

## Evaluation of the activity of a gold catalyst supported on alumina (Au/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub>)

M Barrera<sup>1</sup>, R Gómez<sup>1</sup>, C Caballero<sup>1</sup>, J Oviedo<sup>2</sup> and L C Sánchez<sup>3</sup>

<sup>1</sup> Departamento de Química, Universidad de Córdoba, Carrera 6 # 76 – 103 Montería, Córdoba, Colombia

<sup>2</sup> Departamento de Física y Electrónica, Universidad de Córdoba, Carrera 6 # 76 – 103 Montería, Córdoba, Colombia

<sup>3</sup> Grupo Avanzado de Materiales y Sistemas Complejos (GAMASCO), Universidad de Córdoba, Colombia.

E-mail: ocjm19@gmail.com

**Abstract.** The activity and selectivity of a catalyst (Au/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub>) and the support ( $\gamma$ -Al<sub>2</sub>O<sub>3</sub> cubic) in the oxidation reaction of cyclohexene in the liquid phase to obtain (epoxycyclohexane, 2-cyclohexen-1-ona, 2-cyclohexen-1-ol) were evaluated. The catalyst was prepared by the precipitation-deposition method from aqueous solutions of HAuCl<sub>4</sub>, citric acid (2% m/v) and polyvinyl alcohol. For the adequacy of the support, starting from boehmite calcined at 773 K,  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> phase was obtained. The reaction products and the evaluation of the same were analyzed by gas chromatograph (GC), showing relevant results of the Au/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> system with high conversion levels, mostly to products of 2-cyclohexen-1-one, 2-cyclohexen-1-ol with 31.17% and 25.89% selectivity respectively, and to a lesser proportion to epoxycyclohexane with 13.33% selectivity. Regarding to the system formed by the support, the results reported were 13.31% for 2-cyclohexen-1-ona, 4.28% for 2-cyclohexen-1-ol and 3-23% epoxycyclohexane.

### 1. Introduction

Reactions with supported metals are quite important in the production of many organic compounds [1]. Oxidation of cyclohexane is one of the methods for the synthesis of chemical intermediates which are of great value in the agrochemical and pharmaceutical industries [2].

Obtaining intermediates involved in the oxidation reaction of cyclohexene, lead to very long reaction times and unwanted products which means lost in industrial processes. One way to increase the performance of chemical processes in industrial scale reactions, involves the use of catalysts.

Many heterogeneous catalysts have been evaluated on the oxidation reaction of cyclohexene, within the noble metals supported on porous solids and metalloporphyrins transition metal in homogeneous or supported medium [3]. Gold is very versatile as a catalyst to generate interest products in the chemical and pharmaceutical industry, with high efficiency and less toxic precursors promotes certain reactions at very low metal loadings and small particle sizes [4]. Catalysts of supported gold have been studied for a wide range of oxidation reactions including oxidation of CO, epoxidation of propylene,



direct synthesis of hydrogen peroxide from oxygen and hydrogen, oxidation of cyclohexane to (Ketone/Alcohol) KA oil, among others [5].

## 2. Experimental

The catalyst was prepared by the method of "precipitation-deposition from aqueous solutions of  $\text{HAuCl}_4$ , citric acid (2% mass/volume) and polyvinyl alcohol. Starting from boehmite to obtain the support, it was calcined at 773 K in order to form the  $\gamma\text{-Al}_2\text{O}_3$  phase with surface area BET of  $2.56 \times 10^{-1} \text{ m}^2\text{Kg}^{-1}$ . The amount of deposited gold was determined by atomic absorption, the supported system was calcined at 573 K in air. The surface area and distribution of pore sizes of the catalyst were obtained from adsorption-desorption isotherms of nitrogen at 77 K and transmission electron microscopy (TEM) for dispersion of the metal particles.

