



Hydrotreating catalysts on different supports and its acid–base properties

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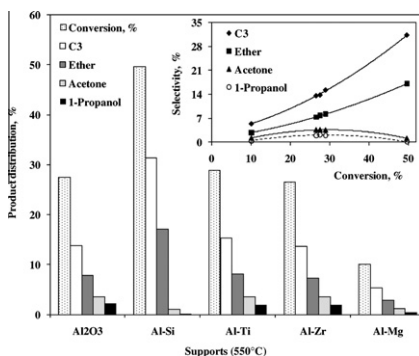
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HIGHLIGHTS

- ▶ The nature of active sites was qualitatively measured in the isopropanol conversion.
- ▶ The selectivity toward propene is higher, indicating strong acidic character.
- ▶ Acetone was produced on basic sites.
- ▶ Al–Si support is the most active support in the isopropanol conversion.

GRAPHICAL ABSTRACT



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ABSTRACT

Pure and mixed oxides (Al_2O_3 , ZrO_2 , $\text{Al}_2\text{O}_3\text{-MgO}$, $\text{Al}_2\text{O}_3\text{-SiO}_2$, $\text{Al}_2\text{O}_3\text{-TiO}_2$, and $\text{Al}_2\text{O}_3\text{-ZrO}_2$) were prepared by homogeneous delayed precipitation. The synthesized supports were impregnated by incipient wetness method to obtain CoMo catalysts. Both supports and catalysts were characterized by N_2 physisorption, X-ray diffraction, among other techniques. Acid–base properties were studied with isopropyl alcohol and cumene decomposition. It was possible to assess qualitatively that nature of Al–Si and its respective catalyst was mainly acidic. Conversion of isopropyl alcohol leads to the dehydration products, mostly propylene with a low amount of di-isopropyl ether and acetone. The CoMo/ $\text{Al}_2\text{O}_3\text{-SiO}_2$ catalyst showed the highest conversion during cumene cracking. CoMo/ $\text{Al}_2\text{O}_3\text{-SiO}_2$ catalyst also was the most active during thiophene hydrodesulfurization followed by CoMo/ $\text{Al}_2\text{O}_3\text{-TiO}_2$ catalyst.

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1. Introduction

The rigorous environmental regulations imposed nowadays for fuels based on fossil sources have been attracting the attention of researchers and refiners to accomplish the ecological specifications. Among the options to process heavy crudes, hydrotreating is considered as one of the most important to reduce the impurities

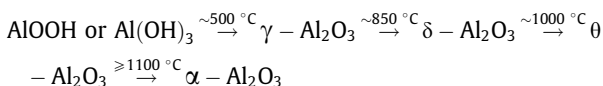
contents present in crudes or in their fractions. The preferred route to produce clean fuels is by using new catalytic materials that is less expensive than increase the pressure and/or temperature in current processes. The influence of new supports such as mixed oxides on the catalytic properties plays an important role because of the improvement of the textural properties of catalysts and modification of the interaction with active metals [1–3].

The preparation of mixed oxide amorphous material was reported using sol–gel [4], homogeneous precipitation [5] and homogeneous delayed precipitation [6] using ammonia solution

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as precipitant. The two major properties (acidity and textural properties) of the specified catalyst can be generated during the preparation of support. The textural and phase transformation (crystalline) of the solid material mainly varied with the calcinations. Alumina showed remarkable series of structural forms due to the dehydrogenation of aluminum hydroxide as follows, where the starting material is boehmite or bayerite:



Different additives such as Zr, Ti, Mg, and Si are known to stabilize the alumina support and modify its mixed oxide properties to its desired acid base nature. These mixed oxides have been used as supports for hydrotreating catalysts, which have been reported to possess a wide range of textural properties and different type of active metal interactions with the support [7]. Considering the importance of acid–base properties of the support, it is worthwhile to study alumina mixed oxides as a catalyst for acid–base reactions, which have been widely applied in various chemical reactions such as hydrotreating and hydrocracking. Acidic nature has been the subject to study in several literature reports, but in some cases, these studies have been carried out over catalysts in the oxide state [8,9]. On the other hand, investigations based on sulfided catalysts also have been reported [10–12].

To investigate the strength and amount of acid–basic sites, different methods can be used to measure the acidity/basicity such as titration [13,14], calorimetry [15], microcalorimetry [16], temperature programmed desorption [17], X-ray photoelectron spectroscopy [18], and infrared spectroscopy [19]. Commonly to obtain the information of acid–basic properties of a catalyst, the probe reaction is considered to be a good method that quantifies catalytic properties being tested by using model molecules, such as cumene, *i*-octene, and alcohols [20].

