



## Full Length Article

# Characterization and HDS activity of sulfided Co—Mo—W/SBA-16 catalysts: Effects of P addition and Mo/(Mo + W) ratio



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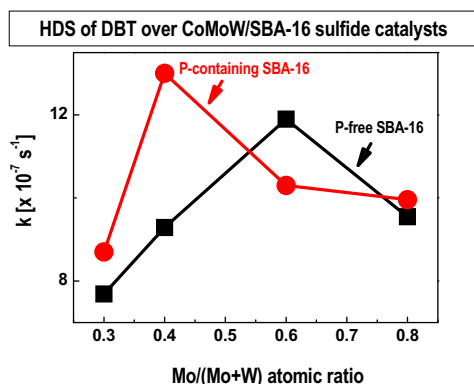
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## HIGHLIGHTS

- HDS activity of CoMoW/SBA-16 sulfide catalysts depends strongly on the Mo/(Mo + W) atomic ratio.
- CoMoW catalyst prepared with Mo/(Mo + W) atomic ratio of 0.4 and supported on SBA-16 modified with P was the most active.
- The most active catalyst exhibited the highest surface exposure and sulfidation degree of W species.

## GRAPHICAL ABSTRACT



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## ABSTRACT

Two series of SBA-16-supported Co—Mo—W ternary sulfide catalysts with atomic ratio  $r = \text{Mo}/(\text{Mo} + \text{W})$  ranging from 0.3 to 0.7 were prepared by the simultaneous impregnation of SBA-16 and phosphated-SBA-16 substrates with metal precursors. The samples were characterized by a variety of techniques (chemical analysis,  $\text{N}_2$  physisorption, SEM, XRD, DRS UV-vis, TPR, TPD- $\text{NH}_3$ , Raman spectroscopy, HRTEM, XPS and coke burning). The catalytic performance was evaluated in the hydrodesulphurization (HDS) of dibenzothiophene (DBT), carried out in a batch reactor at 350 °C and 3.1 MPa of total  $\text{H}_2$  pressure. The maximum activity at the same atomic ratio  $r = 0.4$  was observed for the catalysts supported on SBA-16 modified with phosphorous ( $r = 0.4(\text{P})$ ). HRTEM evidenced that this was because different  $\text{MoS}_2$  crystalline structures were formed: the P-free sample prepared with Mo/(Mo + W) atomic ratio of 0.6 ( $r = 0.6$ ) exhibited the  $\text{MoS}_2\text{-}2\text{H}$  crystalline structure whereas the P-containing samples prepared with Mo/(Mo + W) atomic ratio of 0.4 ( $r = 0.4(\text{P})$ ) exhibited the interplanar distance corresponding to (003) planes of  $\text{MoS}_2\text{-}3\text{R}$  crystalline structure. Additionally, the best activity of the  $r = 0.4(\text{P})$  sulfide catalyst was linked with the enhancement of the  $\text{WS}_2$  species surface exposure accompanied with a larger sulfidation degree of W species (from XPS).

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## 1. Introduction

Typically, the catalysts employed in refineries for hydrodesulphurization (HDS) of gasoline and diesel fuels are based on the

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# Heterogeneous acid conversion of a tricaprylin-palmitic acid mixture over Al-SBA-15 catalysts: Reaction study for biodiesel synthesis



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## ABSTRACT

In this work mesoporous Al-SBA-15 was synthesized by the sol-gel method and used as a solid acid catalyst for the conversion of a model mixture of tricaprylin with 20 wt% of palmitic acid at  $T = 175\text{--}215\text{ }^{\circ}\text{C}$ . The incorporation of aluminum to the SBA-15 through the sol-gel method, gives rise to mesoporous materials with the typical hexagonal arrangement of SBA-15 (XRD). In addition, these materials possess Lewis and Brønsted acid sites (pyridine adsorption), large surface area and wide pore diameter ( $\text{N}_2$  physisorption) being capable of catalyzing simultaneously transesterification of triglycerides (tricaprylin) and esterification of palmitic acid (up to 20 wt%) resulting in FAME yields of 40–87%. A detailed analysis of the reaction products indicates that the conversion of triglyceride to diglyceride is the limiting step during the acid transesterification over Al-SBA-15 catalysts, which results from the difficulty to protonate triglycerides followed by methanol addition. A simplified lumped first order reaction model reproduces well the experimental data for the acid transesterification of tricaprylin in the presence of a high content of free fatty acids (palmitic acid). The calculated activation energy was  $64.7\text{ kJ mol}^{-1}$  which is in the range of  $45\text{--}120\text{ kJ mol}^{-1}$  previously reported for acid catalysts.

