



# Adsorption of CO<sub>2</sub> on mixed oxides derived from hydrotalcites at several temperatures and high pressures



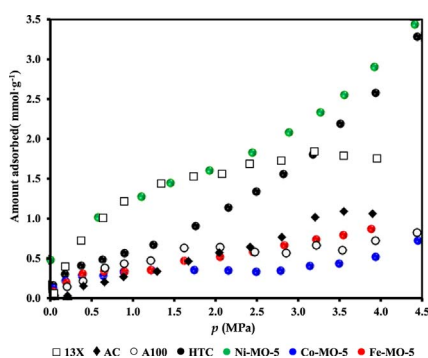
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## GRAPHICAL ABSTRACT



## ARTICLE INFO

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## ABSTRACT

The adsorption of CO<sub>2</sub> on Co, Fe and Ni mixed oxides derived from a commercial hydrotalcite and calcined at 500 °C was measured at several temperatures and pressures. Two types of experiments were considered in this work. In the first one, the adsorption temperatures were 25, 35 and 50 °C, with pressures of up to 1000 kPa. In the second, the adsorption temperature was 300 °C and the pressure up to 4400 kPa. The results obtained were compared with those found for four commercial microporous materials, namely the zeolite 13X, the MOF Basolite A100, an activated carbon and a synthetic alumina pillared clay. The microporous materials showed a higher CO<sub>2</sub> adsorption capacity, from 4.54 to 6.94 mmol·g<sup>-1</sup>, than the mixed oxides, up to 1.44 mmol·g<sup>-1</sup>, at 25 °C and up to 1000 kPa. The calcined hydrotalcite and the Ni mixed oxide presented the highest CO<sub>2</sub> adsorption capacity at 300 °C, 3.28 and 3.44 mmol·g<sup>-1</sup> at 4400 kPa, whereas the rest of materials gave values of up to 1.75 mmol·g<sup>-1</sup>. Ni mixed oxide showed sorption capacity considerably higher than those reported in the literature for hydrotalcite based materials under similar conditions.

## 1. Introduction

The capture and storage of CO<sub>2</sub> is considered to be a potential strategy in the portfolio of mitigation actions required to stabilize

atmospheric greenhouse gas concentrations [1]. Precombustion, post-combustion and oxyfuel combustion are the three main processes for CO<sub>2</sub> capture in industrial and power plant applications. In this context, gas-solid adsorption is one of the technological areas currently in use

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and continuously being developed [2].

The Sorption-Enhanced Reaction Process (SERP) is an emerging concept in precombustion systems. In this process, CO<sub>2</sub> capture is performed *in situ* by combining chemical reaction and separation of the reaction products in the same operation [3]. These processes combine adsorption with conventional hydrogen production reactions (WGS: *water gas shift* and SRM: *steam reforming of methane*) and, depending on the reaction involved, the processes are referred to as SEWGS or SESRM. In both processes, the reactants are fed into a reactor containing a mixture of catalyst and adsorbent at operating conditions of 300–500 °C and 400–2000 kPa (SESRM) or 200–400 °C and 100–2800 kPa (SEWGS). The reaction and removal of CO<sub>2</sub> from the reaction zone occur simultaneously, thereby producing high purity hydrogen. Finally, the adsorbent is regenerated *in situ* using the principles of Pressure Swing Adsorption (PSA) or Thermal Swing Adsorption (TSA) at reaction temperature [3–5].

All current routes for CO<sub>2</sub> capture include several operating conditions. Postcombustion technologies, for instance, can be implemented at temperatures lower than 100 °C, atmospheric pressure and low CO<sub>2</sub> concentrations (< 15%), or directly from the gas stream at 150–400 °C. Similarly, precombustion processes are carried out at temperatures ranging from 40 to 250 °C and a pressure of 3 MPa [6].

The wide range of operating conditions for these technologies leads to the use of a variety of specific adsorbents for each application. Carbonaceous materials, such as activated carbons, exhibit the best adsorption capacity at temperatures lower than 50 °C and pressures higher than 100 kPa, with the amount adsorbed decreasing strongly at higher temperatures [7–10]. Zeolites show the best CO<sub>2</sub> adsorption capacity at low temperatures (0–100 °C) and in a wide range of pressures [7,11,12]. MOF materials, in turn, show a high adsorption capacity at room temperature and high pressures (about 3.5 MPa), although their capacity decreases with increasing temperature and in the presence of moisture and impurities [6,13]. In general, the use of physiorbent materials is limited to SERP technologies and postcombustion at intermediate and high temperatures, between 200 and 400 °C. Chemisorbent materials have gained interest due their high and reversible CO<sub>2</sub> adsorption capacity. Among this group of materials, alkali and alkaline earth metal oxides, double oxides, hydrotalcite compounds and their derived oxides obtained by calcination have attracted increasing attention. Indeed, several reviews have made a detailed comparison of these materials, highlighting the general characteristics of these adsorbents and their maximum adsorption capacity [6,8,14,15]. Specifically, hydrotalcites have been identified as chemisorbents for use at intermediate temperatures [15].