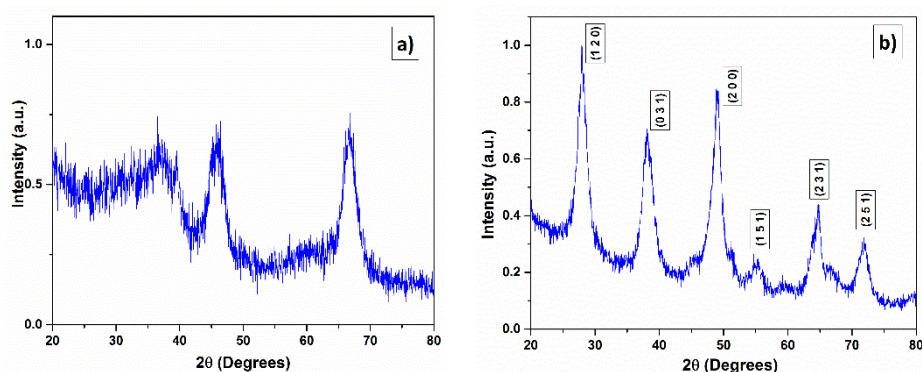
Retention times of each component of the reaction are determined using hexane as an internal standard and dichloromethane as solvent at concentration ranges of 0.1, 0.2, 0.3, 0.4 and 0.5 N. In a reactor  $3.6 \times 10^{-4} \text{ L}$  cyclohexene 0.35 N was added;  $1.4 \times 10^{-4} \text{ L}$  of Hexane 0.1 N;  $2 \times 10^{-4} \text{ Kg}$  of iodosylbenzene (PhIO) as an oxidizing agent;  $5 \times 10^{-5} \text{ Kg}$  of catalyst and  $7.5 \times 10^{-3} \text{ L}$  of dichloromethane. The reaction system was subjected to constant stirring at 298 K and 1 atm for  $1.4 \times 10^4 \text{ s}$ , taking samples of the reaction every  $2.4 \times 10^3 \text{ s}$  and immediately injecting  $2 \times 10^{-6} \text{ L}$  in the gas chromatograph for monitoring the reaction. The reaction products were quantified by gas chromatography (GC) using a DB-5 column, of semi polar character and hexane as the internal standard, under the following conditions: initial temperature of 323 K and final temperature of 433 K, at a heating rate  $1.67 \times 10^{-1} \text{ K/s}$  and held at 433 K for  $3 \times 10^2 \text{ s}$  with nitrogen as a carrier gas, and flow  $2.1 \times 10^{-4} \text{ L/s}$ .

The area of the chromatographic peaks was analyzed by the method of internal standard (hexane), the formation epoxycyclohexane, 2-cyclohexen-1-ona, and 2- cyclohexen-1-ol was determined, formed from the oxidation reaction and the selectivity of the catalyst.

## 3. Results and discussion

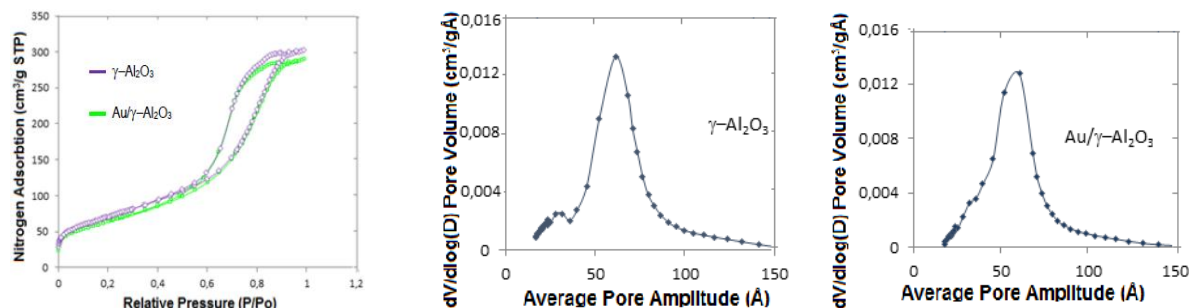
The phase identification was carried out by X-ray diffraction using the X'pert HighScore 2.1 program, and the Match! program (Crystal impact). The X Powder program was also used to facilitate the study of diffraction X-ray obtained by the powder method, considering the data base PDF2-2004.

Figure 1 show X-ray diffractograms for uncalcined and calcined boehmite (773 K) for 4 hours. For the calcined sample, characteristic peaks of the gamma (cubic) phase at  $2\theta = 48.90 - 49.03$  and  $2\theta = 64.50 - 64.68$  positions can be observed. The analysis of the XRD presents characteristic patterns of boehmite phase ( $\text{AlO}(\text{OH})$  21-1307 (ICDD) and  $\gamma\text{-Al}_2\text{O}_3$  phase(50-741 (ICDD) [6]. The results of chemical analysis by atomic adsorption for  $\gamma\text{-Al}_2\text{O}_3$  and  $\text{Au}/\gamma\text{-Al}_2\text{O}_3$  systems were 0,000 and 0,010 % mass of gold respectively.



