Influence of noble metals (Pd, Pt) on the performance of Ru/Al$_2$O$_3$ based catalysts for toluene hydrogenation in liquid phase

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ABSTRACT

Catalytic hydrogenation of aromatic compounds is of great interest due to environmental aspects and the wide range of industrial processes involving such reaction. In this context, the present work aims to study the influence of Pd or Pt addition on the performance of Ru/Al$_2$O$_3$ based catalysts for toluene hydrogenation in liquid phase. For this, catalysts were prepared by wet impregnation from chlorinated precursors and reduced in liquid phase by formaldehyde (H$_2$CO). After impregnation, a part of the catalysts were activated ex situ at 573 K or in situ at 523 K under H$_2$. The studied solids were characterized by N$_2$ physisorption, SEM + EDX, TEM, XPS and TPR techniques. Catalytic tests were conducted in a slurry Parr reactor at 373 K under constant H$_2$ pressure of 5 MPa. Results show that solids reduction by H$_2$CO led to metallic species, while the activation treatments form oxides and decrease the catalytic activity. The initial reaction rate of non-activated monometallic catalysts follows the order: Ru/Al$_2$O$_3 \gg$ Pd/Al$_2$O$_3 \approx$ Pt/Al$_2$O$_3$. A synergistic effect on the activity of Ru/Al$_2$O$_3$ based catalysts is induced by the Pt addition.

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1. Introduction

Catalytic hydrogenation of aromatic compounds is of great interest due to environmental aspects and the wide range of industrial processes involving these reactions. It is an important route to obtain several chemical intermediates as well as to eliminate toxic aromatic compounds present in fuels [1,2]. Indeed, the hydrodearomatization is one of the most important processes in a petroleum refinery [3], having great influence on the final quality of diesel [4,5].

Most of the work found in the specialized literature focuses on the hydrogenation of benzene, notably aiming to obtain the partially hydrogenated product, cyclohexene [6–11]. In a recent paper, Foppa and Dupont [12] presented a thorough review regarding the main advances achieved for the partial hydrogenation of benzene in the last four decades.

However, recent efforts have been made to reduce the use of benzene in researches, since this compound is known to be highly carcinogenic. Hence, toluene has been employed as a substitute of benzene due to its chemical similarities and lower toxicity [13–15]. In addition, the toluene hydrogenation is often used as probe reaction to test the performance of metal catalysts since it is considered insensitive with respect to surface structures [16].

Many catalysts have been tested on the hydrogenation of aromatics, amongst which noble metals such as Pd, Pt and Ru, usually supported on Al$_2$O$_3$, have shown higher activities and stability [3,13]. It is noteworthy that Ru based catalysts have been increasingly employed, since higher yields of the intermediate product are obtained in presence of this metal [11,17–19].

Although the incipient impregnation is a common method to prepare supported catalysts [12,20], the wet impregnation has been acknowledged as a method that leads to solids with higher metallic dispersion and consequently higher activity [8,11,21–23]. The characteristics of the solids prepared by wet impregnation may be affected by variables present in this method [24], such as the suspension temperature and pH. However, the reducing procedure appears to induce effects that are more important since it involves the formation of the active phase of these solids [23].

In wet impregnation, the catalyst reduction procedure is usually carried out in liquid-phase employing reducing agents such as sodium borohydride (NaBH$_4$) [25], hydrazine (N$_2$H$_4$) [24] or formaldehyde (H$_2$CO) [11], under mild conditions. However, high

temperature reduction may also be conducted ex situ under H_2 flow [8,26,27].

Suppino et al. [11] studied the influence of the reduction method on the performance of Ru/Al_2O_3 catalysts prepared by wet impregnation for partial hydrogenation of benzene in liquid phase. Catalyst reduction by H_2CO led to a higher activity and selectivity of cyclohexene than the reduction ex situ under H_2 flow.

Groppo et al. [28] prepared Pd/Al_2O_3 catalysts by wet impregnation using the following reducing agents: sodium formate (HCO_2Na), $NaBH_4$ and H_2. According to the authors, the reducing agents decrease the metal dispersion, which was related to a possible sintering of the Pd. The occurrence of Pd sintering was also suggested by other authors [29,30], according to whom the metallic particles may experience some degree of mobility even in relatively low temperatures, especially when the catalyst reduction is carried out under H_2 atmosphere.

The use of bimetallic catalysts for hydrogenation reactions has been subject of many studies. Bimetallic catalysts often present superior properties than the respective monometallic solids, such as higher tolerance against sulfur poisoning and thermal stability [19,31–34].

Romanenko et al. [31] studied the addition of Ru to Pd/C catalysts in order to prevent the Pd sintering by the solid reduction under H_2 flow. According to the authors, the Ru addition led to an increase of the metallic dispersion on the catalyst. Moreover, the bimetallic Pd-Ru/C catalyst has proven to be more resistant to sintering. Such effect was related to the increase of the potential energy barrier for the mobility of Pd species promoted by the presence of Ru.

More recently, Chen et al. [35] evaluated the effects of the addition of Pd to Ru based catalysts prepared by the wet co-impregnation method and reduced by $NaBH_4$. According to the authors, bimetallic Ru-Pd catalysts presented superior catalytic activity over monometallic ones as well as smaller nanoparticle size with narrower distribution.