Reactions with model compounds used to test acidic catalysts are the cumene cracking or isopropylbenzene. Cumene molecule follows a simple cracking pathway because benzene ring is not attacked under these conditions and only alkyl chain undergoes changes. Therefore, the main products in cumene cracking are propene and benzene. Secondary products of this reaction are diisopropylbenzene, toluene, ethyltoluene, ethylene, ethane, butenes, ethyl- and propylbenzenes, cymene, methane, and *i*-butane. Due to only a part of the Brønsted acid sites is claimed to be active during cumene conversion and some by-products are formed on Lewis acid sites, this reaction can be used to distinguish between Brønsted and Lewis acid sites [21,22]. A wide review regarding to reaction pathways of cumene cracking was published by Corma and Wojciechowski [23]. The strength of the acid sites was qualitatively determined during the cumene cracking and *n*-propanol dehydration as reported by Zi et al. [24]. Cumene cracking was only observed on strongly acidic sites. Choudhary and Akolekar [25] made a comparison of the nature of acid sites by studying the conversion of cumene, *i*-octane, and *o*-xylene over various materials with different silica content and found that *i*-octane cracking required strong acid sites, while *o*-xylene isomerization and cumene cracking were also catalyzed by weaker acid sites. Other studies in which cumene cracking is used to probe the acid–basic nature of supports and catalysts have been reported elsewhere [26–28].

Dehydration of alcohols is considered as the reaction that requires lower strength acid sites to carry out. The acid–basic properties of supports and catalysts can be evaluated by measuring particularly the dehydration of 2-propanol or isopropanol (IPA) that is carried out on both the Lewis and Brønsted acid sites [29]. IPA decomposition products are mostly propene and acetone. Propene represents the acidic character of the material, whereas

acetone corresponds to the basic nature. The reaction is also sensitive to the temperature; therefore, the reaction temperature is kept low during the estimation of selective products yield.

Isopropanol decomposition is an indirect method to test acid–base properties of supports/catalysts, and conversion results are only qualitative because of the contribution of both (acid/base) sites. The amount and nature of active sites can be estimated by calculating the selective yield of reaction products such as propene, diisopropyl ether, and acetone. Hence, 2-propanol decomposition on basic sites proceeds through an elimination reaction yielding acetone, while in acid sites, 2-propanol dehydrates to propylene and diisopropyl ether. The ratio of propylene and diisopropyl ether may further depend on the strength of acid sites where the reaction takes place. Manríquez et al. [30] observed that activity during the isopropanol decomposition showed a good correlation between the acid–basic properties and the selectivity to propene, acetone, and diisopropyl ether. Other studies regarding to the dehydration of isopropanol were conducted by Korah and Viswanathan [31]. The main products were propene, diisopropyl ether, and water. Authors found that the concentration of acid sites did not change by varying the reaction temperature; however, the acid strength varied as function of temperature. Mixed oxides, that is, titania–alumina, titania–silica, titania–zirconia, and ternary mixed oxides such as titania–zirconia–alumina and titania–zirconia–silica, have been evaluated during the IPA dehydration where the silica-containing mixed oxides presented the highest activities [32].

Thus, it is observed that new catalytic materials will have the growing importance in the near future. For this reason, the aim of this work was to synthesize different pure supports and mixed oxides by the homogeneous delayed precipitation to be further characterized and evaluated. Impregnation by incipient wetness method allowed us to obtain different CoMo supported catalysts that were also characterized for their textural, structural phase, and acid–base properties. Acid–basic properties of the supports and catalysts were evaluated on isopropanol dehydration and cumene cracking, whereas HDS activity was tested on the thiophene hydrodesulfurization.

2. Experimental

2.1. Synthesis of supports and catalysts

Supports and catalysts were prepared as reported elsewhere [6]. Briefly, supports such as Al₂O₃, ZrO₂, Al₂O₃(90%)–MgO(10%), Al₂O₃(90%)–SiO₂(10%), Al₂O₃(90%)–TiO₂(10%), and Al₂O₃(90%)–ZrO₂(10%) were prepared by homogeneous delayed precipitation at pH of 8.5 under continuous stirring. Experimental methodology to prepare the supports is schematically shown in Fig. 1. M⁺ corresponds to the cation in different salts, that is, Cl₂OZr·8H₂O, Ti[OCH(CH₃)₂]₄, Mg(NO₃)₂·6H₂O, and (C₂H₅O)₄Si. Extrudates were obtained by the addition of nitric acid (10 vol.%) to be dried overnight and calcined at different temperatures, that is, 300, 550, and 800 °C during 4 h.

The incipient wetness impregnation method was used to prepare molybdenum catalysts on different supports. Ammonium heptamolybdate was used as precursor salt and dissolved in water and ammonium hydroxide to obtain pH ~7.6. The Mo supported catalysts were dried at 120 °C and calcined at 400 °C for 4 h. Catalysts were promoted with cobalt using salts of Co(NO₃)₂. Promoted catalysts were dried at 120 °C and calcined at 450 °C during 4 h.

2.2. Characterization of supports and catalysts

To study the effect on support properties, different temperatures of calcination were evaluated, that is, 300, 550, and 800 °C.

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