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Study of the CO₂/Sorbent Interaction in Sorbents Prepared with Mesoporous Supports and Calcium Compounds

Josefa Fernández,* Fernando González, Carmen Pesquera, Carmen Blanco, and M. Josefina Renedo

Departamento de Ingeniería Química y Química Inorgánica, ETSIIyT, Universidad de Cantabria, Avenida de los Castros s/n, 39005-Santander, Spain

CO₂ chemisorption experiments were used to study the behavior of sorbents prepared from MCM-41 and SBA-15 mesoporous supports and Ca(OH)₂ at different ratios in two main aspects: to determine the capacity of the sorbents to capture CO₂ and to identify the products synthesized in the process. Two different ways of preparation of the sorbents were used: Type I sorbents were prepared by mixing CaO, water, and the support at room temperature, and Type II were prepared by impregnation of the support with calcium nitrate followed by calcination and hydration to form Ca(OH)₂. Static chemisorption experiments at low temperature (323 K) and low CO₂ pressure showed that Type I yielded higher values of CO₂ retention than Type II. MCM-41 support, with a higher specific surface area than SBA-15, achieved the more effective sorbent, 10% Ca(OH)₂/MCM-41. The moles of CO₂ per mole of calcium retained by this sorbent was approximately five times that obtained with unsupported commercial Ca(OH)₂. To determine the form in which CO₂ was retained at this low temperature dynamic chemisorption experiments with CO₂ were performed with commercial Ca(OH)₂ and with 10% Ca(OH)₂/MCM-41 sorbent. The results showed that CO₂ was chemisorbed on both solids as a complex CaO•CO₂, which was reversibly desorbed at 473 K, and as CaCO₃. The 10% Ca(OH)₂/MCM-41 sorbent can be used as a regenerable sorbent at temperatures up to 823 K. At those conditions, only the CO₂ retained as CaO•CO₂ is desorbed, with no relevant loss of capture in the five cycles tested. Experiments varying the adsorption time proved that, in a first step, the CO₂ retention is fast and probably kinetically controlled, making the further uptake much slower in a process controlled by diffusion; the maximum amount of CO₂ retained (56.6% mol CO₂/mol Ca) was obtained at 18 h of exposure with the sorbent prepared at the lowest Ca(OH)₂/MCM-41 ratio tested (2.5%), showing that the reaction at low temperature is favored with a good calcium distribution.

Introduction

Carbon dioxide (CO₂) is the main greenhouse gas that causes global warming. Approximately one-third of the CO₂ emissions to the atmosphere come from the combustion of fossil fuels in power plants, the rest being from automotive engines, industrial use, or heating purposes.¹ To reduce the concentration of CO₂ a variety of measures have been proposed. These include improving the energy efficiency and developing renewable energy sources such as wind and solar power. However, in the short term, fossil fuels will continue to be the main energy supply and technologies associated with CO₂ capture and storage are increasingly considered to be likely contributors to reduce these emissions.^{2,3}

There are three main approaches to capture the CO₂ generated from fossil fuels or biomass, classified as postcombustion (capture from the flue gas), precombustion separations (capture in the gasification process, before the combustion of the gases generated), and oxy-fuel firing (use of oxygen instead of air as comburent gas).^{2–4} Developed postcombustion technology consists in the flue gas absorption in an aqueous solution with amines, mainly in the form of gas–liquid absorption columns. This technology is commonly used in various industries faced with the task of removing CO₂ from gas mixtures containing a wide range of species in different concentrations.^{5,6}

Adsorption at low temperatures (up to 423 K) is considered one potential alternative with the added advantage that solids are easy to handle.⁷

Xu et al.⁸ reviewed the work carried out with various adsorbents, such as zeolites, activated carbons, carbon molecular sieves, pillared clays, and metal oxides.

Calcium oxide and calcium hydroxide are bases commonly considered as good CO₂ adsorbents at high temperatures in precombustion (coal gasification or gas reforming) and post-combustion processes,^{9–14} CaCO₃ being the product of CO₂ capture reported. Sun et al.,¹⁵ to explain the change in the order of the CaO/CO₂ reaction, suggest that an intermediate complex CaO•CO₂ is formed before the synthesis of CaCO₃.

