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STRUCTURE AND MORPHOLOGY OF CALCINED LANTHANUM DOPED HYDROTALCITE

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ABSTRACT

Mg-Al hydrotalcites (Mg/Al molar ratio 3/1) doped with varying amounts of lanthanum were prepared using co-precipitation followed by calcination in order to study the effect of lanthanum on their structure and morphology. Samples were characterized by several methods: XRD, FT-IR, SEM-EDS, LDPSA and MIP. It was found that the addition of lanthanum affects the structure and morphology of the obtained metal oxides derived from La-doped Mg-Al hydrotalcites, making it effective dopant for (Mg/Al/La)O-type materials, being very promising for various catalytic reactions.

INTRODUCTION

Hydrotalcites are environmentally friendly materials which behave as solid bases and can be used in many catalytic reactions, such as transesterification of oils for biodiesel synthesis, ethanol reforming, water gas shift reactions, and CO oxidation [1, 2]. Hydrotalcites are known to be used as support for numerous catalytic species, such as rare-earth metals, alkali metals and even various anions. Their base properties are strongly related to the nature and content of doped metal as well as the temperature of calcinations.

This paper deals with the effect of La content in the mixed oxides derived from La-doped Mg-Al hydrotalcites (Mg/Al = 3/1) on the structure and morphology of prepared (Mg/Al/La)O-type materials.

EXPERIMENTAL

Preparation of HT samples

Three La-doped Mg-Al hydrotalcite samples (Mg/Al molar ratio of 3/1) were synthesized with theoretical La amount of 5, 10, and 15 wt% (calculated with

respect to MgO-Al₂O₃ content) by co-precipitation under stirring at 60°C and pH = 9.75±0.25, using La(NO₃)₃·9H₂O, Mg(NO₃)₂·6H₂O, Al(NO₃)₃·9H₂O, and Na₂CO₃ as a precipitating agent. The obtained hydroxycarbonate precipitates were dried at 105°C for 20 h and subsequently calcined in an air atmosphere at 600°C for 2 h. The prepared samples were denoted as HT-LaX, where X represents the weight percentage of La. Similarly, Mg-Al hydrotalcite reference sample (Mg/Al molar ratio of 3/1) was also prepared under the same preparation conditions and denoted as HT-0.

Characterization of HT samples

X-ray diffraction data were collected using a Bruker D8 Endeavor diffractometer (CoK α radiation ($\lambda = 1.78897 \text{ \AA}$) operating at 40 mA and 40 kV). FT-IR spectra of the samples were recorded in the range of 4000-400 cm⁻¹ on Thermo Scientific Nicolet 6700, diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS) at room temperature under atmospheric conditions. The morphology and composition of the observed particles on the surface were determined by SEM 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 textural characterization of the samples was performed by mercury intrusion porosimetry (MIP) using a Carlo Erba Porosimeter 2000.

RESULTS AND DISCUSSION

The recorded X-ray diffraction lines at 41.1°, 50.4°, and 74.1° for all samples (Fig. 1) corresponded to positions of the crystalline cubic MgO phase (ICDD-PDF file 00-045-0946) indicating the formation of MgO-like phase. It is obvious that after thermal treatment at 600°C, the carbonate-containing HT structure destroyed with formation of mixed MgAl oxide, most probably a solid-solution with cubic structure [3]. The comparison with reference sample (HT-0), the lines' broadening is a consequence of the La presence. For samples with lower La contents, no peaks related to La-oxides can be observed, probably due to La low content or high dispersion of La-oxides. However, the addition of dopant in a larger amount (HT-La15) prompts formation of well-organized La₂O₂CO₃ (lanthanum oxy-carbonate) phase (ICDD-PDF file 00-048-1113) along with Mg-Al mixed oxide. At the applied calcination temperature the structure of La₂O₂CO₃ oxide is not stable, thus the peak intensity variation can be observed.

The broad and strong absorption band in the range of 3725-2570 cm⁻¹, centered at 3410 cm⁻¹ (Fig. 2) appeared in the FT-IR spectra of all calcined samples and is attributed to the H-bonding stretching vibrations of the OH groups in the brucite-like layer. The bands about 1640 cm⁻¹ is ascribed to the

deformation mode of H₂O molecules. It is observed two asymmetric broad bands at 1470 and 1403 cm⁻¹, at 1490 and 1409 cm⁻¹ (HT-La5), at 1494 and 1411 cm⁻¹ (HT-La10) and three ones at 1502, 1454 and 1368 cm⁻¹ for HT-La15. This region is characterized by CO₃²⁻ and NO₃⁻ ions [4]. It is important to note that absorption bands for H₂O and CO₃²⁻ ions are still observed thereby indicating their present in the oxide structure (La₂O₂CO₃). The narrow bands, typical for interlayer NO₃⁻ ions at 1425 and 1385 cm⁻¹ are not registered. It is likely that not all CO₃²⁻ were decomposed at the calcination temperature of 600°C or that CO₂ from the ambient air became re-adsorbed onto the basic sites of the metal oxides. The presence of water bands support the supposition that H₂O molecules could have also physically adsorbed onto the metal oxides. In fact, the HT-La15 sample shows three most intense bands at 1502, 1454 and 1368 cm⁻¹ which are also potential evidence that the addition of a larger amounts of La leads to the formation of more basic sites leading to increased adsorption of CO₂.

