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SYNTHESIS AND CHARACTERIZATION OF MIXED OXIDES DERIVATE FROM Li MODIFIED Mg-Al HYDROTALCITES

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ABSTRACT

Lithium modified Mg/Al hydrotalcite-like samples with different Li content were synthesized using co-precipitation followed by calcination at 500 °C. The samples were characterized by means of XRD, DRIFTS, SEM-EDS, LDPSA and MIP. Results from this study indicated that the addition of Li modifier influences the change in structural, textural and morphological characteristics, more pronounced in samples with higher lithium content.

INTRODUCTION

Hydrotalcite (HT) materials are widely used in a variety of catalytic reactions such as alkylation, isomerization, esterification, polymerization, hydro-dehydrogenation, among which the basic ones are particularly suitable for biodiesel production [1]. By changing the molar ratio of hydrotalcite cations, nature and content of metal modifier, and interlayer anions during the preparation, properties of the obtained as-synthesized hydrotalcite-like materials may be considerably influenced. After calcination, hydrotalcites decompose to mixed oxides with loss of water and CO₂ (carbonate form of HT). Calcined forms of HT are of particular interest due to their increased basicity relative to the as-synthesized HT, increased surface area and homogeneous mixing of the different elements [2].

The aim of this study is to synthesize Mg-Al hydrotalcites modified with different content of Li and to characterize the resulting mixed oxides. The effect of lithium loading on the structural, textural and morphological characteristics of the oxide (Li/Mg/Al)O-type materials as well as their use

as potential solid base catalyst in heterogeneously catalyzed transesterification reaction for biodiesel production is emphasized.

EXPERIMENTAL

Preparation of HT samples

Lithium modified Mg-Al hydrotalcite samples were synthesized in a five-necked glass reactor equipped with a steam jacket, stirrer, pH electrode, thermocouple, and reflux condenser. The carbonate forms of precursors were obtained by co-precipitation at temperature of 60 °C and pH = 9.5-10, using nitrates of the corresponding metals, $\text{LiNO}_3 \cdot 6\text{H}_2\text{O}$, $\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$, and Na_2CO_3 as a precipitating agent. The mixed Li-Mg-Al aqueous solution of nitrate salts (5, 10, and 15 wt% of Li and $\text{Mg}/\text{Al} = 3/1$) and the precipitant were introduced drop-wise simultaneously to the reactor. The resulting slurry was aged for 1 h in the mother liquor under stirring. Then it was filtered off and washed thoroughly with distilled water up to absence of NO_3^- ions in the filtrate. The synthesized precursors were dried at 105 °C for 20 h and subsequently thermally activated in an air atmosphere at 500 °C for 2 h. Neat Mg-Al HT sample (without the addition of Li) was also prepared for comparison purposes. The neat sample was designated as HT, while the nominal 5, 10, and 15 wt% Li-modified HT samples were labelled with 5Li-HT, 10Li-HT and 15Li-HT, respectively.

Characterization of calcined HT samples

The morphology and composition of the observed particles on the surface were determined by SEM-EDS microscopy using JEOL JCM-6610LV with energy dispersive X-ray high vacuum detector (W filament, E = 20 kV). The particle size of the samples was assessed by laser diffraction particle size analyzer (LDPSA) Malvern Mastersizer 3000C. The mercury intrusion porosimetry (MIP) measurements were performed using a Carlo Erba Porosimeter 2000. X-ray diffraction data were collected using a Bruker D8 Endeavor diffractometer ($\text{CoK}\alpha$ radiation, $\lambda = 1.78897 \text{ \AA}$). FT-IR spectra of the samples were recorded in the range of 4000-400 cm^{-1} (DRIFTS, Thermo Scientific Nicolet 6700) at room temperature under atmospheric conditions.

RESULTS AND DISCUSSION

The results of EDS elemental surface analysis, particle size, and mercury intrusion porosimetry measurements are summarized in Table 1. The EDS results revealed that the surface molar ratio of Mg/Al in each calcined sample is the identical, close to the theoretical. Since it is well known that EDS method determines the elemental composition of the mapped part of the SEM micrograph, it can be considered that experimental results satisfactorily correspond to the theoretical bulk ratio of Mg/Al in the samples. The granulometry data showed that the mean diameter of the

Table 1. Mg/Al molar ratio^a, particle size^b and porosimetry^c results

Sample designation	Mg/Al molar ratio		^{b1} d _{p.mean}	^{c1} S _s	^{c2} P
	^{a1} Nominal	^{a2} Experimental	μm	m ² g ⁻¹	vol%
HT	3/1	2.6/1	49	203	83
5Li-HT	3/1	2.5/1	n.d.*	199	86
10Li-HT	3/1	2.4/1	168	187	n.d.*
15Li-HT	3/1	2.5/1	226	179	85

^aEDS microanalysis; ^{a1}theoretical value; ^{a2}elemental surface analysis (EDS); ^bgranulometric analysis; ^{b1}mean particle diameter (LDPSA); ^cMIP; ^{c1}specific surface area; ^{c2}porosity; *not determined.

particles depends on the content of Li. It can be noted that the increase of Li content leads to an increase of the mean particle diameter.

