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CeO_2 nanopowders as solid sorbents for efficient CO_2 capture/release processes

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ABSTRACT

Solid sorbents based on metal oxides have been investigated as an alternative to liquid sorbents for CO_2 capture. Amongst them, acid-base properties of cerium oxide make it an excellent candidate for such applications at rather low temperature. In order to assess the suitability of this material, we quantified CO_2 adsorption/desorption capacities at 25 °C and 0.1 MPa by TGA technique. The adsorption results show the importance of a preliminary thermal treatment of the sorbents under inert gas, in order to maximize the CO_2 capture capacities *via* the thermal cleaning of CeO_2 surfaces (atmospheric and synthetic pollutants) liberating the access to CO_2 adsorption sites. CO_2 capture capacities depend on the specific surface area of the cerium oxide powders, reaching a maximum of 50 mg of CO_2 adsorbed per gram of CeO_2 displaying a specific surface area of 200 $m^2 g^{-1}$. The study also demonstrates the partial reversibility of this adsorption at 25 °C and its quantification, which can represent an important piece of information depending on the application (*e.g.*, catalysis or CO_2 capture). Finally, the CO_2 adsorption/desorption cycling of our best material was investigated exhibiting promising results for the use of CeO_2 powders as CO_2 solid sorbent with moderate temperature-swing conditions (between 25 °C and 150 °C).

1. Introduction

The reduction of greenhouse gases releases (*e.g.*, carbon dioxide—CO_2) has become an important challenge over the past 20 years, in order to reduce or prevent global warming and air pollution [1]. Several studies were conducted for selectively capturing CO_2 at emission points (industries), then releasing it afterwards for its storage (CCS: Carbon Capture and Storage) or reutilizing it as a raw material [2–4]. Two main approaches can be distinguished concerning the reversible capture of CO_2: (i) the use of liquid adsorbents solutions and (ii) the use of solid adsorbents.

The first approach is used in most of today's industrial processes but presents several limitations (*e.g.,* degradation of liquid sorbents over temperature cycles causing regeneration costs) [5] that led industrials and scientists to look for alternative solutions *via* the use of solid sorbents, displaying various absorption capabilities (see Table 1 in the Supporting information). From this perspective, new studies were conducted on the surface modification of materials by oxides (Cs, Ge, La, etc.) [6–8], or the utilization of these oxides alone [9–12], which displayed interesting properties for an efficient CO_2 reversible capture [13,14]. Carbon dioxide indeed possesses the ability to strongly interact with the surface of these oxides. Among them, cerium oxide (CeO_2) displays interesting acid-base properties, which have been extensively studied by Lavalley et al. [15–22].

Based on FTIR analyses during temperature cycles on CeO_2 powders submitted to different gases, they showed that atmospheric pollutants (*e.g.*, water or carbon dioxide) can easily adsorb over cerium oxide surfaces at room temperature (RT), due to the high surface reactivity, making this material an excellent candidate for CO_2 capture (see Figs. 1 and 2 and Table 3 in the Supplementary information). They demonstrated that the CO_2 captured over CeO_2 surface can adopt several configurations, each one of them displaying a different behavior when facing a temperature increase (CO_2 release) [17]. While some configurations will be desorbed at room temperature, some of them may require temperatures up to 500 °C to be released. Thus, knowing that atmospheric carbon dioxide can graft onto CeO_2 surface at RT, along with atmospheric water, it appears essential to thermally treat CeO_2 powders at 500 °C under N_2, in order to fully activate CeO_2 NCs surfaces prior to CO_2 capture/release characterization. Several studies have been conducted in the past few years confirming or completing the

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results of Lavalley et al. [23–30].

While the interaction of cerium oxide with CO_2 has been described and used in many catalytic reactions [31–35], the quantification of the adsorption capacity has not been extensively studied yet. Recently, Yoshikawa et al. described the synthesis and analysis of CO_2 adsorbents based on cerium oxide, proposing for the first time a coherent quantification of the amount of CO_2 adsorbed [36]. In their study, they compared the CO_2 adsorption capacity of three different CeO_2 powders with other CO_2 adsorbents based on single-metal oxide, *i.e.* SiO_2, Al_2O_3 and ZrO_2. From their experimental results, several conclusions can be drawn concerning the important parameters to consider for CO_2 adsorption capacity on metal oxide materials.

First of all, the presence of chemical adsorption sites for CO_2 is obviously the most important parameter. Nevertheless, although SiO_2 exhibited the highest specific surface area (more than 800 $m^2\,g^{-1}$), no CO_2 was adsorbed on this surface. The authors also showed that CeO_2-based materials exhibit the largest amount of CO_2 adsorbed in comparison with the other selected oxides.

It appeared that the adsorption capacity of CO_2 by CeO_2 is dependent on several parameters. The synthesis conditions, and especially the precursor used for the synthesis of the oxide, can generate pollutants on the surface of the oxide preventing the chemical adsorption of CO_2. Indeed, their materials synthesized from a chlorinated precursor displayed chloride pollutants over the surface, which they believe to reduce the adsorption capacity of the material (*via* the occupation of adsorption sites). Morphology, particle sizes, porosity and specific surface area of the materials are also important parameters determining the capture efficiency. Such parameters conditioned not only the number of adsorption sites available for the CO_2 chemical adsorption but also the accessibility of these sites to CO_2 molecules.

The more efficient material they tested towards the CO_2 adsorption was a commercial high-surface-area CeO_2 powder (specific surface are $S_{spe} = 166\ m^2\,g^{-1}$) which is able to adsorb around 5.7 mg of CO_2 per gram of CeO_2 (130 $mmol\,g^{-1}$) at 50 °C. Their study also provided results similar to those of Lavalley et al. concerning the kind of carbonate species interacting with the surface of CeO_2 during the adsorption and desorption of CO_2.

