Hydrotalcite like compounds as tunable surface dispersant precursor to Ce and La active sites

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ABSTRACT

Introduction

The strongest impulse for developing new, more efficient and selective catalyst systems and for the realization of new process technology is strongly related to environmental compatibility The discovery of functional solid materials of high catalytic performance is crucial to most chemical processes. In this context, clay minerals are just a class of inorganic layered compounds, which can be engineered into various functional solid catalysts due to their inherent features in composition and structure. Layered materials, with their structure consisting of stacked sheets, represent an interesting opportunity for developing new materials with a tailored nano-design. Hydrotalcite-like compounds also referred as precursors are anionic clays with the general formula $[M(II)_{1-x}M(III)_x(OH)_2](A^{n-})_{x/n}.mH_2O$. Their structure is based on brucite-like layers in which a fraction of the divalent metal cations (MII: Mg^{2+}) have been substituted by trivalent cations (MIII: Al^{3+}) resulting in positively charged layers balanced by anions in the interlayer. Calcination of precursors leads to formation of mixed oxides. On the other hand, ceria presents particular chemical features such as its redox properties in the presence of transition metals which makes it very attractive for applications in catalytic formulations in numerous reactions. The main role played by ceria is related to the generation of anionic vacancies and to the participation of reactive oxygen species, which can be tuned in the presence of other elements in the lattice [1-4]. This work reports the synthesis and characterization of metal mixed oxides obtained from Hydrotalcite-like compounds, where a constant fraction of Al was substituted by La and Ce.

Experimental

The preparative methods adopted in this study were direct co-precipitation and wet impregnation. In the direct co-precipitation method, the samples were prepared by the low supersaturation procedure at constant pH of 10 ± 0.2, with M^{2+}/M^{3+} constant molar ratio of 3. The resulting solid, washed until pH of 7 and dried, was calcined in open air at 450 ºC for 9 h. In the impregnation method, salt aqueous solution of the metal ion to incorporate was added to the mixed oxide of Mg-Al obtained by co-precipitation. The metal theoretical loading was 10 % wt of the Mg-Al mixed oxide weihgt. The resulting solid was dried at 90 ºC overnight. Then, it was calcined in air flow at 350 ºC for 2 h and finally at 500 ºC for 8 h to obtained the mixed oxide.

All samples were examined by X-ray Diffraction, Surface Area determined by the BET method, Scanning electron microscopy, X-ray photoelectron spectroscopy, Temperature - Programmed Desorption of CO_2 and Inductive Coupled Plasma spectroscopy. Samples were named with the metals in brachet and initial of the synthesis method, for example: $(La-Mg-Al)_C$ and $(La-Mg-Al)_I$.

Results

Precursor samples were analyzed by XRD to assess the presence of crystalline structure depending on the method of synthesis employed. The peaks recorded were attributed to crystalline planes of a hydrotalcite structure. Calcined samples were analyzed by XRD to study the different oxides phases

formed. All patterns of mixed oxides showed the presence of MgO in periclase phase and the oxides of the third metal incorporated. X-ray diffraction patterns are not shown here. Table 1 presents the surface area values of the mixed obtained by co-precipitation and impregnation methods. The area of the oxides was higher than the precursors (not shown here) in all cases. This phenomenon is due to the destruction of the brucite-tipe layer together with the elimination of carbonate anions and water from interlayer space. The carbonate anion is released as carbon dioxide promoting small channels or pores in the solid, which increases the surface area. Oxides with the third metal incorporated specific areas decrease when the metal ion size increases. Chemical composition analysis showed that the sample with Cerium added by co-precipitation molar percent was lower than data synthesis. Furthermore, it could only be incorporated into surface third of the value of synthesis (15%) probably due to the size of the cation. In the same way, Lanthanum could not be observed at the surface. The highest third metal loading at surface level was reached by the impregnation method. Oxides with Cerium incorporated by both methods showed irregular particle size. While samples with embedded Lanthanum showed more homogeneous particle size.

Table 1. Surface area, chemical composition and basic sites density of mixed oxides.

Properties	Area ($m^2 g^{-1}$)	M^{3+} mol %			Basic sites density (μmol $CO_2\,g^{-1}$)
		Synthesis	ICP	XPS	
$(La-Mg-Al)_C$	301	15	16	traces	0.8
$(Ce-Mg-Al)_C$	185	15	12	5.0	0.7
$(La-Mg-Al)_I$	206	2.7	11	4.5	3.5
$(Ce-Mg-Al)_I$	181	2.7	2	1.0	4.5

Conclusions

Hydrotalcites like compounds with La or Ce incorporated by co-precipitation and impregnation methods were synthesized. Heat treatment resulted in the periclase phase MgO formation, together with oxides of the transition metals incorporated. The specific surface areas of the mixed metal oxides were, in all cases, higher than those of the precursors due to dehydroxylation of the brucite type blades and removing carbonate anions as CO_2 interlaminar space. The experimental values of given composition by ICP and XPS for the percentage of third metal were incorporated close to the values of the modified synthesis Ce sample while samples with Lanthanum was markedly superior. The experimental values of composition given by ICP incorporating the third metal by co-precipitation were close to the values of synthesis while the samples obtained by impregnation were markedly higher except in the sample modified with Ce. Comparing both methods of synthesis, the third metal loading at surface level was largest by the impregnation method. All oxides presented basic properties. However, impregnated samples showed highest basic density according with the chemical composition results. Mixed oxides modified with La or Ce presented relevant properties for structured catalyst application in chemistry and energy.

References

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