Ni–Fe and Co–Fe binary oxides derived from layered double hydroxides and their catalytic evaluation for hydrogen production

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ABSTRACT

Binary oxides based on Co–Fe and Ni–Fe were synthesized thermal treatment of layered double hydroxides (LDH) having distinct Ni/Fe and Co/Ni ratios. The solids were characterized through X-ray diffraction (XRD), Raman and Mössbauer spectroscopy, nitrogen adsorption–desorption isotherms, thermoprogrammed reduction (TPR) and thermoprogrammed desorption of CO_2 (TPD-CO_2), scanning electron microscopy (SEM) and evaluated in dry reforming of methane. XRD results revealed the spinel oxides such as $NiFe_2O_4$ and $CoFe_2O_4$ coexisting with γ-Fe_2O_3, α-Fe_2O_3, Co_3O_4 and NiO monoxides. These phases were confirmed by Raman and Mössbauer spectroscopy. Nitrogen adsorption–desorption isotherms showed a porosity within micro-to-meso pores range, with some samples displaying macropores. Catalytic evaluation in the dry reforming of methane by varying the temperature in the 650 and 750 °C range suggested in situ Co°/$CoFe_2O_4$ and Ni°/$NiFe_2O_4$ phases formation, which gives best results with the temperature increment, resulting in H_2/CO ratios close to 1. The elevated resistance to coking showed by Co–Fe series is particularly remarkable, however, sintering effects were observed over these solids.

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1. Introduction

Layered double hydroxides known as hydrotalcite-like compounds or anionic clays have chemical composition represented by the following general formula: $[M^{II}_{1-x}M^{III}_x(OH)_2]^{x+}[A^{n-}_{x/n}\cdot yH_2O]^{x-}$ where M^{II} and M^{III} are divalent and trivalent metal cations, A^{n-} is an n-valent anion and y is the number of interlayer water molecules [1–3].

The structure of hydrotalcite, i.e., $[Mg^{2+}_{1-x}Al^{3+}_x(OH)_2][CO_3{}^{2-}_{x/2}\cdot yH_2O]$, is based on that of brucite, i.e., $Mg(OH)_2$, where each Mg^{2+} cation is octahedrally coordinated with OH^- ligands. The octahedron shares edges to form extended sheets and no net charge is generated. These sheets are indeed stacked on top of each other and held together by hydrogen bonding. The isomorphous substitution in octahedral sites of Mg^{2+} ions by the trivalent Al^{3+} ones results in a positive charge, which is compensated by $CO_3{}^{2-}$ anions. Moreover, these carbonate anions residing in the interlayer region between the two brucite-like sheets can exist in concomitance with water molecules [3,4]. Similarly, hydrotalcite-like compounds possessing several cations and anions in their composition can be obtained.

Upon heating at moderate temperatures, hydrotalcites decompose to form a homogeneous mixture of M^{II} and M^{III} finely dispersed mixed oxides with very small crystal size and stable against thermal treatments [1,4]. Additionally, these mixed oxides derived from hydrotalcite precursors can be transformed into metals possessing high dispersion of the metallic crystallites by a reduction atmosphere [3].

Concerning their applications, hydrotalcites are largely used in catalytic reactions because their structures allow accommodating a wide variation in the M^{II} and M^{III} molar ratio for the resulting oxides. In this sense, oxides based on hydrotalcites have been widely used in many applications such as catalysis, pharmacy as antacids, neutralizing agents and halogen scavengers in polymer processing, adsorbents and anion exchangers [4, 5, 11 and references herein]. In heterogeneous catalysis field, they are used as catalysts, catalyst precursors and support materials for total oxidation of volatile organic compounds, glycerol transformations, oxidation of alkylaromatics to benzylic ketones, transesterification reactions, aqueous-phase reforming of ethanol, dehydrogenation of ethylbenzene, propane oxidative reforming [3–12], among others.

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Table 1
Textural properties of the solids studied: BET surface area, pore volume and pore diameter. The latter parameter was obtained from BJH method.

Sample	Me/Fe ratio	BET surface area ($m^2\,g^{-1}$)	Pore volume ($cm^3\,g^{-1}$)	Pore size (Å)
CF2	2:1	201	0.54	95
CF3	3:1	152	0.22	56
CF4	4:1	102	0.16	59
NF2	2:1	138	0.81	204
NF3	3:1	131	0.35	87
NF4	4:1	51	0.04	45

It is not surprising that a large effort has been devoted in the last years for converting low valuable hydrocarbons into high value-added chemicals via reforming reactions [3,13]. Specifically, the use of oxides based on hydrotalcite for dry reforming of hydrocarbons has been reported before [5,14–17]. These oxides exhibit very good catalytic activity for methane and carbon dioxide reforming due to the enhanced redox properties, elevated textural properties, "memory effect", thermal stability and coking resistance of the solids [14,15,18]. However, little attention has been given to the textural and structural effects of the oxides induced by the reaction on the catalytic performance. In addition, the effect of active centers amount has not been clearly defined and the support–active center interactions are given to explain the improved activity of the catalysts.

A focused examination of the action of promoters (Co, Ni) in either Co–Fe or Ni–Fe mixed oxide catalyst suggests that catalytic properties of these mixed oxides can be considerably improved by using appropriated reaction conditions. Distinct structural properties as well as a good thermal stabilization of the oxides are expected, depending on the active metal content and nature.

