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CeO₂ nano-powders as solid sorbents for efficient CO₂ capture/release processes

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KEYWORDS

Cerium oxide; CO₂ capture; Adsorption; Solid sorbent; High specific surface area.

ABSTRACT

Solid sorbents based on metal oxides have been investigated as an alternative to liquid sorbents for CO₂ 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 CO₂ 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 CO₂ capture capacities *via* the thermal cleaning of CeO₂ surface (atmospheric and synthetic pollutants) liberating the access to CO₂ adsorption sites. CO₂ capture capacities depend on the specific surface area of the cerium oxide powders, reaching a maximum of 50 mg of CO₂ adsorbed per gram of CeO₂ displaying a specific surface area of 200 m².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 CO₂ capture). Finally, the CO₂ adsorption/desorption cycling of our best material was investigated exhibiting promising results for the use of CeO₂ powders as CO₂ solid sorbent with moderate temperature-swing conditions (between 25 °C and 150 °C).

INTRODUCTION

The reduction of greenhouse gases releases (*e.g.*, carbon dioxide – CO₂) 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 CO₂ 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 CO₂: (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 the liquid sorbent 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 modification of the surface 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 CO₂ reversible capture [13-14]. Carbon dioxide indeed possesses the capacity to strongly interact with the surface of these oxides. Among them, cerium oxide (CeO₂) displays interesting acid-base properties, which have been extensively studied by Lavalley *et al.* [15-22].

Based on FTIR analyses during temperature cycles on CeO₂ 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 CO₂ capture (see Figure 1, 2 and Table 3 in the supplementary information). They demonstrated that the CO₂ captured over CeO₂ surface can adopt several configurations, each one of them displaying a different behavior over

temperature increase (CO₂ 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 CeO₂ surface at RT, along with atmospheric water, it appears essential to thermally treat CeO₂ powders at 500 °C under N₂, in order to fully activate CeO₂ NCs surfaces prior to CO₂ capture/release characterization. Several studies have been conducted in the past few years confirming or completing Lavalley *et al.* results [23-30].

While the interaction of cerium oxide with CO₂ 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 CO₂ adsorbents based on cerium oxide, proposing for the first time a coherent quantification of the amount of CO₂ adsorbed [36]. In their study, they compared the CO₂ adsorption capacity of three different CeO₂ powders with other CO₂ adsorbents based on single-metal oxide, *i.e.* SiO₂, Al₂O₃ and ZrO₂. From their experimental results, several conclusions can be drawn concerning the important parameters to consider for CO₂ adsorption capacity on metal oxide materials.

First of all, the presence of chemical adsorption sites for CO₂ is obviously the most important parameter. Nevertheless, although SiO₂ exhibited the highest specific surface area (more than 800 m².g⁻¹), no CO₂ was adsorbed on this surface. The authors also showed that CeO₂-based materials exhibit the largest amount of CO₂ adsorbed in comparison with the other selected oxides.

It appeared that the adsorption capacity of CO₂ by CeO₂ 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 CO₂. 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 CO₂ chemical adsorption but also the accessibility of these sites to CO₂ molecules.

The more efficient material they tested towards the CO₂ adsorption was a commercial high-surface-area CeO₂ powder (specific surface area – S_{spe} = 166 m².g⁻¹) which is able to adsorb around 5.7 mg of CO₂ per gram of CeO₂ (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 CeO₂ during the adsorption and desorption of CO₂.

Another study by Li *et al.* [36bis] reports the capture of CO₂ on CeO₂ nanopowders prepared by a surfactant-templated method over the CO₂ adsorption capacity at room temperature. The results obtained with pure CeO₂ are slightly higher, namely: 700 mmol.g⁻¹ (*i.e.* ~30 mg/g) for S_{spe} = 181 m².g⁻¹.

In our previous work, we described the fast and simple synthesis in near- and supercritical alcohols of CeO₂ nanocrystals aggregated in bigger round shapes [37]. We showed that our powders can display high specific surface area – up to 200 m².g⁻¹ – and keep their particular morphology, after a thermal treatment at 500 °C, required to clean the surface of the CeO₂ powders [38]. Thus, our CeO₂ nanocrystals appear to be excellent candidates as CO₂ solid adsorbents. In this work, we propose a method to quantify the adsorption and the desorption of CO₂ 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 CO₂ adsorption capacity, while demonstrating that an appropriate thermal treatment of the CeO₂ powders is of key importance in order to maximize the activity of CeO₂ towards CO₂ capture.

EXPERIMENTAL SECTION

Materials. The CeO₂ 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 CeO₂ 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 CeO₂ 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 N₂.

The nitrogen flow was provided by the internal gas network in our laboratory, while the CO₂ (purity ≥ 99.5%) was purchased from Air Liquide and filtrated through a SiO₂ sieve tank prior to utilization.

Apparatus and procedure.

Thermal treatment under N₂ flow and CO₂ capture quantification were both performed using a TGA apparatus equipped with a custom-built gas inlet. Approximately 100 mg of CeO₂ 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 Figure 1. The 3-way valve allows switching from N₂ to CO₂ during TGA analysis.

