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Zinc–aluminum hydrotalcites as precursors of basic catalysts: Preparation, characterization and study of the activation of methanol

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ABSTRACT

Monophasic ZnAl hydrotalcite-like layered hydroxycarbonate has been prepared by the urea precipitation method. This material has been characterized by Rietveld refinement of the XRPD pattern, DTA-TG and skeletal IR. ZnAl mixed oxides have been prepared by calcinations of this precursor. According to XRPD, after calcinations at 450 °C this material is constituted by poorly crystallized ZnO phase. IR spectroscopy shows the presence of additional spinel-like domains. The surface of this catalyst is dominated by poorly acidic Zn^{2+} cations and terminal and bridging hydroxy groups bonded to Zn ions. This catalyst adsorbs methanol dissociatively giving rise to two types of methoxy groups. Type A, likely bridging on Al and Zn ions, is more stable to desorption. Type B, likely terminally bonded to Zn^{2+} cations, is more labile with respect to decomposition into CO and H_2. Type B methoxy groups appear to be very ionic and are, likely, those involved in transesterification and polyethoxylation reactions. ZnO and $ZnAl_2O_4$ particles progressively crystallize and sinter by increasing calcination temperature.

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1. Introduction

Zinc aluminates, either stoichiometric or containing an excess of zinc, were characterized in earlier studies as very basic materials [1,2]. In fact, ZnAl mixed oxides find practical application as catalysts for industrial processes which have been classified as typically base-catalyzed, although an acid–base cooperation certainly occurs with solid catalysts [3,4]. They are reported to act as the industrial catalysts of the Institut Français du Pétrol (IFP) process for the biodiesel synthesis by transesterification of fats (Esterfip-H process [5]) as well as of polyethoxylation processes producing non-ionic surfactants (Henckel, BASF [6,7]). Zinc aluminate has also been patented as an optimal catalyst for light olefins double bond position isomerization (Phillips [8]).

Zn aluminates are also supports or components of relevant industrial catalysts such as, in particular, copper containing catalysts for methanol synthesis [9,10], low temperature water gas shift [9,10] and for hydrogen production from methanol steam reforming [10–12]. They are also components of promising Ni catalysts for hydrogen production by ethanol steam reforming [13]. These catalysis behaviors are thought to be assisted by basicity [3].

Like Mg aluminates, Zn aluminates may be prepared by thermal decomposition of hydrotalcite-type precursors. Hydrotalcites (HTs), i.e. Mg–Al layered double hydroxides, and the products of their calcination are very useful and popular basic materials which find industrial application as basic catalysts [14–17]. ZnAl hydrotalcites have been patented as precursors of catalysts for polyethoxylation of alcohols [6,7]. In spite of the relevant industrial interest for these materials, the scientific literature concerning ZnAl HT as catalysts or catalyst precursors is poor.

Both polyethoxylation and transesterification imply the activation of an alcohol as a nucleophilic reactant, to attack the electrophilic carbon of carboxylate esters (transesterification) and of ethylene oxide (polyethoxylation).

In the present communication we will refer about the preparation of ZnAl HT using the urea method, developed in one of our laboratories a few years ago [18]. Additionally, we will refer about characterization of the products of its calcinations as well as on the adsorption and activation of methanol (as a typical alcohol reactant) on them.

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2. Experimental

2.1. Preparation procedure

HT of formula $[Zn_{0.67}Al_{0.33}(OH)_2](CO_3)_{0.165}{\cdot}0.5H_2O$ was prepared by the urea method [18]. Solid urea was dissolved in a solution of 0.165 mol/dm^3 of $Al(NO_3)_3{\cdot}9H_2O$ and 0.335 mol/dm^3 of $Zn(NO_3)_2{\cdot}6H_2O$ to reach a urea/metal ion molar ratio of 3.3. The clear solution was maintained at 100 °C for 36 h. The obtained precipitate was separated from the mother solution, washed with de-ionized water and with small volumes of 0.1 M sodium carbonate in order to exchange residue nitrate ions with carbonate ions. After washings with Na_2CO_3 solution, the solid was recovered, washed with de-ionized water and finally dried at room temperature over P_4O_{10}.

2.2. Characterization techniques

Metal analyses were performed by Varian 700-ES series Inductively Coupled Plasma-Optical Emission Spectrometers (ICP-OES) using solutions prepared by dissolving the samples in concentrated HNO_3 and properly diluted.

Coupled thermogravimetric (TG) and differential thermal (DTA) analyses were performed with a Netzsch STA 449C apparatus, in airflow and heating rate of 10 °C/min.

The morphology of powder was examined with a Philips XL30 Scanning Electron Microscope (SEM) after having deposited a drop of the suspension of the HT in acetone on a holder and having left the solvent to evaporate at room temperature. The samples ware metallized with gold.

X-ray powder diffraction (XRPD) patterns were collected in theta–theta reflection geometry with the Cu Kα radiation on a PANalytical X'PERT PRO diffractometer, PW3050 goniometer equipped with an X'Celerator detector. The Long Fine Focus (LFF) tube operated at 40 KV, 40 mA. Data were collected using a step size of 0.017° and a count time of 40 s per step.

