



Preparation and characterization of Al₂O₃–MgO catalytic supports modified with lithium

L. Escobar-Alarcón^a, T. Klimova^b, J. Escobar-Aguilar^c, S. Romero^a, C. Morales-Ramírez^{d,e},
D. Solís-Casados^{e,*}

^a Departamento de Física, Instituto Nacional de Investigaciones Nucleares, Apdo. Postal 18-1027, México D.F. 11801, Mexico

^b Facultad de Química, Departamento de Ingeniería Química, UNAM, Ciudad Universitaria, México D.F. 04510, Mexico

^c Instituto Mexicano del Petróleo, Eje Central Lázaro Cárdenas Norte 152, Col. San Bartolo Atepehuacan, México D.F. 07730, Mexico

^d Programa de Maestría en Ciencia de Materiales, Facultad de Química UAEMex, Mexico

^e Centro Conjunto de Investigación en Química Sustentable UAEM-UNAM, Carretera Toluca-Atlacomulco Km 14.5, C. P. 50200 Toluca, Estado de México, Mexico

HIGHLIGHTS

- ▶ Lithium addition to Al₂O₃–MgO supports provides textural stability to aged formulations.
- ▶ As a higher content of Li in the formulation a greater variety of basic sites are formed.
- ▶ Li incorporation in the supports favors a structural change from the γ -Al₂O₃ crystalline phase to the δ -Al₂O₃.

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ABSTRACT

Al₂O₃–MgO catalytic supports were modified with different amounts of lithium in order to obtain novel Al₂O₃–MgO–Li(x) formulations containing basic sites. The basic sites on samples surface were identified and quantified through CO₂ chemisorptions. It was found that total amount of basic sites increases as the Li content increases. The Li identification and its content were performed through Non-Rutherford Backscattering Spectroscopy (NRBS). The Li addition to the supports produce surface morphological changes as was observed with Scanning Electron Microscopy (SEM). The addition of lithium produces a decrease in specific surface area, changing the textural properties as N₂-physisorption measurements reveal. Structural characterization by X-ray diffraction (XRD) suggests that Li addition changes the crystalline structure of Al₂O₃ from the γ to the δ phase; additionally, this technique indicate the presence of Li₂CO₃, which could be attributed to the preferential reaction of Li with environmental CO₂. It was not found evidence of magnesium carbonates in the fresh samples by XRD. Raman spectroscopy shows bands attributed to the lithium carbonates species corroborating the found by XRD. The obtained results suggest that these materials could be potentially attractive as catalytic supports for reactions where the basic sites are useful such as selective hydrodesulphurization.

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1. Introduction

In recent years the use of catalysts with acid character has shown an important increase because of the number of reactions that they can catalyze. However, the use of catalysts containing basic sites has not been so extensive mainly due to the difficulties in obtaining catalysts with active basic sites. It has been reported [1] that basic sites react fast with carbon dioxide and water from environment resulting in carbonates and hydroxides. These products

* Corresponding author.

E-mail addresses: dasolisc@uaemex.mx, solis_casados@yahoo.com.mx (D. Solís-Casados).

¹ Personal académico de la Facultad de Química, UAEM.

cover the catalyst surface inhibiting the catalytic response because they are not catalytically active. It is well known that in order to re-activate or generate new basic sites, the catalyst is subjected to a pre-treatment in situ at high temperatures, in vacuum or under an inert gas flow, prior to its use in a catalytic process. The strength of the generated basic sites seems to strongly depend on the temperature of the pretreatment conditions, i.e. if basic sites are generated at low temperature they show a weak strength, while if the basic sites are generated at higher temperatures, their strength is higher. These differences in strength could be used to promote different chemical reactions. It is worth mentioning that due to the scarce of studies involving catalysts containing basic sites, a clear correlation between basic site strength and kind of reaction driven has not been well established. Pines et al. [2] showed that the basic