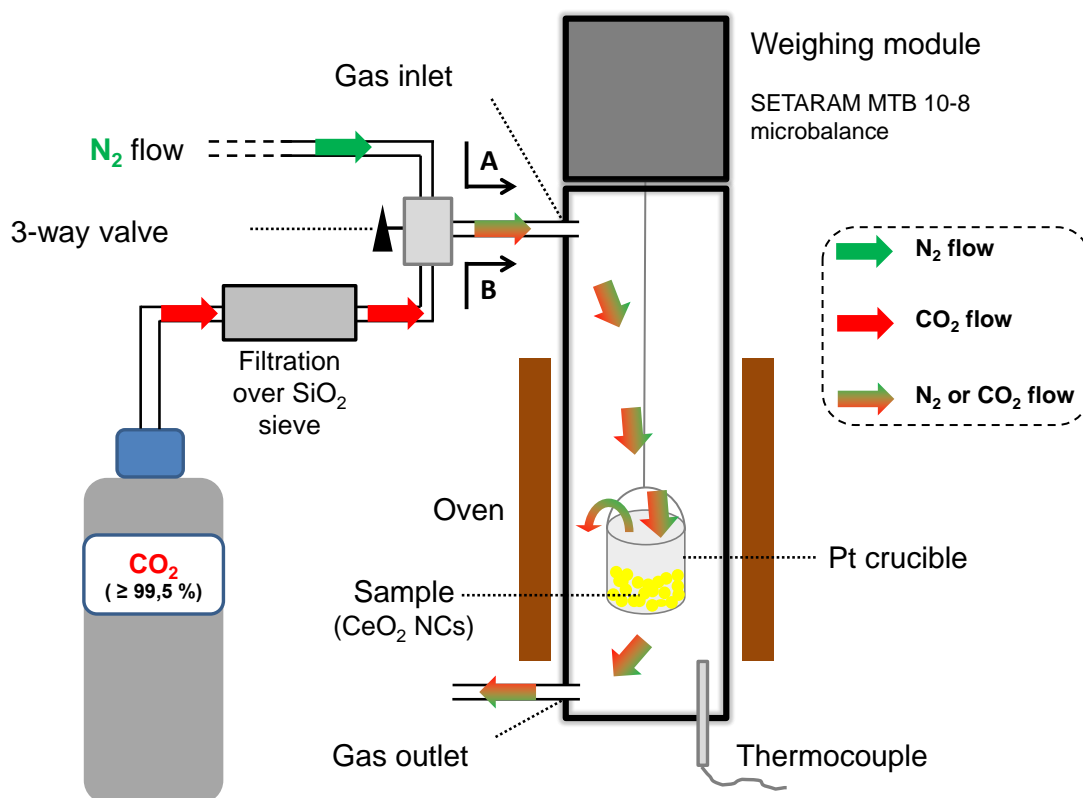


Figure 1. Schematic representation of the TGA apparatus used for CeO₂ powders thermal treatment under N₂ flow (*Gas path A*) and the quantification of CO₂ capture over CeO₂ nanopowders (*Gas path B*)

Prior to the CO₂ capture quantification analysis, CeO₂ powders are submitted to a thermal treatment under a N₂ flow (Figure 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

raised at $5\text{ }^{\circ}\text{C}\cdot\text{min}^{-1}$ up to $500\text{ }^{\circ}\text{C}$. Then, the temperature is kept constant ($500\text{ }^{\circ}\text{C}$) for 5 h, before being finally decreased to RT at $5\text{ }^{\circ}\text{C}\cdot\text{min}^{-1}$.

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.

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 $\text{Cu K}_{\alpha 1, \alpha 2}$ ($\lambda_1 = 1.54060\text{ \AA}$, $\lambda_2 = 1.54441\text{ \AA}$) radiation, equipped with a secondary monochromator and a X'Celerator detector, in the range of 8 – 120° , in continuous scan mode at $3.5 \times 10^{-3}\text{ }^{\circ}\cdot\text{s}^{-1}$. The powder was ground and sieved at $50\text{ }\mu\text{m}$ 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 $150\text{ }^{\circ}\text{C}$ in *vacuo* for a time interval high enough to reach a constant pressure ($<10\text{ }\mu\text{mHg}$). The BET equation was applied between 0.05 and 0.3 relative pressures to provide specific surface areas (S_{sp}).

RESULTS

Characterization and quantification of the CO_2 adsorption/desorption over thermally treated CeO_2 powders synthesized in nc- or sc-alcohols. CO_2 captured over CeO_2 can adopt several configurations, as it has been demonstrated by Lavalley *et al.* [17] (see Figure 1 of Supplementary information). Depending on the configuration adopted by the CO_2 over the CeO_2 surface, its release may require temperatures up to $500\text{ }^{\circ}\text{C}$. 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 $500\text{ }^{\circ}\text{C}$ under N_2 , in order to fully activate the CeO_2 NCs surfaces prior to CO_2 capture/release characterization.

