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Influence of the preparation route on the basicity of La-containing mixed oxides obtained from LDH precursors

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ABSTRACT

A series of La-containing Mg(Al)O mixed oxide catalysts were obtained from layered double hydroxide (LDH) precursors following different La^{3+} incorporation methods, i.e., coprecipitation, impregnation and intercalation. Structural and textural properties investigated by XRD and N_2 physisorption revealed a large range of specific surface areas of the materials and different ordering of the structures. The surface areas were between 18 and 230 $m^2 g^{-1}$ for the coprecipitated and intercalated samples, respectively, and rose to 330 $m^2 g^{-1}$ for the intercalated sample treated by sonication. The base properties of these samples, and for the sake of comparison of Mg(Al)O and Mg(La)O mixed oxides, were investigated by TPD of CO_2 and by performing the highly demanding isomerization reaction of 2,3-dimethyl-1-butene (**1**). Strong base sites are introduced in the mixed oxide, when La^{3+} is incorporated by coprecipitation or intercalation in the Mg/Al LDH precursor. Finally, the relative values of the catalytic activities of the different mixed oxide found in the isomerization reaction of (**1**) showed that not only the densities of strong base sites, but also their accessibility was controlling the catalytic activities.

1. Introduction

An increasing class of catalytic reactions is performed with Mg(Al)O mixed oxides obtained by thermal decomposition of $[Mg_{1-x}Al_x(OH)\ 2]^{x+}(A^{n-})_{x/n}\cdot mH_2O$ layered double hydroxides (LDH) precursors (A^{n-}: interlayer compensating anion) due to the versatility and to the high specific surface area of these catalysts [1–3]. Several parameters, like the ratio of Mg^{2+} and Al^{3+} cations, the activation temperature, the synthesis protocol, allow tuning the acid-base properties of these mixed oxides exhibiting strong base sites (O^{2-}) like MgO and more specifically weak (OH^-) and medium-strength acid-base site pairs ($Mg^{2+}{-}O^{2-}$ and $Al^{3+}{-}O^{2-}$) [4,5]. Nevertheless, further developments of Mg(Al)O mixed oxide catalysts will depend on a careful control of the amounts of the different types of sites with the aim of enlarging the applications to a wider range of differently demanding reactions [6,7]. Following this goal, it was demonstrated that calcination of multicationic Mg/Al/Me LDHs (Me = Y, Dy, Gd, Sm, La) precursors led to a significant improvement of the overall density of base sites of the corresponding mixed oxides in comparison to Mg(Al)O. In the particular case of the La-containing mixed oxide, the presence of a segregated and highly dispersed $La_2O_2CO_3$ phase accounted for its larger content of medium-strength base sites and higher catalytic activity in the reaction of cyanoethylation of ethanol with acrylonitrile [8,9]. In a previous work, we obtained La/Mg(Al)O mixed oxide catalysts by thermal activation of nanocomposite precursors obtained by intercalation of La-containing guest entities into a host Mg/Al LDH. These catalysts were able to perform the transesterification of 1-phenylethanol with diethylcarbonate (DEC), a reaction requiring strong base sites [10]. Therefore, introduction of rare-earth cations into Mg(Al)O mixed oxides improves their basicity and one can assume that the loading and the dispersion of the rare-earth cations are the main governing parameters, which must in turn depend on the incorporation method [10].

The case of La^{3+} is particularly interesting due to the strong intrinsic basicity of the La oxide [11]. High catalytic activities were reported for several La-containing compounds: (i) La-doped hydroxycarbonates in the disproportionation of H_2O_2 [12]; (ii)

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Mg/La mixed oxides in epoxidation of olefins [13], isomerization of isophorone [14] or Wadsworth–Emmons reactions [7]; (iii) La_2O_3 oxide in the synthesis of phytosterol esters [15] and (iv) La_2O_3 supported on γ-Al_2O_3 in the transesterification reaction of rapeseed oil and methanol [16].

Therefore, the aim of this work was to compare the textural and base properties of different La-containing Mg(Al)O mixed oxide catalysts obtained by several routes available in the field of LDHs: (i) impregnation of Mg(Al)O with a La salt; (ii) thermal decomposition of a multicationic Mg/Al/La LDH precursor, (iii) thermal decomposition of a composite obtained by intercalation of guest La anionic complexes between the layers of a host Mg/Al LDH. The negatively charged La-containing guest species that were intercalated were prepared by pre-chelation of La^{3+} with citrate anions ($C_6O_7H_3$) followed by partial hydrolysis employing the approach recently developed by Tichit et al. [10,17,18].

The low accessibility of the active sites situated at the inner surface of the aggregated particles was a main drawback of the catalysts obtained from LDH precursors, whatever the preparation route employed [19–21]. In order to break up these aggregates and increase the accessibility of the reactants to the catalytic sites, vigorous mechanical stirring or sonication treatment were employed. Moreover, formation of defects or distortion in the platelets induced by these treatments can create strong base sites as suggested in the literature [21–24]. Therefore, the influence of a sonication treatment was also examined in this study.

The base properties were investigated by temperature programmed desorption (TPD) of CO_2. Moreover, the catalysts were evaluated and compared in the highly demanding base reaction of isomerization of 2,3-dimethyl-1-butene (**1**) to 2,3-dimethyl-2-butene (**2**) since it was able to reveal the presence of very strong base sites.

