Catalysis Letters Vol. 102, Nos. 1–2, July 2005 (© 2005)
DOI: 10.1007/s10562-005-5206-6

Effect of the support on the selective hydrogenation of benzene over ruthenium catalysts. 1. Al_2O_3 and SiO_2

Vanina Mazzieri[a], Nora Fígoli[a,*], Fernando-Coloma Pascual[b], and Pablo L'Argentière[a]

[a]*INCAPE, Instituto de Investigaciones en Catálisis y Petroquímica (FIQ-UNL, CONICET), Santiago del Estero, 2654 3000 Santa Fe, Argentina*
[b]*Servicios Técnicos de Investigación, Facultad de Ciencias, Universidad de Alicante, Apartado 99, E-03080 Alicante, Spain*

Received 12 May 2004; accepted 3 February 2005

The effect of the support on the liquid phase selective hydrogenation of benzene to cyclohexene over Ru catalysts was studied. Catalysts were prepared using $RuCl_3$ as precursor and characterized by hydrogen chemisorption, XPS and TPR. The reaction was carried out at 373 K and 2 MPa using a stirred tank reactor. It was found that the catalytic activity is not influenced by the Ru dispersion. More electron-deficient Ru species are present on Al_2O_3 than on SiO_2. The electronic state of Ru affects the selectivity to cyclohexene.

KEY WORDS: selective hydrogenation; effect of the support; Ru catalysts; cyclohexene.

1. Introduction

The selective hydrogenation of benzene to cyclohexene is a reaction of scientific and industrial interest because it provides an alternative route to obtain cyclohexene and the possibility to transform a toxic into a non-toxic compound having industrial interest. Cyclohexene is an intermediate in the production of cyclohexanol, raw material for the production of adipic acid and caprolactane as well as in the production of cyclohexanone and lysine because its reactive double bond.

Different catalysts have been proposed for the reaction: Ni, Pd, Pt, Ru, as well as bimetallic and multimetallic ones, appearing Ru as the most promising [1] for activity and selectivity. Ru can be used supported on several materials by the wet impregnation technique and using ruthenium chloride (III) [1,2] or ruthenium acetilacetonate [3] as precursors.

The reaction has been carried out either in the gas [1–4] or in the liquid phase [5–7] using massive or supported catalysts. Several supports have been proposed for the catalysts: ZrO_2 [8], Al_2O_3 [7,9], SiO_2 [1] or TiO_2 [10].

The Objective of this letter is to study the influence of two supports on the activity and selectivity of Ru catalysts during the selective hydrogenation of benzene to cyclohexene.

2. Experimental

2.1. Catalysts preparation

Catalysts were prepared using as supports γ-Al_2O_3 Ketjen CK 300 (cylinders of 1.5 mm diameter and 3 mm length, S_g 180 $m^2\,g^{-1}$ and 0.92 mL g^{-1} pore volume) and SiO_2 W.R. Grace G 57 (S_g 300 $m^2\,g^{-1}$ and 1 mL g^{-1} pore volume). The solids were impregnated by incipient wetness using acid solutions of ruthenium chloride III (Strem Chemicals) in adequate concentration such as to obtain solids containing 4 wt% ruthenium. The samples were dried at room temperature during 24 h and then at 378 k for 3 h, being finally reduced under hydrogen at 673 k for 6 h.

2.2. Catalysts characterization

The ruthenium content on both catalysts was determined spectrophotometrically using a methanol solution saturated with *N*,*N′*-diphenylthiourea (DPTU), based on the Ru capacity to form a complex with DPTU under certain conditions [11].

Ruthenium dispersion was measured by hydrogen chemisorption in a Micromeritics Accusorb 2100e equipment at 373 k following the method proposed by Taylor [12]. A H:Ru atomic ratio 1 was used for calculations.

Ruthenium reducibility was determined by temperature programmed reduction (TPR) using an Ohkura TP 2002S instrument equipped with a thermal conductivity detector. Samples were treated at 373 K for 30 min under an argon stream in order to eliminate humidity; the temperature was then reduced to room temperature and finally heated up to 975 K at 10 K min^{-1} in a gas stream of 5% hydrogen in argon.

