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A study about the effect of the temperature of hydrogen treatment on the properties of Ru/Al_2O_3 and Ru/C and their catalytic behavior during 1-heptyne semi-hydrogenation

Cecilia R. Lederhos,[a] Pablo C. L'Argentière,[a] Fernando Coloma-Pascual,[b] and Nora S. Fígoli[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*

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The 1-heptyne selective hydrogenation carried out at 150 kPa, and at 283 and 303 K using Ru/Al_2O_3 and Ru/C as catalysts, was studied. Catalysts were prepared by the incipient wetness impregnation technique using $RuCl_3$ as precursor. Ru/Al_2O_3 was treated in hydrogen at 373 or 573 K and Ru/C only at the last temperature. Catalysts were characterized by hydrogen chemisorption, TPR and XPS. Ru dispersion after treatment in hydrogen at the highest temperature is similar for both catalysts. Ru is present as Ru^0 in Ru/C, while Ru^0 and Ru electron-deficient species are present on the catalysts surface after hydrogen treatment at the two temperatures using Al_2O_3 as support. The best catalytic behavior was observed for the highest temperature of hydrogen treatment and for 303 K reaction temperature. As a consequence of a shape selectivity effect of the C support, the best conversion is obtained with the alumina supported catalyst.

KEY WORDS: ruthenium; selective hydrogenation; 1-heptyne.

1. Introduction

The potential and utility of alkynes in fine chemicals' manufacture is largely attributed to the selective hydrogenation of the triple bond, opening routes to alkenes.

The partial hydrogenation of acetylenes using homogeneous and heterogeneous catalysts has been widely studied in the last years due to its academic and industrial interest [1]. The transformation of the alkyne to the corresponding alkene is possible because the alkyne is more strongly bond to the metal than the alkene, thus competing for the active sites and limiting the re-adsorption of the alkene or displacing it. A lot of products obtained from these reactions are useful in the synthesis of biological active compounds [2]. One of the most studied systems is the Lindlar catalyst ($Pd/CaCO_3$ modified with $Pb(OAc)_2$), that appeared in 1952 [3]. Other catalysts, mono and bimetallic, as well as several transition metal complexes have been also proposed [4–7].

A major part of the efforts have been devoted to the semi hydrogenation of short chain alkynes such as ethyne [8], with few works related to longer chain alkynes.

Activated carbon is widely used as catalyst support in industrial reactions, especially in hydrogenation and hydro-dechlorination, mainly because of its inertness in liquid reaction media, low cost, the possibility of developing a high surface area and modifying the surface chemistry, besides the easy recovery of the metal phase in the spent catalyst and low deactivation, [9, 10]. It has been published [11] that a reducing treatment with H_2 can strongly modify the properties of an activated carbon.

In previous papers we have studied several aspects related to the use Pd over alumina or carbon as catalysts for the selective hydrogenation of 1-heptyne to 1-heptene [12]. We have also studied Ru supported catalysts [13].

The objective of this paper is to analyze the catalytic behavior of a Ru/C catalyst and to compare the obtained results with those found with a Ru/Al_2O_3 catalyst. The semi-hydrogenation of 1-heptyne, a relatively high molecular weight alkyne presenting a terminal triple bond, was used as test reaction.

2. Experimental

2.1. Catalyst preparation

Al_2O_3 Ketjen CK 300 and Norit GF-45 pelletized carbon (cylinders of 1.5 mm diameter) were used as supports. Both were impregnated by the incipient wetness technique using $RuCl_3$-HCl solutions (pH = 1) in concentrations such as to obtain about 5% Ru on the final catalysts. The samples were dried overnight at 373 K. Ru/Al_2O_3 (from here after named Ru/Al) was then calcined at 773 K.

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

Ru/Al was treated under a hydrogen stream at 373 or 573 K to study the influence of these temperatures (T_{H2}) on the catalytic behavior. Ru/C was only treated at 573 K, the best temperature found for the catalytic behavior of Ru/Al.

2.2. Catalyst characterization

Physical adsorption of gases (N_2 and CO_2 at 273 K) and mercury porosimetry were used to analyze the porous texture of the two supports.

Ruthenium dispersion was measured by hydrogen chemisorption in a Micromeritics Accusorb 2100e equipment at 373 K following the method proposed by Taylor [14]. 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 the sample was heated up to 723 K at 10 K min^{-1} in a gas stream of 5% hydrogen in argon.