Thus, CeO_2 powders were submitted to a 5 h thermal treatment at $500\text{ }^{\circ}\text{C}$ under N_2 , as previously described, prior to the CO_2 capture/release characterization. Once the temperature is back to RT, the CeO_2 samples were submitted to a CO_2 flow at RT (Figure 1 – *Gas path B*) for 3 h, in order to quantify carbon dioxide adsorption over the CeO_2 surfaces. Finally, gas is switched to N_2 for 3 h at RT, in order to quantify CO_2 desorption from CeO_2 surfaces. Weight losses of samples over such treatment cycle are followed by TGA measurements.

All the analyzed CeO_2 powders adopted the same behavior when submitted to such treatment. A general representation of the behavior of these powders is given in Figure 2, along the gas/temperature program used.

During the preliminary thermal treatment under N_2 flow, a drastic weight loss is observed. This phenomenon can be attributed to water and carbon dioxide desorption, which can graft easily at RT, but also to grafted alcohol desorption. Indeed, we previously showed that the alcohol used as solvent during the synthesis in near- or supercritical conditions acts as a surface modifier for the CeO_2 surfaces [37,39], and tends to desorb in this temperature range [38].

Then, when CO_2 is flown over the CeO_2 NCs at RT, a gain in weight is observed, which is attributed to CO_2 adsorption over the CeO_2 surfaces. Finally, a weight loss is witnessed when atmosphere is switched back to N_2 flow, corresponding to a partial desorption of CO_2 from the CeO_2 surfaces.

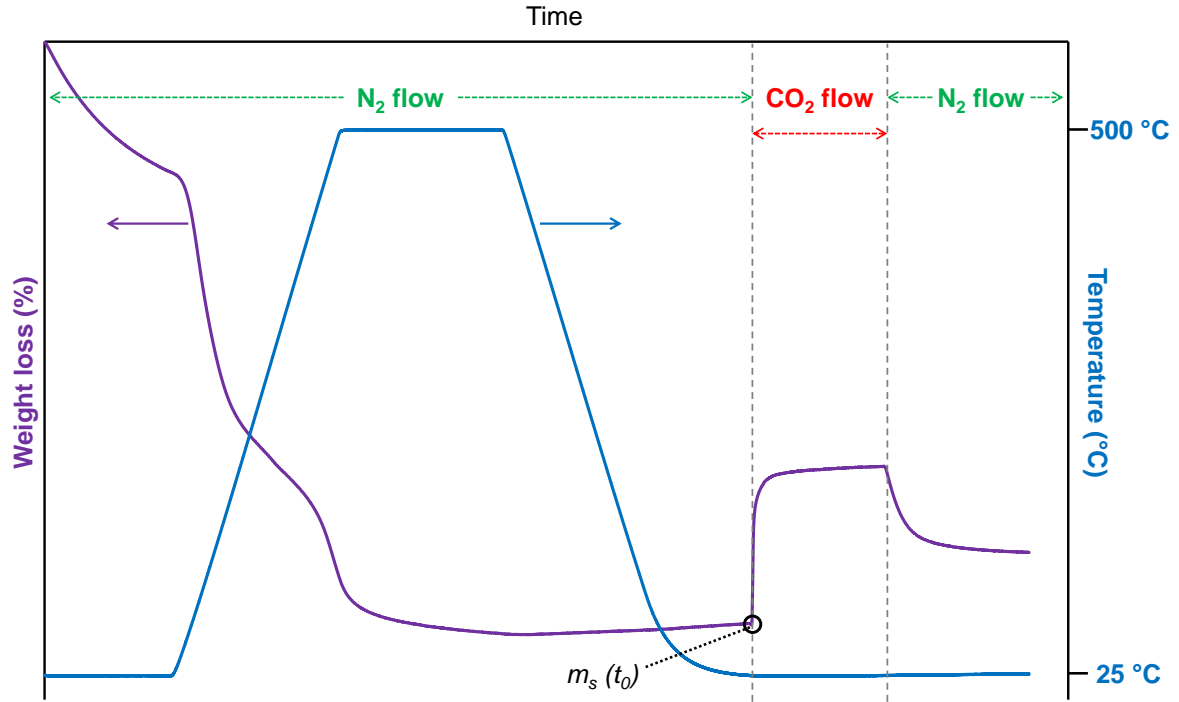


Figure 2. Representation of the general behavior for the weight loss of CeO₂ powders monitored by TGA. The sample is treated under N₂ at RT for 1 h then at 500 °C for 5 h (5 °C.min⁻¹). Back to RT, the sample is submitted to a CO₂ flow for 3 h then to a N₂ flow for 3 h. m_s(t₀): Initial weight of the sample when atmosphere is switched to CO₂.