XPS measurements were made using a VG-Microtech Multilab equipment, using a MgKα (hν: 1253.6 eV) radiation and an energy flow of 50 eV. The XPS system analysis pressure was kept at 5×10^{-7} Pa. Samples were reduced *in situ* following the same procedure as that for

---

* To whom correspondence should be addressed.
E-mail: nfigoli@fiqus.unl.edu.ar

1011-372X/05/0700–0079/0

catalyst preparation. Determinations of the superficial atomic ratios were made by comparing the areas under the peaks after background subtraction and corrections due to differences in escape depth and in photoionization cross sections [13].

2.3. Benzene hydrogenation procedures

The benzene selective hydrogenation was carried out in the liquid phase in a stirred tank reactor equipped with a magnetically driven stirrer. The stirrer has two blades in counter-rotation and was operated at 125 r.p.m. To determine the absence of external diffusional limitations, experiments were carried out at different stirring velocities in the range 100–250 r.p.m. The constancy of the activity and selectivity above 120 r.p.m. ensured that external diffusional limitations were absent at the rotary speed selected. To investigate the possibility of internal diffusional limitation, the catalyst particles were crushed up to 1/4 of their original size. No modifications in activity or selectivity were detected, thus neglecting the existence of internal diffusional limitations. The inner wall of the reactor was completely coated with PTFE in order to neglect the catalytic action of the steel of the reactor found by other authors [14]. The reaction was carried out for 2 h at 373 K and 2 MPa hydrogen pressure using a volume of liquid of 200 cm^3 and 4 g of catalyst. Reactants and products were analyzed by GC-FID and a capillary column CP WAX 52 CB.

3. Results and discussion

The two catalysts contain 4 wt% Ru. Table 1 presents their dispersion. Koopman *et al.* [15] obtained a similar dispersion value for a Ru/SiO$_2$ catalyst.

It was observed during catalyst preparation that the dark red solution of RuCl$_3$ became black after impregnation on alumina, meanwhile the color did not change when being impregnated on silica. Bossi *et al.* [16] also observed this difference and they considered that there exists a higher interaction of the ruthenium salt on alumina than on silica. A weak Ru–SiO$_2$ interaction was also found by Reyes *et al.* [17]. The interaction of the ruthenium species with the basic sites of alumina produces the precipitation of hydrolysis products, such as insoluble oxychlorides and hydroxides, on the external surface of the particles. These compounds inhibit the diffusion of Ru to the interior of the pores. Due to this reason, the dispersion of Ru on Al$_2$O$_3$ is lower than that on SiO$_2$. The activity of both catalyst is almost the same, as shown in table 1. Milone *et al.* [7] also did not find influence of dispersion on activity during benzene selective hydrogenation.

Table 1
Dispersion and activity (expressed as TOF) of Ru/Al$_2$O$_3$ and Ru/SiO$_2$

Catalyst	Dispersion (%)	TOF (s^{-1})
Ru/Al$_2$O$_3$	11	287
Ru/SiO$_2$	35	288

Figure 1 shows the TPR profiles of the two catalysts. Ru/Al$_2$O$_3$ presents a peak with maximum at 415 K which according to the literature [15,18] corresponds to the reduction of unsupported RuCl$_3$. There is also a smaller peak with maximum at 470 K, that can be assigned to the reduction of Ru$_x$O$_y$ [18]. Bentancourt *et al.* [18] and Bossi *et al.* [16] found that RuCl$_3$ can be partially oxidized at the surface after being exposed to the atmosphere at room temperature, justifying the presence of Ru$_x$O$_y$ species in a catalyst that was not calcined. The profile of Ru/SiO$_2$ also presents the RuCl$_3$ reduction peak at 415 K and another at 472 K, which can be assigned to the reduction of Ru oxides.

