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Research paper

Synthesis of transition metal doped lamellar double hydroxides as base catalysts for acetone aldol condensation

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ABSTRACT

Transition metals TM (TM = Fe^{+2}, Zn^{+2}, Ni^{+2} and Cu^{+2}) doped lamellar double hydroxides (LDHs) were prepared by coprecipitation method and characterized with N_2 adsorption–desorption isotherms, X-ray diffraction (XRD), Raman spectroscopy, scanning electron microscopy (SEM), and temperature-programmed desorption of CO_2 (TPD–CO_2). XRD patterns of the dried samples showed that these solids contained the crystallized lamellar double hydroxides (LDHs) after calcination. TPD–CO_2 experiments revealed that these LDHs contain both moderate and strong basic sites varying with transition metal dopants. It was found that the gas-phase acetone aldol condensation was a surface basicity and texture-sensitive reaction. The basicity of the catalysts followed the sequence MgZnAlO > MgFeAlO > MgCuAlO > MgNiAlO, which agreed well with the variation of the catalytic activity in the acetone aldol condensation. The selectivity to isophorone and phorone could be correlated to the textural properties of the catalysts. Catalyst with large surface area and bigger pore diameter favored the formation of isophorone.

1. Introduction

Lamellar double hydroxides (LDHs) attracted great interest because of their wide applications, including their use as catalysts, anion adsorbents and exchangers, medical antacids, and ionic conductors (Dupin et al., 2004; Tanasoi et al., 2009). These materials are composed of a lamellar base structure of magnesium and aluminum hydroxides (Frost et al., 2003; Othman et al., 2006). The general formula of these materials may be represented by $[M^{2+}{}_{1-x}M^{3+}{}_{x}(OH)_2]^{x+}[A^{n-}]_{x/n}\cdot yH_2O$ where M^{2+} are divalent anions (Mg^{2+}, Zn^{2+}, Mn^{2+}, Ni^{2+}, Co^{2+}, Fe^{2+}, etc.), M^{3+} are trivalent metal ions (Al^{3+}, Cr^{3+}, Fe^{3+}, Co^{3+}, Ga^{3+}, etc.), and A^{n-} is the interlayer anion with charge n (Vaccari, 1998). The molecular arrangement and interchange between M^{2+} ions and M^{3+} ions in the layered structure generates excess of positive charge which is compensated by the intercalation of anions, generally carbonates and water. The LDHs have structures similar to brucite ($Mg(OH)_2$) sheet-like crystalline structure due to the presence of divalent small cations in close proximity to the highly polarized OH^- ions. Each Mg^{2+} ion has an octahedral coordinated to six hydroxyl ions and various octahedral species share their edges to form an infinite layer. These layers are stacked on one another and seized together by fragile interactions of hydrogen bonds. If any Mg^{2+} ions are replaced by cations with greater charge but similar ionic radius, the layers are positively charged and its electrical neutrality is maintained by anions in the interlayer region together with water molecules (Braterman et al., 1994; Kloprogge et al., 2001; Kloprogge et al., 2005). Therefore, the space between the stacked brucite-like cation layers is filled with charge compensating anions (CO_3^{2-}, Cl^-, NO^{3-}, SO_4^{2-}, OH^- and many others) and water molecules.

The synthesis methods, the characterizations of crystalline structures, and the catalytic applications of LDHs-related catalysts were reviewed (Vaccari, 1998). Although the LDH materials can be synthesized by various routes, the most frequently used was the economical method of co-precipitation. The conditions of synthesis (temperature, pH, and metal composition) were reported (Constantino and Pinnavaia, 1994; Climent et al., 2004; Didier et al., 2006; Ajat et al., 2008). Thermal treatments of LDHs led to various modifications in the physicochemical properties of the materials. The most important effect of calcination, at temperatures above 600 °C, was the evaporation of water molecules and carbon dioxide, resulting in the loss of the laminar structure with the consequent formation of aluminum and magnesium mixed oxides. However, it is possible, in some cases, to recover the original LDH structure through rehydration, a phenomenon known as memory effect (Prinetto et al., 2000). Calcination of LDH led to the formation of mixed oxides with stronger basic sites, larger specific area, and increased resistance to sintering.