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## 1. Introduction

Traditional homogeneous basic catalysts, even with large reaction rates, are unable to perform simultaneously esterification and transesterification reactions because of the presence of free fatty acids (FFAs) and water [1]. The presence of water favors the formation of FFAs by hydrolysis of triglycerides (TGs) [2], besides FFAs with homogeneous basic catalysts also gives rise to soap formation, making difficult the separation of products and diminishing the activity of the catalysts [1].

In this context, heterogeneous acid catalysts represent an interesting option, because both esterification and transesterification reactions could occur through an acid route [3]. Therefore, several types of heterogeneous acid catalysts have been investigated for the transesterification of different vegetal and animal lipids. These catalysts include zeolites, which are materials whose surface acidity can be modulated with the addition of different atoms to the aluminosilicate structure [4]; despite of

that, zeolites have exhibited low catalytic activity, which has been mainly associated with the restricted transport of TGs into their cavities [5]. Supported heteropoly acids are also materials with strong Brønsted acidity, but their solubility in methanol limits their use for several reaction cycles [6]. Additionally, some resins as Amberlyst 15 have provided good yields for esterification under mild conditions because of their open structure; however, they exhibited low activity for transesterification due to their poor thermal stability at high temperatures [6]. Some other catalysts like superacids, which are materials that use zirconium, titanium and tin oxides as supports, and sulfate or tungsten compounds as active phases [7–9], have been also used for the simultaneous esterification and transesterification, however the leaching of the sulfate compounds from the catalyst was commonly observed [9]. Analyzing these previous works, it can be concluded that large pore diameter, strong acidity, thermal stability and surface hydrophobicity are desirable properties for acid catalysts in order to improve the diffusion of reactants and products and to repel the water, which is formed during the esterification reaction [10].

Therefore, an interesting alternative is the use of amorphous silica with ordered mesoporous structure, such as SBA-15. These materials exhibit a large pore size, high thermal stability

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# Enhancement of dibenzothiophene hydrodesulphurization via hydrogenation route on NiMoW catalyst supported on HMS modified with Ti

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## ABSTRACT

This study shows that ternary Ni-Mo-W sulfide catalysts supported on hexagonal mesoporous silica modified with Ti (HMS-Ti) showed a high enhancement of dibenzothiophene (DBT) transformation via hydrogenation route with respect to their Ti-free counterpart. The reaction of hydrodesulphurization (HDS) of DBT was carried out in a batch reactor at 320 °C and 5.5 MPa of total H<sub>2</sub> pressure. The catalysts were characterized by a variety of techniques (chemical analysis, N<sub>2</sub> adsorption-desorption isotherms, low- and wide-angles XRD, TPR, TPD-NH<sub>3</sub>, DRS UV–vis, TPO/TG and HRTEM). At reaction time of 5 h, all synthesized catalysts exhibited higher DBT conversion (84–100%) than both commercial NiMo/γ-Al<sub>2</sub>O<sub>3</sub> and NiW/γ-Al<sub>2</sub>O<sub>3</sub> catalysts (59 and 69%, respectively). For all catalysts, the DBT transformation occurs via direct desulfurization (DDS) and hydrogenation (HYD) pathways. The DDS was the main reaction route for Ti-free sample whereas for both Ti-containing samples the DBT transformation occurs mainly via HYD reaction route. At a reaction time of 5 h, the best catalyst (NiMoW/HMS-Ti1) exhibited 100% of DBT conversions and the highest yield of hydrogenation route products. From the activity results, it is concluded that only the structure of Ti species is relevant for the catalyst activity, but not the amount of Ti incorporated in the HMS framework. The superior activity of sulfide NiMoW/HMS-Ti1 is linked with the best properties of its oxide precursor: a lowest band energy gap and a large amount of Mo (W)<sup>6+</sup> ions having octahedral coordination. After sulfidation, the best catalyst exhibited the “onion-type” Mo(W) S<sub>2</sub> structures which offer the best conditions for the formation of “bright rim” Mo edge sites, which are known to be active sites for DBT transformation via HYD reaction route.

