o-xylene hydrogenation on supported ruthenium catalysts

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The influence of the support on the surface properties and catalytic activity of finely divided ruthenium catalysts is reported. The catalysts were prepared using an organometallic precursor, Ru(acac)$_2$, and three different supports, Al_2O_3, TiO_2 and SiO_2. In order to study the influence of the particle size on the catalytic performance, the effect of the calcination temperature was also evaluated. XPS suggests that the state of ruthenium is essentially Ru^0, and chemisorption measurements indicate a decrease in metal dispersion from catalysts supported on $Al_2O_3 > TiO_2 > SiO_2$. The turnover number in the *o*-xylene hydrogenation showed significant differences depending on the support and on the particle size. Additionally, an increase in the selectivity to cis-dimethylcyclohexane with particle size was observed.

Keywords: catalysts, ruthenium, acetylacetonates, XPS, hydrogenation

1. Introduction

The hydrogenation of aromatic hydrocarbons on supported noble metal catalysts is of interest because of the commercial use of this reaction [1] and also from a fundamental point of view since some correlations between electronic structure and catalytic properties exist [2–5]. Benzene hydrogenation, considered as a structure-insensitive reaction [6–8], has been the most extensively studied. However, fewer studies dealing with the hydrogenation of toluene and xylene have been reported [9–12]. Both these reactions are of interest to assess the effect of the additional methyl groups on electronic or steric effects. Also, methylcyclopentane [13] and neohexane reactions [14] have yielded information about particle size and support effects on activity and selectivity.

o-xylene hydrogenation is a specially useful test reaction. Even if it is considered a structure-insensitive reaction [15], the reported results show important changes in catalytic activity. Thus, Vannice [11] has reported marked differences in turnover frequency over Pd supported on acidic and non-acidic supports. In those catalysts with higher surface acidity an important enhancement of the activity is observed and this behaviour has been attributed to the presence of additional active sites in the metal–support interfacial region which contributes to the overall rate of hydrogenation. It has been also shown that the selectivity toward the two cyclic products (cis- and trans-dimethylcyclohexane) may be affected by different factors, such as nature of the metal, metal particle size, surface acidity [16,17], etc.

In this work, the influence of the nature of support and the calcination temperature on catalytic activity in *o*-xylene hydrogenation and on surface properties of supported Ru catalysts is studied. As supports, Al_2O_3, SiO_2 and TiO_2 have been used. The catalysts were characterised by H_2 chemisorption, temperature-programmed reduction (TPR), transmission electron microscopy (TEM), surface acidity measurements by TPD of ammonia and X-ray photoelectron spectroscopy (XPS).

2. Experimental

The supports used were: γ-Al_2O_3 Girdler T-126 ($S_{BET} = 192$ m^2/g), SiO_2 BASF D-11-11 ($S_{BET} = 136$ m^2/g) and TiO_2 Degussa CLDD 1434-1 ($S_{BET} = 74$ m^2/g). The catalysts were prepared by impregnation of the support with a toluene solution of ruthenium acetylacetonate (Aldrich), at room temperature. The impregnated solids were dried overnight at 393 K and then calcined in oxygen flow either at 573 or 673 K. Finally, the solids were reduced in hydrogen flow at 773 K. For the sake of simplicity the catalysts calcined at lower temperature, 573 K will be referred to hereafter as L and those calcined at 673 K as H.

Hydrogen chemisorption measurements, temperature-programmed reduction studies and temperature-programmed desorption of ammonia were carried out in a TPR/TPD 2900 Micromeritics apparatus, provided with thermal conductivity detector. H_2 chemisorption at 343 K was evaluated using a pulse method. For TPR experiments, the reducing gas consisted of a mixture of 5% H_2 in argon (50 cm^3/min) and a heating rate of 10 K/min was used. The extent of adsorbed ammonia was evaluated from TPD experiments. Ammonia pulses were dosed in order to saturate catalyst surface at 373 K. Once the sample was cooled to room temperature and the base line was restored, the temperature was linearly increased (10 K/min) up to 773 K. The studies of temperature-programmed desorption of CO were carried out in a TPD apparatus provided with a Balzers QMG 125 quadrupolar mass spectrometer. The Ru catalysts were reduced in situ in H_2 at 773 K for 1 h, and then purged in a 50 cm^3/min of He while cooling till room temperature. At this temperature CO was adsorbed using a flow of CO of 50 cm^3/min. After removal of CO weakly adsorbed, the TPD was performed using a heating rate of 5 K/min up to 773 K.

