

Lithium-based catalysts derived from sol-gel hydrotalcite for ethylic transesterification

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Introduction

Transesterification of vegetable oils or animal fats produces a mixture of fatty acids esters known as biodiesel, which is a promising substitute for fossil diesel fuel because it is renewable, non-toxic and biodegradable [1]. Mixed oxides derived from hydrotalcite are efficient heterogeneous base catalysts for transesterification. Besides, their basicity can be improved by incorporation of an alkaline metal [2]. Particularly, MgAlLi mixed oxides have shown to be very active for transesterification under mild reaction conditions. However, these catalysts prepared by Li impregnation onto an MgAl hydrotalcite (HT MgAl), synthesized through coprecipitation method, followed by calcination presented very low stability in the reaction medium [3]. The present investigation deals with the synthesis of MgAlLi catalysts prepared by sol-gel method with *in situ* lithium addition and their application to transesterification reaction. The influence of the synthesis procedure on texture, structure, catalytic activity and stability is the main purpose of this study.

Materials and Methods

HT MgAl with Mg/Al=4 was prepared by the sol-gel method based on Prinetto et al. [4]. Briefly, 0.15 mol of $\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ was dissolved into ethanol containing 3.2 mL of HCl 35%. Another solution containing 0.038 mol of $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ dissolved into ethanol was added under stirring. The final pH of the mixture was adjusted to 10 by the dropwise addition of NH_4OH 30%. Thus, water in equimolar amounts of $\text{H}_2\text{O}:\text{Mg}^{2+}$ was added. The resulting mixture was constantly stirred until the gel formation (24 h). The obtained gel was then washed and oven dried at 80°C. The Li-based catalysts were prepared using a similar method. Therefore, the precursor of the Li^+ was added *in situ*. For that, LiNO_3 was dissolved into ethanol and added to mixture just before the pH adjusting. After 24 h of stirring, the obtained gel was oven dried at 80°C. Catalysts containing the lithium loadings of 5, 10 and 15 wt% [$\text{Li}^+/(\text{Li}^+ + \text{mixed oxide})$] were prepared (mixed oxide weight was obtained from hydrotalcite calcination was established by TGA analyses). The MgAl and MgAlLi mixed oxides were prepared by the calcination of the HT MgAl and HTs containing Li^+ , respectively. The thermal treatment was performed in an oven EDG (3P-S 1800) at 600°C for 2h, using a heating rate of 5°C.min⁻¹. The materials were characterized by powder X-ray diffractometry in a Rigaku Multiflex using Cu K α radiation. The oxides crystallite size was calculated by Scherrer equation using the main diffraction peak ($2\theta=43^\circ$). N_2 physisorption at 77 K was used for the BET surface area determination (Quantachrome NOVA 1200). The catalytic activity was evaluated in the transesterification model reaction between methyl acetate and ethanol. The experiments were performed in a batch reactor (2 mL) using a mol ratio of ethanol/methyl acetate=6/1, 4 wt% of catalyst, 50°C and 30 min of reaction. The reaction products were analyzed in a gas chromatograph Shimadzu (GC 2010) equipped with FID and Rtx[®]-1 capillary

column. The reuse of the catalysts was also investigated. After the first reaction cycle, the catalyst was separated by centrifugation and a new reaction mixture was placed in contact with the used catalyst. The following reaction was performed under the same conditions described before.

Results and Discussion

The XRD for HT MgAl showed characteristic diffractions of the hydrotalcite [JCPDS 14-0191]. Figure 1 (a) shows the XRD of the MgAl and MgAlLi mixed oxides. The XRD of MgAl exhibits diffractions of an $\text{Mg}(\text{Al})\text{O}$ mixed oxide with periclase-type structure (MgO) [JCPDS 75-1525] [3]. In the MgAlLi oxides, the presence of some low intensity diffraction peaks, possible related to LiAlO_2 , Li_2CO_3 and LiOH can be observed. The last two compounds can be formed, respectively, by carbonation and hydration of the Li_2O (arising from thermal decomposition of LiNO_3). Diffractions related to LiNO_3 were also detected. The XRD analysis of the MgAlLi oxides revealed more intense and narrower diffractions than the oxides without Li. Furthermore, the crystallite size tend to increase with the Li addition (13.2 nm for $\text{Mg}(\text{Al})\text{O}$ and 18.9 nm for MgAlLi-5) in the catalysts. On the other hand, the specific surface area tend to decrease (155 m².g⁻¹ for $\text{Mg}(\text{Al})\text{O}$ and 16 m².g⁻¹ for MgAlLi-5). This result suggest that the Li causes the oxides sintering, probably due to the reduction in the materials thermal stability [5]. The $\text{Mg}(\text{Al})\text{O}$ showed insignificant transesterification activity (Fig. 1(b)), as also observed by Fraile et al. and Castro et al. [2, 3]. Nevertheless, all the MgAlLi catalysts revealed to be very active. It is interesting to note that high conversions (ca 86%) were reached even in the presence of the catalyst with the lowest Li loading (MgAlLi-5). Reuse experiments showed a gradual catalyst deactivation with lower conversion after three reaction cycles.

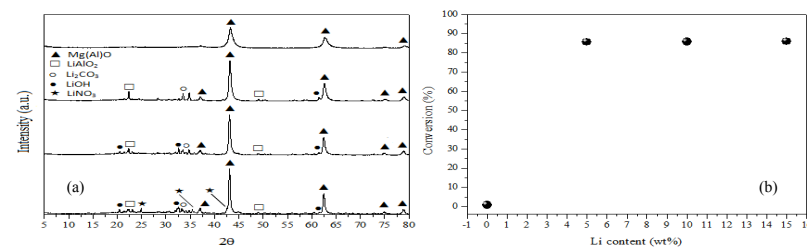


Figure 1. XRD and catalytic tests (b) for MgAl and MgAlLi mixed oxides.

Significance

$\text{Mg}(\text{Al})\text{O}$ mixed oxide showed, under mild reaction conditions, negligible transesterification activity. However, all MgAlLi catalysts were found to be very active. Reuse tests showed catalyst deactivation after the third cycle.

References

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