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Layered double hydroxides as base catalysts for the synthesis of dimethyl carbonate

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ABSTRACT

In this work, we have prepared two series of layered double hydroxides (LDHs) based on three different divalent cations (Zn²⁺, Ni²⁺ and Mg²⁺), that were ion-exchanged by a trivalent cation (Al³⁺). The charge was balanced with interlayer anions, either silicate or carbonate. Thus, we have synthesized six different samples and we have studied their physicochemical properties by a wide range of techniques, in order to elucidate their properties. Finally, we have used the prepared materials as catalysts in the transesterification of ethylene carbonate with methanol to produce dimethyl carbonate and ethylene glycol. We have found that materials containing Ni as divalent cation present better catalytic activity due to their basic properties, whereas catalysts containing silicate as interlayer anion yield better selectivity, since they have a lower amount of acid sites.

1. Introduction

Dimethyl carbonate (DMC) is an organic compound classified as carbonate ester. It has high industrial importance due its versatile reactivity and unique physical properties [1]. DMC is characterized by its low toxicity, good biodegradability and high oxygen content [2]. Therefore, it is used as a substitute agent for phosgene, dimethyl sulfate or methyl iodine reagents in methylation and carbonylation reactions [3,4]. DMC has also been used as an additive in gasoline due to its high oxygen content [5], and as an electrolyte in lithium batteries due to its high electric constant [6].

Conventionally, DMC has been synthesized by oxidative carbonylation of methanol (non-phosgene route, harmful CO is needed) or by phosgenation of methanol [7]. The DMC production by phosgenation of methanol was the most successful method until the 1980s [8]. However, it has been replaced in recent years due to the high toxicity of phosgene [9]. Currently, DMC production is commonly carried out through the oxidative carbonylation of methanol, a process which is based on the catalytic reaction between methanol and carbon monoxide/oxygen [10]. Again, the use of CO generates health and environmental concerns.

An alternative for such toxic and dangerous processes to synthesize DMC is the unexplored transesterification of ethylene carbonate with

methanol, in which ethylene glycol is co-produced. Transesterification reactions can be catalyzed by bases (NaOH, KOH, metallic oxides, etc.), by acids (sulfuric acid, zeolites, hydrochloric acid, etc.) or by enzymes [11–13]. In base-catalyzed reactions the catalyst deprotonates the alcohol, which becomes activated? On the other hand, in acid-catalyzed reactions the catalyst gives a proton to the carbonyl group to activate it.

Ethylene carbonate is produced by the reaction between CO₂ and ethylene oxide. This is a well-known reaction and a variety of catalysts drives this reaction properly. EC carbonate is easily prepared and in each molecule of EC formed consuming one molecule of CO₂. EC is the ideal platform produce DMC since came from CO₂.

Different alternative homogeneous and heterogeneous catalysts have been studied for this reaction in recent years. The most interesting ones are basic metal or metal combinations like cerium–zinc [14], cerium–cobalt [14] or copper–zinc–aluminum [15], and basic metal oxides or mixed oxides like mesoporous ceria [16], basic alumina [17], TS-1 [18], Zn–CeO₂ [19] or CeO₂–MgO [20]. Additionally, other metal-free catalysts have also been used include emerging compounds like DABCO-ionic liquid [21], ionic liquid/silica [22] and graphitic carbon nitrides [23].

Layered double hydroxides (LDHs) are hydrotalcite-type materials with octahedral brucite-type structure expressed by the formula [M_{1-x}M³⁺_x(OH)₂]^{x+}[Aⁿ⁻]_{x/n}·yH₂O, where M²⁺ = Mg²⁺, Ni²⁺,

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Zn^{2+} or Fe^{2+} , and $M^{3+} = Al^{3+}$ or Fe^{3+} [24]. In this kind of materials, a part of the divalent cation is isomorphically substituted by a trivalent cation, giving place to a wide group of materials whose properties and characteristics depend on the metal used in the layer structure and the interlayer anion [25]. LDH has several advantages with respect to other heterogeneous catalyst for this reaction in particular. They are intrinsically basic (hydroxides), are insoluble in many solvents and they can be finely tuned to get the desired basicity. Regarding to the simple and economic synthesis methods LDHs and their derive have been studied as a heterogeneous base catalyst in biodiesel production [26], Knoevenagel condensation reaction [27], VOC total decomposition [28], etc.

In this work, we report the synthesis and characterization of XALDHs ($X = Mg, Zn$ y Ni) using carbonate or silicate as interlayer anions, and the catalytic evaluation of these materials as catalysts in the transesterification of ethylene carbonate with methanol. The effect of the divalent metal and interlayer anion in the catalyst structure has also been studied.

2. Experimental

2.1. Catalysts preparation

Two different groups of LDHs were synthesized by the co-precipitation method at constant pH using carbonate or silicate as interlayer anion, and a cation to aluminum molar ratio X/Al of 3:1 ($X = Mg, Zn$ and Ni) [29,30].

Two solutions containing the cation's precursors ($[X^{2+}] = 0.15$ M, $X = Mg^{2+}, Zn^{2+}$ and Ni^{2+}) and the anion's precursors ($[A^{n-}] = 0.5$ M, $A = CO_3^{2-}$ and SiO_4^{4-}), respectively, were added dropwise to a beaker under constant stirring at 70 °C. Five milliliter of NaOH 1 M were added every 0.5 h to the beaker to keep the pH close to 10. The precipitated was aged at 70 °C during 18 h. The solid was filtered and washed with water at 80 °C until neutrality, and finally dried at 60 °C overnight. Within this manuscript, the hydroxalite type catalysts are identified by the code XAl-CO₃ or XAl-SiO₃ ($X = Mg, Zn$ or Ni).