The adsorption capacity of CO₂ for each sample as the function of time (Ads_{CO₂}(t), in mg of CO₂/g of CeO₂, or mg/g) can be calculated from the TGA curves. The mass of the sample at the beginning of CO₂ flow switch (m_s(t₀), in mg) is used as a reference (**Figure 2**). The mass of CO₂ adsorbed by the CeO₂ as a function of time (m_{CO₂-ads}(t), in mg) can be therefore obtained by subtracting the initial mass m_s(t₀) to the mass at the time *t* (m_s(t), in mg), as described by the Equation (1).

Thus, the adsorption capacity of CO₂ by the sample as a function of time (Ads_{CO₂}(t)) is easily calculated as the ratio of the mass of CO₂ adsorbed by the sample over the mass at t₀ (Equation (2)).

$$m_{\text{CO}_2\text{-ads}}(t) = m_s(t) - m_s(t_0) \quad (1)$$

$$\text{Ads}_{\text{CO}_2}(t) = \frac{100 \cdot m_{\text{CO}_2\text{-ads}}(t)}{m_s(t_0)} \quad (2)$$

Based on these considerations, a general representation of the variation of the CO₂ quantity adsorbed on the CeO₂ surface as a function of time (Ads_{CO₂}(t)) is given in Figure 3. Several observations and conclusions can be withdrawn from such curve.

First, as observed by Lavalley *et al.* [17], about 15 min are needed to reach the maximum CO₂ adsorption quantity (Ads_{max}, in mg CO₂/g CeO₂). Such phenomenon is led by both the diffusion kinetics of CO₂ in the material and the thermodynamics of CO₂-CeO₂ interactions.

When the atmosphere is switched from a CO₂ to a N₂ flow, a decrease of the adsorbed CO₂ quantity is observed. Yet, this phenomenon is not only slower than the adsorption but also not complete, *i.e.* a considerable amount of CO₂ remains adsorbed over CeO₂ surfaces after several hours of N₂ flow at 25 °C. Regarding the works of Lavalley *et al.*, such phenomenon can easily be explained by the broad range of CO₂-CeO₂ interaction species forming during the adsorption at 25 °C under a CO₂ flow (Figure 1 of Supplementary information). Some of them will desorb spontaneously at 25 °C when the CO₂ flow is stopped (*i.e.*,

hydrogenocarbonates and bridged carbonates mainly) while other will require temperatures up to 500 °C to be desorbed (*i.e.*, bidentate, monodentate and polydentate carbonates mainly).

