameter was calculated: $d_n = \sum n_i d_i / \sum n_i$ where n_i is the number of particles of diameter d_i .

Temperature-programmed reduction (TPR) measurements were performed using a conventional TPR apparatus. The dried samples (50 mg) were heated at a linear rate of 10 K/min from 273 to 1273 K in a 5 vol. % H₂/Ar mixture at a flow rate of 20 cm³/min. H₂ consumption was monitored by a thermal conductivity detector (TCD). A

molecular sieve cold trap (maintained at 193 K) and a tube filled with KOH, placed before the TCD, were used to block water and CO₂, respectively. The calibration of signals was made by injecting in the carrier a known amount of H₂.

Powder X-ray diffraction (XRD) data were acquired, at room temperature, on a Philips X-Pert diffractometer, by using the Ni β-filtered Cu-Kα radiation ($\lambda = 0.15418$ nm). Analyses were performed on reduced samples and registered in the 2θ range of 10° – 80° at a scan speed of 0.5° min⁻¹. Diffraction peaks were compared with those of standard compounds reported in the JPCDS Data File.

X-ray photoelectron spectroscopy (XPS) analysis was performed on reduced samples, by using a Physical Electronics GMBH PHI 5800-01 spectrometer, equipped with a monochromatic Al Kα X-ray source. The binding energies were set taking the C 1s peak (284.6 eV) as reference.

2.3 Catalytic tests

Liquid phase hydrogenation of aromatic alcohols (benzyl alcohol, 1-phenylethanol and diphenylmethanol) was generally carried out at 0.1 MPa partial hydrogen pressure in a 100 ml five-necked batch reactor fitted with a reflux condenser. When the reaction was carried out at lower hydrogen pressures, nitrogen was used to balance the total pressure at 0.1 MPa. The reaction temperature was maintained at a constant value (323 K) by circulation of silicone oil in an external jacket connected with a thermostat. The temperature of the reaction mixture was monitored by placing a thermocouple inside the vessel. A typical run was carried out as follows. The catalyst (about 300 mg), previously activated under H₂ at 473 K was added to the required amount of solvent (25 ml of ethanol, 99.8% analytical grade), and further reduced in “situ” at 323 K for 1 h under H₂ flow (50 ml/min). Then, a solution of the aromatic alcohol in ethanol (0.6 M, 15 ml), containing tetradecane as internal standard, were added through one arm of the flask. The reaction mixture was stirred with a magnetic stirrer head coupled with a gas stirrer at a rate of 500 rpm.

Preliminary runs, performed with different amounts of catalyst, sample grain size and stirring rate, indicated that, under the experimental conditions adopted, the reaction was carried out in absence of external and internal mass-transfer limitations.

The progress of the reaction was followed by analyzing a sufficient number of samples withdrawn periodically from the reaction mixture. Products analysis was performed

with a gas chromatograph (HP model 5890), equipped with a wide-bore capillary column (CP-WAX 52 CB, 50 m, i.d. = 0.53 mm) and a flame ionization detector. Quantitative analyses were carried out by calculating the areas of the chromatographic peaks with an electronic integrator (HP model 3396).

3 Results and Discussion

3.1 Catalysts characterization

Table 1 reports the real wt% of palladium, determined by X-ray fluorescence analysis, and BET surface area values relative to each catalyst. Surface area changes in the order Pd/SiO₂ > Pd/Co₃O₄ > Pd/TiO₂, whereas the particles diameter varies as Pd/Co₃O₄ > Pd/TiO₂ > Pd/SiO₂.

3.1.1 Temperature-programmed reduction (TPR) measurements

The TPR profile of Pd/Co₃O₄ (Fig. 1a) shows a broad and intense peak located at ~535 K. This peak can be related to the simultaneous reduction of both palladium and cobalt cations, causing an upward shift relative to that of palladium, as compared to palladium oxide (PdO can be easily reduced by H₂ at room temperature) [20] and downward relative to that of cobalt oxides (739 K) [8]. This suggests that: (i) the Pd²⁺ species is stabilized within the cobalt oxide support and (ii) the presence of palladium catalyzes the reduction of cobalt oxide more readily. This phenomenon is well documented in the literature and is attributed to a strong interaction between well dispersed palladium particles and the metal oxide support [21].

