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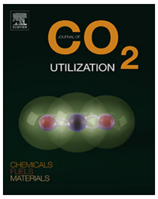

Enhanced CO_2 chemisorption at high temperatures via oxygen addition using (Fe, Cu or Ni)-containing sodium cobaltates as solid sorbents

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ABSTRACT

Sodium cobaltates containing Fe, Cu or Ni were synthesized, characterized and evaluated for CO_2 capture at high temperatures. Initially, $NaCoO_2$ and metal-containing samples were characterized by XRD, XPS, SEM and N_2 adsorption-desorption, where it was probed that Fe, Cu and Ni were partially incorporated into the $NaCoO_2$ structure. All these ceramics were able to trap CO_2, but only Fe-containing sample presented an important CO_2 chemisorption improvement in comparison to the pristine $NaCoO_2$ sample. Based on these results, a second set of samples was prepared and characterized, varying the iron concentration (10, 20 and 30 mol%). Results showed that CO_2 chemisorption was improved by iron addition up to 20 mol%, but higher amounts of iron did not continue enhancing the chemisorption process. Afterwards, the gas flow was modified adding oxygen ($P_{CO2} = 0.95$ and $P_{O2} = 0.05$), resulting in higher CO_2 chemisorption efficiencies and kinetics. These analyses were complemented by CO_2 cyclic experiments, where different gas flows were used, analyzing thermal stability and efficiency evolution.

1. Introduction

Since Nakagawa and Ohashi published in 1998 that lithium metazirconate (Li_2ZrO_3) reacts with carbon dioxide (CO_2) at high temperatures [1], different reports have shown that several alkaline-containing ceramics, especially lithium and sodium ones, are able to chemically trap CO_2 in a wide temperature range [2–20]. Moreover, it has been proposed that these ceramics would be used in different bifunctional sorption-catalytic processes, such as the sorption enhanced steam methane reforming (SE-SMR), which involves the catalytic steam methane reforming (SMR) and water-gas shift reaction processes, as well as carbon monoxide or dioxide sorption by a solid sorbent [21–24]. Within this context, the use of alkaline-containing ceramics, where the heteroatom is supposed to present active catalytic properties, is becoming an important issue. For example, sodium cobaltate ($NaCoO_2$) was recently reported as a possible bifunctional ceramic for the CO oxidation and subsequent CO_2 chemical capture, where different cobalt phases are responsible of the catalytic process [25,26].

Based on the importance of having heteroatoms on the crystal structure of alkaline ceramics, the solid solution syntheses have been evaluated [27–32], where the heteroatom can be an alkaline element (for example $Na_{2-x}Li_xZrO_3$) [32] or other metal or metalloid element (for example $NaZr_{1-x}Al_xO_3$) [33]. When these solid solutions are tested as CO_2 captors, in general, most of them improve different physicochemical properties, such as CO_2 capture temperature range, kinetic and efficiency, among others. The improvements observed on solid solutions are attributed to specific modifications in the crystal structure of ceramics or secondary phases formation [5]. Most of crystal structure modifications imply the formation of crystal point defects, which induce better atomic diffusion and release processes [17,20]. On the contrary, formation of different secondary phases usually modifies microstructural and diffusion properties of the external shell [5,7]. For example, $Li_{4+x}(Si_{1-x}Al_x)O_4$ solid solution importantly improved the CO_2 capture temperature range and chemisorption kinetics, in comparison to Li_4SiO_4 [29]. In this case, carbonation process produces Li_2SiO_3 and $LiAlO_2$ as secondary phases, where $LiAlO_2$ has a better lithium diffusion coefficient than Li_2SiO_3, improving the bulk carbonation processes.

In the same way, as it was already mentioned above, $NaCoO_2$ was recently reported as a possible CO_2 and CO captor material [25,26]. CO_2 capture in $NaCoO_2$ presented an efficiency of 55.9% at 700 °C. Moreover, $NaCoO_2$ catalytic activity was evidenced during the CO oxidation and subsequent CO_2 chemisorption. Furthermore, this ceramic has a hexagonal crystal system composed of $(CoO_2)^{1-}$ pillared layers with sodium atoms at the interlayers [25]. This kind of structure should favor the introduction of different heteroatoms, which consequently may modify CO_2 capture and catalytic properties.

