

Hydrotreating of carboxylic acids using SBA-15 mesoporous supported NiMo catalyst by micro waves in a fixed bed reactor

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Abstract:

In the present study, hydrogenation of carboxylic acid was performed in a continuous manner, using Micro Waves (MW), and a sulfide catalyst. SBA-15 supported NiMo hydrotreating catalysts were prepared by incipient wetness impregnation method and synthesized NiMo on AlSBA-15 and ZrSBA-15 in order to investigate the role of support acidity. Extrudates of the supported NiMo powders were prepared and sulfided. Octanoic acid in dodecane (10%) was introduced in the continuous flow reactor by the mean of an HPLC pump and co-fed with hydrogen at a working pressure of 0.5 MPa, while varying the reaction parameters such as temperature and feed flow rate (0.1, 0.25, and 0.5 ml/min). Power applied to the monomodal cavity varies in the range of 15-150 W and corresponding temperature from 200-350°C. Catalysts and supports were characterized by small- and wide-angle XRD, N₂-physisorption (BET, BJH), HRTEM, ICP-MS, UV-vis, ²⁷Al MAS-NMR and NH₃-TPD. The result of thermal response of MW found that the extrudates of SBA-15 (with or without Al or Zr) exhibit a strong MW response. The comparison of catalytic activity shows that all SBA-15 supported NiMo catalysts exhibit the same activity but the selectivity as compared to NiMo/Al₂O₃ catalysts was different.

Keywords: Hydrotreating; Octanoic acid; SBA-15; Microwave; Sulfide catalyst

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1. Introduction

Despite being an exhaustible fossil resource, crude oil currently remains as the main source of transportation fuels. One alternative is provided by biofuels and more specifically for diesel by the transesterification of vegetable oils. However, biodiesel has some drawbacks such as a limited content in conventional gas oil, a smaller heating value, For these reasons, biodiesel is not fully compatible with existing diesel engines and it is commercialized as a mixture with conventional diesel (Mikulec et al., 2010; Serrano-Ruiz, Ramos-Fernandez and Sepulveda-Escribano, 2012). In order to circumvent these drawbacks, vegetable oil can be hydrotreated (so called green diesel) to eliminate the oxygen and yield a renewable fuel with features similar to conventional diesel (Snåre et al., 2006; Šimáček et al., 2010; Huber and Corma, 2007). Hydrodeoxygenation (HDO) of triglycerides leads to carboxylic acids. Their conversion proceeds on conventional hydrotreating catalysts by three general routes that consist of ketonization, hydrogenolysis and decomposition (decarboxylation and decarbonylation). SBA-15 has been studied as support for a NiMo hydrotreating catalyst by various researchers (Badoga et al., 2012). In order to utilize the ordered mesoporous structure various modifications are done with SBA-15. The important modification included the incorporation of hetero atoms such as Ti, Zr, and Al in the frame work of SBA-15 (Klimova et al., 2008; Lizama and Klimova, 2009), modifying acidity, texture and dielectric properties. Hence, in the present study, we investigated the hydrotreating of octanoic acid, under MW, in a fixed-bed reactor using NiMo on SBA-15, ZrSBA-15, and AlSBA-15 catalysts. Micro Wave heating is known to bring a larger temperature gradient between catalyst and surrounding species leading to acceleration of desorption and species transport in the system (Suttisawat et al., 2012).

2. Material and methods

2.1 Material

P123, poly (ethylene oxide)-block-poly (propylene oxide)- block-poly(ethylene oxide), TEOS (tetraethyl orthosilicate), aluminum iso-propoxide, zirconyl chloride, Ammonium heptamolybdate,

nickel nitrate, octanoic acid, dodecane, hexadecane.

2.2 Support Preparation

-The SBA-15 was synthesized with 4g of P123 that was dissolved in the solution of deionized water and 4 mol/L of HCl and stirred at 40°C for 0.5 h and then TOES was slowly added to the mixture with vigorous stirring at 40°C for 24 h to get gel. The gel mixture was transferred into a Teflon bottle and aged at 100°C for 24 h. After that the sample was calcined at 550°C for 5 h to remove the organic template.