Another study by Li et al. [36b] reports the capture of CO_2 on CeO_2 nanopowders prepared by a surfactant-templated method over the CO_2 absorption capacity at room temperature. The results obtained with pure CeO_2 are slightly higher, namely: 700 $mmol\,g^{-1}$ (*i.e.* ~30 mg/g) for $S_{spe} = 181\ m^2\,g^{-1}$.

In our previous work, we described the fast and simple synthesis in near- and supercritical alcohols of CeO_2 nanocrystals aggregated in bigger round shape structures [37]. We showed that our powders can display high specific surface area – up to 200 $m^2\,g^{-1}$ – and keep their particular morphology, after a thermal treatment at 500 °C, required to clean the surface of the CeO_2 powders [38]. Thus, our CeO_2 nanocrystals appear to be excellent candidates as CO_2 solid adsorbents. In this work, we propose a method to quantify the adsorption and the desorption of CO_2 over cerium oxide powders at 25 °C and 0.1 MPa, and to draw a relation between the specific surface area of the powders and their CO_2 adsorption capacity, while demonstrating that an appropriate thermal treatment of the CeO_2 powders is of key importance in order to maximize the activity of CeO_2 towards CO_2 capture.

2. Experimental section

2.1. Materials

The CeO_2 powders used in this work were previously synthesized in our custom-built continuous process and characterized, as described in our previous work [37]. As a reminder, they were synthesized from ammonium cerium nitrate in near- or supercritical alcohols: methanol (scMeOH), ethanol (scEtOH), propanol (scPrOH), butanol (scButOH), pentanol (ncPentOH), hexanol (ncHexOH) and isopropanol (sciPrOH). The experimental conditions were set at 300 °C and 24.5 MPa, with a residence time (t_s) of 55 s. The recovered dry powders were used as produced, without any post-treatment.

Three additional samples of CeO_2 powders synthesized in near- and supercritical water were also studied as a matter of comparison with powders synthesized in alcohols [37]. The experimental conditions were set at 300 °C, 24.5 MPa and 45 s for the first sample and 400 °C, 24.5 MPa, 10 s and 45 s for the two other samples. The recovered dry powders were also used as produced.

All dry powders were grinded and sieved before further utilization.

The synthesis conditions, the crystallite sizes and the specific surface areas of the as-synthesized CeO_2 nanocrystals (NCs) are reminded in Table 2 of Supplementary information, along with their crystallite sizes and specific surface areas after 5 h of thermal treatment under N_2.

The nitrogen flow was provided by the internal gas network in our laboratory, while the CO_2 (purity ≥ 99.5%) was purchased from Air Liquide and filtrated through a SiO_2 sieve tank prior to utilization.

2.2. Apparatus and procedure

Thermal treatment under N_2 flow and CO_2 capture quantification were both performed using a TGA apparatus equipped with a custom-built gas inlet. Approximately 100 mg of CeO_2 powders were placed in a Pt crucible, itself placed in a microbalance SETARAM *mtb 10-8*. A schematic representation of the apparatus is given in Fig. 1. The 3-way valve allows switching from N_2 to CO_2 during TGA analysis.

Prior to the CO_2 capture quantification analysis, CeO_2 powders are submitted to a thermal treatment under N_2 flow (Fig. 1 *Gas path **A***). First, the temperature is maintained for 1 h at room temperature (RT), in order to stabilize the microbalance atmosphere, before being increased at 5 °C min^{-1} up to 500 °C. Then, the temperature is kept constant (500 °C) for 5 h, before being finally decreased to RT at 5 °C min^{-1}.

Once the temperature is back to RT, a CO_2 flow is injected into the microbalance for 3 h at RT (*Gas path **B***), in order to quantify the CO_2 capture over the CeO_2 powders. Finally, the gas flow is switched back to N_2 (*Gas path **A***), in order to quantify the CO_2 desorption from the CeO_2 surface.

2.3. Characterization techniques

Crystallite sizes (d_{cr}) of the CeO_2 nanocrystals were calculated using XRD patterns. The XRD patterns were recorded on a PANalytical X'Pert MPD powder diffractometer (θ–θ Bragg–Brentano geometry using Cu $K_{\alpha1,\alpha2}$) ($\lambda_1 = 1.54060$ Å, $\lambda_2 = 1.54441$ Å) radiation, equipped with a secondary monochromator and a X'Celerator detector, in the range of 8–120°, in continuous scan mode at $3.5 \times 10^{-3\circ}\,s^{-1}$. The powder was ground and sieved at 50 μm before being subjected to XRD.

The texture of the CeO_2 nanocrystals was analyzed by nitrogen adsorption isotherm (77 K) measurements. Data collection was performed by the static volumetric method, using an ASAP2010 apparatus (Micromeritics). Prior to each measurement, the samples were degassed at 150 °C in *vacuo* for a time interval high enough to reach a constant pressure (< 10 μmHg). The BET equation was applied between 0.05 and 0.3 relative pressures to provide specific surface areas (S_{sp}).

3. Results

CO_2 captured over CeO_2 can adopt several configurations, as it has been demonstrated by Lavalley et al. [17] (see Fig. S1 of Supplementary information). Depending on the configuration adopted by the CO_2 over the CeO_2 surface, its release may require temperatures up to 500 °C. Knowing that atmospheric carbon dioxide can graft onto CeO_2 surface at RT, along with atmospheric water, it appears essential to thermally treat CeO_2 powders at 500 °C under N_2, in order to fully activate the