A study about the effect of the temperature of hydrogen treatment on the properties of Ru/Al$_2$O$_3$ and Ru/C and their catalytic behavior during 1-heptyne semi-hydrogenation

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The 1-heptyne selective hydrogenation carried out at 150 kPa, and at 283 and 303 K using Ru/Al$_2$O$_3$ and Ru/C as catalysts, was studied. Catalysts were prepared by the incipient wetness impregnation technique using RuCl$_3$ as precursor. Ru/Al$_2$O$_3$ 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$_2$O$_3$ 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$_2$O$_3$ 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$_2$O$_3$ 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$_2$O$_3$ (from here after named Ru/Al) was then calcined at 773 K.

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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 (hv: 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