TEM studies were carried out in a Jeol model JEM-1200 EX II system. The samples were prepared by the extractive replica procedure.

Photoelectron spectra were recorded using an Escalab 200R spectrometer provided with a hemispherical analyzer, operated in a constant pass energy mode and unmonochromatized Mg $K\alpha$ X-ray radiation ($h\nu = 1253.6$ eV), operated at 10 mA and 12 kV. The samples were pressed in a hydraulic die to form thin, smooth discs and then mounted in the pretreatment chamber. The samples already reduced as mentioned previously, were prereduced in situ in hydrogen at 673 K to avoid any surface reoxidation.The residual gas pressure was maintained below 3×10^{-9} Torr during data acquisition. Each spectral region was signal-averaged for a number of scans, depending on the peak intensity, in order to obtain good signal-to-noise ratios. The adventitious C 1s line at 284.9 eV was used as an internal standard. The intensities of the XPS peaks were determined after subtracting an S-shape background and integrating peaks areas. The surface Ru/M ratios were estimated from the integrated intensities of Ru $3d_{5/2}$, Al 2p, Si 2p and Ti $2p_{3/2}$ lines using the Wagner et al. sensitivity factors [18].

o-xylene hydrogenation was studied in a fixed-bed microcatalytic reactor working at atmospheric pressure. For this reaction a flow of 50 cm^3/min of a H_2/*o*-xylene = 1000 (molar ratio) mixture was fed into the reactor. The reaction was studied at 373 K. Only 10–25 mg catalysts samples were used in order to keep low conversion levels and to avoid heat and transfer limitation. The analyses were carried out by an on line gas chromatograph.

3. Results and discussion

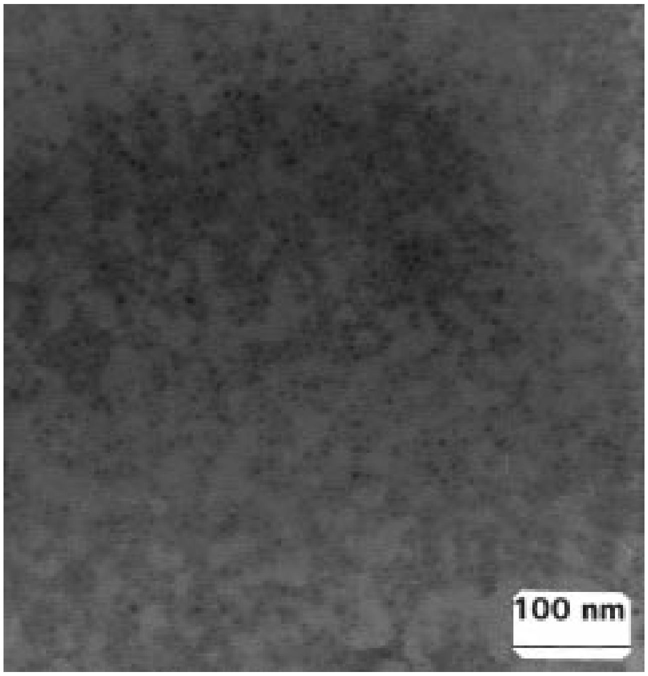
Table 1 summarizes H/Ru ratios, the estimated particle size evaluated from both chemisorption and TEM measurements, and surface acidity obtained from TPD of ammonia. To estimate the particle size, it was assumed that the hydrogen is adsorbed by the ruthenium atoms with a stoichiometry $Ru_s : H = 1 : 1$ and the particle size was evaluated from the equation $d = 5/S\rho$ where S is the metal surface area and ρ is the density of the metal. Significant differences in H/Ru ratios are observed. Alumina-supported ruthenium catalysts display the highest dispersion. In contrast, those supported on silica are poorly dispersed. These results can be explained in terms of strength of the metal–support interactions. For all catalysts, calcination at higher temperatures induces a migration of the RuO_2 species leading to a sintering of the Ru particles. The particle size evaluated from chemisorption data follows the same trend as the values obtained from TEM. Although particle sizes measured by both procedures do no match precisely, differences comparing particle size are not too important. Figures 1a and 1b show TEM micrographs. Ru particles are very small and in alumina-supported catalysts simultaneously the distribution is more homogeneous than in all the other catalysts. Surface acidity, expressed as the amount of NH_3 desorbed, follows the expected trends, $Ru/Al_2O_3 > Ru/TiO_2 > Ru/SiO_2$. Additionally, an increase in surface acidity in the samples calcined at higher temperatures is also observed. This may be attributed to an increase in the density of Lewis sites upon increasing temperature.