Figures 2 and 3 present the Ru 3d XPS spectra for Ru/Al$_2$O$_3$ and for Ru/SiO$_2$, respectively. Peaks 1 and 2 correspond to the Ru 3d$_{5/2}$ and Ru 3d$_{3/2}$ signals, respectively. The peaks under 1 and 2 are the corresponding deconvolution peaks. In both cases, the Ru 3d$_{5/2}$ and Ru 3d$_{3/2}$ peaks appear separated approximately 4.2 eV, in accordance with literature values [19,20]. The Ru 3d$_{5/2}$ position was followed. The binding energy reference is difficult in the case of Ru because the Ru 3d$_{3/2}$ peak appears at the same value than the C 1s one. For this reason, the Al 2p peak at 74.5 eV and the Si 2p peak at 103.5 eV were taken as internal standards for Ru/Al$_2$O$_3$ and Ru/SiO$_2$, respectively. The C 1s line was omitted in figures 2 and 3 in order to improve the presentation.

In the case of Ru/Al$_2$O$_3$ (figure 2) two Ru species were detected after a careful deconvolution: Ru° at

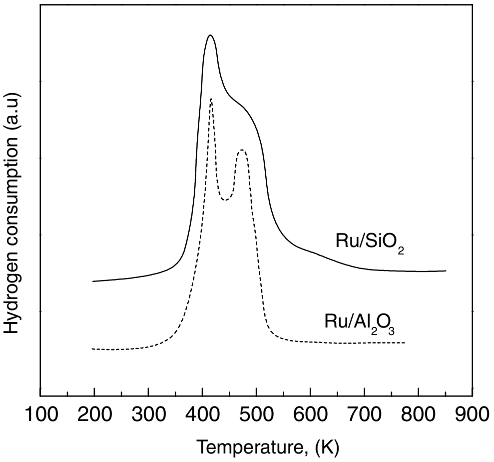

Figure 1. TPR profiles of Ru/Al$_2$O$_3$ and Ru/SiO$_2$. Heating rate: 10 K min^{-1} in a 5% hydrogen in argon stream.

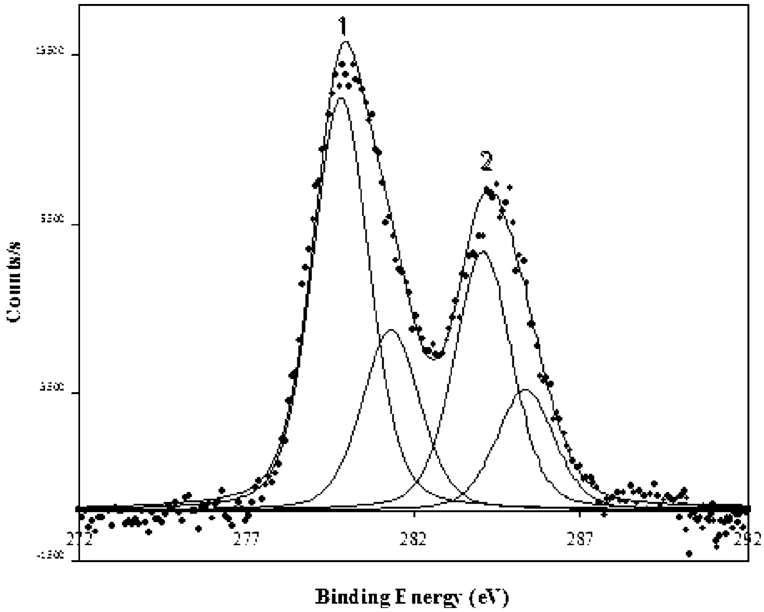

Figure 2. Ru 3d XPS spectra of Ru/Al_2O_3. Peaks 1 and 2 correspond to the Ru $3d_{5/2}$ and Ru $3d_{3/2}$ signals, respectively. The peaks under 1 and 2 are the corresponding deconvolution peaks.

279.9 eV and another corresponding to electron-deficient Ru species ($Ru^{\delta+}$) at 281.4 eV.

The XPS spectrum of Ru SiO_2 (figure 3) also shows the presence of two Ru species: Ru° at 279.6 eV and $Ru^{\delta+}$ at 282.3 eV. It can be noted that the peak corresponding to $Ru^{\delta+}$ is much smaller than the corresponding one in Ru/Al_2O_3, thus indicating that ruthenium species are more easily reduced on Ru/SiO_2.