The Pd/TiO₂ TPR profile (Fig. 1b) shows two peaks: the first one at ~ 310 K and the second more intense at ~ 375 K. Both can be ascribed to different species of palladium: the first one can be attributed to the presence of larger agglomerations of the palladium species and the other to smaller particles [22]. H₂ uptake quantitative analysis thoroughly supports this conclusion. Accordingly, it can be assumed that a not uniform distribution of palladium particles occurs, as verified by TEM measurements.

3.1.2 Transmission electron microscopy (TEM) analysis

Catalysts were also characterized by using TEM analysis (Fig. 2) and the average size and the relative size distribution were calculated on the basis of, at least, 100 particles for each sample. In particular, the co-precipitated Pd/Co₃O₄ shows the presence of faceted metal particles and is characterized by a broader size distribution with a mean diameter of 10.7 nm, higher than that of the other samples. Conversely, TEM micrographs of the TiO₂ supported palladium catalyst exhibit Pd particles dispersed on the matrix and also particles agglomeration spots. Moreover a particles size distribution in the range of 2 - 16 nm, with a mean value, d_n , of 5.2 nm was observed.

3.1.3 Powder X-ray diffraction (XRD) analysis

XRD spectra of all investigated catalysts, after reduction with H₂ at 473 K, are reported in Fig. 3. The impregnated Pd/TiO₂ and Pd/SiO₂ systems, in addition to diffraction patterns related to oxides carriers (those belonging to the anatase structure of Pd/TiO₂ and a broad peak at $2\theta = 22^\circ$, characteristic of the quite amorphous SiO₂, on Pd/SiO₂) show the peak at $2\theta = 40.1$, corresponding to the most intense diffraction line of the (111) plane of metallic palladium. Furthermore peaks at $2\theta = 46.8^\circ$ and 68.1° are detected on the XRD spectrum of Pd/SiO₂ sample, ascribed to diffraction lines relative to the (200) and (220) plane of Pd⁰, respectively. Conversely the co-precipitated palladium – cobalt oxide catalyst spectrum shows the typical reflections of Co₃O₄ crystalline phase and a very broad Pd (111) peak, slightly shifted towards higher angles than that observed in pure Pd, suggesting an interaction of palladium particles with the cobalt support.

3.1.4 X-ray photoelectron spectroscopy (XPS) measurements

XPS results of different palladium catalysts, after reduction, are summarized in Table 2. The binding energy values of 458.8 eV (Ti 2p_{3/2}), corresponding to the Ti⁴⁺ formal oxidation state and of 103.6 eV (Si 2p_{3/2}), typical of Si⁴⁺ in SiO₂, are observed on the spectrum of Pd/TiO₂ and Pd/SiO₂ catalysts, respectively [23]. The Co 2p_{3/2} spectrum of the Pd/Co₃O₄ catalyst evidences a broad peak at 780.0 eV. The absence of any shake-up satellite peak at about 5.0 - 6.0 eV higher binding energy values confirms the Co₃O₄ structure for the support [24, 25]. The binding energy value, relative to the Pd 3d_{5/2} peak for Pd/TiO₂ and Pd/SiO₂, is 334.9 eV, very close to that reported for pure

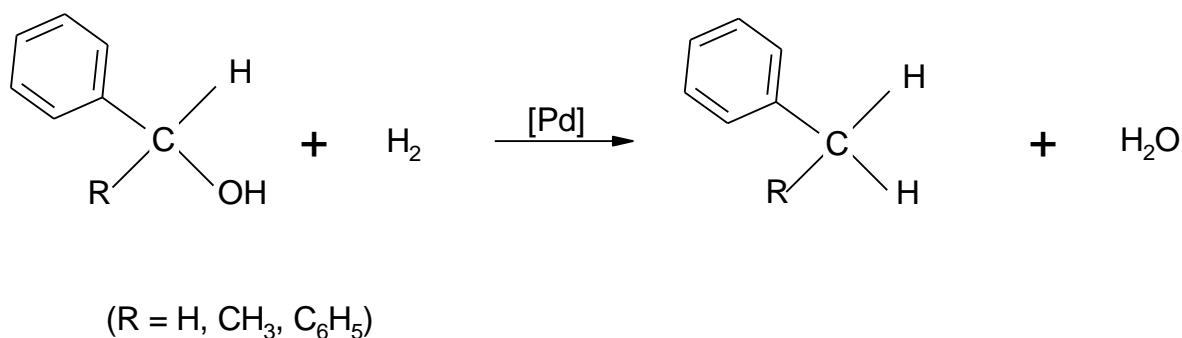
metallic palladium [23], confirming a lack of palladium-support interaction, in accordance with TPR and XRD data. Conversely, a shift toward higher values of the Pd 3d_{5/2} peak is observed on Pd/Co₃O₄ and a value of 335.2 eV is found. Higher binding energy values than that of metallic palladium suggest that an electron transfer from Pd to the support occurs, consequent to a strong metal-support interaction.