Table 1
H/Ru ratios, metal particle size and surface acidity for supported Ru catalysts

Catalyst [a]	H/Ru	d (nm)		NH_3 des. ($\mu mol/m^2$)
		CHEM	TEM	
Ru/Al_2O_3 L	0.334	33	33	33
Ru/Al_2O_3 H	0.193	57	57	98
Ru/SiO_2 L	0.177	62	62	66
Ru/SiO_2 H	0.102	108	108	94
Ru/TiO_2 L	0.204	54	54	50
Ru/SiO_2 H	0.111	99	99	75

[a] L and H refer to low and high calcination temperature, respectively.

Figure 2 shows TPR profiles of calcined supported Ru catalysts. For catalysts calcined at 573 K the TPR profiles are rather complex, showing a doublet peak centered at 370 and 420 K. In all these samples calcined at low temperature, a wide peak at higher temperature also appears. The peak positions for Al_2O_3-, SiO_2- and TiO_2-supported Ru are, respectively 475, 490 and 560 K. In all these samples, the hydrogen consumption is higher than that required for the stoichiometric reduction of RuO_2 particles. Therefore, it is likely that part of the H_2 consumed has been used to hydrogenate the remaining organic residue from the organometallic precursor located close to the metallic particle. As the hydrogenation of this residue may take place at temperature close to 400 K, a certain overlapping with the reduction peak of RuO_2 species is expected to occur. Additionally, the high temperature peak may be responsible for the hydrogenation, via hydrogen spillover, of other fragments placed on the support. In the samples calcined at higher temperatures, 673 K, the profiles exhibit essentially a single peak, of lower intensity, centered at 360 K attributed to the reduction of RuO_2 species [19]. A very small and wide peak in the temperature range 540–560 K, due a



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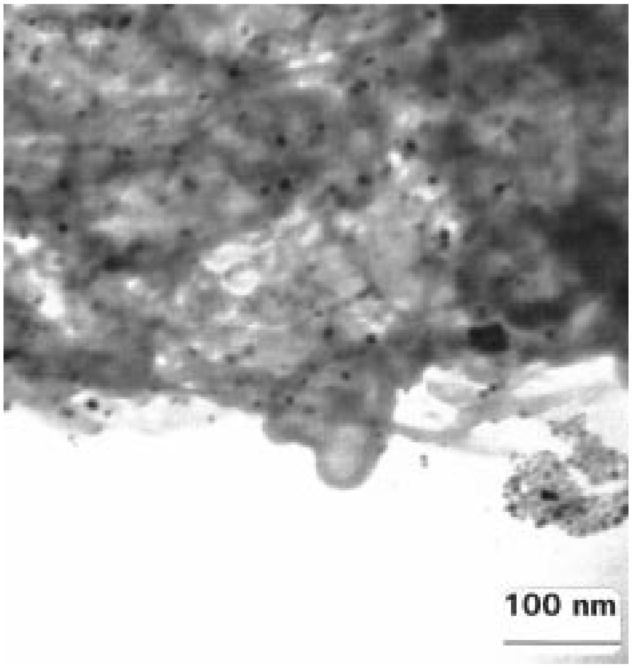

Figure 1. TEM micrographs of prereduced supported Ru catalysts. (a) Ru/Al_2O_3 L, (b) Ru/SiO_2 L.