Mesoporous molecular sieves represent a new class of inorganic materials, first recognized by scientists from Mobil Corporation. Since then, MCM-41 has become the most popular member of the family of mesoporous silicates. The structure represents a hexagonal ordering of cylindrical channels consisting of amorphous silica with pore diameters ranging between 15 and 100 Å, depending on the template and synthesis conditions. SBA-15, another mesoporous material, is synthesized by using triblock copolymer surfactant as a template under acidic conditions, which gives mesoporous materials with a much larger pore size (up to 30 nm) and better stability than MCM-41. These new materials have great technological importance.

These mesoporous materials, with high surface areas and well-defined pore structures, have been found to have reasonably high CO₂ adsorption capacity at low temperatures.¹⁶ Investigations have been conducted to modify these materials with basic amines in order to increase their adsorption capacity and mainly their selectivity to acid gases.^{8,17–20} A work recently published²¹ used the MCM-41 material, with no calcium base supported, to separate CO₂ from binary mixtures at low temperature and

* To whom correspondence should be addressed. Tel.: 34-42-202026. E-mail: fernandj@unican.es.

Table 1. BET Specific Surface Area (SSA) and CO₂ Chemisorption Results in (mol CO₂/mol Calcium) × 100 for Static Experiments

		BET SSA (m ² /g)	CO ₂ chemisorbed (mol CO ₂ /mol Ca) × 100
supports	MCM-41	1236	
	SBA-15	660	
calcium base	CaO	3	0.1
	Ca(OH) ₂	16	2.4
sorbents Type I	10% Ca(OH) ₂ /MCM-41	238	11.0
	10% Ca(OH) ₂ /SBA-15	181	4.2
sorbents Type II	5% Ca(OH) ₂ /MCM-41	499	8.0
	5% Ca(OH) ₂ /SBA-15	255	3.1
	10% Ca(OH) ₂ /MCM-41	412	3.1
	10% Ca(OH) ₂ /SBA-15	251	2.4
	15% Ca(OH) ₂ /MCM-41	158	4.5
	15% Ca(OH) ₂ /SBA-15	231	1.8

different pressures, and a preferential CO₂ adsorption was reported. In a previous work,²² MCM-41 with Ca(OH)₂ supported has been used to capture SO₂ at low temperature, but no work has been found using calcium bases supported on these materials for CO₂ capture at low temperature.

In the present work, the capture of CO₂ with CaO or Ca(OH)₂ supported on these mesoporous materials is studied. The amount of CO₂ captured and its relation to the sorbents characteristics or the experimental conditions is reported; the products formed in CO₂ capture are discussed.

Experimental Section

Preparation of the Sorbents. The synthesis procedure and chemical products used in the preparation of the mesoporous materials, MCM-41 or SBA-15, used as support of the sorbents, were described in previous works.^{23,24} The MCM-41 used in this work was identified as MCM-41-2 in these previous works.

Commercial CaO and Ca(OH)₂ were supplied by Calcinor S.A., with a purity of 90%, and calcium nitrate was from Panreac PA.

Type I sorbents consisted of a mixture of calcium oxide, water, and the support at room temperature. Type II sorbents were prepared by impregnating the support with calcium nitrate salt followed by calcination and hydration to form Ca(OH)₂ in amounts ranging from 5% to 15% by weight. The sorbents were sieved through a 60 μm mesh, ensuring a particle size lower than 60 μm. Detailed procedures for preparation of the sorbents were reported in previous work.^{25,26}

Characterization. The specific surface area (SSA) of the supports and sorbents prepared was obtained using a Micromeritics ASAP-2000 apparatus by N₂ adsorption at 77 K and calculated following the BET standard method. The whole adsorption isotherm of N₂ was only obtained for the supports to confirm the textural properties characteristics of MCM-41 and SBA-15 materials.

CO₂ Static Chemisorption Tests. Experiments of pure CO₂ static chemisorption were performed in a Micromeritics ASAP 2010C volumetric apparatus, equipped with a turbomolecular pump, at a constant temperature of 323 K for the CO₂ adsorption and desorption processes. This test was carried out with the sorbents reported in Table 1 in order to quantify the gas chemisorbed.