sites present in sodium supported in alumina are active for reactions such as the migration of the double bond in alkenes that could be attributed to the strong tendency of sodium as donor of electrons. Kokes and Dent [3] reported that hydrogen molecules adsorbed on the active sites of ZnO through acid–base interactions can dissociate hydrogen by heterolysis and then promote alkenes hydrogenation reactions. On the other hand, Tanabe et al. [4] reported that MgO and CaO showed catalytic activity for the isomerization of 1-butene when the basic sites in these catalysts were activated through a pre-treatment under conditions of high temperature and vacuum. Brunet et al. [5] reported that nature of the basic sites in some supports has also an influence on the selectivity in reactions as hydrocarbons hydrodesulphurization giving to basic supports, such as magnesium oxide, an important role in order to improve HDS/olefin hydrogenation selectivity. In that research work, Brunet et al. mentioned that the presence of a promoter (Co in particular) favors the HDS/olefin hydrogenation selectivity of the catalyst, but it is clear that electronic effects due to a decrease in acidity of the support would decrease the hydrogenation activity of the catalyst. From the reported by Hattori et al. [1–4], it can be concluded that simple metal oxides, such as MgO and ZnO, can have active sites with basic character. Several groups have reported over the last ten years the use of acidic supports modified with MgO, mostly for applications as supports for selective hydrodesulphurization [5–10]. In a previous work, we have studied Al₂O₃-based supports modified with different amounts of MgO in order to decrease their acidity [10]. These materials were evaluated in a selective hydrodesulphurization process using thiophene as a model molecule. The prepared Al₂O₃-MgO(*x*) supports showed textural and structural instability when were exposed to environmental moisture, particularly the supports prepared with molar ratios, MgO:Al₂O₃, greater than 0.25. In a subsequent study [11], we showed that the MgO exposed on the surface support reacted with environmental CO₂ and water, resulting in a mixture of magnesium carbonates and hydroxides. The transformation of MgO into MgCO₃ and Mg(OH)₂, resulted in a strong decrease of specific surface area, from 130 to 10 m²/g, diminishing drastically the catalytic response. Therefore, textural and structural instability of MgO-containing formulations was found to be their major problem. Therefore, investigate a way to avoid such MgO transformation is an important issue to obtain MgO containing catalytic supports that preserve their surface areas as a result of exposure to environmental conditions. Additionally, it was shown that specific surface area can be recovered with thermal treatments in situ, however, depending on the conditions of the thermal treatment active sites with different characteristics were generated. The purpose of our previous works [12,13], was to improve the selectivity of Al₂O₃-MgO mixed oxides formulations by the addition of alkaline metals, such as potassium or lithium. It was found that although the basic sites were not identified and quantified, it was assumed that their presence decrease the acid character of the obtained formulations. From the aforementioned, the aim of this work is to contribute to the understanding of low acidity supports containing basic sites. For this purpose, the effect of addition of different lithium contents on freshly prepared Al₂O₃-MgO supports on their physical and chemical properties was studied. Also it was investigated if lithium addition to the supports can provide textural stability to the obtained formulations after exposition to environmental conditions.

2. Experimental

2.1. Precursors

The catalytic supports were prepared using the following chemical precursors: Mg(OEt)₂ (magnesium ethoxide Sigma,

Mg(OC₂H₅)₂ ACS reagent), AlOOH (pseudo-boehmite Catapal B TM Sassol), HCOOH (formic acid Sigma, ACS reagent, ≥96.0%), citric acid (Aldrich, ACS reagent, ≥99.5%). Supports were modified using LiOH (lithium hydroxide, Sigma–Aldrich, ACS reagent). Formic acid (HCOOH, 5 vol.%) was used to produce the gelation of AlOOH, which was employed as a binder.

2.2. Al₂O₃-MgO support

About 24 g of Al₂O₃-MgO support were prepared from the mechanical mixture of 27.7 g of AlOOH and 1.4 g of Mg(OEt)₂ to obtain a molar ratio MgO:Al₂O₃ of 0.05, which results in the optimum magnesium content reported previously [10–13]. 5.7 g (20%) of the total quantity of AlOOH required, were gelled by using 5 ml of formic acid solution (5 vol.%). This gel was used as a binder to agglutinate the rest of the AlOOH and Mg(OEt)₂ mixture. Afterwards, the obtained paste was extruded by pushing it through a syringe. The obtained pellets were dried overnight and then thermally treated in an air convection oven at 500 °C (4 h) reached by using a heating rate of 3 °C/min, in order to obtain the Al₂O₃-MgO support. This is the support of all formulations and is used as a reference materials as well as the Al₂O₃ support.

2.3. Al₂O₃-MgO-Li(*x*) supports

The Al₂O₃-MgO pellets were impregnated, by the incipient wetness technique, with an aqueous solution containing lithium hydroxide (LiOH). Solutions with different concentrations of LiOH (0.38, 1.90, 3.90, 7.70 g, dissolved in the impregnation volume) were prepared to obtain formulations, Al₂O₃-MgO-Li(*x*), with different lithium load being *x* = 0, 1, 5, 10 and 20 wt.% of Li₂O with respect to the Al₂O₃-MgO. The prepared lithium-containing supports were dried overnight and after annealed at 500 °C for 4 h in an air convection oven. Hereinafter, modified supports will be referred to as Al₂O₃-MgO-Li(*x*), where *x* is the nominal loading of Li₂O (wt.%) used to prepare the support.

2.4. Supports characterization

Chemical and also physical properties of the Al₂O₃-MgO-Li(*x*) supports were characterized by means of different techniques.

2.4.1. Compositional characterization

The elemental composition of the elements present in the supports was determined from Non-Rutherford Backscattering Spectroscopy (NRBS). Measurements were performed in a Tandem Van de Graff accelerator using a proton beam of 2.8 MeV and a detection angle of 165°.

2.4.2. Basic sites characterization

Number of basic sites was measured by the concentration of gaseous CO₂ adsorbed on the samples taken from infrared spectroscopy [1,14,15]. The basic sites were generated on the support's surface with pretreatment conditions to active basic sites. Surfaces before pretreatment were covered with carbon dioxide, water, oxygen, etc., from the environment and no showed the basic sites, thus for generate or activate the basic sites was applied in situ in a DRIFT cell at high-temperature pretreatment (500 °C) in a flow of inert gas such as N₂ to remove carbon dioxide, water and in some cases oxygen interacting weakly in surface. Then a CO₂ (g) flow at room temperature was passed through the pretreated samples. Monitoring of CO₂ adsorbed on surfaces by Infrared Spectroscopy is a well-established tool to investigate the basicity of solids. This technique is able to identify interactions between CO₂ and the different kind of basic sites on the sample surface, such as CO₂ physisorbed on the surface, carbonates mono, bi- and tridentated

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