The electronic state of superficial ruthenium and chlorine and their atomic ratios were studied by X-ray Photoelectron Spectroscopy (XPS) following the Ru 3d and Cl 2p peaks position, respectively. Measurements were made using a VG-Microtech Multilab equipment, a MgK_α ($h\nu$: 1253.6 eV) radiation and a pass energy of 50 eV. The XPS system analysis pressure was kept at 5×10^{-7} Pa. Samples were treated in H_2 *in situ* following the same procedure as that for catalyst preparation. The areas of the peaks were estimated by calculating the integral of each peak after subtracting a Shirley background and fitting the experimental peak to a combination of Lorentzian/Gaussian lines of 30–70% proportions. The binding energy (BE) reference is difficult in the case of ruthenium because the Ru 3d peaks appear at the same region than the C 1s peak. There are also discrepancies in the BE reported in the literature for ruthenium compounds. The Al 2p peak at 74.5 eV for Ru/Al_2O_3 and the C1s signal at 285.0 eV for Ru/C were taken as internal standards. A careful deconvolution of the spectra was made. 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 [15].

2.3. Catalyst evaluation

The 1-heptyne selective hydrogenation was performed in a stainless steel stirred tank reactor equipped with a magnetically driven stirrer. The stirrer has two blades in counter-rotation and was operated at 750 rpm. 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 [16]. The reaction was carried out at 283 and 303 K using a volume of liquid of 100 ml and a mass of catalyst of 1 g. The hydrogen pressure in all the experiments was 150 kPa; it is well established in the literature [3] that high alkene selectivities require low hydrogen pressures. A 5% (v/v) solution of 1-heptyne (Fluka, Cat. No. 51950) in toluene (Merck, Cat. No. TX0735-44) was used as feed.

The possibility of diffusional limitations during the catalytic tests was investigated following procedures previously described [17]. Experiments were carried out at different stirring velocities in the 180–1400 rpm range. The constancy of the activity and selectivity above 500 rpm ensured that external diffusional limitations were absent at the rotary speed selected (750 rpm). To ensure that the catalytic results were not influenced by intra-particle mass transfer limitations, the catalyst particles were crushed up to 1/4 of their original size. Then, several runs using the crushed catalysts were made. In every case, the conversion and selectivity values obtained were the same than those corresponding to the catalyst that was not crushed. Hence, it can be accepted that internal diffusional limitations were absent in the operational conditions of this work.

Reactant and products were analyzed by Gas Chromatography using a Flame Ionization Detector and a Chrompack CP WAX 52 CB capillary column.

3. Results and discussion

Table 1 presents the Brunauer-Emmett-Teller (BET) surface area and the super-micro, micro, meso and macro pores volume, S_{BET}, V_{sm}, V_{micro}, V_{meso} and V_{macro}, respectively [18]. It can be observed that the activated carbon has almost the same amounts of the four type of pores. γ-Al_2O_3 is a mesoporous solid having a poor contribution of super-micro, micro and macropores.

Ru dispersion is 11% in Ru/Al and 14% in Ru/C after the hydrogen treatment at 573 K.

The TPR profile of Ru/Al (figure 1) [19] shows a peak with maximum at about 415 K, which can be attributed to $RuCl_3$ reduction [20]. This indicates that chlorine was not completely eliminated after calcinations at 773 K. A shoulder at 425 K is also observed, which according to the literature [21] corresponds to ruthenium oxychloride [21]. Another peak appears at about 470 K, which can be related to Ru oxides reduction; Koopman *et al.* [20] assigned a peak between 450 and 478 K to the reduction of RuO_2.

Figure 2 presents the TPR profile of Ru/C. Two peaks can be noted at 408 and 460 K. These peaks have been assigned to the reduction of Ru(III) species to Ru^0 and to the decomposition of the support surface oxygen functional groups [22, 23]. As the profile of our C

Table 1
BET surface area and pore volumes of the supports

Sample	S_{BET} ($m^2\ g^{-1}$)	V_{sm} (ml g^{-1})	V_{micro} (ml g^{-1})	V_{meso} (ml g^{-1})	V_{macro} (ml g^{-1})
GF-45	1718	0.498	0.345	0.449	0.400
γ-Al_2O_3	180	0.030	0.048	0.487	0.094

support, also shown in figure 2, does not show peaks up to 700 K we can only assigned those peaks to the reduction of Ru(III) species. By analogy with Ru/Al, the peaks could be assigned to the reduction of $RuCl_3$ and Ru oxides. It has been reported that no hydrogen consumption could be found during TPR of carbons up to temperatures between 923 and 1223 K [24].

