



Tin-containing hydrotalcite-like compounds as catalysts for the Meerwein–Ponndorf–Verley reaction

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ABSTRACT

Hydrotalcite-like compounds (HTs) containing Mg/Al or Mg/Al/Sn were prepared and used as precursors to obtain basic catalysts by calcination at 450 °C. The catalysts were used in the Meerwein–Ponndorf–Verley (MPV) reaction of benzaldehyde and cyclohexanone in the presence of 2-propanol as hydrogen donor. The mixed oxide obtained by calcining the tin-containing HT was found to be more catalytically active than that obtained from the Mg/Al HT and the pure magnesium oxide. This result can be ascribed to the mechanism of the reaction, which involves acid–base sites on the catalyst surface. The most active catalyst was used in the MPV reactions of other carbonyl compounds including aldehydes and ketones with excellent conversion and selectivity.

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1. Introduction

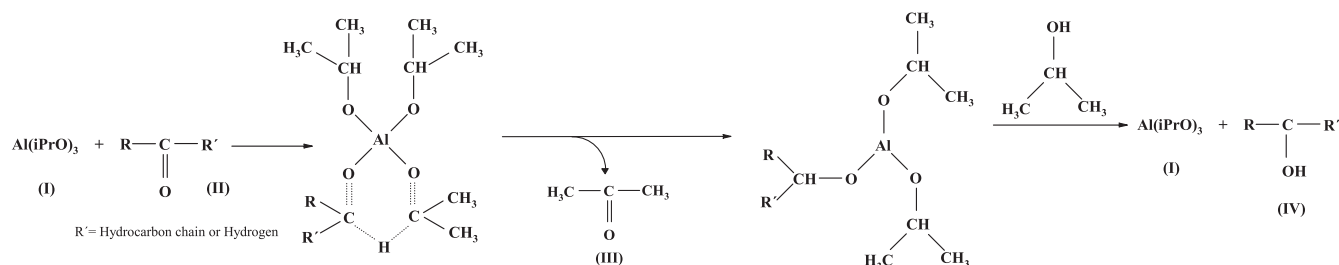
Hydrotalcite-like compounds, also known as “layered double hydroxides” or, simply, “hydrotalcites” (HTs), are anionic clays which have aroused much interest in recent years for a number of uses in various scientific fields [1–3]. Structurally, hydrotalcites are similar to brucite, $\text{Mg}(\text{OH})_2$, where a fraction of Mg^{2+} ions is substituted by trivalent metals with an ionic radius similar to that of magnesium [4,5]. This substitution introduces a charge deficiency that causes the brucite-like layers to be positively charged. Electroneutrality in the interlayer region can be restored by the presence of a wide variety of anions in addition to molecules of water (crystal water) [2]. The parent compound for HTs is the natural mineral hydrotalcite, of formula $\text{Mg}_6\text{Al}_2(\text{OH})_{16}\text{CO}_3 \cdot 4\text{H}_2\text{O}$. The magnesium can be replaced not only with trivalent metals, but also with divalent ones. Therefore, hydrotalcites can be generically formulated as $[\text{M}(\text{II})_{1-x}\text{M}(\text{III})_x(\text{OH})_2]^{x+}[\text{A}_{x/m}]^{m-} \cdot n\text{H}_2\text{O}$, where $\text{M}(\text{II})$ and $\text{M}(\text{III})$ are a divalent and trivalent metal, respectively, lying at octahedral positions of Mg^{2+} in brucite-like layers and A is the interlayer anion – which can vary widely in nature and be either inorganic or organic. x , which represents the ratio $\text{M}(\text{II})/[\text{M}(\text{II}) + \text{M}(\text{III})]$, usually ranges from 0.17 to 0.33.

There are two main types of HTs. One consists of divalent and trivalent cations plus various interlayer anions; the other, contains lithium and aluminium (i.e., a univalent metal and a trivalent

one) [6,7]. However, some HTs reported in the last decade contain tetravalent metals such as tin [8–10], zirconium [11–13] or titanium [14,15]; in any case, these require the presence of a trivalent metal in addition to the divalent one since high concentrations of the tetravalent metal can cause the formation of various phases (particularly mixed hydroxides of the di- and tetravalent metals) in addition to the hydrotalcite. The tetravalent metals confer HTs special properties of catalytic interest. In fact, our research group has successfully used calcined HTs of this type in organic syntheses such as the Meerwein–Ponndorf–Verley (MPV) reaction of heterocyclic carboxaldehydes [16] and uncalcined HTs in the Baeyer–Villiger oxidation of cyclohexanone [17].

The catalytic transfer of hydrogen from an alcohol to a carbonyl compound that is reduced as a result is widely used in organic synthesis. This process is known as the Meerwein–Ponndorf–Verley (MPV) reaction and has traditionally involved the use of 2-propanol as hydrogen donor and aluminium isopropoxide $[\text{Al}(\text{iPrO})_3]$ as catalyst. The hydrogen transfer from the alcohol to the carbonyl compound takes place via the pericyclic mechanism of Scheme 1, which involves the formation of a 6-membered intermediate between the isopropoxide (I) and the carbonyl compound (II). The reaction gives acetone (the oxidation product of 2-propanol) (III) and a new alcohol (IV) [18]. The MPV reaction has also been performed with other catalysts of both the homogeneous [19,20] and the heterogeneous type [21,22]. Heterogeneous catalysts have aroused increasing interest in recent years by virtue of their providing conversion and selectivity results similar to or even better than those of homogeneous catalysts.

