

Selective hydrogenation of carvone and *o*-xylene on Pd–Cu catalysts prepared by surface redox reaction

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Abstract

A series of Pd and Pd–Cu bimetallic catalysts were prepared by surface redox reaction and coimpregnation methods. A comparison between the preparation methods in the activity and selectivity for *o*-xylene and carvone hydrogenation was done. FTIR studies showed that the Cu is deposited mainly in the low coordination Pd sites when the catalyst was prepared by redox, whereas a random distribution of Cu on the Pd surface was obtained for the catalyst prepared by coimpregnation. The activity and selectivity of bimetallic catalysts, were found to depending on the method of preparation used. For *o*-xylene hydrogenation in redox catalyst, the selectivity to *trans*-1,2-dimethylcyclohexane was lower than that obtained in the Pd/SiO₂ reference catalyst, whereas in the coimpregnated catalyst, the *trans* isomer selectivity was higher. In the redox preparation, the selective hydrogenation of carvone favors the formation of carvotanacetone, whereas the coimpregnated catalyst favors the selectivity to carvomenthone. © 2000 Elsevier Science B.V. All rights reserved.

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1. Introduction

In heterogeneous catalysis the selective hydrogenation of organic molecules plays an important role in the synthesis of the fine chemicals [1]. The attractive features include reactions under mild conditions, easily handled and catalyst recycling. Platinum, palladium or rhodium are generally the most effective metals for these reactions. It was also reported that metal promoters (e.g., Au, Cu) modify their selectivity and deactivation behaviors [2,3].

On the other hand, since the classical preparation methods of bimetallic catalysts (e.g., successive impregnation or coimpregnation) are unsatisfactory in providing homogeneous catalysis in surface as well in volume properties, new techniques are being proposed [4–9]. One of these methods is the surface redox reaction proposed by Barbier et al. [10]. In order to obtain a greater metal–metal interaction, direct reduction of the second metal was made by the hydrogen preadsorbed on the surface of the monometallic catalyst. A strong Pt–Re interaction, larger than that obtained by the traditional methods was obtained by the surface redox

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reaction occurring between the prereduced parent metal and the oxidized modifier [11]. In the Pt–Au catalysts prepared by the redox method, energy dispersive spectrometry X-ray (EDX) results shown that the second (Au) metal was preferentially deposited on the vertexes and edges of the platinum parent metal [12]. In the hydrogenation of carvone the selectivity of platinum was modified by the addition of gold. These results were explained assuming that gold was selectively deposited in the surface planes [13].

In the present work, we prepared Pd–Cu bimetallic catalysts supported on silica by a surface redox reaction and by coimpregnation in order to study the effect of the method of preparation on the activity and selectivity of *o*-xylene and carvone hydrogenation.

2. Experimental

2.1. Catalysts preparation

The monometallic Pd catalyst (1.42 wt.%) was prepared by ion exchange. Silica (spheralite 540 of surface area, 250 m²/g) was used as support and Pd (NH₃)₄ · (NO₃)₂ (Johnson Matthey) as precursor. The palladium precursor was maintained in contact, at pH 11, with the support for 2 h under stirring; afterwards the solvent was eliminated in a rotating evaporator at 70°C. The solid was dried at 120°C for 12 h. The catalyst was calcined in flowing air at 300°C for 4 h and then reduced under flowing hydrogen at 400°C for 4 h.

The Pt–Cu bimetallic catalysts were prepared by surface redox reaction and coimpregnation methods. For the surface redox reaction, the second metal was deposited by the oxidation–reduction reaction carried out on the surface of the metal between the hydrogen preadsorbed on the Pd and the cation of the second metal (Cu⁺²) [10]. The necessary quantity of the prereduced monometallic Pd/SiO₂ catalyst was placed on a Pyrex glass specially designed reac-

tor. The monometallic catalysts were purged with N₂ for 15 min, at room temperature; afterwards, the N₂ was replaced by a H₂ stream, then the temperature was raised to 300°C and maintained for 1 h, then cooled to room temperature. At the same time the solution of Cu (NO₃)₂ · 3H₂O (Prolabo) was bubbled with N₂ at room temperature. This solution was added to the Pd/SiO₂ catalyst and maintained continuously in stirring under N₂ flow for 1 h. The catalyst was washed with distilled water, filtered, and dried in N₂ flow at 120°C for 12 h, then calcined under air stream at 200°C and reduced under flowing hydrogen at 400°C. The Cu⁺² was reduced by the chemisorbed H atoms over Pd atoms as follows: 2[Pd(s)–H(ad)] + Cu⁺²(aq) → 2H⁺(aq) + Pd–Cu–Pd(s).