Figure 3 presents the XPS spectrum of Ru in Ru/Al treated in hydrogen at 573 K showing the peaks corresponding to the Ru $3d_{5/2}$ and Ru $3d_{3/2}$ signals. The peaks appearing at 285.1 and 286.4 eV correspond to carbon. The points are the experimental data and the curves under them are the corresponding deconvolution peaks. The Ru $3d_{5/2}$ and Ru $3d_{3/2}$ peaks appear separated by approximately 4.2 eV, in accordance with literature values [25]. The spectrum of the catalyst treated in hydrogen at 373 K has a similar shape.

Table 2 presents the Ru $3d_{5/2}$ XPS results after deconvolution. It can be seen that the hydrogen treatment temperature influences the electronic state of ruthenium. According to the literature [26], the binding energy for the Ru^0 $3d_{5/2}$ contribution is 279.9 eV. Different ruthenium species for Ru/Al treated in hydrogen were detected at both temperatures (373 and 573 K). This suggests the presence of different amounts of ruthenium electron-deficient species (Ru^{n+}) at the surface. The XPS results also show the presence of chlorine in Ru/Al treated in hydrogen at both temperatures (373 and 573 K) as the Cl $2p_{3/2}$ peak at 199.0 eV, corresponding to a chloride, was detected. The results displayed in

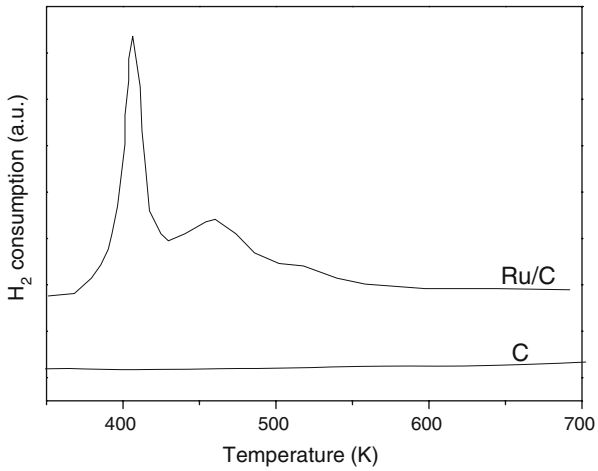

Figure 2. TPR profile of Ru/C and of the carbon support (C).

table 2 show that ruthenium in Ru/Al is more electron-deficient when the catalyst was treated in hydrogen at the lowest temperature (373 K). At T_{H2} = 373 K two peaks, corresponding to ruthenium electron-deficient species, can be detected after deconvolution: one at 280.9 eV and the other at 283.0 eV. According to the literature [19] the peak at 280.9 eV could be assigned to ruthenium oxychloride; however, as the Cl $2p_{3/2}$ signal appears 199.0 eV we can only suggest the presence of Ru-chlorine-containing species. The peak at 283.0 eV can be assigned to ruthenium in RuO_3 [26]. At T_{H2} = 573 K, Ru^0 was detected at 279.6 eV; another peak at 280.9 eV was observed, which could be assigned to ruthenium oxychloride [19]. Other authors [20] have reported that chlorine modifies the electronic state of Ru, favoring the formation of electron deficient Ru species. The assignment of the Ru^{n+} line is not easy because of the small difference between the ruthenium binding energy in oxides, oxychlorides and chlorides and also due to discrepancies in the literature [25]. The Cl/Al atomic ratio changes when varying the temperature of hydrogen treatment, as also shown in table 2. A lower