The aim of this work was to evaluate the CO<sub>2</sub> adsorption capacity of Co, Fe and Ni mixed oxides obtained from aqueous impregnation a commercial hydrotalcite as potential adsorbents in precombustion processes. The results are compared with four microporous materials selected from previous studies. Information related to several materials and their CO<sub>2</sub> adsorption capacity under several conditions of temperature and pressures are given in Table S1 of the Supporting Information. To the best of our knowledge, there are very few reports of CO<sub>2</sub> adsorption on mixed oxides derived from hydrotalcites under the experimental conditions studied in this work, high temperatures and pressures.

## 2. Experimental

### 2.1. Materials, reagents and gases

Materials and reagents used for the synthesis of mixed oxides derived from the hydrotalcite were: Co(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O (Panreac, PA), Fe(NO<sub>3</sub>)<sub>3</sub>·6H<sub>2</sub>O (Sigma-Aldrich), Ni(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O (Panreac, PA) and Mg<sub>6</sub>Al<sub>2</sub>(CO<sub>3</sub>)(OH)<sub>16</sub>·4H<sub>2</sub>O (Sigma-Aldrich). Four commercial adsorbents were used as reference: a zeolite 13X (Sigma-Aldrich), a MOF (Basolite A100 (MIL-53-Al) purchased from Sigma-Aldrich), an

activated carbon (AC; Sigma-Aldrich, Darko KB-B) and a synthetic alumina pillared clay (Al-PILC) [16]. Pure oxides (NiO, 99.999%, Sigma-Aldrich; Co<sub>3</sub>O<sub>4</sub>, 99.9985%, Strem Chemicals; Fe<sub>2</sub>O<sub>3</sub>, 99.99%, Sigma-Aldrich) are also included for comparison in the characterization section. Carbon dioxide (AGA, 99.996%), nitrogen (Air Liquide, 99.999%) and helium (Air Liquide, 99.999%) were also used.

### 2.2. Preparation of the materials

The materials selected in this study include three mixed Co, Fe and Ni oxides with a content of 5 wt%, Ni-MO-5, Fe-MO-5 and Co-MO-5, obtained from a commercial hydrotalcite, HT. These oxides were initially prepared from HT previously calcined at 500 °C and impregnated with aqueous solutions of the corresponding nitrate salt. The resulting material was then dried at 100 °C and finally calcined at 500 °C for 4 h in order to obtain the mixed oxides.

### 2.3. Characterization techniques

In order to characterize the crystalline phases of the mixed oxides, the powder X-ray diffraction (PXRD) patterns were recorded using a Siemens D-5000 diffractometer equipped with a Ni-filtered Cu K $\alpha$  radiation source ( $\lambda = 0.1548$  nm). The working conditions used were 30 mA, 40 kV and a scanning rate of 2° (2 $\theta$ )/min from 4 to 90°.

The textural properties of the mixed oxides in the micro-mesoporous region were obtained from N<sub>2</sub> adsorption-desorption experiments at –196 °C using a static volumetric apparatus (Micromeritics ASAP 2010 adsorption analyzer). Prior to the adsorption measurements, 0.3 g of sample was degassed at 200 °C for 24 h at pressures lower than 0.133 Pa. In the case of HT, the sample was pretreated at 100 °C. The textural characteristics of the meso-macroporous region were also obtained by Hg intrusion-extrusion experiments using an intrusion porosimeter apparatus (Micromeritics AUTOPOR-III). Prior to analysis, 0.5 g of sample was degassed at room temperature up to 7 Pa. Hg was introduced at a fill pressure of 2 kPa. The analysis at low pressure was performed from 3.4 to 206 kPa, followed by high pressure measurements up to 413 MPa, thus allowing the identification of pore sizes from 360  $\mu$ m to 3 nm.

Temperature-programmed reduction (TPR) studies were performed using a Micromeritics TPR/TPD 2900 equipment instrument. TPR tests were then carried out from room temperature to 1000 °C, at a heating rate of 10 °C min<sup>–1</sup>, under a total flow of 30 cm<sup>3</sup> min<sup>–1</sup> (5% H<sub>2</sub> in Ar, Praxair).

The thermogravimetric analysis of Ni-MO-5, before and after CO<sub>2</sub> adsorption at 300 °C, was performed using a Hi-Res TGA2950 apparatus from TA-Instruments. The measurements were carried out at a heating rate of 10 °C min<sup>–1</sup> from room temperature to 800 °C under nitrogen atmosphere and a flow of 60 cm<sup>3</sup>/min.

### 2.4. CO<sub>2</sub> adsorption experiments

Carbon dioxide adsorption experiments at 25, 35 and 50 °C were performed using a static volumetric apparatus (Micromeritics ASAP 2050) at pressures up to 1000 kPa. The samples (0.5 g) were previously degassed under vacuum at 200 °C for 24 h, except for the HT material, which was degassed at 100 °C to avoid any structure modification. The adsorption temperature was controlled using a circulating thermostatic bath containing ethylene glycol solution as the heat-transfer medium.

Adsorption experiments at 300 °C and pressures up to 4400 kPa were performed using a different static volumetric apparatus (VTI HPA-100). The degassing conditions were similar to those at low temperatures. The density of CO<sub>2</sub> gas under these experimental conditions was obtained using REFPROP v. 8.0 software, which contains the NIST *Standard Reference Database*. The excess CO<sub>2</sub> adsorption isotherms were calculated using these density data.

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