As catalysts, the LDH materials present considerable advantages in low production costs since their synthesis is relatively inexpensive and in terms of environmental pollution, thus they can replace the use

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of mineral bases in catalytic reactions. A large number of organic reactions were carried out using LDHs as solid base catalysts and adsorbents (Yamamoto et al., 1995; Schulze et al., 2001; Lima et al., 2014). Several transition metal cations introduced into the LDH can generate Lewis centers, giving rise to catalytic activity. LDHs containing copper and cobalt were reported as successful traps for NOx and SOx, and those containing nickel were active catalysts for the partial oxidation of paraffins (Li et al., 2004). It was reported that BiOCl dispersed on NiFe-LDH was very active for photo-degradation of Rhodamine B dye (Ma et al., 2015).

In recent years, the fine chemical industry has developed growing interest in the utilization of solid catalysts in reactions catalyzed by solid bases. The replacement of homogeneous alkaline bases by a solid base catalyst, offers, among others, the advantages of solid reuse and waste stream reduction. The LDHs with basic sites were capable of catalyzing aldol condensation reactions with high conversion (Celaya-Sanfiz et al., 2015). The aldol condensation of acetone (Ac) produces 4-methyl-4-hydroxy-2-pentanone, which was also known as diacetone alcohol (DAA). Dehydration of DAA leads to 4-methyl-3-pentenone, commonly known as mesityl oxide (MO). Heavier products such as phorones (P) result from additional condensation reactions between MO and acetone. At this point, due to their basic properties, LDHs are promising catalysts for commercial applications in the production of fine chemicals. With this in mind, the use of LDHs for aldol condensation reactions, the synthesis of LDHs solids MgMAlO (M = Zn, Fe, Cu Ni) by the co-precipitation method was reported in the present paper. Their crystalline structures were characterized by XRD, nitrogen adsorption isotherms, SEM, Raman spectroscopy as well as by TPD–CO_2 analysis. Aldol condensation of acetone was used as test reaction and the catalytic efficiency and selectivity in function of the surface basicity and textural properties of the transition metal cations incorporated LDHs was explored.

2. Experimental

2.1. Sample preparation

The MgAl based hydrotalcite and the transition metal doped lamellar double hydroxides were prepared by co-precipitation method at 65 °C. All samples were prepared as follows: An aqueous solution containing the nitrates of the metallic salts (solution A) was prepared. Another aqueous solution containing KOH and K_2CO_3 (solution B) was prepared separately. The M^{2+}/M^{3+} molar ratio was established to a value of 3 in all cases. Solutions A and B were added drop-wise simultaneously into a glass reactor, maintaining the final pH between 9 and 10. Afterwards, the mixture was aged at 65 °C for 18 h under vigorous stirring. Then the precipitate was washed several times with hot deionized water, and dried at 100 °C in air overnight. The obtained solids were calcined at 450 °C in static air.

The metallic nitrate salts employed for the preparation of hydrotalcite-like materials were: M^{2+}: $Mg(NO_3)_2 \cdot 6H_2O$, $Ni(NO_3)_2 \cdot 6H_2O$, $Cu(NO_3)_2 \cdot 6H_2O$, $Zn(NO_3)_2 \cdot 6H_2O$, and M^{3+}: $Al(NO_3)_3 \cdot 9H_2O$, and $Fe(NO_3)_3 \cdot 9H_2O$. The keys used for synthesized hydrotalcite-like materials are MFA (MgFeAlO), MNA (MgNiAlO), MCA (MgCuAlO), and MZA (MgZnAlO). For comparison purpose, MA (MgAlO) was prepared similarly by co-precipitation using $Mg(NO_3)_2 \cdot 6H_2O$ and $Al(NO_3)_3 \cdot 9H_2O$ as Mg and Al precursor; while, the sample MOHA was prepared with $Mg(OH)_2$ and $Al(NO_3)_3 \cdot 9H_2O$.