2. Experimental

2.1. Preparation of samples

Hydrotalcites were prepared by co-precipitation method. Detailed synthesis procedure can be found elsewhere [4]. A typical synthesis of hydrotalcites consists in adding dropwise 200 mL of a mixed aqueous solution of nickel nitrate (or cobalt nitrate) and iron nitrate into a 200 mL of sodium hydroxide and carbonate mixed solution, under vigorous mechanical stirring until pH close to 11. The suspension was stirred for additional 30 min at room temperature and pH was 11. The product was filtered off, thoroughly washed with distilled water until pH equal to 7. After being dried at 60 °C overnight, samples were crushed and then calcined at 700 °C for 6 h in air. The obtained catalyst with nickel-to-iron molar ratio of 2:1 was represented as NF2. The Ni/Fe molar ratio was adjusted to 3:1 and 4:1 and the catalysts were accordingly denoted as NF3 and NF4, respectively. Cobalt-based catalysts were prepared according to the same methodology and labeled as CF2, CF3 and CF4, for molar ratio 2:1, 3:1 and 4:1, respectively. The description of the solids obtained is shown in Table 1.

2.2. Characterization of solids

XRD patterns of the hydrotalcite precursor and the calcined solids were obtained on a Bruker D8 Advance diffractometer using Cu Kα radiation (1.5405 Å), time for step 1 s, and 0.05° per the step.

Nitrogen adsorption–desorption isotherms at −196 °C were determined in an ASAP 2000 equipment. The calcined samples were firstly degassed at 120 °C for 12 h and then the measurements were performed.

Scanning electron micrographs (SEM) of the samples were performed in a scanning electron microscope FEI Quanta 200 FEG

at a magnification of about 20000–100000 times. EDS analyses were performed in the same equipment. The accelerating voltage was about 30 kV. No conductive layer was applied for coating of observed samples.

The Raman measurements of both calcined and spent samples were recorded using a Witec confocal spectrometer with alpha 300 microscope over a range of 4000–50 cm^{-1}. A 532 nm laser line for the spectral excitation was used. For each sample spectrum, 16 accumulated spectra were collected at a resolution of 4 cm^{-1}, with a power of 10 mW in the sample.

Mössbauer spectra were collected at room temperature with the spectroscopy system from Wissel, which was calibrated using α-Fe. The measurements were carried out for the samples calcined at 700 °C by standard transmission geometry, using a constant acceleration spectrometer with a radioactive source of ^{57}Co in Rh matrix and activity of 50 mCi. The spectra were fitted using the Fit routine, which makes use of a set of Lorentzian profile peaks. The analyses allowed the calculation of amplitude and width (G) of each peak, isomer shift (δ), electric quadrupole splitting (Δ) and hyperfine magnetic fields (BFH). In addition, the isomer shift (δ) values of the solids are reported against α-Fe at room temperature.

Temperature-programmed reduction (TPR) was carried out in a home-made equipment. Around 100 mg of the calcined sample was used for each run, in a fixed-bed quartz tube and heated under nitrogen at 100 °C for 2 h. Afterwards, the reactor was cooled down to room temperature and was then heated from room temperature to 1000 °C using a heating rate of 10 °C min^{-1} in the presence of a 8% H_2/N_2 mixture. The same equipment was used for temperature-programmed desorption of CO_2 (TPD-CO_2) experiments. Prior to the CO_2 adsorption, all catalysts were preheated in He flow at 700 °C for 2 h; subsequently, 5% of CO_2 in N_2 flow was passed through the samples and then CO_2 desorption was performed from 50 to 700 °C.

2.3. Catalytic activity tests

The dry reforming of methane reaction was used to evaluate the catalytic properties of the solid at 650 °C, initially. About 50 mg of catalyst and a reactant mixture ($CH_4/CO_2 = 1$) were used. Previously, the calcined catalysts were reduced in situ at 700 °C in a flow of hydrogen (50 mL min^{-1}) for 1 h. After reduction, the catalysts were purged with nitrogen for 30 min to remove physically adsorbed hydrogen from the surface. The temperature conditions were varied from 650 to 750 °C in order to know the stability of selected samples. The products of the reaction were analyzed using a gas chromatograph (GC) connected to a thermal conductivity detector (TCD).

Conversion of methane and carbon dioxide was obtained according to previous papers [19,20].

3. Results and discussion

3.1. Structural properties of the catalysts by XRD and Raman

The XRD patterns of the catalysts are shown in Fig. 1.

As shown in Fig. 1a, the representative symmetric peaks of hydrotalcite-type compounds at around $2\theta = 11.8$, 23.7 and 34° attributable to the (0 0 3), (0 0 6) and (0 0 9) for their basal crystal planes, respectively appear in the as-prepared sample in concomitance with those of the asymmetric reflections for non-basal (0 1 2), (0 1 5), (0 1 8), (1 1 0) and (1 1 3) ones located at about $2\theta = 35.3$, 39.1, 47.0, 60.5 and 61.0°, respectively [3,4]. Indeed, all the aforesaid peaks can be indexed to the $R - 3M$ space group revealing that the synthesized hydrotalcite-like compounds are crystallized in a rhombohedral structure. The NF3 reflections (not shown in Fig. 1a) suggest that the chemical composition is close to that reevesite, (i.e.,