The results of mercury porosimetry showed that there is no significant difference between neat and modified samples. The porosity is varied between 83 and 86%, while the specific surface area is changed from 203 to 179 m²g⁻¹ and decreasing slightly with increasing the content of lithium.

The morphology of the selected Mg/Al and Mg/Al/Li mixed oxides (neat HT and 10Li-HT) is shown in Fig. 1. The neat HT presents flat structure with “platelet” morphology, representative of layered materials, whereas the

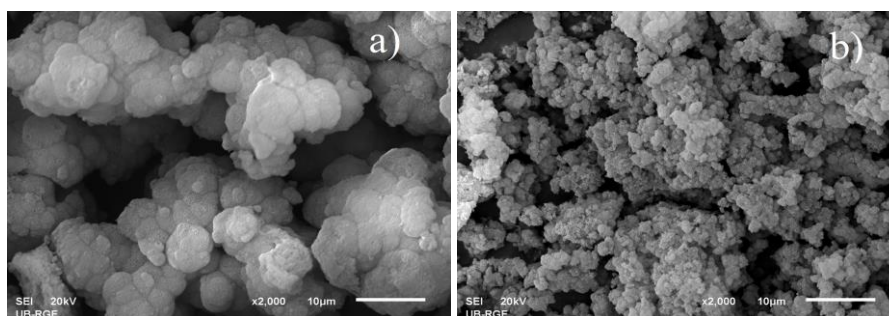


Figure 1. SEM micrographs of neat and Li-modified Mg-Al hydrotalcites: (a) neat HT and (b) 10Li-HT.

sample 10Li-HT is morphologically modified in which the large aggregates composed by round particles are observed (Fig. 1b).

Fig. 2 shows XRD diffractograms of the calcined samples. The XRD of neat HT exhibits diffractions of an Mg(Al)O mixed oxide with MgO cubic crystal structure (ICDD 00-045-0946). For the MgAlLi oxides, new diffractions were not observed (Fig. 2). The expected Li₂O was not detected, which can be due to the low scattering factor for the light atom of Li or due to high dispersion of Li₂O over the oxide matrix. Another explanation for the absence of diffractions related to the Li compounds may be found in the vicinity of the ionic radii of Li¹⁺ (0.76 Å) and Mg²⁺ (0.72 Å), which allows a simple isomorphic replacement of Mg²⁺ by Li¹⁺ in the MgO structure [3].

Fig. 3 illustrates the FT-IR spectra of calcined samples. All samples show a broad and intense band between 4000 and 3000 cm⁻¹ due to OH stretching

vibration of layer hydroxyl groups and interlayer water molecules. The bands at 1635 cm^{-1} are originated by the bending mode of interlayer water molecules. The broad and intense bands in the region $1490\text{--}1390\text{ cm}^{-1}$ are due to the antisymmetric stretching mode of interlayer carbonate ions. The intensity of this band is different for modified samples and increases with increasing lithium content (Fig. 3). In fact, the 15Li-HT sample shows the most intense band centered at 1384 cm^{-1} , which is also potential evidence that the addition of larger amounts of Li leads to formation of more basic sites, leading to increased adsorption of CO_2 .

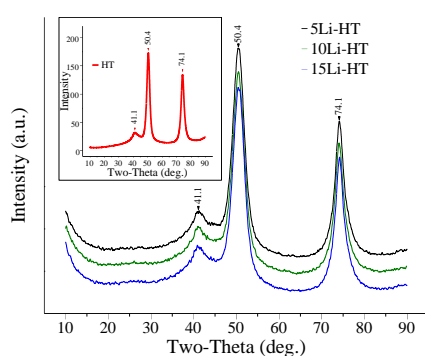


Figure 2. XRD patterns of calcined samples

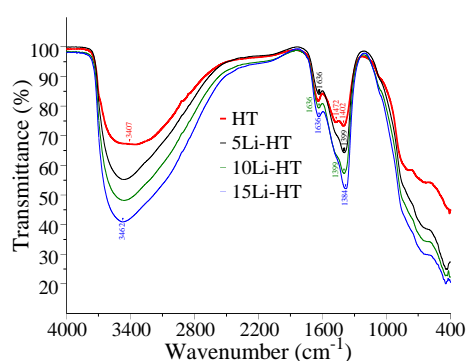


Figure 3. FT-IR spectra of calcined samples

CONCLUSION

Lithium modified Mg/Al hydrotalcite-like samples with different Li content were synthesized using co-precipitation followed by calcination at $500\text{ }^{\circ}\text{C}$. It was disclosed that the structure, texture and morphology of the mixed oxides, formed by calcination of co-precipitated Li modified Mg-Al hydrotalcites were altered by the content of Li. This finding is more significant in the MgAlLi oxides with higher Li content, thus allows obtaining of favorable catalysts for use in various organic conversions, especially in the reaction of oils transesterification for biodiesel production.

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