The IR spectra were recorded with a Nicolet Nexus Fourier Transform instrument. A conventional manipulation/outgassing ramp connected to the IR cell was used. For the analysis of the skeletal vibrations KBr pressed disks were used. For adsorption experiments pressed disks of pure catalyst powders (15 mg, 2 cm diameter) were used. The samples were thermally pre-treated in the IR cell by heating in air at 450 °C for 2 h and later by outgassing 1 h at 450 °C. The adsorption procedure involves contact of the activated sample disk with CO at 130 K in the conventional IR cell cooled with liquid nitrogen. Desorption is carried out by outgassing upon warming from 130 K to room temperature. Methanol adsorption experiments were performed at r.t., followed by outgassing at r.t. and at 110 °C. Methanol decomposition experiments were performed at 30–350 °C in static conditions with methanol 5 Torr pressure.

2.3. Rietveld refinement

Rietveld refinement of the structural model taken from Ref. [18] for the product of precipitation was performed using the GSAS program [19]. Sample displacement, cell parameters and background were first refined. Then fractional coordinates and profile shape were also refined. The profile was modeled using a pseudo Voigt profile function [20]. Inspection of the diffraction profile revealed that the pattern was affected by anisotropic peak broadening. The *00l* reflections were noticeably broader than other reflections, suggesting that the coherent diffraction domains preferentially extend along the [00l] crystallographic planes, that is the direction of growth of inorganic layers. Fixing the anisotropic broadening axis along the *00l* direction, the refined anisotropy broadening coefficients X_e and Y_e assumed positive values (0.06° and 0.66°, respectively) attesting the presence of a certain amount of shape anisotropy and defects along the direction of layer packing. Isotropic thermal factors were set to a reasonable value and not refined. Soft restraints were applied to O–H and carbonate C–O bond lengths, in order to avoid refinement unstability. The metal atom occupancies were set according to stoichiometry and were not refined. At the end of the refinement the shifts on all parameters were less than their standard deviations.

3. Results and discussion

3.1. TG-DTA and SEM analyses

Fig. 1 shows the coupled TG-DTA curves of ZnAl HT. The TG curve is characterized by a continuous mass loss without well-defined plateaux between the decomposition steps. The first mass loss of 1.8% at 100 °C, corresponding to a broad endothermic peak, can be ascribed to the loss of adsorbed water and it is followed by a second more pronounced and sharp endothermic phenomenon, due to loss of hydration water from the interlayer region at 190 °C, corresponding to the 8.5% of the total mass. A second step extends up to 400 °C, and it is assigned to the overlapped mass losses due to the dehydroxylation of the layers and the decomposition of the carbonate counter-anions as carbon dioxide. In addition, the small mass loss observed around 600 °C can be ascribed to the loss of residual surface carbonate anions and/or dehydroxylation water [21,22]. Being known the Zn/Al molar ratio and that at 1000 °C the ZnO and $ZnAl_2O_4$ are formed, it was possible to assign to the sample the following composition: $[Zn_{0.67}Al_{0.33}(OH)_2](CO_3)_{0.165}{\cdot}0.5H_2O$. SEM analysis (Fig. 2) clearly reveals the lamellar morphology of the sample. The layered microcrystal aggregates are evident and a rough estimation indicates that the thickness of the each layered microcrystals is of the order of few hundreds of nm, the size being of the order of few microns.

3.2. XRPD analysis of ZnAl HT

Tables 1–3 show the refinement details, structural parameters and selected bond lengths and angles for $[Zn_{0.67}Al_{0.33}(OH)_2](CO_3)_{0.165}{\cdot}0.5H_2O$ while Fig. 3 shows the Rietveld plot. In spite of the difficulties reported by some authors [23] in preparing monophasic Zn-containing HT with the urea method, monophasic ZnAl HT has indeed been obtained. Major crystallographic features are in good agreement with those reported for MgAl–CO_3 HT [18]. The structure originates from the packing of inorganic layers along the *c* crystallographic axis. These layers are made of edge connected MO_6 octahedra. These octahedra are slightly distorted, since O-M-O

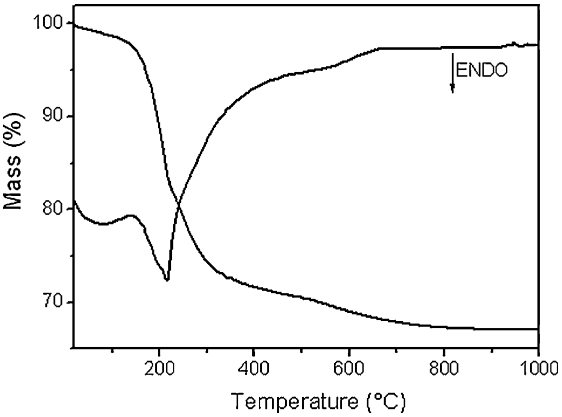

Fig. 1. TG and DTA curves of ZnAl hydrotalcite.

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