



ELSEVIER

Journal of Molecular Catalysis A: Chemical 96 (1995) 155–161

JOURNAL OF  
MOLECULAR  
CATALYSIS  
A: CHEMICAL

## Probing Ru–Pd/SiO<sub>2</sub> catalysts by gas phase *o*-xylene hydrogenation

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Received 24 June 1994; accepted 8 November 1994

### Abstract

Ru–Pd/SiO<sub>2</sub> catalysts were characterized by hydrogen chemisorption, XPS and TPD of CO, and their catalytic activity was obtained for the gas phase hydrogenation of *o*-xylene at atmospheric pressure. A small maximum in activity appeared in the bimetallic catalysts at temperatures at which palladium is inactive. The stereoselectivity of the bimetallic catalysts differed markedly from that of monometallic ruthenium. A ligand effect between surface Ru and Pd atoms is suggested to be responsible for the catalytic behaviour of the bimetallic catalysts.

**Keywords:** Gas phase; Hydrogenation; Palladium; Ruthenium; Silica; Supported catalysts; *o*-Xylene

### 1. Introduction

In previous papers we reported the results of the hydrogenation of *o*- and *m*-xylenes on supported palladium catalysts [1,2] and on supported ruthenium catalysts [3]. It was observed that the selectivity towards the thermodynamically preferred product *trans*-1,2-dimethylcyclohexane (*t*-1,2-DMCH) in the case of *o*-xylene, increased with temperature, acidity of support and dispersity [1–3] and decreased in the presence of electron-donor molecules [1]. Taking into account the ‘roll-over’ model proposed by Inoue et al. [4], it was concluded that the bond strength between the reactive species and the surface determines the stereoselectivity in such a way that an increase in the bond strength leads to a product composition

closer to that predicted by thermodynamics [1].

On the other hand, concerning the Ru–Pd/system, we reported that in the hydrogenation of benzene a volcano curve appeared for the activity as a function of bimetallic composition at temperatures at which Pd was completely inactive [5]. In this work it was shown that the deactivation of the catalysts was responsible for this behaviour. To explain this, two possibilities were suggested: first, dilution of Ru ensembles by ‘inactive’ Pd and second, an increase in the hydrogen pool of the surface available for the reaction due to Pd atoms.

However, new approaches are under development to understand alloying effects, which demphasize the role of ensembles in heterogeneous catalysis and rather prefer to view reactions, in almost all cases, as occurring on single metal atoms, where ligand effects and degree of coor-

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dinative unsaturation of metal atoms may be of great importance [6].

With this in mind and taking into account that the stereoselectivity of a metal in the hydrogenation of *o*-xylene seems to be a parameter very sensitive to the chemical environment of the active sites, we report here the hydrogenation of *o*-xylene on Ru–Pd/SiO<sub>2</sub> catalysts.

## 2. Experimental

### 2.1. Catalyst preparation

RuCl<sub>3</sub> · 3H<sub>2</sub>O and PdCl<sub>2</sub> · 2H<sub>2</sub>O from ICN Pharmaceuticals were used as precursors of the supported catalysts. The support used was silica (Ketjen F-2 180 m<sup>2</sup>/g) from Akzo Chemie, previously calcined in air (3.6 l/h) at 723 K for 12 h.

The catalysts were prepared by the co-impregnation technique from aqueous solutions (deionized water) of the metal precursors in appropriate amounts to give a total (nominal) loading of 4 wt.-% metal (Ru + Pd). Following the evaporation of the solvent the samples were dried in air at 383 K overnight. The powders (80–120 mesh) were reduced in flowing hydrogen at 573 K for Pd and 673 K for Ru and bimetallic catalysts.

### 2.2. Catalyst characterization

The number of accessible surface atoms was determined by hydrogen chemisorption at 343 K in a conventional (grease-free) volumetric apparatus. Prior to chemisorption experiments the catalysts were treated under flowing hydrogen at 673 K (573 K for Pd) for 2 h, outgassed at the same temperature for the same period of time and cooled in vacuum to the adsorption temperature. The pressure in the system was  $1.3 \times 10^{-3}$  Pa. Isotherms of hydrogen adsorption on the fresh catalysts were determined in the range 0.1–10 kPa. The total hydrogen uptake was obtained by extrapolating the linear portion of the isotherm to zero pressure.