Table 2 presents the $Ru°/Ru^{\delta+}$and Cl/Al surface atomic ratios obtained from XPS and the selectivity to cyclohexene (S_{CHE}) at 5 min of operation during the benzene selective hydrogenation. Selectivity, calculated from gas chromatography data, is defined as:

$$S_{\mathrm{CHE}} = \frac{(A_{\mathrm{CHE}} \times F_{\mathrm{CHE}})(A_{\mathrm{BZ}} \times F_{\mathrm{BZ}} + A_{\mathrm{CHE}} \times F_{\mathrm{CHE}} + A_{\mathrm{CHA}} \times F_{\mathrm{CHA}})}{A_{\mathrm{CHE}} \times F_{\mathrm{CHE}} + A_{\mathrm{CHA}} \times F_{\mathrm{CHA}}} \times 100$$

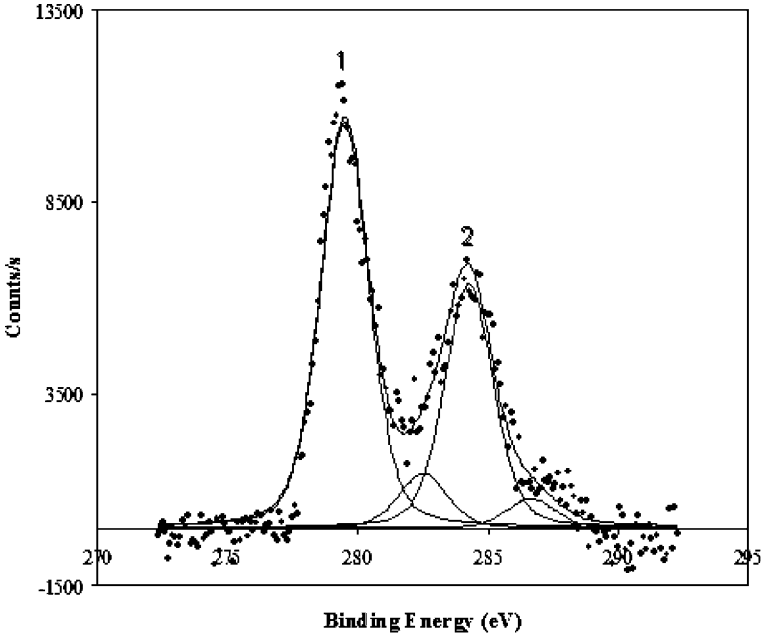

Figure 3. Ru 3d XPS spectra of Ru/SiO_2. Peaks 1 and 2 correspond to the Ru $3d_{5/2}$ and Ru $3d_{3/2}$ signals, respectively. The peaks under 1 and 2 are the corresponding deconvolution peaks.

where: A_{CHE}, A_{CHA}, A_{BZ}: Area of the cyclohexene, cyclohexane and benzene peaks, respectively. F_{CHE}, F_{CHA}, F_{BZ}: Chromatographic response factors for cyclohexene, cyclohexane and benzene, respectively.

Chlorine was not detected by XPS on Ru/SiO_2. It is known that alumina adsorbs more chlorine than silica [21]. Bossi *et al.* [16], using $RuCl_3$ as precursor, also did not detect chlorine on a similar catalyst and they considered that chlorine is eliminated during the reduction treatment because of the low interaction of the precursor with the support. A higher selectivity is observed when chlorine is present than when it is not. The highest selectivity also corresponds to the catalyst having the lowest $Ru^{\circ}/Ru^{\delta+}$ ratio. This result can be assigned to the fact that the $Ru^{\delta+}$ sites have a lower hydrogenation capacity than Ru° ones, more easily allowing the desorption of cyclohexene before it is further hydrogenated to cyclohexane [22].

4. Conclusions

A higher interaction of $RuCl_3$ with alumina than with silica was observed. The difference can be attributed to the presence of basic sites in alumina, that induce the precipitation of hydrolysis products, such as insoluble oxychlorides and hydroxides on the external surface of the pellets, thus decreasing dispersion.