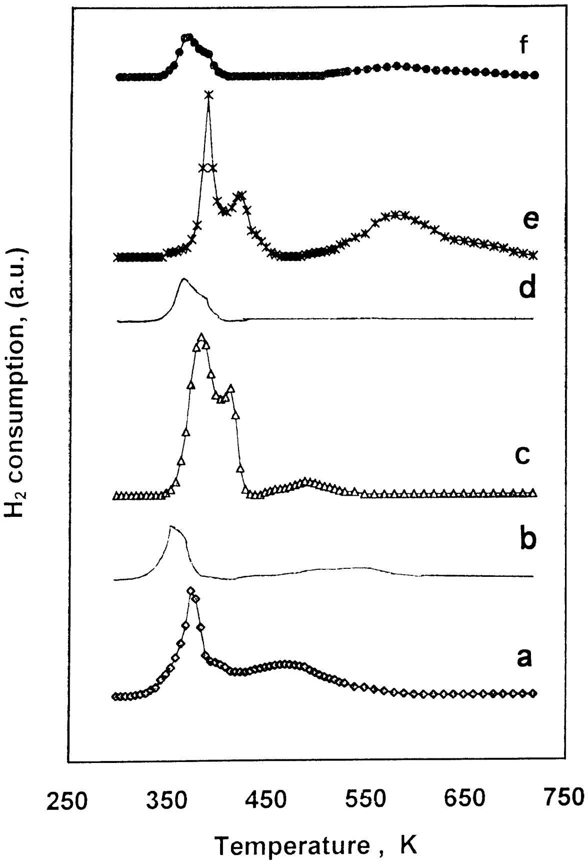

Figure 2. Temperature-programmed reduction profiles of supported Ru catalysts. (a) Ru/Al_2O_3 L, (b) Ru/Al_2O_3 H, (c) Ru/SiO_2 L, (d) Ru/SiO_2 H, (e) Ru/TiO_2 L, (f) Ru/TiO_2 H.

to hydrogenation of C-residue, also appears in Ru/Al_2O_3 and Ru/TiO_2 catalysts. The hydrogen uptake is close to the stoichiometric requirement. It seems that the C-residues are associated to the calcination temperature and also to the surface acidity. Therefore, a small contribution of this species is expected to occur on a non-acidic support such as SiO_2, when using a high calcination temperature which results in an almost complete decomposition of the organometallic precursor. Temperature-programmed desorption of carbon monoxide on Ru catalysts with mass detection showed, besides the desorption of CO, the evolution of H_2O, CO_2 and small amount of CH_4. The intensity of the masses $m/e = 28$, 18, 44 and 16 became smaller in those catalysts calcined at higher temperature. These findings confirm the presence of a carbonaceous residue on the catalyst surface still present in small amounts even after calcination and reduction treatments.

The Ru $3d_{5/2}$ core level spectra for two representative Ru/TiO_2 catalysts of the studied series are shown in figure 3. It can be seen that the binding energy of the Ru $3d_{5/2}$ peak in both samples is essentially constant and corresponds to Ru^0 species. An important overlap of the less intense Ru $3d_{5/2}$ component with the C 1s line is observed. As this component has a somewhat higher intensity in the samples calcined at lower temperature, an important contribution of this C 1s peak comes from the remaining residue. Table 2 summarizes XPS results for all the Ru samples. The Ru $3d_{5/2}$ line profile and the binding energy of the maxima point to the presence of completely reduced ruthenium species. From the integrated Ru $3d_{5/2}$ peak and that of the carrier (Al 2p, Si 2p

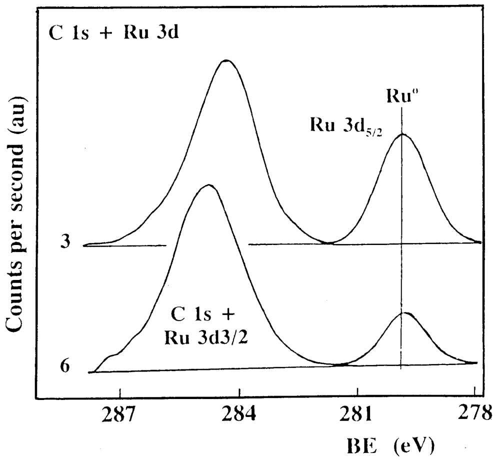

Figure 3. XP spectra for supported Ru catalysts. (a) Ru/TiO_2 L, (b) Ru/TiO_2 H. As C 1s and Ru $3d_{3/2}$ peaks overlap, only the $3d_{5/2}$ peak was considered for quantitative calculations.

and Ti 2p), together with the atomic intensity factors (18), Ru/M (M 0 Al, Si or Ti) atomic ratios have been calculated. These values are also summarised in table 2. For alumina- and silica-supported Ru catalysts, the Ru/M surface ratios are much lower than the bulk ratios. This finding does not mean a poor dispersion of Ru samples, which was accuracy measured by TEM and chemisorption. This can be explained considering that XPS is essentially a surface technique, therefore the Ru crystals located in the porous structure of the supports with higher surface area such as Al_2O_3 or SiO_2 are not detected. However, in the case of Ru/TiO_2 catalysts, the location of Ru particles in external position of the solid is more likely and consequently a higher extent of Ru can be detected.