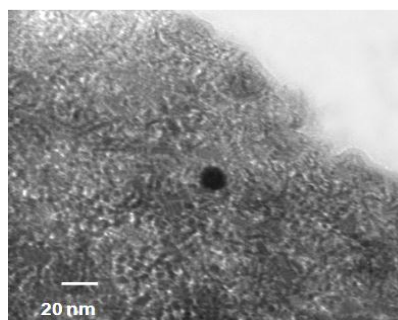
**Figure 1.** X-ray diffractograms for a) uncalcined boehmite and b) calcined boehmite (773 K)

Figure 2 corresponds to the adsorption-desorption isotherms of type IV nitrogen for the support  $\gamma$ - $\text{Al}_2\text{O}_3$ , and the catalyst  $\text{Au}/\gamma$ - $\text{Al}_2\text{O}_3$  synthesized. Additionally, are shown: the surface areas, calculated by the BET model and pore size distributions by the BJH model. The support has an area of  $2.56 \times 10^{-1} \text{ m}^2 \text{ Kg}^{-1}$  and average pore size of  $58 \text{ \AA}$  according to Figure 4a. The system comprised of the  $\text{Au}/\gamma$ - $\text{Al}_2\text{O}_3$  has a  $2.33 \times 10^{-1} \text{ m}^2 \text{ Kg}^{-1}$  area and an average pore size of  $56 \text{ \AA}$ .



**Figure 2.** Isotherms of nitrogen adsorption of the catalyst and support  $\gamma$ - $\text{Al}_2\text{O}_3$  and pore size distribution for the  $\gamma$ - $\text{Al}_2\text{O}_3$  support and  $\text{Au}/\gamma$ - $\text{Al}_2\text{O}_3$ .

Additionally, transmission electron microscopy (TEM) image of the catalyst  $\text{Au}/\gamma$ - $\text{Al}_2\text{O}_3$  catalyst (Figure 3), evidence a particle size of less than  $20 \text{ nm}$ .



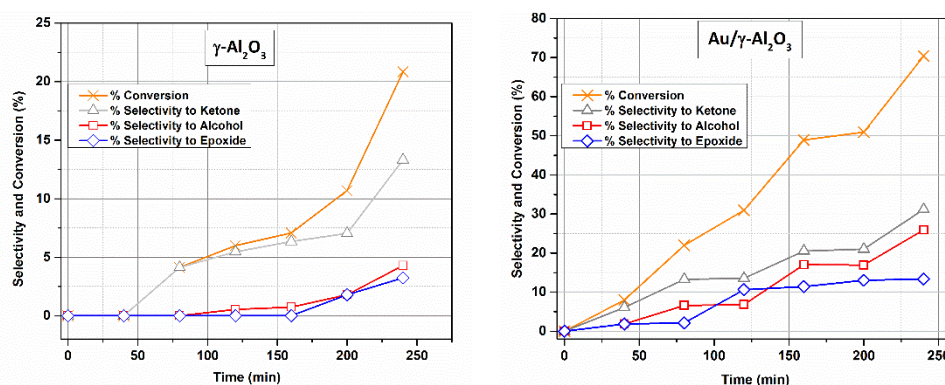
**Figure 3.** TEM image of the  $\text{Au}/\gamma$ - $\text{Al}_2\text{O}_3$  catalyst.

The products obtained in the evaluation of the catalytic activity in the oxidation reaction of cyclohexene with respect to support  $\gamma$ - $\text{Al}_2\text{O}_3$  were: epoxycyclohexane, 2-cyclohexene-1-ol and 2-cyclohexene-1-ona which are summarized in Table 1. All reactions were performed with  $3.6 \times 10^{-4} \text{ L}$  of cyclohexene at a concentration of  $0.35 \text{ N}$ ;  $1.4 \times 10^{-4} \text{ L}$  of Hexane  $0.1 \text{ N}$ ;  $2 \times 10^{-4} \text{ Kg}$  of iodosylbenzene (PhIO) as an oxidizing agent;  $5 \times 10^{-5} \text{ Kg}$  of catalyst and  $7.5 \times 10^{-3} \text{ L}$  of dichloromethane as solvent.