For the coimpregnation method, the aqueous solutions of Pd (NH₃)₄ · (NO₃)₂ and Cu (NO₃)₂ · 3H₂O were put on contact with the support silica, during the 2-h stirring at room temperature, in an ammoniacal solution with a pH of 11. The catalyst was dried at 120°C, calcined, and then reduced under air and hydrogen at 300°C and 400°C, respectively. The catalyst metal loading was determined by atomic absorption spectroscopy.

2.2. Catalyst characterization

The metal accessibility was determined by volumetric hydrogen chemisorption in a conventional glass system equipped with a turbomolecular pump. Prereduced samples were reactivated

Table 1
Loading catalysts and metal accessibility

Catalyst	wt.% Pd	wt.% Cu	Accessibility (%)
Pd/SiO ₂	1.46	–	54
Pd–Cu/SiO ₂ (surface redox reaction)	1.42	0.14	33
Pd–Cu/SiO ₂ (coimpregnated)	0.85	0.28	46

Table 2

Values of ν_i and the ratio of S_i/S_t obtained in the FTIR spectra for Pd and Pd–Cu catalysts

Bands	1.42% Pd		1.42% Pd–0.14% Cu (redox)		0.85% Pd–0.28% Cu (coimpregnated)	
	ν_i (cm ⁻¹)	S_i/S_t (%)	ν_i (cm ⁻¹)	S_i/S_t (%)	ν_i (cm ⁻¹)	S_i/S_t (%)
A1	2094	18	2086	11	2094	24
A2	2056	6	2056	4	2056	9
A1 + A2		24		15		33
B	1959	5	1977	5	1962	4
C	1910	64	1929	55	1929	25
D	1846	5	1865	24	1869	38
X	1775	2				
C + D + X		71		80		63

in H₂ at 400°C for 1 h, then the system was evacuated at this temperature and cooled to 70°C. The H₂ chemisorption was carried out at this temperature to avoid the formation of Pd hydride [14]. A H/Pd stoichiometric ratio of one was assumed. At these conditions, Cu did not chemisorb hydrogen. The catalysts characterization is reported in Table 1.

The FTIR spectra were obtained in a Nicolet 10-MX spectrometer (resolution 1 cm⁻¹) equipped with CaF₂ windows. Samples were placed in a holder (KBr) and introduced in the IR cell, which was coupled to the vacuum system. After thermal treatments, air calcination at 300°C and reduction in hydrogen at 400°C, a flow of CO was introduced, and the FTIR spectra were obtained at room temperature. The spectra shown correspond to the difference between the reference and the catalyst samples in the IR range 2300–1400 cm⁻¹. The CO vibration spectra were deconvoluted as elemental Gaussian bands in order to obtain the maximum of the various picks (ν_i), their surface (S_i) and the ratio S_i/S_t , where S_t was the total surface. The surface picks estimation was calculated employing a software (Peakfit) which decompose the IR picks in elementary bands, obtaining directly the S_i and S_t surfaces, see Table 2 [15].