## 1. Introduction

To reduce the air pollution by S produced from the combustion of transportation fuels, nowadays, there are more stringent environmental regulations on the S content for diesel fuel and gas-oil. This is a technological challenge for current commercial hydrotreatment process because the most of the sulfur compounds present in middle distillates are dibenzothiophene and alkyl-substituted dibenzothiophenes, which are highly refractory for the S-removal by catalytic hydrodesulphurization (HDS) reaction [1,2]. The difficult S removal from those molecules is believed to be due the steric hindrance of the C-S bond scission in the partially hydrogenation intermediates leading to inhibition of the direct desulfurization (DDS) reaction route [1,2]. In order to solve this problem, the catalysts with improved hydrogenation function are needed.

Nowadays, the world's most active hydrotreating catalyst is

considered to be a bulk-like catalyst, called as NEBULA, which was developed in 2001 by Akzo Nobel, ExxonMobil and Nippon Ketjen [3,4]. The NEBULA catalyst has a NiMoW formulation and its porous structure is formed during decomposition of metal's precursors [3,4]. As compared with classical alumina-supported catalysts, the bulk-like catalysts are more expensive due to the elimination of support from the catalyst formulation. Thus, the challenge is to development trimetallic catalysts, which can be more cost effective than unsupported ones.

One of the current strategies for the design of heterogeneous catalysts is the variation of the support. In the selection of support, the important factors to be considered are: surface area, pore size distribution, acidity and stability during on-stream reaction. In most reports in the literature, hybrid supports were used because a major drawback of the use of mesoporous alumina as support is the strong metal-support interaction leading to the loss of active phase due to the formation of spinel-like structures (NiAl<sub>2</sub>O<sub>4</sub>). Taking into account the

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# The Role of Composition for Cobalt Molybdenum Carbide in Ammonia Synthesis

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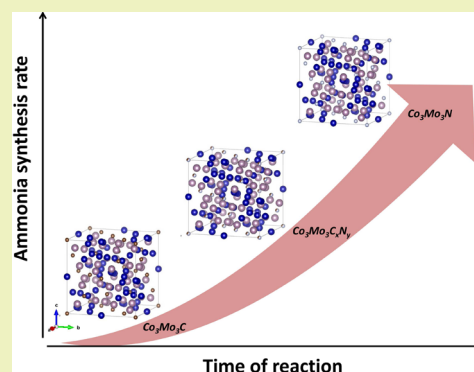
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**ABSTRACT:** The performance of  $\text{Co}_3\text{Mo}_3\text{N}$ ,  $\text{Co}_3\text{Mo}_3\text{C}$ , and  $\text{Co}_6\text{Mo}_6\text{C}$  for ammonia synthesis has been compared. In contrast to  $\text{Co}_3\text{Mo}_3\text{N}$ , which is active at 400 °C, a reaction temperature of 500 °C, which was preceded by an induction period, was necessary for the establishment of steady state activity for  $\text{Co}_3\text{Mo}_3\text{C}$ .  $\text{Co}_6\text{Mo}_6\text{C}$  was found to be inactive under the conditions tested. During the induction period, nitridation of the  $\text{Co}_3\text{Mo}_3\text{C}$  lattice was found to occur, and this continued throughout the period of steady state reaction with the material transforming in composition toward  $\text{Co}_3\text{Mo}_3\text{N}$ . Taken together, these observations demonstrate that ammonia synthesis activity in ternary cobalt molybdenum systems is associated with the presence of N in the 16c Wyckoff lattice site.