Some catalysts were characterized by TPD of CO in a conventional TPD/TPR/TPO apparatus with a thermal conductivity detector (TCD). The samples (0.100 g) were pretreated 'in situ' under flowing hydrogen at 673 K for 1 h; at this time H<sub>2</sub> was switched for He and, after 1 h, the samples were allowed to cool to ambient temperature. The adsorption of CO was carried out under a continuous flow of pure CO (50 cm<sup>3</sup>/min) for 45 min. Desorption was performed under flowing He (31 cm<sup>3</sup>/min) with a heating rate of 10 K/min up to 773 K. The desorbed CO was measured with the TCD. All of the gases employed were of ultra high purity (Linde).

XPS spectra were obtained using a Fisons ESCALAB Mk II 200R electron spectrometer employing MgK $\alpha$  X-rays (photon energy = 1253.6 eV) operated at 120 W. The analyzer was operated in fixed analyzer transmission (FAT) mode with a pass energy of 20 eV for the individual spectra. Data analysis was performed on a VGS5000 data system based on the DEC PDP11 computer. The methodology employed for peak fitting consisted in selecting 1.8–2.0 eV line widths and a gaussian/lorentzian mix with a lorentzian contribution of 25%. Atomic percentages values were calculated from the peak areas using the sensitivity factors provided with the data system and background subtraction.

### 2.3. Catalytic activity

The hydrogenation of *o*-xylene was performed in a differential flow reactor operated at low conversions in order to avoid heat and mass transfer limitations. After passing through the reactor the reaction mixture was analysed by sampling on line to a gas chromatograph, equipped with a flame ionization detector and a stainless steel column, 4 m long and 1/8 in. o.d., packed with 10% Carbowax 20M on Chromosorb W. An aliquot (10–100 mg) of the catalyst was reactivated 'in situ' under flowing hydrogen at the reduction temperature for 2 h. The reaction was carried out at 301 K and 323 K. The partial pressure of *o*-xylene and the flow rate were fixed at 488 Pa and 3.6 l/h,

respectively. The products detected under these conditions were *trans*-1,2 dimethylcyclohexane (t-DMCH), *cis*-1,2 dimethylcyclohexane (c-DMCH) and 1,2-dimethylcyclohexene (DMChE).

### 3. Results

#### 3.1. Catalysts characterization

Table 1 lists the series of Ru–Pd catalysts prepared, their bulk (nominal) composition and the

Table 1  
Dispersion values of the Ru–Pd/SiO<sub>2</sub> Catalysts

Catalyst	Ru	Pd	Dispersion (H/M)
RP-1.00	4.0	0.0	0.12
RP-0.75	3.0	1.0	0.13
RP-0.50	2.0	2.0	0.18
RP-0.15	0.6	3.4	0.22
RP-0.00	0.0	4.0	0.29

Table 2  
The binding energies (eV) of core level spectra for the Ru–Pd catalysts

Catalyst	Ru 3d <sub>5/2</sub>	Pd 3d <sub>5/2</sub>	Si 2p	Ru 3p <sub>3/2</sub>
RP-0.50	279.8	335.1	103.4	461.6
RP-0.75	279.9	335.1	103.4	461.5
RP-0.90	280.0	335.3	103.4	461.6

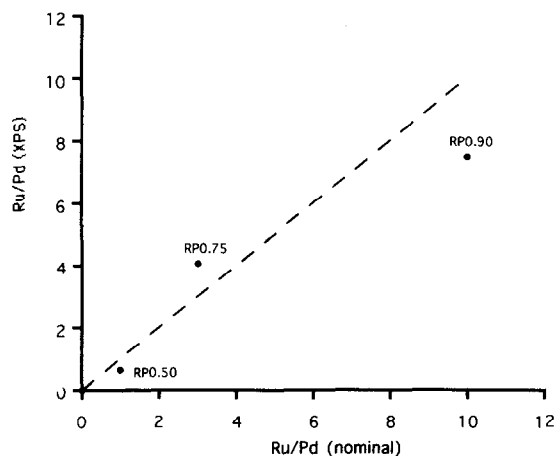


Fig. 1. XPS composition vs. nominal composition of Ru–Pd/SiO<sub>2</sub> catalysts.