2. Experimental

2.1. Preparation of the catalysts precursors

2.1.1. Preparation of NO_3-Mg/Al LDH precursor

A NO_3-Mg/Al LDH was synthesized by a conventional coprecipitation method under ambient atmosphere. In a typical synthetic run, 200 mL aqueous solution of $Mg(NO_3)_2{\cdot}6H_2O$ (0.41 M) (Panreac 98%) and $Al(NO_3)_3{\cdot}9H_2O$ (0.21 M) (Fluka ≥ 98%) in deionized water was added dropwise at a rate of 2 mL min^{-1} and room temperature into a beaker. Simultaneously, appropriate volume of NaOH (2 M) (Panreac 98%) was added at a controlled rate to maintain the pH close to 10 using a pH-STAT Titrino (Metrohm, France) apparatus. After complete precipitation, the gel obtained was refluxed at 353 K for 24 h. It was then repeatedly washed with distilled water (~6 L) at 298 K, and finally dried overnight at 353 K. This solid was labeled NO_3-Mg/Al LDH.

2.1.2. Preparation of CO_3-Mg/Al/La LDH precursor

A multicationic CO_3-Mg/Al/La LDH was obtained following the coprecipitation protocol using 200 mL of an aqueous solution of $Mg(NO_3)_2{\cdot}6H_2O$ (0.41 M), $Al(NO_3)_3{\cdot}9H_2O$ (0.19 M) and (0.016 M) $La(NO_3)_3{\cdot}7H_2O$ (Mg:Al:La = 0.65:0.30:0.025 molar ratio) precipitated with NaOH (2 M) and Na_2CO_3 (0.2 M) aqueous solution [8]. This solid was labeled CO_3-Mg/Al/La LDH.

2.1.3. Preparation of La-impregnated Mg(Al)O mixed oxide precursor

Impregnation of Mg(Al)O mixed oxide (3 g) calcined at 923 K (heating rate: 10 K min^{-1}) under air flow (100 mL min^{-1}) for 4 h was performed using the required amount of $La(NO_3)_3{\cdot}7H_2O$ dissolved in ethanol (0.26 M). This solid was labeled La_{imp}Mg(Al)O.

Table 1
Synthesized precursors and the mixed oxides obtained by their calcination.

Precursor	Mixed oxide
NO_3-Mg/Al LDH	Mg(Al)O
CO_3-Mg/Al/La LDH	Mg(Al,La)O
La_{int}Mg/Al LDH	La_{int}Mg(Al)O
$La_{int/us}$Mg/Al LDH	$La_{int/us}$Mg(Al)O
La_{imp}Mg(Al)O	La_{imp}Mg(Al)O
Mg/La	Mg(La)O

2.1.4. Preparation of La-intercalated Mg/Al LDH precursor

The first step in the preparation of the La-containing LDH composite is the preparation of La hydroxy citrate complexes. This was achieved by dissolving in 20 mL of water the required amounts of $La(NO_3)_3{\cdot}7H_2O$ (0.12 M) (Sigma–Aldrich 99%) and $Na_3C_6O_7H_3$ (0.12 M) (Fluka ≥ 98%) salts (complexation degree $[La]/[C_6O_7H_3] = 1$) at room temperature followed by hydrolysis performed by addition of the appropriate amount of NaOH (0.12 M) (hydrolysis degree $[OH]/[La] = 1$) under vigorous stirring for 0.5 h. This led to stable and clear suspensions of La hydroxycitrate complexes, which have been used freshly prepared for intercalation.

The nanocomposite was prepared from NO_3-Mg/Al LDH by anionic exchange of the nitrate ions by a solution containing a mixture of competing free citrate anions ($C_6O_7H_3{}^{3-}$) and La complexes $[La(C_6O_7H_3)(OH)]^-$ under hydrothermal conditions (50 bar of N_2, 423 K, 4 h). For this purpose, the NO_3-Mg/Al LDH (3 g) was dispersed in the required amount (100–150 mL) of the aqueous mixture of the La complexes and $Na_3C_6O_7H_3$ at a $(C_6O_7H_3)^{3-}/[La(C_6O_7H_3)(OH)]^-$ molar ratio of 4. Such mixture of anionic species allowed controlling the amount of La ions to be intercalated. The solid was then recovered and washed by dispersion and centrifugation in deionized water, and finally dried at 353 K for 12 h. This sample was labeled LaintMg/Al LDHLa_{int}Mg/Al LDH.

2.1.5. Preparation of sonicated La-intercalated Mg/Al LDH precursor

An ultrasonic treatment (2 h) was performed on a dispersion of 0.2 g of La_{int}Mg/Al LDH in 10 mL of dimethylformamide (DMF). After treatment the solid was separated by centrifugation, washed 3 times with water and dried at 423 K for 0.5 h. This sample was labeled $La_{int/us}$Mg/Al LDH.

2.1.6. Preparation of Mg/La hydroxy carbonate precursor

A Mg/La hydroxy carbonate material was prepared by co-precipitation of Mg and La nitrates: a solution containing 0.26 mol $Mg(NO_3)_2{\cdot}6H_2O$ and 0.13 mol $La(NO_3)_3{\cdot}7H_2O$ (Mg/La = 2) dissolved in 0.5 L of water was poured into a mixture of NaOH (1 mol) and Na_2CO_3 (0.26 mol) in 0.52 L of distilled water maintained at a constant pH 10. This sample was labeled Mg/La.

2.2. Preparation of the catalysts

The catalysts were obtained by calcination of the precursors into a quartz glass fixed-bed reactor in a dry synthetic air flow (100 mL min^{-1}). The temperature was raised at the rate of 10 K min^{-1} up to 923 K, and then maintained for 4 h. The calcined samples were cooled down to room temperature in argon flow (100 mL min^{-1}) and then maintained isolated under argon.

The precursors and the catalysts obtained by calcination of the precursors are presented in Table 1.

2.3. Characterization techniques

Chemical analyses of the materials were carried out at the Central Analysis Service of the CNRS (Solaize, France).