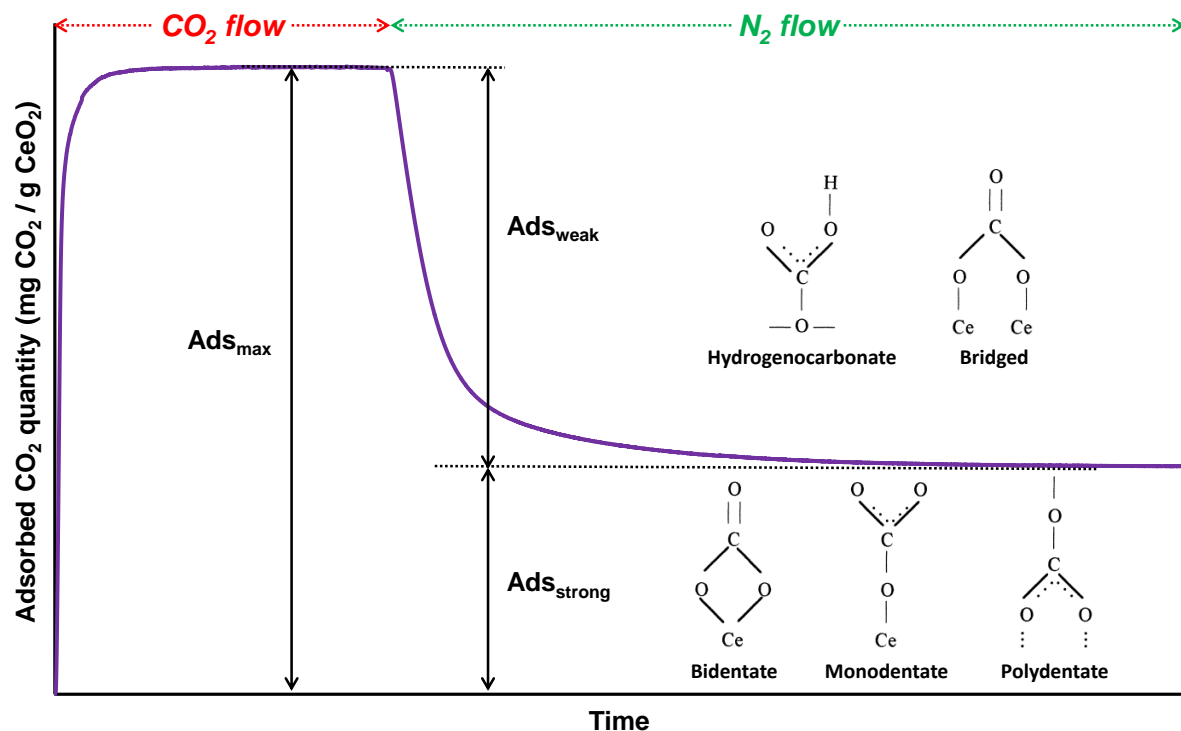


Figure 3. General overview of the quantity of adsorbed CO₂ over CeO₂ samples as a function of time. Representations of the most probable configurations for CO₂-CeO₂ interactions are also pictured. Hydrogenocarbonates and bridged carboxylates are desorbed at RT under N₂ flow (weak CO₂ adsorption, Ads_{weak}). Bidentate, monodentate and polydentate carboxylates remains at the surface of CeO₂ after N₂ flow at RT (strong CO₂ adsorption, Ads_{strong}).

Thus, the maximum quantity of CO₂ adsorbed can be considered as the sum of two kinds of CO₂ interactions with CeO₂ surface. First, the hydrogenocarbonates and bridged carbonates form weak interactions at 25 °C, and desorb by simply stopping the CO₂ flow over the CeO₂ samples. Those species can be quantified as the quantity of CO₂ desorbed from CeO₂ surfaces during the purge at 25 °C (Ads_{weak} , in mg CO₂/g CeO₂, or mg/g). Then, bidentate, monodentate and polydentate carbonates create a strong interaction with CeO₂ surfaces and cannot be desorbed from these surfaces at 25 °C. They can be quantified as the quantity of CO₂ still adsorbed over CeO₂ surfaces during the purge at 25 °C (Ads_{strong} , in mg CO₂/g CeO₂, or mg/g). Such differentiation can be very useful for applications such as CO₂ storage, which may require a stable adsorption even when CO₂ flow is stopped (*i.e.*, Ads_{strong}) or which may require CO₂ desorption at low temperatures (Ads_{weak}), depending on the utilization.

The experimental values of Ads_{max} and Ads_{strong} are plotted as a function of the CeO₂ NCs specific surface area in **Figure 4** (The exact values can be found in Table 3 of the Supplementary information, along with those of the Ads_{weak}).

The cerium oxide powders synthesized in near- and supercritical alcohols allow reaching a maximum quantity of adsorbed CO₂ up to 48 mg/g of CeO₂, for samples developing high specific surface areas.

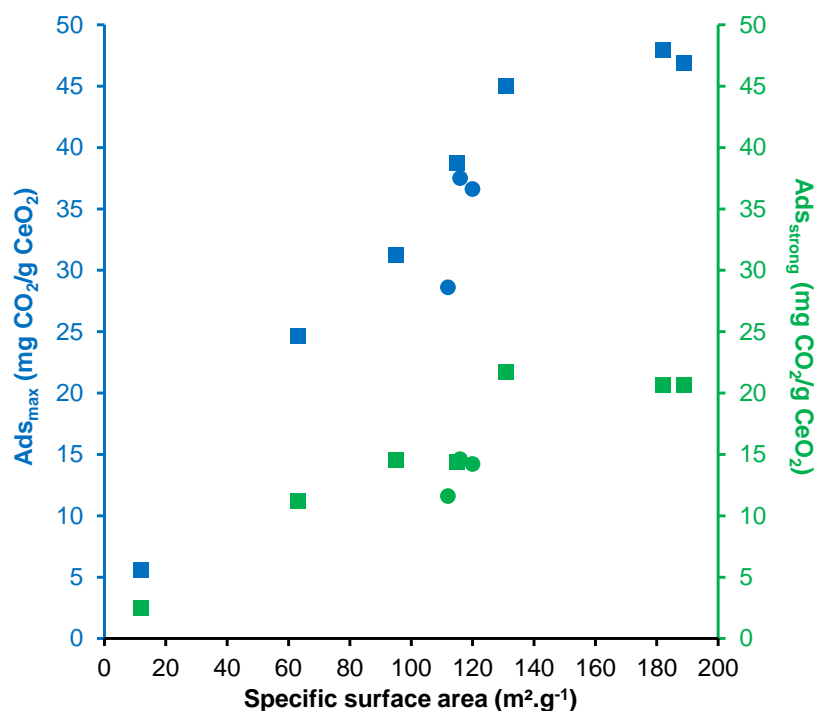


Figure 4. Experimental values of the Ads_{max} and the Ads_{strong} as a function of the surface specific areas of the CeO_2 powders thermally treated at 500 °C under N_2 flow. Squares are CeO_2 powders synthesized in nc- or sc-alcohols and circles the ones synthesized in nc- or sc-water.

CeO_2 powders synthesized in near- and supercritical water have also been submitted to the same N_2 thermal treatment at 500 °C and CO_2 adsorption/desorption cycle at RT. Similar behaviors are observed and the measured Ads_{max} validate that it exists a relationship between the quantity of CO_2 adsorbed over CeO_2 surfaces and the specific surface area, disregarding their syntheses conditions. The Ads_{max} and Ads_{strong} of these samples as a function of their specific surface areas are presented in Figure 4, along with the results with alcohols (The exact values can also be found in Table 4 of the Supplementary information, along with those of the Ads_{weak}).