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Scheme 1. General mechanism for the Meerwein-Ponndorf-Verley reduction using $\text{Al}(\text{iPrO})_3$.

In this work, we used Mg/Al and Mg/Al/Sn hydrotalcites calcined at 450°C as catalysts for the Meerwein-Ponndorf-Verley reaction of aldehydes and ketones with 2-propanol as hydrogen donor. The results were compared to those provided by a magnesium oxide widely used in this reaction [23–25].

2. Experimental

2.1. Preparation of hydrotalcite-like compounds

Hydrotalcites containing Mg/Al or Mg/Al/Sn were prepared by using a coprecipitation method described elsewhere [26]. In a typical synthetic run, a solution containing 0.3 mol of $\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ and 0.15 mol of $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ in 250 mL of de-ionized water (Mg/Al = 2) was slowly dropped over 500 mL of an Na_2CO_3 solution at pH 10 at 60°C under vigorous stirring, the pH being kept constant by adding appropriate volumes of 1 M NaOH during precipitation. The suspension thus obtained was kept at 80°C for 24 h, after which the solid was filtered and washed with 2 L of de-ionized water. An Mg/Al/Sn hydrotalcite with $\text{Mg}(\text{II})/[\text{Al}(\text{III}) + \text{Sn}(\text{IV})] = 2$ was obtained by following the same procedure but using appropriate amounts of Mg(II) and Al(III) nitrates, and Sn(IV) chloride.

The HTs thus obtained were ion-exchanged with carbonate to remove nitrate or chloride ions intercalated between layers. The procedure involved suspending the solids in a solution containing 0.345 g of Na_2CO_3 in 50 mL of bidistilled, de-ionized water per gram of HT at 100°C for 2 h. Then, each solid was filtered off in vacuo and washed with 200 mL of bidistilled, de-ionized water. The resulting HTs were subjected to a second ion-exchange operation under the same conditions. The exchanged Mg/Al solid was named HT-Mg/Al and its Mg/Al/Sn counterpart HT-Sn (see Table 1). These solids were calcined at 450°C in the air for 8 h, using a temperature gradient of $1^\circ\text{C}/\text{min}$.

The magnesium oxide used for comparison was prepared by calcining commercial magnesium hydroxide in the air at 600°C for 2 h. The calcined solid was rehydrated in refluxing water for 6 h to obtain a new hydroxide that was re-calcined at 600°C to obtain the catalyst designated MgO-600.

2.2. Experimental techniques

Hydrotalcites and their calcination products were characterized by using various instrumental techniques. Thus, the metal contents of the hydrotalcites were determined by inductively coupled plasma-mass spectrometry on a Perkin-Elmer ICP-MS instrument under standard conditions.

All catalysts were subjected to X-ray diffraction (XRD) analysis to check for crystallinity. Powder patterns were recorded on a Siemens D-5000 diffractometer using $\text{CuK}\alpha$ radiation. Scans were performed over the 2θ range from 5° to 70° , using a resolution of 0.02° and a count time of 2 s at each point.

Thermogravimetric analyses were performed on a Setaram Set-sys 12 instrument by heating in an argon atmosphere from 25 to 800°C at $10^\circ\text{C}/\text{min}$.

BET surface areas, pore radii and pore volumes were calculated from nitrogen adsorption-desorption isotherms obtained at -196°C on a Micromeritics ASAP 2010 instrument. Samples were outgassed in vacuo at 100°C for 12 h prior to use. The amount of CO_2 chemisorbed on each solid was measured on a Micromeritics 2900 TPD/TPR analyser. Prior to analysis, samples were heated at 450°C in argon stream for 1 h. Measurements were made at room temperature by alternate passage over argon, and the same gas containing 5% CO_2 , over the sample; the amount of chemisorbed CO_2 was calculated as the difference between the first adsorption peak (physisorbed plus chemisorbed CO_2) and the arithmetic mean of the adsorption and desorption peaks. Basicity was assessed under the assumption that one molecule of CO_2 was adsorbed at one basic site. The number of basic sites found was thus a measure of basicity.

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2.3. Reaction conditions

The Meerwein-Ponndorf-Verley reaction was conducted in a two-necked flask furnished with a condenser and a magnetic stirrer. 2-propanol (0.06 mol) was treated with 0.003 mol of the aldehyde and the reaction mixture heated at reflux temperature with stirring (1000 rpm). The reaction was started by introducing 1 g of freshly calcined catalyst. The products of the reactions were analyzed by GC-MS using an HP 5890 GC instrument furnished with a Supelcowax 30 $\text{m} \times 0.32 \text{ mm}$ column and an HP 5971 MSD instrument.

3. Results and discussion

3.1. Characterization of catalysts

The solids used were characterized in previous work [17,26]. Table 1 shows the chemical composition and empirical formula of each hydrotalcite and the magnesium oxide.

The XRD patterns for both the Mg/Al and the Mg/Al/Sn solid (Fig. 1) are typical of layered clay minerals.

Calcining Mg/Al hydrotalcite at 450°C has been reported to cause deep structural changes leading to the formation of perfectly crystalline periclase MgO phases [27] the a values for which are

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