**KEYWORDS:** Ammonia synthesis, Mars-van Krevelen,  $\text{Co}_3\text{Mo}_3\text{N}$ ,  $\text{Co}_3\text{Mo}_3\text{C}$ , In situ neutron diffraction



## INTRODUCTION

The development of the Haber–Bosch Process for the industrial-scale synthesis of ammonia from  $\text{N}_2$  and  $\text{H}_2$  feedstock was a landmark 20th century achievement.<sup>1</sup> This process employs an iron-based catalyst and is operated at very high pressure (>100 atm) and moderate temperatures (ca. 400 °C) to accomplish acceptable process yields. It is also necessary to use highly pure feed gases. Taking the whole process into consideration (including the generation of feedstock), as operated on the industrial scale, the process is currently responsible for ca. 1–2% of global energy demand producing more than 1.5 tonnes of  $\text{CO}_2$  per tonne of  $\text{NH}_3$  made.<sup>2</sup> While the process is well integrated and iron is a widely abundant and cheap catalyst which exhibits, under the correct conditions, a significant lifetime, the search for new catalytic materials and/or processes for ammonia synthesis is an area of topical interest. A strong driver for this is the development of routes with enhanced sustainability and/or facilitating more localized production requiring smaller distribution networks. On the industrial scale, a more highly active carbon-supported ruthenium-based catalyst was developed, and it forms the basis of the Kellogg Advanced Ammonia Process (KAAP). To date, while there has been some industrial uptake of this system, this has been limited. The development of this ruthenium catalyst has recently been outlined.<sup>3</sup> Given the fact that thermodynamically ammonia synthesis is favored by lower reaction temperatures, the development of more active catalysts

which could lead to exploitation of this thermodynamic window and a concomitant reduction in the severity of the conditions required for operation of ammonia synthesis continues to be a major focus of attention. The performance of a number of different materials has been reported in the literature including  $\text{Co}_3\text{Mo}_3\text{N}$ ,<sup>4,5</sup>  $\text{Ni}_2\text{Mo}_3\text{N}$ ,<sup>4,6</sup>  $\text{Co-Re}$ ,<sup>7,8</sup>  $\text{BaH}_2/\text{Co}$ ,<sup>9</sup>  $\text{Ru}/\text{electride}$ ,<sup>10</sup> and lithium hydride–transition metal (nitride) combinations.<sup>11</sup> In making an activity comparison between the  $\text{Fe-K}_2\text{O-Al}_2\text{O}_3$  and  $\text{Co}_3\text{Mo}_3\text{N}$  catalysts at atmospheric pressure and 400 °C, Kojima and Aika have reported rates of 330 and 652  $\mu\text{mol h}^{-1} \text{g}^{-1}$ , respectively,<sup>5</sup> and in a study at elevated pressure and with a feed containing ammonia, Jacobsen has also reported the  $\text{Co}_3\text{Mo}_3\text{N}$  to exhibit better ammonia synthesis performance than a commercial multipromoted iron catalyst.<sup>4</sup>

Among the different systems investigated, we have been interested in the possibility that Mars–van Krevelen mechanisms may be operative for metal nitrides.<sup>12</sup> To this end, the reactivity of lattice N in  $\text{Co}_3\text{Mo}_3\text{N}$  with hydrogen has been investigated where it was found that some  $\text{NH}_3$  could be produced in the absence of gas-phase  $\text{N}_2$ .<sup>13,14</sup> Furthermore, at elevated reaction temperature, 50% loss of lattice N occurred resulting in the  $\eta$ -12 carbide-structured  $\text{Co}_6\text{Mo}_6\text{N}$  phase, which was previously unprecedented.<sup>15</sup> The residual lattice N was

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## Heterogeneous acid conversion of a tricaprylin-palmitic acid mixture over Al-SBA-15 catalysts: Reaction study for biodiesel synthesis

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# *Synthesis and characterization of iron and iron nitride microtubes obtained from biogenic iron oxide*

**J. L. Rico & J. S. J. Hargreaves**

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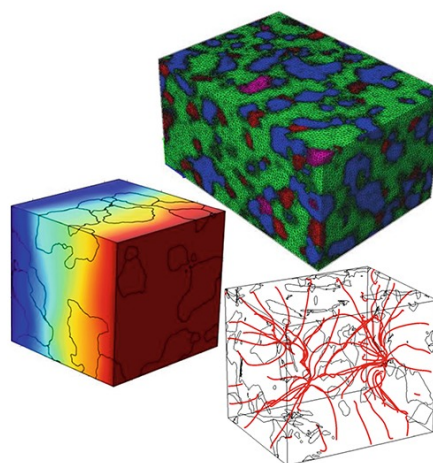
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# Potential Routes to Obtain Value-Added Iron-Containing Compounds from Red Mud