DISCUSSION

Concerning the CO_2 adsorption capacity of the thermally treated CeO_2 NCs, the TGA analyses under CO_2 flow at 25 °C showed that the maximum quantity of CO_2 adsorbed on the surface of CeO_2 NCs increases linearly with the specific area of CeO_2 powders in the range 0-150 $m^2.g^{-1}$. This work is the first demonstration of such a relationship between CO_2 adsorption capacity over CeO_2 and specific surface area.

However, we noticed that this adsorption reaches its limits at 48 mg of CO_2 captured by gram of CeO_2 powders (synthesized in nHexOH). But this limit appears at high specific areas, when ButOH, PentOH and HexOH are used for the synthesis. Now, we previously showed that not all organic species are desorbed from such CeO_2 samples at 500 °C, which limits their specific surface areas but also makes a hard path for CO_2 diffusion through the round shaped structures.

Playing with thermal treatment to increase the adsorption rates. Our previous work showed that a treatment under N_2 flow at a temperature higher than 500 °C can enhance the desorption of organic species and thus leads to CeO_2 NCs with higher specific surface areas [38]. Nonetheless, a temperature too important can also lead to sintering which will have the opposite effect, *i.e.* a decrease of the specific surface areas of the materials.

This treatment temperature also plays an important role to improve the CO_2 adsorption capacities of the CeO_2 powders, alongside with the specific surface areas of the materials. As previously shown, the CeO_2 NCs synthesized in nHexOH reach a S_{sp} of 182 $m^2.g^{-1}$ and display

an Ads_{max} of 47.9 mg/g after a thermal treatment at 500 °C. When submitted to a thermal treatment at 540 °C, the S_{sp} of these materials increases from 182 to 199 $m^2.g^{-1}$ owing to a better desorption of surface pollutants and the Ads_{max} also increases alongside from 47.9 mg/g versus 49.6 mg/g. On the contrary, the CeO_2 NCs exposed to a thermal treatment at 600 °C undergo sintering and thus, the S_{sp} of these materials decreases (from 199 $m^2.g^{-1}$ to 185 $m^2.g^{-1}$) and the Ads_{max} declines accordingly from 47.9 mg/g to 36.7 mg/g. The Ads_{weak} and Ads_{strong} of these materials are given in the Table 5 of Supplementary information.

These results show the importance of choosing an appropriate temperature for the thermal activation of the CeO_2 (mandatory to remove surface pollutants and thus activate the material towards CO_2 capture) prior to their use for CO_2 capture.

Cyclability of the CeO_2 powders. We have further investigated the suitability of our materials as potential CO_2 solid sorbents by checking their cyclability. Indeed, we showed that our materials can display high specific surface area and interesting CO_2 adsorption capacity at low temperature (25 °C and 0.1 MPa), but to be suitable as CO_2 solid sorbents, they need to be regenerable for continuous use with an acceptable thermal treatment cycle.

In this regard, a longer experiment was led on crude CeO_2 powders synthesized in nHexOH with 3 CO_2 adsorption tests and different regeneration steps under N_2 . The weight loss of the sample and thus, its CO_2 adsorption/desorption during this experiment were followed by TGA and the results are presented in Figure 5, along with the experimental conditions (temperature, time and gas flow). Numerical values of these results are also given in Table 1.

The first step was a classical thermal treatment at 500 °C under N_2 flow in order to eliminate pollutants from the surface of CeO_2 powders, resulting in a weight loss from the sample (-12.7 %). Of course, this temperature is not sufficient to achieve a complete desorption of the pollutants, as previously demonstrated, but allows avoiding the sintering of the powders. Once the sample is back to RT, the gas flow was switched to CO_2 (Step 2), which resulted in a gain of weight of the sample (+ 3.8 %), corresponding to an adsorption of 44.0 mg of CO_2 per gram of CeO_2 , which is comparable to the value previously obtained with similar treatment and samples (Table 2 of Supplementary information).

In a third step, gas flow was switched back to N_2 to characterize the CO_2 desorption from the sample at 25 °C. It resulted in a weight loss of the sample (- 2.0 %) corresponding to a CO_2 desorption of 24.0 mg/g, which is in good agreement with previous experiments.