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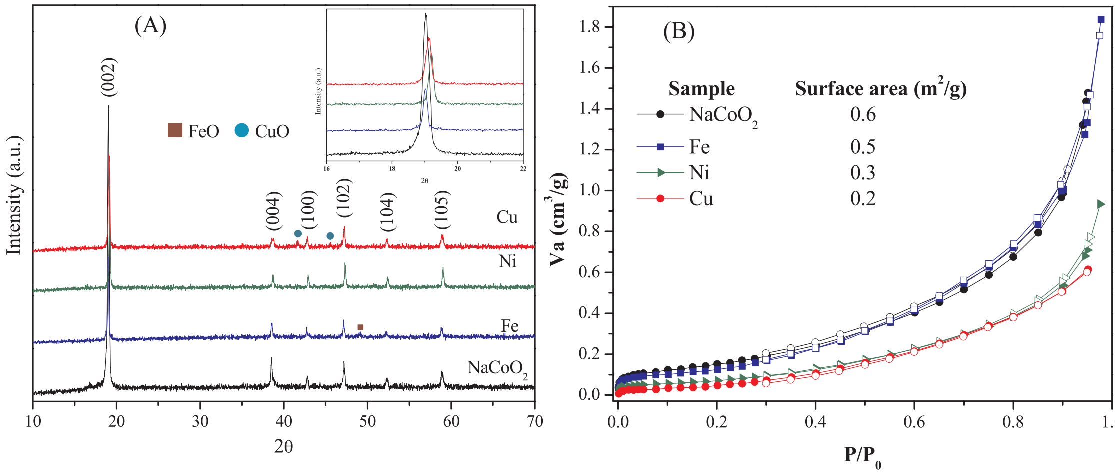

Fig. 1. XRD patterns (A) and N_2 adsorption-desorption isotherms (B) of pristine $NaCoO_2$ and M-$NaCoO_2$ samples (M = Fe, Ni or Cu).

Hence, it has been reported that alkaline ceramics, structural and chemically modified, enhance different CO_2 chemisorption properties, such as kinetics and capture temperature range, among others. Based on that, the aim of this work was to synthesize, characterize and evaluate as CO_2 captors different materials with $NaCo_{1-x}M_xO_2$ chemical composition (M = Cu, Fe or Ni). CO_2 capture process was performed in absence or presence of oxygen. This analysis may be considered an initial step for evaluating other alkaline ceramics as CO_2 captor materials to further utilize them as possible bifunctional catalytic-capture materials in different industrial processes, such as sorption enhanced reforming or H_2 enrichment from syngas flows.

2. Experimental

2.1. Sample synthesis

$NaCo_{1-x}M_xO_2$ (M = Fe, Ni, Cu) samples were synthesized by solid-state reaction method using sodium carbonate (Na_2CO_3, J.T. Baker), cobalt carbonate ($CoCO_3$, Aldrich), iron oxide (Fe_2O_3, MEYER), nickel oxide (NiO) obtained from the calcination of nickel nitrate hexahydrate at 600 °C for 4 h ($Ni(NO_3)_2 \cdot 6H_2O$, Aldrich) or copper oxide (CuO, Sigma Aldrich), adding 27 wt% excess of sodium carbonate to compensate the sublimation effect [33–35]. The corresponding stoichiometric amounts were mixed and calcined at 850 °C for 12 h, adding metallic heteroatom mole contents of $x = 0.1$ for Ni and Cu, while for Fe the mole content varied between 0.1 and 0.3. $NaCoO_2$ was also synthesized for comparison purposes.