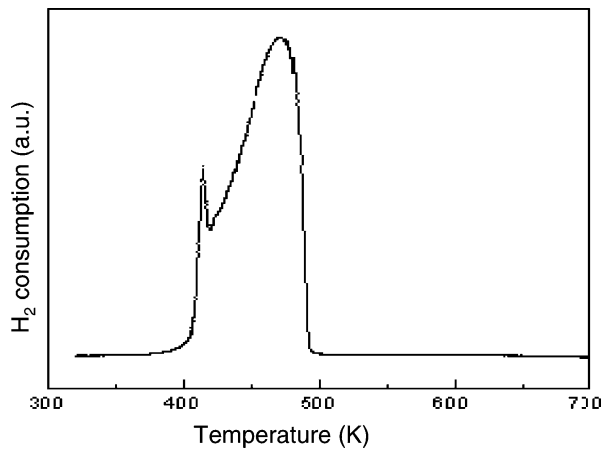

Figure 1. TPR profile of Ru/Al_2O_3.

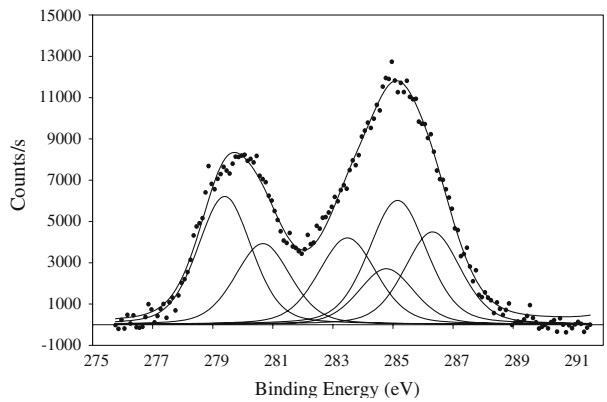

Figure 3. Ruthenium XPS spectrum of Ru/Al_2O_3 treated in hydrogen at 573 K.

Table 2
XPS results for Ru/Al_2O_3 and Ru/C

Catalyst	T_{H2}(K)	Ru $3d_{5/2}$ (eV)		Cl $2p_{3/2}$ (eV)		Ru/S (% at/% at)	Ru^0/Ru^{n+} (% at/% at)	Cl/S (% at/% at)	N/C (% at/% at)
		BE	FWHM	BE	FWHM				
Ru/Al	373	280.9	2.07	199.0	2.30	0.080	0	0.13	0
		283.0	2.16						
	573	279.6	2.12	199.0	2.05	0.050	1.6	0.07	0
		280.9	2.18						
Ru/C	573	280.0	1.60	199.1	1.96	0.003	–	0.09	0.006

S = Al/C.

Cl/Al ratio can be seen at the highest temperature. Nevertheless it must be taken into account that under these treatments, chlorine was not completely eliminated. Other authors [16] also found that it is very difficult to eliminate chlorine from catalysts prepared from $RuCl_3$.

The XPS spectrum of the C supported catalyst treated in hydrogen at 573 K is presented in figure 4. The peaks at 284.4 eV and those at 286.0 eV and 288.8 eV have been assigned to C 1s signals [24]. The first one corresponds to graphitic carbon, the second one to C=C, CNH_2, COH and COC signals and the last one to C=O. The peaks at 280.0 and 284.1 eV correspond to the Ru $3d_{5/2}$ and Ru $3d_{3/2}$ signals, respectively. The Ru binding energies correspond to Ru^0 [27]. The difference in the Ru 3d binding energies in Ru/C with those corresponding to Ru/Al treated in H_2 at the same temperature can be due to the fact that carbon is a good reductor; C is capable to completely reduce Pt even at room temperature [28]. The surface of carbons is usually complex, presenting several groups, specially oxygenated, like phenols, carbonyls, carboxyles, etc. and also nitrogen-containing groups. These groups can be modified during thermal treatments, either in the presence of hydrogen or not. Although no Ru-chlorine-containing species were detected in Ru/C, chlorine is present because of the carbon adsorption capacity. Table 2 presents the Ru, N and Cl/C surface atomic ratios.