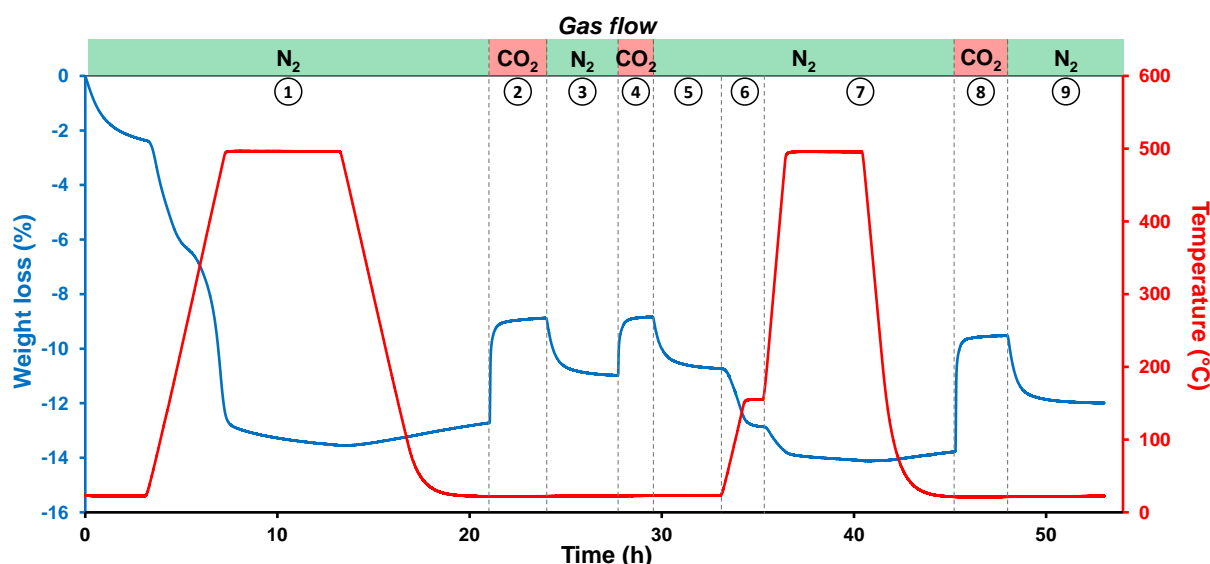


Figure 5. Experimental conditions and weight loss of CeO_2 powders synthesized in nHexOH and submitted to cycling tests of CO_2 adsorption/desorption.

Another CO_2 adsorption/desorption cycle at RT was then performed in order to compare the values of Ads_{weak} for pristine and reused CeO_2 powder (Step 4). A gain of weight of + 2.0 % was witnessed corresponding to an adsorption of 24.4 mg of CO_2 per gram of CeO_2 . This

means that all the CO₂ that was desorbed during the previous step under N₂ at 25 °C can be adsorbed again at the CeO₂ surface, *i.e.* there is no loss of CO₂ adsorption capacity after a desorption step at 25 °C. This CO₂ is once again desorbed under N₂ flow at 25 °C during a fifth step (weight loss of - 1.9 %, *i.e.* a CO₂ desorption of 22.6 mg/g during this step). This may mean that each CeO₂ adsorption sites will favor a specific type of interaction for the capture of CO₂ (*e.g.*, hydrogenocarbonate or bidentate carbonate) which remains the same over cycling.

Table 1. Cycling experiments performed on the CeO₂ powders synthesized in nHexOH.

| Step | Gas | T (°C) | Duration (h) | Total weight loss (%) ^[a] | ΔAds(CO ₂) (mg/g) ^[b] |
|------|-----------------|------------|--------------|--------------------------------------|--|
| 1 | N ₂ | 25 | 3 | - 12.7 | - |
| | | 25 to 500 | 4 | | |
| | | 500 | 6 | | |
| | | 500 to 25 | 7 | | |
| | | 25 | 1 | | |
| 2 | CO ₂ | 25 | 3 | - 8.9 | + 44.0 |
| 3 | N ₂ | 25 | 4 | - 10.9 | - 24.0 |
| 4 | CO ₂ | 25 | 2 | - 8.9 | + 24.4 |
| 5 | N ₂ | 25 | 4 | - 10.8 | - 22.6 |
| 6 | N ₂ | 25 to 150 | 1 | - 12.9 | - 24.2 |
| | | 150 | 1 | | |
| 7 | N ₂ | 150 to 500 | 2 | - 13.7 | - |
| | | 500 | 4 | | - |
| | | 500 to 25 | 4 | | - |
| | | 25 | 1 | | - |
| 8 | CO ₂ | 25 | 3 | - 9.5 | + 49.3 |
| 9 | N ₂ | 25 | 5 | -12.0 | - 20.7 |

^[a] Total weight loss of the material recorded from the beginning of the experiment by TGA.

^[b] Calculated values of the adsorption (positive values) and desorption (negative values) of CO₂ by CeO₂ powders, deduced from the total weight loss values. The ΔAds(CO₂) values are cumulative, which means that after the Step 3, for example, 24.0 mg of CO₂ per gram of CeO₂ are desorbed ($Ads_{weak} = 24 \text{ mg.g}^{-1}$) while $(+44.0 + (-24.0) =) 20.0 \text{ mg of CO}_2 \text{ per gram of CeO}_2 \text{ remain on CeO}_2 \text{ powders (} Ads_{strong} = 20 \text{ mg.g}^{-1}\text{)}$.