For the sample conditioning (approximately 250 mg), air at a flow rate of 50 cm³/min passed through the samples for 1 h followed by evacuation at 10⁻⁶ Torr at the same temperature (323 K). The CO₂ chemisorbed was analyzed using the adsorption–backdesorption isotherm method proposed by Boudart et al.²⁷ CO₂ chemisorbed was obtained from the total and reversible adsorption isotherms taken in a pressure range of 25 – 400 mmHg. The apparatus provides the volume of CO₂

captured per gram of solid at 273.16 K and atmospheric pressure, and it is transformed to (mol CO₂/mol Ca) × 100 as a measure of the sorbent calcium utilization in the CO₂ reaction. The total time required for each experiment was approximately 8 h.

CO₂ Dynamic Chemisorption Tests. Experiments of CO₂ dynamic adsorption and desorption varying the experimental conditions were performed by using an AutoChem II 2920 apparatus with Type I, Ca(OH)₂/MCM-41 sorbents (approximately 250 mg) prepared with 2.5%, 5%, or 10% Ca/(OH)₂. Results of these tests allowed us to determine the influence of the experimental variables on the CO₂ capture, on the regenerability of the sorbents, and on the products obtained in the process of capture.

The support or Ca(OH)₂/MCM-41 sorbents were pretreated in a helium flow at a rate of 50 cm³/min at temperatures ranging from room temperature to 823 K. After being cooled, the solids were brought into contact with a mixture of CO₂ in He (normally 10% CO₂, but some experiments were performed with 50% CO₂) flowing at a rate of 50 cm³/min for times varying from 5 to 1440 min (24 h) at 323 K. The CO₂ physisorbed was removed (desorbed) by treatment of the sample in He flow, normally for 30 min (desorption time) at the adsorption temperature. Then, temperature-programmed desorption (TPD) was carried out by heating the sample at a rate of 10 °C/min normally up to 823 K (but 923, 1073, or 1173 K were also used in some experiments) in He flow. The signals for the CO₂ desorbed at different temperatures (indicating the products of the chemisorption) were recorded. These signals were integrated to obtain the amounts of CO₂ desorbed, previous calibration of the device.

The regenerability of the sorbents was studied by repeating the adsorption–desorption cycle, after holding the sample temperature at 823, 923, 1073, or 1173 K for 30 min and cooling, within consecutive cycles.

Results and Discussion

Results of Physical Characterization. The isotherms of the supports showed an inflection zone at relative pressures of $P/P_0 = 0.2–0.4$ for MCM-41 and $P/P_0 > 0.80$ for SBA-15. This indicates a pore size distribution in the mesoporous range with a pore medium size higher for SBA-15 than for MCM-41 materials, as is usual. Figures of isotherms are omitted.

Table 1 shows the results of the BET specific surface area for the prepared sorbents, for the supports, and for commercial CaO and Ca(OH)₂. The BET specific surface area is high for the supports and lower for all the sorbents. A drastic reduction is found mainly in sorbents of Type I, prepared by mixing the calcium base and the support in an aqueous medium at room temperature. It seems that the calcium hydroxide formed in the preparation process deposited in the support produces the closure

Table 2. Experimental Conditions (CO₂ adsorption time and desorption time of CO₂ physisorbed) for Dynamic Chemisorption Consecutive Experiments with Type I, 10% Ca(OH)₂/MCM-41 Sorbent and the MCM-41 Support (last line) and Results of CO₂ Chemisorbed^a

adsorption time (min) gas, 10% CO ₂ in He	desorption time of CO ₂ physisorbed (min) Gas, 100% He	CO ₂ chemisorbed (mol CO ₂ /mol Ca) × 100
5	30	4.1
30	30	4.1
120	30	4.2
240	30	7.5
480	30	11.2
480	120	11.2
480	240	11.5
480	480	10.7
960	30	12.4
1080	30	12.7
1440	30	12.7
30	30	irrelevant for support

^a Adsorption temperature: 323 K.

of some pores, causing this reduction. For Type II sorbents, Table 1 shows a general decrease in the SSA values as the percentage of calcium base increases.

Results of CO₂ Static Chemisorption Tests. Results of CO₂ static chemisorption are shown in Table 1, expressed as (chemisorbed mol CO₂/mol Ca) × 100, as this value is a measure of the calcium utilization in the CO₂ reaction.