2.2. Characterization

Specific surface area, pore volume, and pore size distribution were obtained from nitrogen adsorption–desorption isotherms at −196 °C in an automatic Micromeritics ASAP-2100 analyzer. The chemical composition of solids was determined by inductively coupled plasma atomic emission spectrometry (ICP-AES, Perkin-Elmer model Optima 3200 Dual Vision). The adsorption was carried out using calcined solids, after outgassing at 400 °C under a pressure of 10^{-5} Torr for 4 h. X-ray diffraction (XRD) patterns of the solids were obtained by an Empyrean Multi-Purpose Research X-ray diffractometer (PANalytical) with a Cu Kα radiation ($\lambda = 0.15418$ nm) source. Scanning electron microscopy (SEM) analysis was made with a Quanta 3D FEG Environmental Scanning Electron Microscope and Focused Ion Beam. For Raman spectroscopy studies, a MicroRaman, Jobin Yvon-Horiba Labram 800 was used. The basicity of the samples was determined by means of temperature programmed desorption of CO_2 (TPD–CO_2) employing a Micromeritics 2900 device. A CO_2–Ar mixture (Praxair Inc.) was employed for the TPD study. The typical procedure consists of catalyst (0.1 g) pretreatment under argon gas flow (30 mL/min) at 200 °C for 2 h, and subsequently, a step of cooling down the sample to room temperature. Finally the sample was saturated under the CO_2–Ar mixture. Desorption of carbon dioxide was performed after flushing the system with the carrier gas at an increasing temperature from 200 °C to 500 °C with a heating rate of 10 °C/min.

2.3. Catalytic evaluation

Acetone aldol condensation was performed using a fixed-bed reactor at atmospheric pressure. Catalyst sample (200 mg) was loaded in the middle of the reactor and heated in situ at 350 °C in flowing He for 1 h before cooling to the reaction temperature of 300 °C. Acetone was delivered to the reactor at a rate of 0.7 mL h^{-1}. The reaction products were collected in a cold trap and the liquid samples were collected and analyzed with a Varian-3600 CX Gas Chromatograph (Flame Ionization Detector and PONA capillary column). All products were identified by in comparison with their retention times of commercially available pure compounds. The main products detected in the reaction were mesityl oxide (MO), isophorone (IP) and phorone (P). Some deactivation was observed as reaction time increased and the values for activity and selectivity were calculated in the first 60 min. The acetone conversion C and product selectivity S_i were calculated as follows:

$$C(\text{mol }\%) = \frac{\sum_i^n \mathrm{Y_i}}{\mathrm{C_{out}} + \sum_i^n \mathrm{Y_i}} 100,$$

selectivity S_i to compound i:

$$S_i(\text{mol }\%) = \frac{\mathrm{Y_i}}{\sum_i^n \mathrm{Y_i}} 100$$

where C_{out} is acetone mole percent in the outlet of reactor and Y_i are yields to the different products.

3. Results and discussion

In catalyst preparation, a M^{2+}/M^{3+} molar ratio of 3 was established in all cases. Elemental chemical analysis data of the LDH samples determined by ICP-AES are summarized in Table 1. Actually, the M^{2+}/M^{3+} molar ratios in the solids varied from 2.4 to 3.1. The textural properties of the calcined LDHs obtained from the nitrogen adsorption–desorption isotherms were reported in Table 1. All the samples showed surface areas greater than 200 m^2/g. It seems that the surface area of the samples was related to the ionic radius of the doping transition metal ions. It was noted that the ionic radius of transition metal M^{2+} (with 6-fold coordination and low spin state) increased with an order as: Fe^{2+} (0.61 Å) < Ni^{2+} (0.69 Å) < Cu^{2+} (0.73 Å). The surface area of the samples decreased as the ionic radius increased from Fe^{2+} to Ni^{2+} and Cu^{2+}. Similarly, the pore volume and pore size gradually decreased as the ionic radius of the divalent cation increased, except for the MZA sample which had a relatively large surface area (234 m^2/g), big pore diameter (134 Å), and pore volume (0.78 cm^3/g).