-The Zr-SBA-15 was prepared in the absence of HCl and using $ZrOCl_2 \cdot 8H_2O$ as zirconium precursor with the same procedure used for SBA-15, but was aged at 100°C for 2 days.

-The Al-SBA-15, P123 was added to 30 mL of water. After stirring for few hours, a clear solution was obtained. Thereafter, the required amount of HCl (pH=1.5) was added, and the solution was stirred for another 2 h. Then, TEOS and required amount of aluminum iso-propoxide were added and then the resulting mixture was continuously stirred at 40°C for 24 h, and finally crystallized in a Teflon-lined autoclave at 100°C for 2 days. The crystallized product was filtered off, dried and calcined in air at 550°C for 6 h.

2.3 Catalyst Preparation

All the catalysts were prepared by standard incipient wetness impregnation (IWI) technique. Molybdenum and nickel were impregnated into support. After each impregnation, the catalysts were dried at room temperature for 24 h and at 100°C for 24 h and then calcined at 500°C for 5 h. All catalysts were extruded by syringe that 3g of boehmite AlOOH (binder) were mixed with 1 g of catalyst, and then added nitric acid as solvent. This mixture was extruded by syringe, dried and calcined at 500°C for 2 h.

2.4 Hydrodeoxygenation (HDO) in fixed-bed reactor under single-mode MW

A monomodal cavity has been designed to perform, under H_2 pressure, in a continuous manner. The apparatus consists of a generator (2kW), circulators, a Tristan automatic tuning system linked to an adapted waveguide resonant cavity. Temperature was measured with a pyrometer focused on the reactor. The cylindrical volume of the quartz reactor interacting with the MW that was filled with a sulfided NiMo/SBA-15 hydrotreating catalyst extrudates deposited on a quartz frit (volume 24 cm³). Octanoic acid in dodecane (10%) was introduced in the continuous flow reactor by the mean of an HPLC pump and co-fed with hydrogen. Power applied to the cavity varies in the range of 15-150 W and corresponding temperature from 200-350°C. Various flow rates (0.1, 0.25, and 0.5 ml/min) were also used. Under these conditions, the octanoic was converted and hydrogenation products were analyzed by GC-FID.

3. Results and discussion

The thermal response of the catalytic solids to MW irradiation is given in Fig 1. We observed that alumina has a stronger response than silica based catalysts and that sulfidation of the catalysts enhances also this property. The preparation of extrudates leads systems which reacted rapidly to MW excitation, a few tenth of watts providing rapidly temperature of interest for our reaction.

The active phase of the catalysts is based on lamellar nanocrystallites of MoS_2 as illustrated by Fig 2. The distribution of stacking degree and slab length, metal dispersion follows the order $ExNiMo/AlSBA-15 > ExNiMo/ZrSBA-15 > ExNiMo/SBA-15$ (Fig. 2). A higher number of MoS_2 stacks and longer slab length indicate a poorer dispersion than conventional HDT catalysts (Badoga et al., 2014).

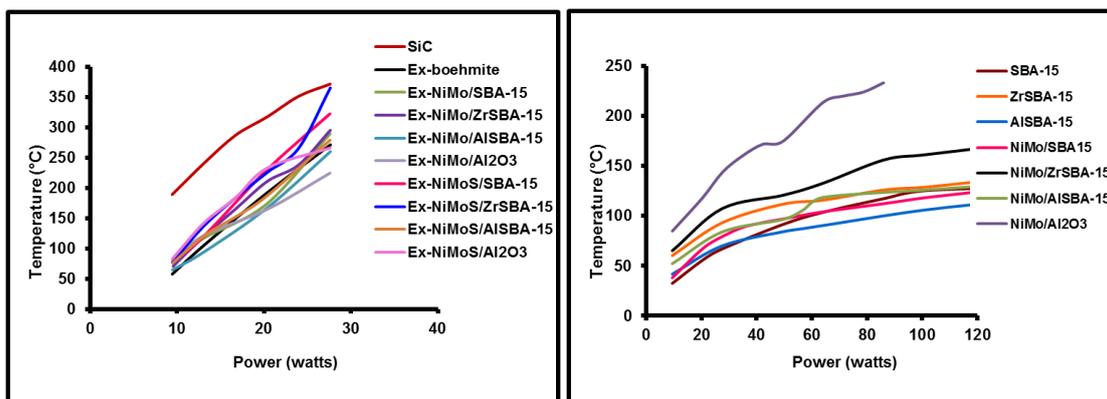


Fig. 1 Thermal response of MW of NiMo on different supports before and after extrudates.