H. Gu<sup>1</sup> · J. S. J. Hargreaves<sup>2</sup> · J. -Q. Jiang<sup>3</sup> · J. L. Rico<sup>4</sup>

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**Abstract** Red mud, an aluminum industry large-scale waste, was used as a precursor to prepare sodium ferrate(VI) and sodium ferrite following different reaction pathways. Ferrous oxalate extracted from red mud has been used as an intermediate for the preparation of these compounds. The conversion rate to sodium ferrate(VI) from ferrous oxalate was as high as 64% in sodium hydroxide solution with sodium hypochlorite. Furthermore, sodium ferrite was formed after performing the solid–solid reaction at 600 °C using a 1:1 weight ratio of iron oxide (prepared via the ferrous oxalate extraction route from red mud) and sodium peroxide. In contrast, sodium iron silicon oxides were formed when red mud was reacted directly, following similar experimental procedures. These results present an

interesting alternative to convert an environmentally unfriendly waste to new value-added products. It is envisaged that sodium ferrate(VI) might be of great interest in terms of wastewater treatment, whereas sodium ferrite and  $\text{Na}_w\text{Fe}_x\text{Si}_y\text{O}_z$  might be of interest in the development of new materials for energy storage.

**Keywords** Red mud · Ferrate(VI) · Ferrite · Ferrous oxalate

## Introduction

Red mud is an alkaline waste generated in the process of alumina extraction from bauxite ores by the Bayer process [1]. Discharge of red mud is damaging to the environment because of its high alkalinity and heavy metal content [2]. The issues of red mud are a big challenge to the aluminum industry as well as society as a whole. Typically, red mud contains 6–8 major constituents and more than 50 trace elements. The major constituents are  $\text{Fe}_2\text{O}_3$ ,  $\text{Al}_2\text{O}_3$ ,  $\text{SiO}_2$ ,  $\text{TiO}_2$ ,  $\text{Na}_2\text{O}$ ,  $\text{CaO}$ , and, sometimes,  $\text{K}_2\text{O}$  and  $\text{MgO}$  [3, 4]. The content of each chemical constituent of red mud from different origins differs significantly because of the variation in the composition of bauxite ore and the process parameters, for example, typical compositional ranges are (wt%)  $\text{Al}_2\text{O}_3$  5–30,  $\text{Fe}_2\text{O}_3$  5–60, and  $\text{CaO}$  2–14 [4]. The identity and quantity of mineralogical components in red mud are important for its properties [5], which are diverse and not easy to examine. It is estimated that less than 4 million tons of the current annual production of 150 million tons of red mud are used in a productive manner [4]. In India alone, more than 4 million tons of red mud are generated annually and the development of its large-scale utilization is a major area of interest [6].

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# Investigación en catálisis en la Universidad Michoacana

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**RESUMEN:** En este trabajo se hace una breve reseña de la investigación y actividades relacionadas con la catálisis llevadas a cabo en la Facultad de Ingeniería Química de la Universidad Michoacana de San Nicolás de Hidalgo. Se mencionan los proyectos y las tareas de investigación, la infraestructura disponible, así como las colaboraciones con diferentes instituciones. Finalmente, se mencionan los principales logros.

**PALABRAS CLAVE:** Catálisis, proyectos de investigación, infraestructura.

**Abstract:** A brief review of the research activities on catalysis at the Department of Chemical Engineering of the University of Michoacan is herein described. The approved research projects, the available infrastructure in the laboratory and the collaboration with other institutions are also mentioned. The main achievements are finally commented.