Table 2 XPS data of reduced palladium catalysts

Catalyst	BE (eV)			
	Pd 3d _{5/2}	Ti 2p _{3/2}	Si 2p _{3/2}	Co 2p _{3/2}
Pd/TiO ₂	334.9	458.8		
Pd/SiO ₂	334.9		103.6	
Pd/Co ₃ O ₄	335.2			780.0

3.2 Hydrogenolysis reactions

The catalytic reduction of aromatic alcohols was carried out in ethanol at 323 K and 0.1 MPa H₂ pressure and follows the reaction pathway reported in Scheme 1.



Scheme 1 Reduction of aromatic alcohols

Initial reaction rates, r_i , expressed as moles of substrate/grams of palladium per second, are reported in Table 3. A typical composition against time plot is shown in Fig. 4. A different kinetic behaviour arises from the observed results. When Pd/TiO₂ and Pd/SiO₂ catalysts, prepared by impregnation, are considered, the activity changes

in the order: benzyl alcohol > 1-phenylethanol \geq diphenylmethanol. Conversely, on using the co-precipitated Pd/Co₃O₄ the hydrogenolysis activity is totally reversed and follows the order: diphenylmethanol > 1-phenylethanol > benzyl alcohol.

Table 3 Activity of supported Pd catalysts in aromatic alcohols hydrogenolysis at 323 K and 0.1 MPa H₂ pressure, using ethanol as solvent

Catalyst	r_1 (mol _{sub} /g _{Pd} · s) 10 ⁵		
	Benzyl alcohol	1-phenylethanol	Diphenylmethanol
Pd/TiO ₂	30.5	8.38	9.52
Pd/SiO ₂	1.14	0.67	0.03
Pd/Co ₃ O ₄	9.95	12.8	15.8

Physico-chemical properties (BET, TEM, TPR, XRD and XPS) suggest different structural peculiarities in our substrates, useful for interpreting the link between the observed reactivity and the catalysts structure. The co-precipitated Pd/Co₃O₄ evidences a strong metal-support interaction, confirmed by the higher binding energy value (335.2 eV) of the Pd 3d_{5/2} peak and the shape of the TPR profile, whereas on impregnated Pd/TiO₂ and Pd/SiO₂ samples only bare metal clusters are detected and no interaction with support occurs. On this basis, it appears that the steric influence observed on the activity of Pd/TiO₂ and Pd/SiO₂ systems should be the result of an adsorption of the aromatic ring of alcohols on the palladium surface. As a consequence, the C-O bond is into close proximity to palladium atoms and strictly subject to the steric hindrance of the substrate. This mode of adsorption is well documented in literature and thoroughly explains the observed results [10]. Analogous results were also reported for hydrogenolysis reactions carried out using the Pd/B(OH)₃ catalyst [26]. Conversely on Pd/Co₃O₄, structural and electronic properties of palladium make the previous supposed geometry less likely and the activity should depend more on the electronic peculiarities of the organic substrates. Thus, in our opinion, the different geometric configuration of organic molecules on the catalytic surface and/or on the transition state could explain the different activity order of aromatic alcohols on changing the properties of metal substrates.

In principle, the hydrogenolysis of aromatic alcohols can occur through one of two possible mechanisms: i) an associative mechanism, in which the surface palladium

bonded hydrogen displaces the hydroxyl group bonded to the carbon atom, or ii) a more stepwise mechanism starting with the dissociation of the C-OH bond and temporary bonding of the OH group and the hydrocarbon residue on the Pd surface, followed by the transfer of a metal-bonded H atom to the unsaturated hydrocarbon intermediate.