2.2. Characterization techniques

All samples were characterized by powder X-ray diffraction (XRD), nitrogen (N_2) adsorption-desorption, scanning electron microscopy (SEM) and X-ray photoelectron spectroscopy (XPS). XRD patterns were obtained in a D-5000 Siemens diffractometer coupled to Co-K_α anode working at 34 kV and 30 mA. This radiation was used in order to avoid iron fluorescence. Compounds were identified using the Powder Diffraction File (PDF) database. Then, N_2 (Praxair, grade 4.8) adsorption-desorption isotherms were obtained on a Bel-Japan Minisorp II instrument at 77 K with a multipoint technique. Respective specific surface areas were obtained using the Brunauer-Emmet-Teller (BET) model. Microstructural characterization was complemented by scanning electron microscopy, using an equipment JEOL JMS-7600F. Afterwards, XPS analysis was performed in an ESCA2000 Multilab equipment (VG Microtech, from UK) with UHV system, Al K X-ray (1486.6 eV) and CLAM4 MCD analyser. Sample surface was sputtered for 5 min with 0.33 $\mu A/mm^2$ argon ions produced at 4.5 kV. The peak positions on the XPS spectra were referenced to C 1s core-level localized at 285.00 eV. XPS spectra were deconvoluted using SDP v4.1 software. The curve fitting procedure was performed as follows: (i) All spectra were calibrated to C 1s peak at 285.00 eV as carbon is ubiquitous and present on any surface; (ii) the linear method for background subtraction was employed in the binding energy (BE) range; (iii) the Gaussian-Lorentzian ratio was fixed to 0.95 to simulate peak profiles; iv) the asymmetry factor was fixed to 0.2; v) the peak positions for Co^{3+} $2p_{3/2}$ and Co^{3+} $2p_{1/2}$ were obtained from the first fit of data for $x = 0$ sample and then fixed for following analyses; (vi) the full width at half maximum (FWHM) was initially determined on the original sample and then used as initial parameter and; (vii) the best fit was selected by its minimum χ^2 value.

2.3. CO_2 chemisorption tests

CO_2 chemisorption was evaluated in a thermobalance (Q500HR, from TA Instruments) using dynamic, isothermal and cyclic experiments. Initially, $NaCo_{1-x}M_xO_2$ samples were dynamically heated from 30 to 900 °C (5 °C/min), under different gas flows; CO_2 (60 mL/min) or CO_2-O_2 (57-3 mL/min). For isothermal analyses, samples were heated up to desired temperature (between 200 and 800 °C, each 100 °C), under a N_2 flow (60 mL/min, Praxair grade 4.8). Then the gas flow was switched to CO_2 or CO_2-O_2 for 3 h. Finally, different cyclic experiments were performed at 700 °C. In these cases, sorption steps were produced into CO_2 (60 mL/min) or CO_2-O_2 (57-3 mL/min) for 90 min, while desorptions were produced with N_2 (60 mL/min) or N_2-O_2 (57-3 mL/min). Isothermal and cyclic products were characterized by XRD.

3. Results and discussion

XRD patterns of the synthesized compounds ($NaCo_{0.9}M_{0.1}O_2$, where M = Ni, Cu or Fe) are shown in Fig. 1A. All these diffractograms matched to 01-087-0274 PDF file, which corresponds to $Na_{0.74}CoO_2$ phase, with a hexagonal crystal system. It is well known that sodium cobaltate is a non-stoichiometric phase [36,37]. While XRD pattern identification showed the $Na_{0.74}CoO_2$ phase, the sample was labeled as $NaCoO_2$ in the whole work. It was also observed that samples synthesized with Fe and Cu presented secondary phases; iron (II) oxide (FeO, 99-101-0507 PDF file) and copper (II) oxide (CuO, 01-089-5895 PDF file), respectively. Nevertheless, their intensities were very low compared to $NaCoO_2$. The square inset in Fig. 1A presents the XRD reflections corresponding to plane (0 0 2), located at 19.03° for $NaCoO_2$ and $NaCo_{0.9}M_{0.1}O_2$ samples. Fe-containing $NaCoO_2$ sample presented a negligible shift (0.03°), as expected, since both Co^{3+} and Fe^{3+} cations possess the same oxidation state and ionic radius (0.55 Å). On the other hand, samples with Ni and