The EDS results (Table 1) disclosed that the molar ratio of Mg/Al in each

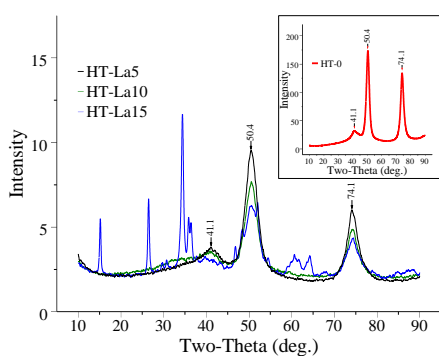


Figure 1. XRD patterns of calcined samples

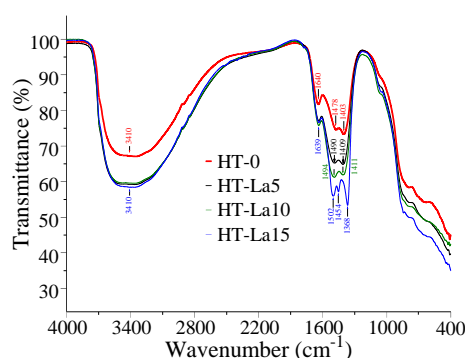


Figure 2. FT-IR spectra of calcined samples

sample is lower than the theoretical value. Bearing in mind that SEM analysis is surface one and also the limited accuracy of EDS, the obtained results correspond to the theoretical bulk ratio of Mg/Al in the samples. The La surface content increases with La loading.

The granulometry data determined by laser diffraction technique show mean particle diameters around 40 μm except for the HT-La 5 sample (Table 1). The particle diameter is roughly independent of the La content.

Sample	Mg/Al molar ratio		La content		^{b1} D _{p,mean} μm	^{c1} ρ _{bulk} gcm ⁻³	^{c2} P vol%
	^{a1} Nominal	Experimental (Mg/Al)	^{a1} Nominal	^{a2} wt%			
HT-0	3/1	2.83/1 (26.89/9.50)	-	-	42.3	0.42	83
HT-La5	3/1	2.76/1 (24.80/9.00)	5	4.75	26.9	0.48	80
HT-La10	3/1	2.65/1 (25.62/9.67)	10	12.92	40.8	0.62	79
HT-La15	3/1	2.82/1 (24.41/8.64)	15	16.31	41.4	0.55	87

^aEDS microanalysis; ^{a1}theoretical value; ^{a2}elemental surface analysis (EDS); ^bgranulometric analysis; ^{b1}LDPSA; ^cMIP mercury intrusion porosimetry; ^{c1}bulk density; ^{c2}porosity.

Mercury intrusion porosimetry results showed that all calcined samples represent high-porosity materials with a porosity about 80 vol% (Table 1). SEM micrographs of calcined samples (Fig. 3) indicate the uniform hexagonal platelet structure partly destroyed due to the H₂O removal from the brucite-like layers (OH groups), interlayer H₂O molecules and CO₂ from the interlayer carbonates as well. Nevertheless, the lamellar like morphology is still kept, although with smaller platelets. The mixed Al/Mg/La oxides obtained by calcinations of La-doped Mg-Al hydrotalcites showed a different morphological structure in relation to the reference sample (Fig. 3).

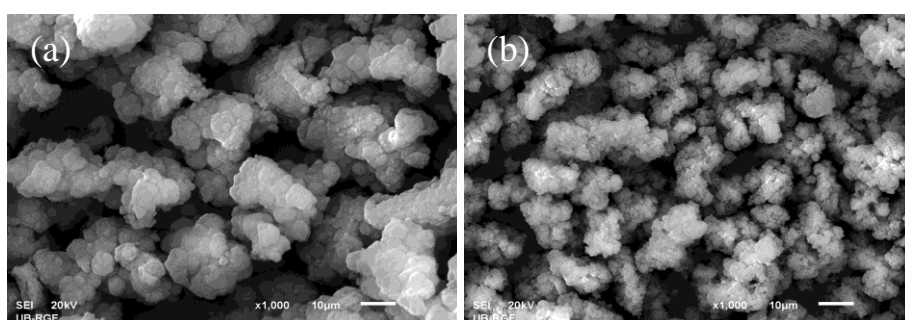


Figure 3. SEM micrographs of reference and La-doped samples

CONCLUSION

The characterization study revealed that the structure and morphology of the mixed oxides, resulting from calcination of co-precipitated La-doped Mg-Al hydrotalcites were affected by the content of La. The impact of La supplement is more significant in the oxides with higher La loading, thus permits obtaining of promising catalysts for different catalytic processes.

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