Catalytic experiments were run at 373 K under differential conditions at atmospheric pressure. Under the used conditions no deactivation was detected after 4 h on stream and only trans- and cis-1,2-dimethylcyclohexane were detected. Previous studies on Ru catalysts have shown an important deactivation during the catalytic reaction [2,15,16]. To avoid catalyst deactivation in the present work a much higher H_2/*o*-xylene molar ratio was used. Table 3 compiles the activity results, expressed as turnover number, TON, as the number of *o*-xylene molecules converted per second and per active site. Additionally, the selectivity to the cis product is also given. Although the reaction has been considered as structure insensitive, marked differences can be noted. Comparing the catalytic behaviour of Ru on different supports, it appears that the more acidic supports (Al_2O_3 and TiO_2) display lower activity. On the other hand, an increase of the calcination temperature is paralleled with an increase in the activity. The interpretation of this behaviour can be made by assuming that carbonaceous species close to the metal particle alter the adsorption of the aromatic molecule. As this effect may be higher in catalysts with higher surface acidity, it should be expected that in the case of Ru/SiO_2 minor or no restriction occurs and consequently the TON should be higher. Similar results have been reported by Gomez et al. [16] who found significant differences in TON in *o*-xylene hydrogenation on different metal supported catalysts and by Boitiaux et al. [20] who reported changes in TON in factor of 10–15 in the hydrogenation of highly unsaturated hydrocarbons. With regard to the selectivity to the cis product the trends observed agree with those previously reported for Pt, Pd, Ru and Rh supported on Al_2O_3 and SiO_2 [16], the selectivity to cis being higher as particle size increases. This behaviour is independent of the support and implies that small particles are less effective to obtain the cis product, this being explained on the basis of the roll-over model proposed by Inoue et al. [21]. Thus, for the formation of the trans product a long stay of the olefin precursor on the surface is required. This may be achieved by reinforcing the interaction of this intermediate with the active site, which may occur on a highly dispersed metal. Therefore, as particle size increases (or dispersion decrease), the interaction between the olefin and the metal particle is lower making easier the formation of the cis product.

4. Conclusions

Metal dispersion of supported Ru catalysts is affected by the calcination temperature and by the nature of the

Table 2
Binding energies (eV) of core electrons and surface atomic ratios of reduced supported ruthenium catalysts

Catalyst[a]	Ru $3d_{5/2}$	M 2p	$(Ru/M)_s$[b]	$(Ru/M)_b$[b]
Ru/Al_2O_3 L	279.9	74.5	0.0028	0.0051
Ru/Al_2O_3 H	279.9	74.5	0.0023	0.0051
Ru/SiO_2 L	279.8	103.4	0.0014	0.0060
Ru/SiO_2 H	280.0	103.4	0.0012	0.0060
Ru/TiO_2 L	279.9	458.5	0.0142	0.0080
Ru/SiO_2 H	279.8	458.5	0.0154	0.0080

[a] L and H refer to low and high calcination temperature, respectively.

[b] s: surface; b: bulk

Table 3
Activity per site (TON) and selectivity for Ru/support in *o*-xylene hydrogenation at 373 K

Catalyst[a]	TON 10^3	Selectivity %cis
Ru/Al_2O_3 L	0.87	79.8
Ru/Al_2O_3 H	3.07	83.9
Ru/SiO_2 L	3.34	82.5
Ru/SiO_2 H	10.00	85.0
Ru/TiO_2 L	0.80	89.0
Ru/SiO_2 H	1.71	89.5

[a] L and H refer to low and high calcination temperature, respectively.

support. An increase of the metal dispersion is obtained as surface acidity increases. The calcination temperature also affects metal dispersion making easier the agglomeration of Ru particles as temperature increases. XPS results indicate that ruthenium species are mainly in a reduced state. Catalytic activity results show significant changes in TON depending on the type of support. Moreover, the selectivity to cis product increases slightly with the particles size.

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