In this context, the present work aims to study the influence of Pd or Pt addition on the performance of Ru/Al_2O_3 based catalysts for toluene hydrogenation in liquid phase.

2. Experimental

2.1. Catalysts preparations

Alumina (Al_2O_3) of commercial grade was used as received as catalysts support. According to the manufacturer (Alfa Aesar), the solid (99.9 wt%) is in the gamma phase, with an average particle diameter of 40 μm.

Mono and bimetallic catalysts were prepared from the precursors $RuCl_3 \cdot xH_2O$, $PdCl_2$ (Aldrich Chemical Co.) and $PtCl_2$ (Santa Cruz Biotechnology), all with 99.9 wt% of purity, in order to obtain a total metal mass fraction of 5 wt%.

Wet impregnation was used for the preparation of monometallic catalysts. In the procedure, deionized water was added to the support resulting in a suspension continuously agitated by a magnetic stirrer at room temperature.

Since both the Pd and Pt chlorides are insoluble in water, the precursors of such metals were previously dissolved in aqua regia (1 HCl:1 HNO_3). The resultant solution was then heated under constant stirring until its complete vaporization, thus remaining a metal salt of Pd or Pt that was dissolved in water.

The aqueous solution of the metal (Pd, Pt or Ru) was then slowly added to the support suspension. Afterwards, the resultant suspension was heated until 353 K and then its pH was adjusted to 10 by adding a 2 M aqueous solution of NaOH.

In sequence, an aqueous solution of formaldehyde (H_2CO, Merck, 37 wt%), used as reducing agent, was added to the sus-

pension. After this reduction in liquid phase, the suspension was filtered in a Büchner funnel and the remaining solid was thoroughly washed with deionized water in order to remove residual chlorine, sodium and formaldehyde. During the washing procedure, the chlorine and sodium eliminations were respectively observed by $AgNO_3$ and flame tests.

Afterwards, the solids were dried in an oven at 358 K for 24 h. After drying, a part of the obtained catalysts were submitted to ex situ or in situ activation. In the ex situ activation, the catalyst was placed in a Pyrex glass cell and heated at 10 K/min under H_2 flow of 40 mL/min from the room temperature until 573 K, remaining at this temperature for 3 h. Catalysts submitted to ex situ activation have the E abbreviation on its denominations.

In situ activation took place in the reactor itself, where the catalyst reduced by H_2CO was submitted to the H_2 pressure of 3 MPa at 523 K during 1 h. Catalysts submitted to in situ activation have the I abbreviation on its denominations.

Bimetallic catalysts were prepared by co-impregnation, employing the wet impregnation procedure described above. It is noteworthy that only the ex situ activation was studied for bimetallic catalysts because of the little effect induced by in situ activation on the active phase formation of monometallic solids, as discussed hereafter.

2.2. Support and catalysts characterization

The support γ-Al_2O_3 was characterized by potentiometric titration in order to determine its isoelectric point, an important parameter for the wet impregnation procedure. A digital microprocessed pH meter (Marconi, model MA522) was used to take pH measurements according to the procedure of Strelko and Malik [36].

The specific surface area (Sg) of the solids was determined through N_2 physisorption (B.E.T. method). A sample of 1.00 g of each solid was previously dried at 473 K under vacuum and the physisorption was conducted at 77 K in a Tristar Micromeritics ASAP 2010 equipment.

Scanning Electronic Microscopy (SEM) coupled with spectrometric X-ray analysis (SEM + EDX) was used mainly with the purpose of evaluating the chemical composition of the catalysts. The analyses were conducted in a LEO 440i Leica equipment. Before insertion in the SEM, all samples were covered with a fine layer of gold atoms using a 3 mA current for 180 s in order to obtain a gold film thickness of 92 Å.

Transmission Electronic Microscopy (TEM) analyses were carried out on a Libra 120 Zeiss microscope with Cantega 2k/Olympus CCD camera and iTEM data acquisition platform. The samples were gently grinded and then dispersed in water. The dispersion was placed on ultrasound for 10 min and then left to rest for another 10 min. A drop of the solution was placed on a 300 mesh cupper grid coated with parlodium and carbon. The grids were dried at ambient temperature and examined at 80 kV using the energy filter at zero loss, 25 eV, 30 eV or 50 eV. The energy positions of 25 eV and 50 eV correspond to the first and second plasmon.

X-ray Photoelectrons Spectroscopy (XPS) was employed in order to study the chemical compounds on the catalysts surfaces. A spherical analyzer VSWHA-100 with aluminum anode (Al K_α, h_v = 1486.6 eV) was used. The pressure during the analyses was lower than 2.10^{-12} MPa. To correct binding energies, the line Al 2p with binding energy of 74.0 eV was used as reference.

The formation of the catalysts active phases was studied through temperature programmed reduction (TPR). A Micromeritics Auto Chem 2910 equipment was used to obtain the TPR profiles. In these analyses, a sample of 50 mg of each solid was heated at 10 K/min from 298 to 573 K under 50 mL/min flow of a 10% H_2 in N_2 mixture.