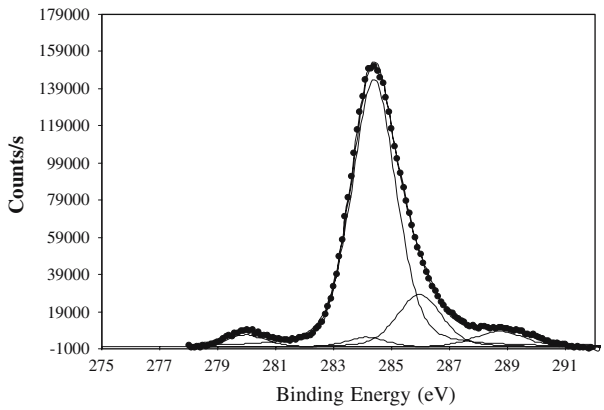

Figure 4. Ruthenium XPS spectrum of Ru/C treated in hydrogen at 573 K.

Comparing the total conversion and the selectivity to 1-heptene as a function of time for Ru/Al treated in hydrogen at 373 and 573 K and run at 303 K it was found that the total conversion, as well as the selectivity are higher at the highest temperature of hydrogen treatment. At T_{H2} = 573 K the total conversion measured at the final operational time (240 min) was 73% with a selectivity to 1-heptene equal to 98%. At T_{H2} = 373 K the total conversion measured at the same operational time was 27% with a selectivity to 1-heptene equal to 84%. The higher conversion obtained at the highest temperature of H_2 treatment may be attributed to the fact that ruthenium is more electron-deficient after H_2 treatment at 373 K than at 573 K. The Ru^{n+} species, having less available electrons, could not interact so strongly with the alkyne molecules as Ru^0 does, thus decreasing activity.

The alkyne is much more strongly adsorbed than the alkene and there exists a competitive adsorption between both species. Due to the preferential adsorption of the alkyne, the alkene, once formed, is easily desorbed; hence its further over hydrogenation is decreased. Because of the strongest alkyne adsorption at 573 K, the selectivity of this catalyst is higher.

Figure 5 compares the total conversion and selectivity to 1-heptene for Ru/Al treated in H_2 at 573 K and run at 283 and 303 K. The highest values correspond to the catalyst run at the highest temperature. The highest selectivity for the catalyst run at 303 K can be attributed to a decrease in the strength of adsorption of the unsaturated molecules which favors the alkene desorption before the undesired complete hydrogenation reaction occurs.

As the best catalytic results for Ru/Al were obtained after hydrogen treatment at 573 K, this temperature was the only one used for Ru/C. Figure 6 presents the results of Ru/C evaluation during reaction at 283 and 303 K. The highest conversion is obtained when working at the highest reaction temperature. Selectivity to 1-heptene at the end of the experience (240 min) is almost the same at the two reaction temperatures.

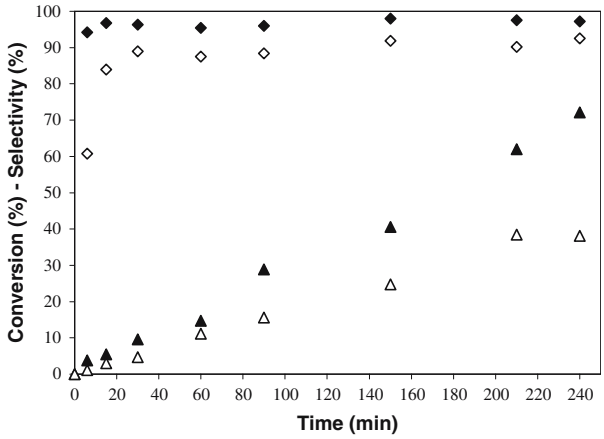

Figure 5. Total conversion (▲) and selectivity to 1-heptene (◆) for Ru/Al_2O_3 treated in hydrogen at 573 K and run at two temperatures: full signs; 303 K; empty signs 283 K.

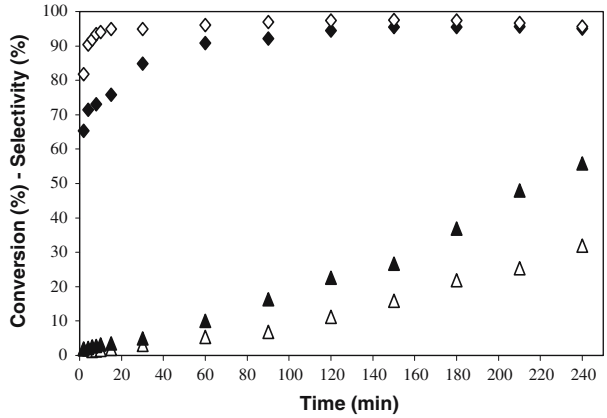

Figure 6. Total conversion (▲) and selectivity to 1-heptene (◆) as a function of time for Ru/C treated in hydrogen at 573 K and run at two temperatures: full signs; 303 K; empty signs 283 K.