The supports essayed in the same conditions showed a negligible CO₂ static capture meaning that, in the CO₂ chemisorption, the causticity of CaO or Ca(OH)₂ is implied. Commercial calcium bases were also tested to compare their CO₂ retention with that obtained by using the same bases dispersed on the supports. Results confirm that calcium hydroxide is a stronger base than calcium oxide. The values of CO₂ chemisorbed obtained are low at the experimental conditions used, according to other authors' works.²⁸ These authors studied the CO₂ uptake by CaO in a temperature range from 300 to 973 K, finding that at temperatures lower than 573 K the CO₂ was retained by CaO in low amounts and no CaCO₃ peaks were observed by the XRD technique. Although carbonation reaction is thermodynamically favored at low temperatures as it is an exothermic process, the chemical reaction is slow. Chen et al.²⁹ studied the CO₂ uptake by Ca(OH)₂ at room temperature and concluded that no appreciable formation of CaCO₃ occurs at a relative humidity lower than 80%. According to these authors,^{28,29} the low values of CO₂ capture found in these tests can be related to the low experimental temperatures and the absence of humidity.

Sorbents of Type I have the highest calcium utilization values and lowest SSA. The basic centers are more accessible to CO₂ with the simplest preparation method, even when the Ca(OH)₂ formed plugs the support pores with the corresponding surface area reduction. As Table 1 shows, the CO₂ chemisorbed with the best sorbent [11.0 (mol CO₂/mol Ca) × 100] is nearly five times higher than that obtained with unsupported Ca(OH)₂ [2.4 (mol CO₂/mol Ca) × 100]. The MCM-41 support produces sorbents with higher SSA and CO₂ retention than the SBA-15 support, probably due to a better distribution of the calcium in a support with higher SSA.

Among Type II sorbents, the highest values of CO₂ chemisorbed are obtained with the lower amount of calcium, thus providing a better distribution on the support. In a previous study²⁶ conducted with sorbents prepared in a similar way with these and other MCM-41 supports, it was found that, in general, the chemisorbed CO₂ per mol of calcium increases with decreasing amount of calcium.

The low retention values and increase of the values as the amount of base decreases suggest that the CO₂ does not reach

the calcium base. Yue et al.¹⁹ using MCM-41 supports modified with amine found that the CO₂ retention was a process controlled by diffusion, as the amine particles supported on the solid surface are those which react more readily than the inside ones. On the other hand, Shih et al.³⁰ suggest pore plugging, surface coverage of a CaO particle, and formation of a product layer as a more plausible justification of the low values of CO₂ capture.

Results of CO₂ Dynamic Chemisorption Tests. The Type I 10% Ca(OH)₂/MCM-41 sorbent (that showed the highest CO₂ capture in static chemisorption) and other Type I sorbents prepared with 2.5% or 5% Ca(OH)₂/MCM-41 weight ratios were submitted to dynamic chemisorption experiments of carbonation/decarbonation at different experimental conditions. Consecutive cycles were also carried out. The aim was to study the chemisorption of CO₂ at different experimental conditions to elucidate the product of CO₂ capture and probe the behavior of these solids in regenerable processes.³¹

Table 2 shows the experimental conditions and CO₂ chemisorbed obtained from TPD data in consecutive cycles for Type I 10% Ca(OH)₂/MCM-41 sorbent. As the sample was pretreated up to 823 K, CaO is the calcium base that retains the acid gas and not the initial Ca(OH)₂.