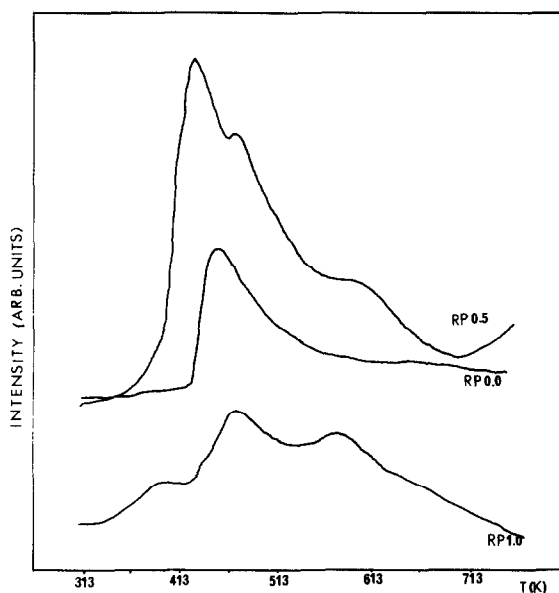


Fig. 2. CO TPD profiles for some Ru–Pd/SiO<sub>2</sub> catalysts. CO adsorption, temperature = 298 K, He flow rate = 31 cm<sup>3</sup>/min, heating rate = 10 K/min.

dispersion values. Dispersion values are defined as  $H/(Ru + Pd)$ , i.e., the ratio of total hydrogen atoms chemisorbed with respect to the total ruthenium plus palladium atoms. Dispersion values were small for all of the catalysts in the series, therefore particle size effects are not likely to appear.

The binding energies of core level spectra for prerduced catalysts are summarized in Table 2. For the catalysts reduced in H<sub>2</sub> at 673 K the BE of Pd 3d<sub>5/2</sub> and Ru 3p<sub>3/2</sub> peaks are characteristic of Pd<sup>0</sup> and Ru<sup>0</sup>, respectively. From the intensity of the peaks and atomic sensitivity factors, surface atomic ratios have been calculated. In order to see if there is surface enrichment of one component, the dependence between bulk and surface Ru/Pd atomic ratios has been examined in Fig. 1. It may be observed that there is not a clear enrichment in any of the two metal components.

CO TPD profiles for some Ru–Pd/SiO<sub>2</sub> samples are shown in Fig. 2. Desorption of CO from Ru/SiO<sub>2</sub> showed three well defined peaks at 393, 474 and 576 K. Three adsorption states have also been reported by others [7,8] on similar Ru/SiO<sub>2</sub> catalysts. It seems that low-temperature peaks cor-

Table 3  
Ru–Pd/SiO<sub>2</sub> catalysts. Activity and selectivity in the hydrogenation of *o*-xylene at 323 K and atmospheric pressure

Catalyst	TOF × 10 <sup>3</sup> mmol/ site · s	Selectivity <sup>a</sup>		
		St	Sc	Sa
RP-1.00	6.35	6.4	90.0	3.6
RP-0.75	18.90	10.9	85.0	4.0
RP-0.50	6.50	25.9	71.4	2.7
RP-0.15	0.50	27.7	65.5	6.8
RP-0.00	0.15	40.0	60.0	0.0

<sup>a</sup> St = selectivity to *trans*-1,2-dimethylcyclohexane, Sc = selectivity to *cis*-1,2-dimethylcyclohexane, Sa = selectivity to the alkene (1,2-dimethylcyclohexene).

respond to molecularly adsorbed CO [9], that could present strong CO–CO repulsive interactions [7], while high-temperature desorption arises from recombination of dissociated (or side-ways bonding) CO [8]. For monometallic palladium (RP0.0) only one peak was observed centred at 455 K. Gillet et al. [10] reported only one desorption peak for a Palladium/mica model catalyst (particle size = 6 nm) which appeared in the 449–453 K temperature range, depending on the CO surface coverage. Rieck and Bell [11] observed four desorption peaks, for a Pd 9%/SiO<sub>2</sub> catalyst, on a rather broad spectrum. They assigned the high-temperature peaks (638 and 773 K) to CO bridge bonded, and the low-temperature peaks (410 and 530 K) to linearly adsorbed CO. If this is so, only linear adsorption would be pres-

Table 4  
Activity and selectivity in the hydrogenation of *o*-xylene at 301 K on Ru–Pd/SiO<sub>2</sub>

Catalyst	Dispersion H/ (Ru + Pd)	TOF × 10 <sup>3</sup> (mmol/site · s)	Selectivity		
			St	Sc	Sa
RP-1.00	0.12	4.06	3.1	92.2	4.6
RP-0.75	0.13	14.20	9.1	88.5	2.4
RP-0.50	0.18	3.40	21.5	77.0	1.5
RP-1.00 + RP-0.00 (50–50 wt.%)	–	4.90 <sup>b</sup>	4.4	92.4	3.2
RP-0.15	0.22	0.25	16.7	80.2	3.1
Ru <sup>a</sup> (0.3 wt%)	1.00	2.10	10.0	84.6	5.8

<sup>a</sup> At 343 K.