**Table 1.** Catalytic evaluation on cyclohexene oxidation for catalysts

System	Time (min)	Conversion	Selectivity (%)		
			Epoxidation	Via Allylic	
			Cy-Epoxy	Cy-1-ol	Cy-1-ona
$\gamma$ - $\text{Al}_2\text{O}_3$	240	20.83	3.23	4.28	13.31
$\text{Au}/\gamma$ - $\text{Al}_2\text{O}_3$	240	70.40	13.33	25.89	31.17

Having account conversion of cyclohexene and the selectivity of the products to the oxidation reaction, the results exhibit a higher catalytic performance for  $\text{Au}/\gamma\text{-Al}_2\text{O}_3$  respecting to  $\gamma\text{-Al}_2\text{O}_3$ , presenting higher levels of conversion to products 2-cyclohexen-1-ol, 2-cyclohexen-1-ol and a lower proportion of epoxycyclohexane.



**Figure 4.** Results of the catalytic activity for the  $\gamma\text{-Al}_2\text{O}_3$  and  $\text{Au}/\gamma\text{-Al}_2\text{O}_3$  systems.

Figure 4 shows the results of the catalytic activity for  $\gamma\text{-Al}_2\text{O}_3$  and  $\text{Au}/\gamma\text{-Al}_2\text{O}_3$  systems. At  $4.8 \times 10^3$  s (80 min) of reaction,  $\gamma\text{-Al}_2\text{O}_3$  promotes allylic oxidation, showing selectivity for 2-cyclohexen-1-one. At  $7.8 \times 10^3$  s (120 min), the catalytic activity is observed towards allylic oxidation and epoxidation. At  $1.44 \times 10^4$  s (240 min) of reaction, the conversion is 20.83%, with percentages of 3.23%, 4.28% and 13.31% for epoxycyclohexane, 2-cyclohexen-1-ol and 2-cyclohexen-1-ona, respectively. For  $\text{Au}/\gamma\text{-Al}_2\text{O}_3$ , a tendency to the formation of allylic oxidation during the reaction is observed, with some epoxidation products. At end of reaction, a conversion of 70.40% is obtained with selectivity rates of 13.33%, 25.89% and 31.17% for epoxycyclohexane, 2-cyclohexen-1-ol and 2-cyclohexen-1-ona respectively.

During the process, a marked competitiveness between the two reactions is observed, this behavior can be attributed to the nature of the catalyst used. The oxidation of allylic carbon occurs by influence of the increased acidity of the catalyst [7], where the alumina acts as a support of Au, presenting an appreciable catalytic activity due to its surface acidity and resulting intermediates reactive molecules adsorbed on metal support interfaces [1].

#### 4. Conclusions

In this work, products obtained in the oxidation reaction of cyclohexene due to catalytic activity and selectivity of the  $\gamma\text{-Al}_2\text{O}_3$  and  $\text{Au}/\gamma\text{-Al}_2\text{O}_3$  were identified and quantified.

The catalytic activity of the  $\text{Au}/\gamma\text{-Al}_2\text{O}_3$  system is increased compared to  $\gamma\text{-Al}_2\text{O}_3$  support, associated with the presence of gold particles, possibly related to surface acidity and removing of OH groups.

#### References

- [1]. Caballero C, Valencia J, Barrera M and Gil A 2010, *Powder Technol.* **203**(2) 412
- [2]. Zhen-Yu C, et al 2011, *Adv. Che. Eng. Sci.* **1** 15.
- [3]. Karimipour G, Rezaei M, and Ashouri D 2013, *J. Mex. Chem. Soc* **57**(4) 276.
- [4]. Kouachi K, Lafaye G, Especel C, Cherifi O and Marécot P 2008, *J. Mol. Catal. A. Chem* **280** 52.
- [5]. Xu Li-Xin, et al 2008, *Catal. Commun* **9**(5) 816.
- [6]. Paglia G et al 2004, *Chem. Mater* **16** 220.
- [7]. Radman et al 2015, *Orient. J. Chem* **31**(4) 2277.