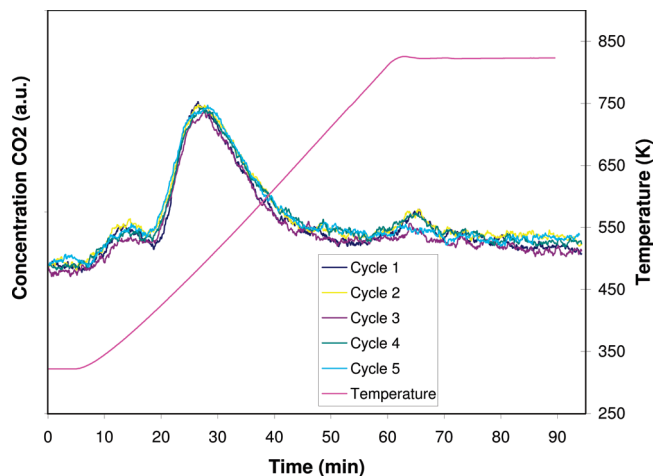
The results show that the same amount of CO₂ was retained at 5 or 30 min. When the adsorption time increased, the CO₂ chemisorbed increased slowly. These results agree to those found by Barker,³² who proposes two steps for the CO₂ adsorbed by CaO being the initial step fast and kinetically controlled and the second step slower and diffusionally controlled. The maximum CO₂ chemisorbed with this sample (12.7%) was found at about 1080 min (18 h) and is similar to the value found in the static experiment (11%, Table 1). These values represent the maximum amount of CO₂ retained at the equilibrium. Table 2 also shows that no influence of the time of desorption (experiments at 30, 120, 240, and 480 desorption times) was observed, with 30 min being time enough to eliminate all physisorbed CO₂.

When the sorbent Type I 10% Ca(OH)₂/MCM-41 was exposed at two different CO₂ concentrations in the flue gas, 50% CO₂ in He at atmospheric pressure (partial CO₂ pressure of 50 kPa) and 10% CO₂ (partial CO₂ pressure of 10 kPa) in a five cycles experiment, no influence of the partial CO₂ pressure was found. This result confirms the findings of Sun et al.,¹⁵ indicating that when the CO₂ partial pressure exceeded 10 kPa, the CaO–CO₂ reaction rate was zero order with respect CO₂.

Table 3 shows the CO₂ chemisorbed for three Type I Ca(OH)₂/MCM-41 sorbents in these dynamic experiments. The sorbent with the lowest amount of Ca(OH)₂, 2.5%, exhibits the maximum CO₂ retention at both adsorption times. The CO₂

Table 3. Data of CO₂ Chemisorbed Expressed as (mol CO₂/mol Ca) × 100 Obtained in TPD Experiments up to 823 K after Exposure to 10% CO₂ in He^a

sorbent Type I	(mol CO ₂ /mol Ca) × 100; adsorption time 30 min	(mol CO ₂ /mol Ca) × 100; adsorption time 1080 min
2.5% Ca(OH) ₂ /MCM-41	15.0	56.6
5%Ca(OH) ₂ /MCM-41	8.5	25.7
10%Ca(OH) ₂ /MCM-41	4.1	12.7

^a Adsorption temperature: 323 K.**Figure 1.** TPD results up to 823 K for Type I 2.5% Ca(OH)₂/MCM-41 sorbent after adsorption for 30 min with 10% CO₂ in He corresponding to five cycles. CO₂ concentration is expressed in arbitrary units (au).

retention is favored, as in the static experiments, with a good calcium base distribution and not with a high amount of base.

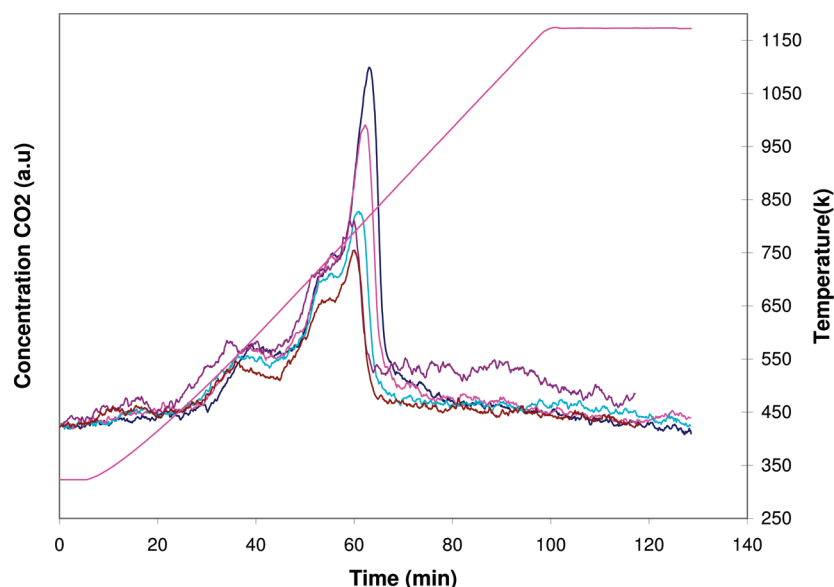
Figure 1 shows the results of TPD up to 823 K obtained with 2.5% Ca(OH)₂/MCM-41 sorbent in five cycles after 30 min exposure to 10% CO₂ in He flow. Three desorption peaks were obtained, with maxima at 373, 473, and 823 K, with the most important peak centered at 473 K. The same outline for all cycles was obtained, meaning that all CO₂ chemisorbed detected at these TPD conditions was desorbed reversibly up to 823 K with the maximum desorption peak at 473 K. Similar profiles were obtained with 5% or 10% Ca(OH)₂/MCM-41 sorbents. These desorption peaks of the CO₂ chemisorbed at low