The CO IR adsorption bands have been assigned on Pd monocrystals [16,17] and they were used to identify the bands in the deconvoluted spectra in the present work (Fig. 1 and Table 3).

o-Xylene hydrogenation was accomplished in a conventional flow reactor used in differential mode at low conversion (< 10%). Reactants were *o*-xylene from Phillips (99%) and hydrogen (UHP). Reaction conditions were: partial pressure for *o*-xylene and hydrogen, 3.7 and

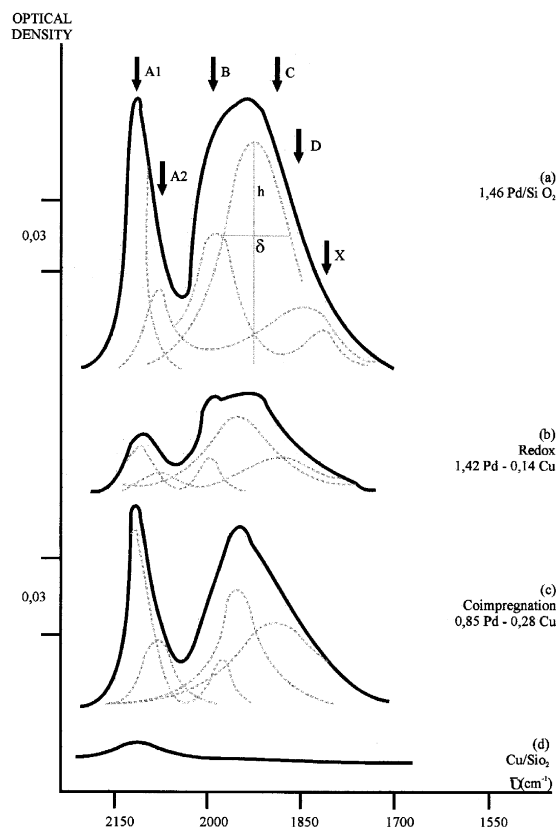


Fig. 1. The FTIR spectra of CO adsorbed for Pd, Cu and Pd–Cu catalysts.

756 Torr, respectively; mass of catalyst 0.050 g; reaction temperature 100°C.

An aliquot of the sample used for the dispersion measurements was reactivated under H₂ flow at 400°C for 2 h; afterwards, the catalyst was brought to the reaction temperature. The hydrogen gas saturated with *o*-xylene was passed through the reactor; the products were analyzed by on-line gas chromatography using an 8% carbowax 20 M on chromosorb W packed column (diameter: 2 m and 1/8 in.). The only products detected under these conditions were *cis*- and *trans*-1,2-dimethylcyclohexane. The activities were reported as turnover frequency (TOF), at $t = 0$. The selectivity defined as the molar ratio of *cis*-1,2-dimethylcyclohexane or *trans*-1,2-dimethylcyclohexane to *o*-xylene reacted, is given in mol% and reported at $t = 0$.

Carvone hydrogenation was carried out in a Parr reactor of 1.0 l of capacity at 100°C and 20 atm using 200 ml of a 0.02976 M carvone (Aldrich) solution in n-hexane (Aldrich). The catalyst (0.05 g), previously reactivated at 400°C was placed directly in the reactor, then the system was purged with N₂ and stirred for 20 min at 20 atm. Afterwards, the nitrogen was evacuated from the reactor and the hydrogen (UHP) was then introduced. The reaction sequence was followed by analyzing samples at time intervals. The chemical analysis was per-

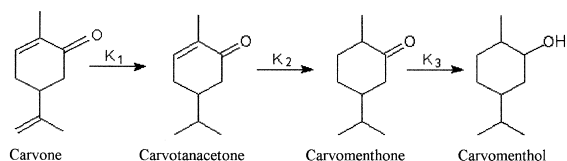


Fig. 2. Scheme of reaction for carvone hydrogenation.

formed in a gas chromatograph using a packed column of 30 m and 1/8 in. with Chromosorb W on 5% of FFAP. Carvotanacetone and carvomenthone were the only products detected. The formation of carvomenthol was not observed (Fig. 2). Activities are expressed as TOF (number of molecules of reactant transformed per unit time per surface metal atom). These were determined from Pd accessibility values and initial activities ($t = 0$) calculated from the slopes of the straight lines that result from plotting the amount of carvone versus time. The selectivity, defined as the molar ratio of carvotanacetone, or carvomenthone formed, to carvone reacted, is given in mol% and reported at initial time ($t = 0$).