2.2. Catalysts characterization

Powder X-ray diffraction patterns were measured in a Bruker D8-Advance spectrometer with a Kristalloflex K 760-80F X-ray generator mA (power: 3000 W, voltage: 20–60 KV and current: 5–80 mA) with a tube of X-ray with a copper anode. The data were recorded from 5° to 80° with scanning rate of 2°min⁻¹ and an angular step size of 0.05, as well as a counting time of 3 s. FT-IR spectra were obtained in the range of 400 to 4000 cm⁻¹ using KBr pellets in a spectrometer BRUKER IFS 66/S. The chemical composition of the catalysts was determined by X-ray fluorescence (XRF) in a sequential X-ray spectrometer (Phillips Magic Pro and PW2400).

Thermogravimetric analyses were carried out in a simultaneous thermal analyzer TG-DSC Mettler-Toledo, from room temperature to 800 °C. The morphology of the samples was observed in a field emission scanning electron microscope (FE-SEM) (ZEISS Merlin VP Compact). TEM images were obtained in a transmission electron microscope (JEOL JEM-2010). Textural properties (BET surface area [31], micropore area (t-plot method), BJH, average pore volume) of the samples were derived from the N₂ isotherms carried out at -196 °C using a volumetric physisorption analyzer QUANTACHROME AUTOSORB-6.

X-ray photoelectronic spectroscopy experiments were collected using a Scientific K-ALPHA with Al-K radiation (1486.6 eV), monochromatized by a twin crystal monochromator, yielding a focused X-ray spot with a diameter of 400 μm, at 3 mA × 12 kV when charge compensation was achieved with the system flood gun that provides low energy electrons and low energy argon ions from a single source. The alpha hemispherical analyzer was operated in the constant energy mode with survey scan pass energies of 200 eV to measure the whole energy band, and 50 eV in a narrow scan to selectively measure the

particular elements. An estimation of the intensities was done after the calculation of each peak integral, S-shaped background subtraction and fitting the experimental curve to a combination of a Lorentzian (30%) and Gaussian (70%) lines. Binding energies (BE), referenced to the C 1s line at 284.6 eV, have an accuracy of ± 0.1 eV.

The basic sites in the samples were characterized by CO₂ temperature-programmed desorption (CO₂-TPD). An amount of 100 mg of each catalyst was deposited in a U-shape quartz reactor. The LDHs materials were first pre-heated at 120 °C with a He flow of 50 cm³min⁻¹ for 1 h to remove the physisorbed molecules. Subsequently, the sample was cooled down to room temperature prior to being exposed to a He/CO₂ mixture flow (10% v/v in He) for 1 h. The system was heated at 80 °C during 0.5 h under He flow (50 cm³min⁻¹) and cooled to room temperature. Finally, the temperature was increased in the system from room temperature to 1000 °C at a heating rate of 10 °Cmin⁻¹. The CO₂ liberated by the sample was measured with a mass spectrometer (Pfeiffer, OmniStar GSD 301).

A blank measurement was made for the carbonate LDHs samples to subtract the CO₂ liberated by carbonate decomposition [32].

Acid sites were determined by temperature-programmed desorption of ammonia (NH₃-TPD), which was performed following the same procedure described above for CO₂-TPDs, but saturating the surface with a flow of NH₃/He (10% v/v in He) and then measuring the desorbed NH₃ with a mass spectrometer.

2.3. Catalytic behavior

The transesterification of ethylene carbonate with methanol was performed in a two-neck round-bottom flask adapted in one side with a temperature sensor and in another one with a reflux system. The flask was filled with methanol (≥ 99.98% Sigma-Aldrich), ethylene carbonate (≥ 98% Sigma-Aldrich) and the catalyst. The test was carried out using a methanol/ethylene carbonate ratio of 10/1, an amount of catalyst which was 10% w/w of ethylene carbonate, temperature of 90 °C and a reaction time of 4 h [33]. During the test, six samples were taken from the reaction flask. The liquid sample was passed through a micro-filter prior to depositing it into the chromatography vial. The samples were analyzed in a SHIMADZU GCMS-PQ2010S gas chromatograph coupled with a mass spectrometer.

Finally, a recycling test was performed. To this end, the catalysts were thermally treated at 300 °C for 6 h after the first run, and then the reaction experiment was repeated under the same conditions.

3. Results and discussion

3.1. Catalysts characterization

After these materials are synthesized, the first thing one must check is that their chemical composition corresponds to the nominal one. For this reason, samples were studied by XRF. Table 1 shows the metal percentage in each material. It can be seen that the carbonate-containing materials maintain a metal ratio close to the nominal value (3:1) providing a hint that the materials were successfully prepared. In the case of the silicate-containing LDHs, although the values of x are close to the nominal ones, it is not possible to calculate the theoretical formula due to the distortion of the structure in these materials (see below, XRD results). It can then be concluded that all the prepared compounds have the desired chemical composition.

The second point to be checked is the nature of the functional groups present in the materials. For this purpose, FT-IR spectroscopy has been applied and the corresponding spectra are shown in Fig. 1. All materials, i.e. those synthesized with carbonate (Fig. 1(a)), and those prepared with silicate (Fig. 1(b)), present very similar FT-IR spectra. The free carbonate has three characteristic peaks in the infrared spectrum: non-planar bending (ν_2), antisymmetric stretching (ν_3) and angular bending (ν_4) at 880, 1415 and 680 cm⁻¹, respectively [36]. In

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