temperature can be explained considering the mechanistic explanation proposed by Sun et al.,¹⁵ who assumes that the reaction between CaO and CO₂ involves a first step of reversible formation of a CaO•CO₂ complex with gaseous CO₂ molecules adsorbing on CaO sites.

To perform a deeper study of the products formed in the CO₂ chemisorption, experiments of dynamic chemisorption with a TPD up to 923 or 1073 K were carried out with commercial Ca(OH)₂ and Type I 10% Ca(OH)₂/MCM-41 sorbent.

Figure 2 shows the peaks obtained with calcium hydroxide at standard conditions (30 min of adsorption at 323 K and a flue gas with 10% CO₂) in an experiment of five cycles with a TPD up to 1173 K. As the sample was pretreated up to 1173 K, the base is CaO instead of Ca(OH)₂ and the CaCO₃ present in the commercial sample as impurity is not present at the beginning of the cycles. The peak desorbed at about 473 K is the same that it was found with the sorbent previously essayed (Figure 1); the other peak with a maximum at about 800 K corresponds to the CO₂ obtained by calcination of the CaCO₃ synthesized. These results show that at a sorption temperature of 323 K the CaO retains CO₂ as a complex CaO•CO₂ but also and in higher amounts as CaCO₃, although the retention diminishes in further cycles as it was previously stated.^{9,15,31}

To determine if CaCO₃ is also produced at the same chemisorption conditions with the prepared sorbents, experiments were carried out with a Type I sorbent, 10% Ca(OH)₂/MCM-41. Because the sorbent contained CaCO₃ as an impurity in commercial Ca(OH)₂ one experiment was performed without CO₂ to distinguish between the CaCO₃ formed in the process and that contained in the sorbent initially. Figure 3 shows the results of TPD obtained.

**Figure 2.** TPD results up to 1173 K for commercial Ca(OH)₂ after adsorption for 30 min with 10% CO₂ in He corresponding to five cycles. CO₂ concentration is expressed in arbitrary units (au).