A desorption temperature of 25 °C is obviously not sufficient enough to desorb all the CO₂ captured by the CeO₂ powders. Indeed, the work of Lavalley *et al.* showed that the CO₂ species adsorbed at the surface of CeO₂ can require temperatures up to 500 °C to be desorbed [17]. A temperature difference of 475 °C (between 25 °C for the CO₂ adsorption and 500 °C for the CO₂ desorption) would hardly make CeO₂ suitable as a solid sorbent from an energy point of view compared to classical use of liquid monoethanolamine, which can adsorb CO₂ at 25 °C and can be regenerated at 150 °C. Fortunately, not all CO₂ species required temperature of 500 °C to desorb and some of the species, which do not desorb at RT, could be desorbed around 150 °C, according to the work Lavalley *et al.*

In order to check what could be the desorption efficiency with a thermal treatment at 150 °C (comparable to conventional liquid sorbent desorption process), a sixth step was performed under N₂ with a 1 h threshold at 150 °C. A weight loss of - 2.1 % is observed during this step, corresponding to a CO₂ desorption of 24.2 mg/g. Unexpectedly, this temperature increase from 25 °C to 150 °C under N₂ flow allows retrieving the weight of CeO₂ in presence after the initial

N₂ thermal treatment (500 °C) and before the two CO₂/N₂ cycles at 25 °C. This means that the amount of CO₂ species present at the surface in the CeO₂ powders, which requires a thermal treatment over 150 °C, is negligible. Thusly, CeO₂ powders would make great candidate at low temperature as CO₂ solid sorbent for replacing liquid adsorbent systems.

Then, a seventh step was performed under N₂ flow with a 4 h threshold at 500 °C, witnessing a weight loss of - 0.8 % after the temperature is back to RT. This weight loss is attributed to desorption of remaining organic species from the synthesis (alcohol grafts). This hypothesis is confirmed by the gain in weight (+ 4.2 %) observed during a final step (Step 8) under CO₂ at 25 °C (Step 8), which corresponds to a CO₂ adsorption of 49.3 mg/g. This adsorption capacity is higher than the one recorded after the first CO₂ adsorption (Step 2, 44.0 mg/g), which is **coherent** with the previous hypothesis. Indeed, not all the organic species from the synthesis are desorbed during the first step at 500 °C under N₂, which limits the CO₂ adsorption capacity of the material. During this second threshold at 500 °C (Step 7), more surface pollutants are removed from the surface creating more available adsorption sites for CO₂ and thus increasing the maximum CO₂ adsorption capacity of the CeO₂ powders.

In brief, cerium oxide powders with high specific surface areas appear as great candidates for temperature-swing reversible capture of CO₂ at low temperature – between 25 and 150 °C – compared to most of the other metal oxides studied so far, which required higher temperatures for cyclability (e.g., CaO/CaCO₃ between 700 and 800 °C [2,40]). This dramatically enhances the energy efficiency of the process.

CONCLUSION

The suitability of CeO₂ materials as CO₂ solid sorbent has been examined on powders displaying a large array of different specific surface areas (from 12 up to 199 m².g⁻¹). This study showed that the adsorption efficiency of the CeO₂ materials is primarily dependent on its specific surface area, with an almost linear relationship.

The adsorption of CO₂ requiring the access of CO₂ to the surface atoms of CeO₂, we also showed that a thermal activation of the materials before their use as a solid sorbent is mandatory. This thermal treatment requires knowing well the material in order to wisely choose the operating temperature and thusly, maximize the CO₂ capture capacity of the materials. Indeed, the preliminary treatment temperature must respect two major conditions: (i) being high enough to remove most of the surface pollutants from the material (e.g., atmospheric water and CO₂ and synthesis residues), which are blocking potential CO₂ adsorption sites and (ii) being low enough to avoid the sintering of the material, which will drastically decrease the CO₂ adsorption capacity of the material along with its specific surface area [38].

This way, our CeO₂ powders, displaying a specific surface area of 199 m².g⁻¹ after a thermal treatment at 540 °C under N₂ flow, exhibited at 25 °C and 0.1 MPa a maximal CO₂ adsorption capacity around 50 mg of CO₂ per gram of CeO₂ (i.e., around 1130 mmol of CO₂/kg of CeO₂). It was also demonstrated that the adsorption of CO₂ by CeO₂ is partially reversible at 25 °C and gave a quantification of the CeO₂-CO₂ species that can be desorbed just by stopping the CO₂ flow and those which remains at the surface. Such distinction may be of key importance depending on the sought application for this material, e.g. catalysis requiring weak adsorption or capture requiring strong adsorption.

Eventually, the possible CO₂ adsorption/desorption cycling over CeO₂ powders has been examined. The preliminary analyses show that it is possible to adsorb CO₂ at 25 °C and to regenerate almost completely the material at 150 °C under inert gas atmosphere, without losing the CO₂ capture capacity. That way, we believe that high specific surface area CeO₂ materials can be future great candidates as reversible low temperature CO₂ solid sorbents (25 – 150 °C), making them competitive alternative to conventional liquid sorbents systems.

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Notes

The authors declare no competing financial interest.

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