3. Results and discussion

In Table 1, the accessibilities obtained by H₂ chemisorption are shown. As expected, the addition of a second metal causes a decrease in the Pd accessibility. The monometallic catalyst showed a value of accessibility of 54%, whereas the bimetallic catalysts prepared by redox and by coimpregnation are 33% and 46%, respectively. As we can see, the decrease in the surface metal area is more important for the catalyst prepared by redox method. This method of preparation allows us to obtain bimetallic catalysts in which the two metals are in closer interaction [8].

The FTIR vibration spectra of the CO for Pd and Pd–Cu catalysts are shown in Fig. 1, and the assignment of the elemental bands of the deconvoluted spectra are reported in Table 3.

Table 3
FTIR spectra band assignment for CO adsorption on Pd and Pd–Cu catalysts supported on silica

Elemental bands	Absorption range (cm ⁻¹)	Assignment
A1	2050–2100	Linear adsorption on: • Low coordination atoms • Discontinuity between planes
A2	2030–2050	• Edges and corners
B	1970–1990	Bridged adsorption on: • Two-fold sites planes (100)
C	1920–1940	Bridged adsorption on: • Two-fold sites, planes (111)
D	1860–1880	• Two-fold sites, planes (111)
X	1690–1790	• Two-fold sites, planes (111)

Fig. 1a corresponds to the Pd monometallic spectra, and Fig. 1b and c corresponding to bimetallic catalysts, prepared by redox and coimpregnation, and Fig. 1d to the Cu monometallic catalyst. Studies of CO adsorption have correlated the CO frequency with the coordination of the Pd atoms at the surface of the metal [17], and the assignment is as shown in Table 3. The A_1 and A_2 bands correspond to the CO lineal adsorption on sites of lower coordination while the B bands correspond to a bridged CO adsorption assigned to planes (100) and finally the C, D, X bands which are assigned to a bridged CO adsorption on faces (111). In Cu/SiO₂ the IR spectrum showed only one broad absorption band at 2130 cm⁻¹.

The addition of Cu to the Pd leads to a decrease of the intensity of spectra of CO adsorption. This decrease is more important for the catalyst prepared by redox method. The redox method (Fig. 1b) leads to a diminution of the intensities of the IR bands A_1 and A_2 and therefore to a lower S_i/S_t (15%) ratio with respect to the Pd monometallic catalyst (24%). It is also observed that the bands corresponding to the CO adsorption on the (111) planes is higher for the redox catalyst, showing the higher value of S_i/S_t (80%), since 63% was obtained for the coimpregnated catalyst and 71% for the monometallic one. This means that the adsorption of the CO on the sites of low coordination is diminished due to a preferential deposition of the Cu on such sites, thus leaving free the sites of high coordination as the dense planes. For the catalysts prepared by coimpregnation, the IR of CO adsorption spectra for A_1 and A_2 is only slightly modified, the S_i/S_t ratio is higher with respect to the Pd monometallic while a decrease of the intensity of the CO adsorption bands for the planes (111) is observed. It could be assumed then that the Cu deposited in this catalyst is not selective and a random distribution on the surface is proposed.

The activity and selectivity for the *o*-xylene hydrogenation on Pd and Pd–Cu catalysts are reported in Table 4. The main products of this

Table 4

Activity and selectivity in the *o*-xylene hydrogenation on Pd and Pd–Cu catalysts

Catalyst	TOF × 10 ³ (molecule/ site · s)	Selectivity (%) ^a		
		<i>cis</i> - dchxa	<i>trans</i> - dchxa	dchxe
Pd/SiO ₂	87	44	52	4
Pd–Cu/SiO ₂ (surface redox reaction)	42	52	48	–
Pd–Cu/SiO ₂ (coimpregnated)	39	42	58	–

^aProducts of the hydrogenation of *o*-xylene: *cis*- and *trans*-1,2-dimethylcyclohexane [*cis*- and *trans*-(dchxa)] and 1,2-dimethylcyclohexene (dchxe).