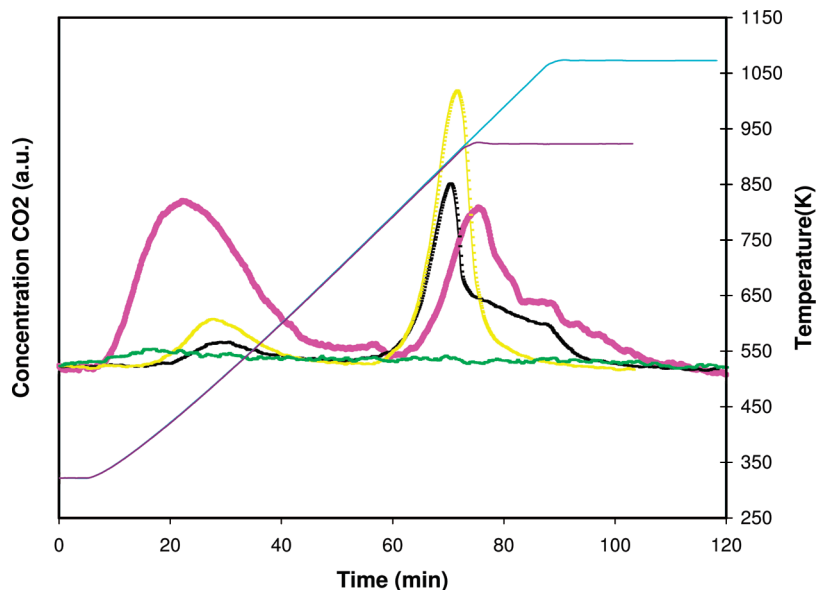


Figure 3. TPD results at different experimental conditions for Type I 10% $\text{Ca}(\text{OH})_2/\text{MCM}-41$ sorbent: (black) TPD up to 1073 K of the sorbent pretreated with He (without CO_2); (yellow) TPD up to 923 K of the sorbent exposed for 5 min at 10% CO_2 in He; (pink) TPD up to 1073 K of the sorbent exposed for 18 h at 10% CO_2 in He; (green) second cycle at the same conditions as previous. CO_2 concentration is expressed in arbitrary units (au).

With a flue gas free of CO_2 (black pointed) and a TPD step up to 1073 K, a peak with a maximum at 873 K due to the CaCO_3 of the sorbent is found; the shoulder of the peak is due to the dehydroxylation of the support that takes place at about 1023 K (data obtained from the TPD of the support). At this temperature the collapse of the support is produced, losing the sorbent its main structure and SSA. When the sorption time was 5 min, with the standard flue gas and a TPD step up to 923 K (yellow color) the mass loss due to the dehydroxylation was not found and the peak with the maximum at about 873 K was due to the CO_2 captured as CaCO_3 and also to the CaCO_3 present initially in the sorbent. It can be concluded that CaCO_3 is synthesized at 323 K. As the peak of calcination and peak of dehydroxylation overlap, it is not possible to quantify the CO_2 retained as CaCO_3 .

Comparing the intensity of the first peak corresponding to the $\text{CaO} \cdot \text{CO}_2$ complex, a great difference was found for 5 or 1080 min of sorption time (curves yellow and pink) according to the results of Table 2.

According to all the experiments, it can be concluded that at an adsorption temperature of 323 K, CO_2 is retained in the sorbent as a $\text{CaO} \cdot \text{CO}_2$ complex that can be reversibly desorbed mainly at 473 K and also as CaCO_3 in amounts that cannot be easily quantified.

After a TPD up to 1073 K in a first cycle of 1080 min (pink curve), the structure of the sorbent was collapsed and no CO_2 was retained in the following cycle (green color). As the CaCO_3 calcination needs to reach more than 900 K and at this temperature the structure of the sorbent collapses, it is not possible to release the CaCO_3 formed maintaining the structure of the sorbent. Figure 1 shows the results of TPD up to 823 K for five cycles. Even when the CaCO_3 is not desorbed at this temperature, the uptake of CO_2 as $\text{CaO} \cdot \text{CO}_2$ does not diminish in the five cycles. Because of that, if the regeneration process stops at this temperature, it is possible to use these solids as

regenerable sorbents, recovering only the CO_2 retained as $\text{CaO} \cdot \text{CO}_2$ complex.

Conclusions

Sorbents prepared by mixture of CaO , water, and MCM-41 support at room temperature achieve higher CO_2 retention and calcium utilization values at 323 K than sorbents prepared by impregnation of a soluble calcium salt and posterior calcination or than commercial calcium hydroxide, probably due to a more accessible and better distributed calcium base on a support with higher specific surface area.

At low temperature (323 K), CO_2 is retained in the sorbents as a $\text{CaO} \cdot \text{CO}_2$ complex and also as CaCO_3 in a process fast at the beginning and slow until obtaining equilibrium.

Values of CO_2 retained as $\text{CaO} \cdot \text{CO}_2$ complex do not vary with CO_2 partial pressure (from 10 to 50 kPa) or with physidesorption time. They depend mainly on the time of exposure to the CO_2 flow. The 2.5% $\text{Ca}(\text{OH})_2/\text{MCM}-41$ sorbent achieved a maximum value of 56.6% ($\text{mol CO}_2/\text{mol Ca}$) $\times 100$ after 18 h of exposition.

Even when the amount of CO_2 chemisorbed as $\text{CaO} \cdot \text{CO}_2$ complex is low, the sorbents can be regenerated at a temperature of 823 K and used cyclically without appreciable loss in activity.

The dynamic chemisorption experiments with a TPD step are a good tool to investigate the products formed in the process of CO_2 capture and the influence of the experimental conditions.

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