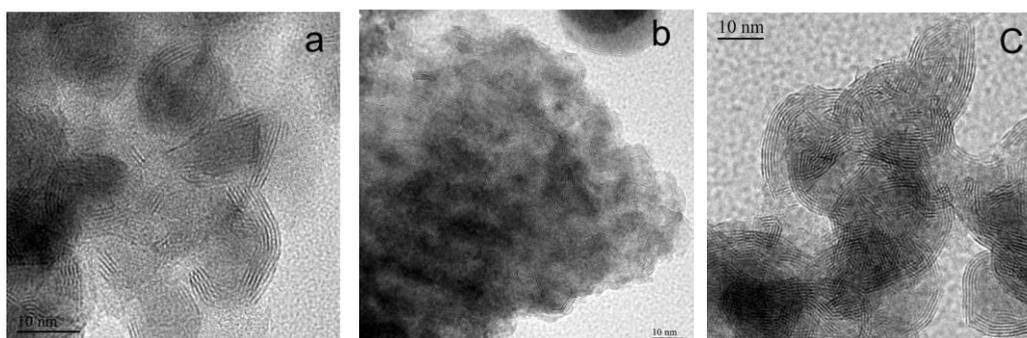


Fig. 2 HRTEM micrograph for (a) Ex-NiMoS/SBA-15, (b) Ex-NiMoS/ZrSBA-15, (c) Ex-NiMoS/AlSBA-15.

Concerning the catalytic performances, Fig. 3 illustrates the selectivity observed with the different catalysts at close levels of conversion. We can notice that C8/C7 ratio is close to 0.4 for all based SBA-15 catalysts whereas it reached 1.6 for the NiMo on alumina catalyst. Al containing SBA-15 exhibits also a higher yield of octyloctanoate, suggesting a contribution of stronger acid sites.

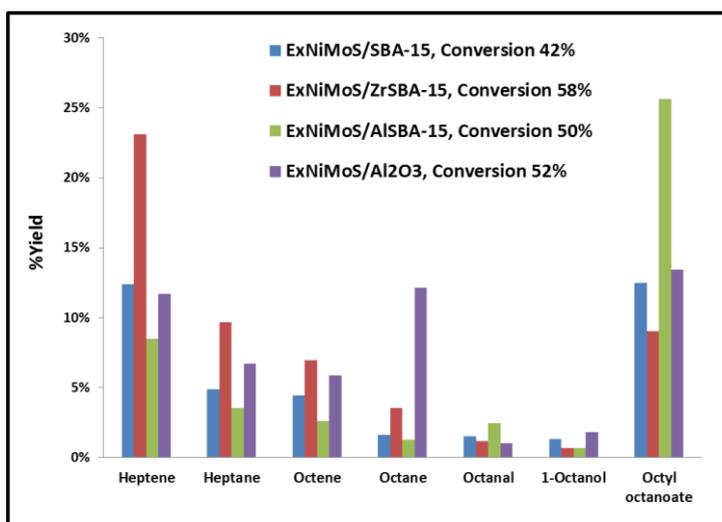


Fig. 3 Activities of supported NiMo hydrotreating catalysts at 350°C (catalyst = 3g, Flow rate = 0.25 mL/min, P = 0.5 MPa, and [OA]₀ = 0.7 mmol/g).

4. Conclusion

The use of MW activation allowed to convert octanoic acid (the main intermediate of triglyceride hydrogenation) with a low input power (50-150 w). Even if the dispersion of sulfide catalysts diminishes by using SBA-15, the catalytic activities remains close to that of the reference catalyst. The use of SBA-15 based catalyst provides a favored route with respect to decarboxylation as compared to NiMo on alumina catalyst. However, a higher acidity obtained by Al substitution in SBA-15 is unfavorable since it promotes the condensation route.

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