The catalytic activity is not influenced by the Ru dispersion. Ru appears more electron-deficient when supported on Al_2O_3 than on SiO_2. The electronic state of Ru affects the selectivity to cyclohexene. Cyclohexene is more weakly adsorbed over electron-deficient Ru species and it can be more easily desorbed, reducing the possibility of its further hydrogenation to cyclohexane, thus increasing selectivity.

Table 2
Surface atomic ratios from XPS and selectivity to cyclohexene (S_{CHE}) at 5 min of operation

Catalyst	$Ru^{\circ}/Ru^{\delta+}$ (%at/%at)	Cl/Al (%at/%at)	S_{CHE}(%)
Ru/Al_2O_3	1.50	0.40	33
Ru/SiO_2	3.10	0	23

Acknowledgments

The experimental assistance of C. Mázzaro and the financial assistance of CAI + D (UNL), CONICET and ANPCyT are greatly acknowledged.

References

[1] M. Schoenmaker-Stolk, J. Verwijs and J. Scholten, Appl. Catal. 30 (1987) 339.
[2] M. Reinikamen, M. Nimela, N. Kakuta and S. Sichomen, Appl. Catal. A 174 (1998) 61.
[3] E. Dietzsch, P. Claus and D. Honicke, Topics Catal. 10 (2000) 99.
[4] P. Vander Steen and Scholten, J. Appl. Catal. 58 (1990) 291.
[5] J. Struik, R. Moene, T. Vander Kamp and J. Scholten, Appl. Catal. A 89 (1992) 77.
[6] H. Nagahara, M. Ono, M. Konishi and Y. Fukuoka, Appl. Surf. Sci. 121(122) (1992) 448.
[7] C. Milone, G. Neri, A. Donato, M. Musolino and L. Mercandante, J. Catal. 159 (1996) 253.
[8] F. Pinna, M. Scarpa, G. Strukul, E. Guglielminott, F. Boccuzzi and M. Manzoli, J. Catal. 192 (2000) 158.
[9] M. Johnson and G. Nowack, J. Catal. 38 (1975) 518.
[10] J.W. da-Silva and A.J.G. Cobo, Appl. Catal. A 252 (2003) 9.
[11] S. Knight, R. Parks and S. Leidt, Anal. Chem. 29 (1957) 571.
[12] K. Taylor, J. Catal. 38 (1975) 299.
[13] R. Borade, A. Sayari and S. Kaliaguine, J. Phys. Chem. 94 (1990) 5989.
[14] S. Hu and Y. Chen, J. Chin. Chem. Engr. 29 (1998) 387.
[15] P.G.J. Koopman, P.G.J. Kieboom and H. Bekkum, J. Catal. 69 (1981) 172.
[16] A. Bossi, F. Garbassi, A. Orlandi, G. Pettrini and L. Zanderighi, Stud. Surf. Sci. Catal. 3 (1979) 405.
[17] P. Reyes, M.E. Koning, G. Pecchi, I. Concha, M.L. Granados and J.L.G. Fierro, Catal. Lett. 46 (1997) 71.
[18] Betancourt P., A. Rives, R. Hubaut, C.E. Scott and J. Goldwaser, Appl. Catal. A 170 (1998) 307.
[19] D. Briggs and M.P. Search, *Practical Surface Analysis*, 2nd Ed. (J. Willey and Sons, 1993).
[20] C.D. Wagner, W.M. Riggs, L.E. Davis and J.F. Moulder, in *Handbook of X-ray Photoelectron Spectroscopy*, G.E. Muilenberg (ed.) (Perkin Elmer Corporation, Eden Prairie, Minessota, USA, 1978).
[21] H. Noller and J.M. Parera, J. Res. Inst. Catal. Hokkaido Univ. 29 (1981) 95.
[22] V. Mazzieri, F. Coloma-Pascual, A. Arcoya, P.C. L'Argentière and N.S. Fígoli, Appl. Surf. Sci. 210 (2003) 222.