Figure 7 compares the behavior of the two catalysts treated in H_2 at 573 K and run at 303 K, the most convenient temperature found for Ru/Al. A better yield (measured as the conversion to 1-heptene) was found for the alumina supported catalyst. The selectivity is excellent for both catalysts, as can be seen comparing the data presented in figures 5 and 6.

Although the results mentioned in previous paragraphs draw attention on the relationship existing between the surface electronic state of ruthenium and activity and selectivity when alumina is used as support, comparing the two quite different supports it appears that the electronic state of ruthenium is not the only property that determines the catalytic behavior. The best behavior using Ru/Al is when more Ru^0 is present. Nevertheless Ru/C, where all Ru is present as Ru^0, presents a lower conversion. The difference could be assigned to a higher Ru accessibility in Ru/Al.

The influence of the support on the physicochemical properties and, therefore, on the catalytic behavior of metals is well established in the literature [29]. Specific support properties such as chemical nature, texture, pore structure, surface state, etc., can indeed modify the morphology and/or localization of the metal particles, electronic structure of the surface metal atoms, adsorption-desorption equilibrium of reactants, etc., in a different way whereby different values of conversion and selectivity can arise. Thus, as our results suggest, the catalytic behavior of ruthenium-supported catalysts is a complex property of the whole catalyst and cannot be related to a single parameter.

According to these considerations, the differences in selectivity observed for Ru/Al and not for Ru/C at the two reaction temperatures (see figures 5 and 6) can be assigned to differences in adsorption-desorption equilibrium between the double and triple bond compounds. We have found a higher conversion using Ru/Al than using Ru/C. As previously mentioned, the difference can

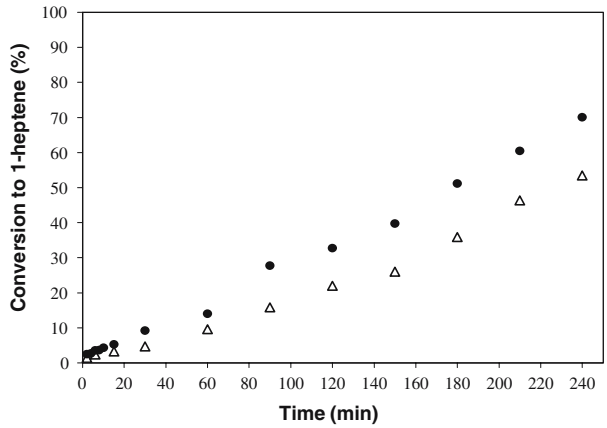

Figure 7. Conversion to 1-heptene as a function of time for Ru/Al_2O_3 (•) and Ru/C (Δ) treated in hydrogen at 573 K and run at 303 K.

not be ascribed to electronic effects. We might suggest that the lower conversion found in Ru/C is due to the presence in the carbon support of micro and supermicro pores where the reacting molecules can not enter. Moreover, 1-heptene that can be generated in bigger pores also could not enter to the narrower ones; then, its transformation in n-heptane is forbidden.

4. Conclusions

Chlorine is not completely eliminated from Ru/Al_2O_3 prepared using $RuCl_3$ as a precursor, even after treatment in H_2 at 573 K. Treating the catalyst at this temperature strongly decreases the chlorine content. As a consequence of the different T_{H2} treatments after impregnation, Ru species with different electronic states appear in the catalyst: Ru^0 and oxychloride and ruthenium oxides. The catalytic activity and selectivity during 1-heptyne selective hydrogenation are related to the different T_{H2} and reaction temperature. An increase in

catalyst selectivity as well as in the activity have been obtained treating the catalyst in hydrogen at 573 K. Under these conditions, the catalyst contains different Ru species and a low content of chlorine.

Ruthenium is completed reduced in Ru/C after hydrogen treatment at 573 K. The differences observed between the two supports can be ascribed to their porosity, although the influence of characteristic superficial functional groups cannot be neglected. More work is necessary to reach a better understanding about the effect of surface chemistry and porosity of the carbon on the conversion and selectivity.

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