Table 4 Aromatic alcohols hydrogenolysis over 5% Pd/TiO₂ catalyst at 323 K and at different partial H₂ pressure, using ethanol as solvent

$\sqrt{P_{H_2}}$ (MPa)	r_i (mol _{sub} /g _{Pd} · s) 10 ⁵		
	Benzyl alcohol	1-phenylethanol	Diphenylmethanol
0.32	30.5	8.28	9.52
0.22	20.7	9.75	9.55
0.14	16.7	7.33	3.85

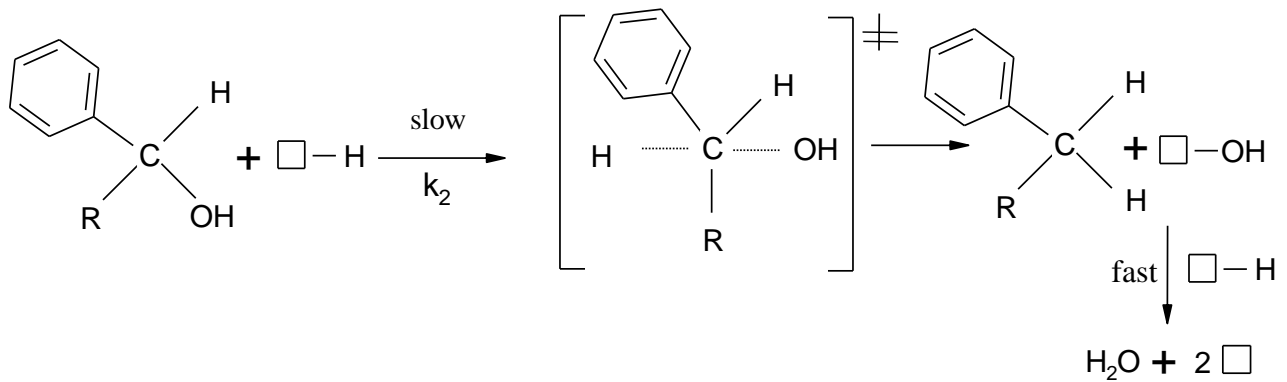
In order to elucidate the possible contribution of one or both of the accounted mechanisms new kinetic experiments were carried out at different H₂ pressures and using Pd/TiO₂ as test catalyst. Table 4 reports the results and fig. 5 shows the relation between r_i values and $\sqrt{P_{H_2}}$. We recall that the amount of hydrogen active sites, Θ_H , on a metal surface, is given by:

$$\Theta_H = \frac{\sqrt{K_H P_{H_2}}}{1 + \sqrt{K_H P_{H_2}}};$$

$$\text{if } 1 \gg \sqrt{K_H P_{H_2}}, \quad \Theta_H = \sqrt{K_H P_{H_2}}$$

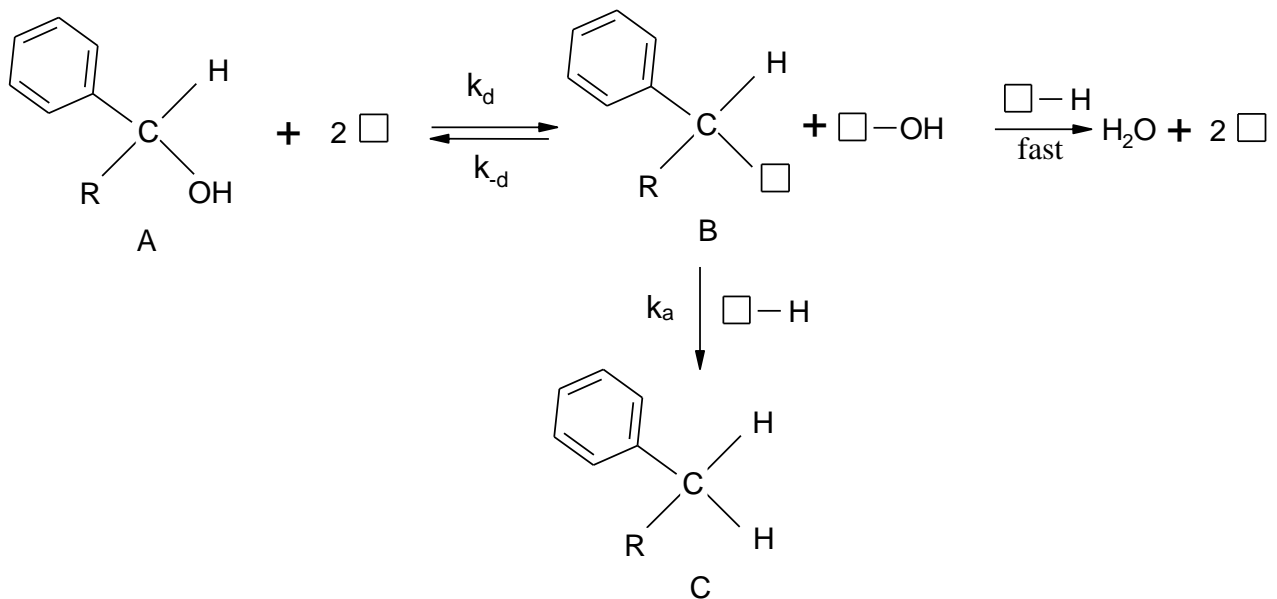
where K_H is the adsorption equilibrium constant of H₂ on the surface. Therefore $\sqrt{P_{H_2}}$ is proportional to Θ_H . Furthermore Table 4 reports initial rate values, r_i , calculated in conditions where the substrate concentration can be, reasonably, considered constant. Plots in fig. 5 allow to formulate the following general hydrogenolysis mechanism:

Associative mechanism



(R = H, CH₃, C₆H₅; \square = palladium site)

Dissociative-competitive mechanism



(R = H, CH₃, C₆H₅; \square = palladium site)

If both of them are simultaneously operating, on applying the steady-state approximation to the intermediate B the following kinetic rate law can be derived:

$$r_i = k_2[\text{alcohol}]\Theta_{\text{H}} + \frac{k_a k_d [\text{alcohol}]\Theta_{\text{H}}}{k_a \Theta_{\text{H}} + k_{-d} \Theta_{\text{OH}}} \quad (1)$$

where Θ_{OH} is the amount of OH active sites.

Equation (1), if $k_a Q_H \gg k_{-d} \Theta_{OH}$ reduces to:

$$r_i = k_2 [\text{alcohol}] \Theta_H + k_d [\text{alcohol}] \quad (2)$$

Comparison of data referring to Pd/TiO₂ evidences that only in the case of the unhindered benzyl alcohol both k_2 term (associative) and k_d term (dissociative) occur whereas the activity of both 1-phenylethanol and diphenylmethanol depends only on the k_d term and, if the reaction of diphenylmethanol at lower pressures of H₂ is considered, a dissociative-competitive mechanism occurs being comparable $k_a \Theta_H$ and $k_{-d} \Theta_{OH}$ terms. Interestingly, values of the k_d term for all aromatic alcohols investigated converge towards the approximate term ($\sim 9.25 \times 10^{-5}$) as it can be expected considering that the C-OH bond breaking energy for all alcohols is of the same order of magnitude.

4 Conclusions

The catalytic reduction of aromatic alcohols, promoted by impregnated Pd/TiO₂, Pd/SiO₂ catalysts and Pd/Co₃O₄ (prepared by co-precipitation) is carried out at 323 K and at 0.1 MPa H₂ pressure. A different kinetic behaviour is noticed. The hydrogenolysis activity follows the order benzyl alcohol > 1-phenylethanol \geq diphenylmethanol in presence of impregnated Pd/TiO₂ and Pd/SiO₂ systems whereas it is totally reversed in presence of the co-precipitated Pd/Co₃O₄. The results reported indicate that the reactivity strongly depends on the nature of the support, the preparation method of catalysts and the aromatic alcohols structure. Kinetic experiments allow to elucidate the reduction mechanism of alcohols that occurs through a radical substitution of the carbon bonded OH group by an incoming hydrogen atom from the metal surface “via” associative and dissociative paths.

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Figure Captions

- Fig. 1** H₂-TPR profiles of different supported palladium catalysts: (a) Pd/Co₃O₄, (b) Pd/TiO₂
- Fig. 2** TEM microphotographs and metal particles size distribution histograms of Pd/Co₃O₄ and Pd/TiO₂ catalysts
- Fig. 3** XRD patterns of different supported palladium catalysts investigated
- Fig. 4** Composition-time plot of the hydrogenolysis reaction of 1-phenylethanol over Pd/Co₃O₄ at 323 K and 0.1 MPa H₂ pressure, using ethanol as solvent
- Fig. 5** Hydrogenolysis initial rate values versus $\sqrt{P_{H_2}}$