<sup>b</sup> Calculated considering Ru surface atoms only.

ent in our monometallic Pd catalyst (RP0.0).

For the bimetallic catalyst (RP-0.50) three desorption peaks were obtained located at 417, 468 and 585 K. As it may be observed, the last two peaks are very similar in shape to those produced by monometallic Ru, while the shape of the first peak resembles that of Pd. This first peak is shifted to lower temperatures by ca. 38 K compared with that of monometallic Pd. With these considerations we may say that the CO adsorption states on Pd are modified by the presence of Ru atoms. This is not a particle size effect since it has been reported [10] that for small Pd particles, the CO desorption temperature is shifted to higher values.

### 3.2. Catalytic activity

Activity values at 323 K are reported in Table 3 as turnover frequencies (molecules converted per (site · second)) and selectivity values are defined as:

$$\%Si = \frac{r_i}{r_c + r_t + r_a} \times 100$$

where,  $r_i$  = rate of formation of the  $i$ th product, and c, t and a, stand for c-DMCH, t-DMCH and DMCH<sub>e</sub> respectively.

A small maximum in activity appeared at 75 atomic per cent of Ru in the bulk. At high dilutions of Ru with Pd the activity decreased sharply (one order of magnitude) and Pd was slightly active at 323 K. The composition at which the maximum in activity was observed coincides with that of benzene reported previously [5].

The selectivity values changed smoothly on going from pure Ru to pure Pd. However, being Ru about 40 times more active than pure Pd, the changes in selectivity for the first two bimetallic catalysts (RP-0.75 and RP-0.50) cannot be accounted exclusively by the presence of Pd active sites.

In order to facilitate the analysis of the results the reaction was carried out at 301 K, temperature at which pure Pd was found to be completely inactive, and this data is reported in Table 4. Besides

Table 5  
Deactivation of RP-1.00/SiO<sub>2</sub> with time on stream at 323 K

Time on stream (min)	Total Conversion % Ct	Selectivity		
		St	Sc	Sa
20	4.63	5.6	88.3	6.1
27	3.28	5.5	87.5	7.0
35	2.50	5.6	86.0	8.4
43	1.93	5.2	85.5	9.3
51	1.58	5.1	84.8	10.1
59	1.32	5.3	83.3	11.4
67	1.12	4.5	83.0	12.5
78	0.92	4.3	81.5	14.2
100	0.65	4.6	78.5	16.9
110	0.56	4.2	78.6	17.2

the catalysts listed in Table 1 two other sources of information were used: a mechanical mixture of pure Ru + pure Pd and a highly dispersed Ru monometallic catalyst (RP-1.00 wt.%). It may be observed that the mechanical mixture of Ru + Pd showed a catalytic behaviour very similar to that of monometallic Ru (RP-1.00) with the selectivity of formation of the *cis* isomer being 92.4 and 92.2%, respectively.

Nevertheless, variation of selectivity was observed for the bimetallic catalysts, although pure Pd is inactive at this temperature. In order to see if the diminution in size of Ru ensembles caused by dilution with Pd was responsible for the behaviour of the bimetallic catalysts, a highly dispersed Ru monometallic catalyst was tested. Two facts arose from this catalyst: firstly, there was an important decrease in the turnover frequency. In fact, the value reported is at  $T=343$  K since at 301 K the catalyst was inactive, and secondly, although there was a change in selectivity, increasing the production of the *trans* isomer and decreasing the formation of *c*-DMCH, the variation was not as important as it was observed for the bimetallic catalysts.

Monometallic Ru catalysts suffer important self deactivation in hydrogenation reactions [12], and the hydrogenation of *o*-xylene is not an exception [3]. Table 5 shows the behaviour of RP-1.00 catalyst with time on stream. The conversion decreased as well as the selectivity to *c*-DMCH

Table 6  
Hydrogenation of *o*-xylene at 301 K on Ru-Pd/SiO<sub>2</sub>. Activity and selectivity after 80 min of reaction

Catalyst	TOF × 10 <sup>3</sup> (molecules/site · s)	Selectivity			Residual Activity
		St	Sc	Sa	
RP-1.00	0.71	2.8	83.1	14.1	0.17
RP-0.75	4.70	8.6	86.5	4.9	0.33
RP-0.50	1.50	18.0	77.8	4.2	0.44
RP-0.15	0.19	16.6	75.0	8.4	0.76
Ru 0.3 wt% <sup>a</sup>	0.64	10.7	81.1	8.1	0.30

<sup>a</sup> At 343 K.

and *t*-DMCH, and the selectivity to DMCH increased with the time of reaction. The behaviour of the Ru-Pd series of catalysts after 80 min time on stream is represented by the data in Table 6.