**KEYWORDS:** Catalysis, research projects, infrastructure.

## Introducción

Las actividades de investigación en el área de catálisis comienzan en la Universidad Michoacana de San Nicolás de Hidalgo (UMSNH) con la incorporación del autor de esta reseña a la Facultad de Ingeniería Química (FIQ), perteneciente a esta institución, en 1993. Sin embargo, y debido a las dificultades encontradas en todo comienzo, fue hasta el año de 1996 que se realizó el primer trabajo de tesis relacionado con catálisis. Los primeros temas de investigación fueron sobre la síntesis de materiales y su caracterización. Cabe mencionar que gracias a los apoyos recibidos del Instituto de Investigaciones Metalúrgicas de la UMSNH, nuestras actividades de investigación fueron posibles y continúan siendo apoyadas en la actualidad. Esto se debe a que dicho instituto cuenta con infraestructura muy importante para nuestros fines, como son, por ejemplo, los equipos de microscopía electrónica, difracción de rayos X, espectroscopía de infrarrojo, entre otros. Asimismo, del 22 al 24 de noviembre de 1998, conjuntamente con la Academia de Catálisis A.C., organizamos por primera vez en nuestra institución, el IV Encuentro Nacional de Catálisis Heterogénea, lo cual vino a robustecer el desarrollo de esta área de investigación en la región occidente de nuestro país. Actualmente, somos

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## Reaction study for the esterification of oleic acid over M-SBA-15-SO<sub>3</sub>H (M=Al, Ti) catalysts.

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### Abstract

Mesoporous M-SBA-15-SO<sub>3</sub>H materials with molar ratios of Si/M=10 (M=Al, Ti) and Si/S=10 were synthesized by sol-gel. The materials were characterised by SAXRD, nitrogen physisorption, UV-Vis-DRS, FT-IR, using pyridine as a probe molecule, and the H<sup>+</sup> content was determined by sodium hydroxide titration. The incorporation of -SO<sub>3</sub>H groups resulted in Ti or Al mesoporous materials with the typical hexagonal arrangement of SBA-15. In addition, the materials possess Lewis and Brønsted acid sites, large surface areas and wide pores, being capable of catalyzing the esterification of oleic acid with high conversions (~97%) at 140°C. It was also demonstrated that the SBA-15-SO<sub>3</sub>H is more resistant to deactivation than Al-SBA-15-SO<sub>3</sub>H or Ti-SBA-15-SO<sub>3</sub>H catalysts. A simplified lumped first order reaction model reproduces well the experimental data for the acid esterification of oleic acid over SBA-15-SO<sub>3</sub>H at 60°C, 80°C, and 100°C. The calculated activation energy was 31.5 kJ mol<sup>-1</sup>, similar to other values reported for analogous systems.

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**Keywords:** M-SBA-15-SO<sub>3</sub>H; acidity; esterification; reaction study.

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## ZnAl-Zr hydrotalcite-like compounds activated at low temperature as solid base catalyst for the transesterification of vegetable oils

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### Abstract

ZnAl hydrotalcite-like compounds were modified through the incorporation of Zr<sup>4+</sup> using molar ratios of Zr/Al(X)=0.0, 0.10 and 0.25. The synthesis of these materials was performed by the co-precipitation method and their physicochemical properties were characterized by XRD, UV-Vis-DRS, N<sub>2</sub> physisorption, TGA, and finally, the basic properties were analyzed by titration with benzoic acid and adsorption of methanol analyzed by FT-IR. It was found that 200°C is the most appropriate activation temperature, since the catalytic activity of ZnAl-Zr(X) materials on the transesterification reaction was enhanced, obtaining FAME yields ranging from 68% to 82%. This high catalytic activity at low activation temperature (200°C) was attributed to the presence of a mixture of the active phases: hydrotalcite, zincite, and hydrozincite; as well as the formation of Brønsted and Lewis basic sites when the hydrotalcite-type materials are dehydrated. In addition, it was possible to calculate the apparent reaction rate constants by means of a simplified lumped first-order reaction model. The reaction rate constant for the ZnAl-Zr(0.25) catalyst was  $12.4 \times 10^{-3} \text{ L/g}_{\text{cat}} \cdot \text{min}$  which is 1.5 times greater than that of the catalyst without Zr.

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**Keywords:** ZnAl-Zr hydrotalcites; zincite; hydrozincite; basicity; transesterification

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