reaction are the *cis*- and *trans*-1,2-dimethylcyclohexane. The initial activity per site (TOF) for the *o*-xylene hydrogenation decreases with the addition of the Cu, independent of the method of preparation. With respect to the selectivity the formation of *trans*-1,2-dimethylcyclohexane decreases when the catalyst is prepared by redox and the opposite is observed when the catalyst is prepared by coimpregnation. The addition of the Cu modifies the selectivity depending of the method of preparation. The hydrogen *trans* addition is a reaction that involves a roll-over, as suggested by Inoue et al. [18]. Considering the roll-over model, the *o*-xylene hydrogenation involves the formation of 1,2-dimethylcyclohexene in the last step. This olefin can isomerized to 2,3-dimethylcyclohexene which by a roll-over process can produce the 1,2-*trans*-dimethylcyclohexane. It has been proposed that the formation of *trans*-dimethylcyclohexane needs a higher residence time of the precursor olefin on the surface of the metal [2,19]. Since the benzene ring has high electron density, the *o*-xylene can be strongly adsorbed on an electrodefficient surface. Then the reaction will be favored in the low coordination sites of the metal, and the unfavored on the sites with higher electron density as the dense planes (111) of the Pd. As was observed by IR results, the catalyst prepared by redox shows the higher number of (111) planes which is responsible for

the lower selectivity towards the *trans*-1,2-dimethylcyclohexane. The higher selectivity to *trans*-1,2-dimethylcyclohexane observed on the coimpregnated catalyst is explained by a dilution of the Pd metal surface by Cu atoms.

The activity and selectivity for carvone hydrogenation over Pd and Pd–Cu are reported in Table 5. The products obtained in the hydrogenation of carvone were carvotanacetone and carvomenthone. The activity per site (TOF) of the Pd monometallic catalyst is modified by the Cu addition only in the catalyst prepared by coimpregnation while for the catalyst prepared by redox the activity was not modified. In the selectivity pattern we observed an increase of the carvotanacetone formation for the catalyst prepared by redox, while a diminution of this product in the coimpregnated catalyst. The carvone has two double C=C bonds (exo and endo) and a C=O function in which the hydrogen addition could be done. It has been reported [13] that the formation of carvotanacetone, (hydrogenation of the exo C=C bond) is produced mainly in the sites of high coordination where the desorption of the molecule is favored. If the adsorption of the unsaturated molecule in the surface of the metal is stronger, as will occur in the sites of low coordination, the residence time of the molecule adsorbed increases, then deep hydrogenation will be obtained. The different selectivity behavior showed by the bimetallic catalysts are then a result of the sites where the

Cu was deposited and then an effect of the method of preparation.

As was discussed above in the catalyst prepared by redox, it is proposed that the Cu is placed preferentially in the low coordinated sites of the Pd surface. High coordinated sites are available for the reaction and an increase of the carvotanacetone product will be expected. These results are supported by the values reported in Table 5. For the coimpregnated catalysts, the random Cu deposited in the surface of the dense planes leads to dilution of the Pd ensembles.

The sites of low coordination are higher in coimpregnated catalyst, therefore the carvone molecule increases the residence time of carvone on the surface, which is higher due to the strong adsorption on the Pd surface. This leads to the hydrogenation of both exo and endo C=C bonds, leaving the carvomenthone as main product. The C=O bond was not hydrogenated at the present reaction conditions.

4. Conclusions

The FTIR studies of the bimetallic catalyst showed that the Pd–Cu bimetallic catalyst prepared by redox reaction leads to a preferential deposit of the Cu on the surface of Pd. The Cu is deposited at the sites of lower coordination (edges and vertex). In the coimpregnated catalyst, a random distribution on the surface of the dense planes (111) is observed.

This model of Pd–Cu catalyst prepared by redox explains the lower selectivity towards *trans*-1,2-dimethylcyclohexane for *o*-xylene hydrogenation and the higher carvotanacetone selectivity for carvone hydrogenation.

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Table 5
Activity and selectivity in the carvone hydrogenation on Pd and Pd–Cu catalysts

Catalyst	TOF $\times 10^2$ (molecule/ site \cdot s)	Selectivity (%)	
		Carvotan- acetone	Carvo- menthone
Pd/SiO ₂	7.0	64	36
Pd–Cu/SiO ₂ (surface redox reaction)	6.9	73	27
Pd–Cu/SiO ₂ (coimpregnated)	12.8	32	68

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