It may be observed, that the bimetallic catalysts were more resistant to the self-poisoning process, and the changes in selectivity did not follow the pattern of the monometallic Ru, i.e., an important increase in the selectivity to the formation of the alkene.

#### 4. Discussion

We shall first recall the first two conclusions drawn in the previous paper [5] dealing with the Ru-Pd/SiO<sub>2</sub> system:

(1) the catalytic data for the hydrogenation of benzene is consistent with the formation of bimetallic particles in spite of the large miscibility gap in the Ru-Pd phase diagram, and

(2) the synergism found for the activity of this bimetallic system can be explained by a self deactivation process, with the bimetallic catalysts being more resistant to the deposit of carbonaceous residues than pure ruthenium.

These two facts are also evident in the hydrogenation of *o*-xylene since a maximum in activity appears at RP-0.75 (Tables 3 and 4) and the bimetallic catalysts showed a higher residual activity after 80 min of reaction (Table 6).

It was postulated that either the decrease in size of Ru ensembles by dilution with Pd or the formation of mixed metal surface sites – where Pd

served as a source of hydrogen – could be responsible for the catalytic behaviour of the bimetallic system.

With the information obtained from the selectivity values in the hydrogenation of *o*-xylene, it is possible to rule out the first assumption, i.e., the decrease in the Ru ensemble size by dilution with Pd as being responsible for the synergism found on this system. It was observed that highly dispersed Ru (Ru 0.3 wt.%) had a very small TOF and it also deactivated (Tables 4 and 6). Moreover the selectivity of this catalyst was different from that observed with the bimetallic catalysts.

As can be observed in Fig. 1, there is not a clear segregation of either metal on the surface of the bimetallic catalysts, therefore the increase in selectivity to the *trans* isomer cannot be explained by an increase in the palladium content at the surface of the catalysts with respect to the bulk composition.

On the other hand, the shift in the desorption temperature of CO from palladium observed when comparing monometallic catalyst and the bimetallic one, could point to the existence of a ligand effect on the bimetallic catalysts. However, it is important to remark that the binding energies for both metals in the bimetallic catalysts, are essentially the same as for the individual metals.

The interaction between Ru and Pd was studied by Rodriguez et al. [13] on a well defined Pd–Ru surface (Pd evaporated onto Ru (0001)). They found an increase in the Pd ( $3d_{5/2}$ ) binding energy of 0.3 eV with respect of the surface layer of Pd (100). Moreover, the desorption temperature of adsorbed CO on Pd/Ru(0001) is 330 K [14], much lower than that from Pd(100) (480 K) [15]. According to Rodriguez et al. [13], the electron density of the supported monolayer of Pd on Ru is smaller than that at the surface atoms of Pd(100), producing a weaker Pd–CO bond.

The ligand effect in Ru–Pd catalysts, has already been claimed by Ryndin et al. [16], who studied the hydrogenation of CO and the hydrogenolysis of  $C_2H_6$  on Ru–Pd/SiO<sub>2</sub> catalysts. The results obtained for the hydrogenolysis reaction was explained in terms of the dilution of Ru atoms

by less active atoms of Pd. However, the activity decrease of Pd in the methanol synthesis, could not be attributed to dilution by Ru, since the molecular adsorption of CO (and its hydrogenation) seems to take place on a single Pd atom as well. These authors ascribed this phenomenon to the ligand effect, i.e., to variations in the electronic properties of the Pd atoms due to presence of Ru in its first coordination sphere [16,17].

This ligand effect could affect the adsorption strength of the xylene molecule. As proposed earlier [1–3], a modification in the adsorption strength of the reactive species on the metal surface would produce a change in the stereoselectivity of the active sites. This would be a good explanation for the selectivity behaviour shown by the bimetallic catalysts compared to monometallic Ru (or Pd).

## 5. Conclusions

The catalytic behaviour of Ru–Pd/SiO<sub>2</sub> catalysts is consistent with the formation of bimetallic particles. The interaction between these two metals implies more than a geometric dilution of the active metal (Ru) with the inactive one (Pd).

The formation of mixed metal sites, with the presence of a ligand effect, is a good explanation for the resistance of the bimetallic catalysts to the self deactivation process, and also for the variation observed in the stereoselectivity values.

## Acknowledgements

We thank Mr. Luis Cedeño (UNAM) for the TPD measurements.

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