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TPD study of the reversible retention of carbon dioxide over montmorillonite intercalated with polyol dendrimers

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ABSTRACT

Organoclays with improved affinity towards carbon dioxide were obtained via montmorillonite intercalation with polyol and amino dendrimers having respectively hydroxyl or amino groups that act as adsorbing sites. Measurements through thermal programmed desorption (TPD) show that higher amounts of CO_2 than predicted by stoichiometry were retained by polyol organoclays, suggesting that more than one CO_2 molecule adsorb on each OH group. The latter displayed optimal base properties tailored for: (i) improved retention capacity of CO_2 by increasing their number; (ii) easy consecutive gas release upon slight heating owing to their weak basicity. Unlike amines, polyols display sufficiently weak basicity to exert only physical interaction towards carbon dioxide molecules. The reversible CO_2 adsorption–desorption equilibrium is discussed here in terms of acid–base interactions between the organoclay surface and surrounding CO_2 molecules. The results obtained herein open new prospects in obtaining microporous materials able to act as lungs that fix reversibly polluting gases.

1. Introduction

Attempts to capture carbon dioxide from major emission sources using liquid amines as adsorbents turned out to be ineffective due to amine leakage and oxidation during regeneration. Even amine immobilization over solid supports cannot avoid completely these shortcomings [1–3], and large-scale processes need high amines consumption [4]. Anionic clays (hydrotalcites) with intrinsic base properties appear as being interesting alternatives to amine sorbents for CO_2 retention [5–7], but they produce strong chemical reactions with CO_2, and regeneration still requires heating, unless achieved at room temperature at the expense of the effectiveness.

The major issue to be tackled here is how to simultaneously achieve effective capture of CO_2 and easy gas release through low energy consumption. In this regard, a growing interest is focused towards cationic clays, and more particularly, montmorillonite [8–13]. Here, the weak base character of the oxygen atoms surrounding the ion-exchange sites [14] should promote physical interactions towards CO_2. Nonetheless, high retention capacity cannot be envisaged because of the small number of adsorption sites and diffusion hindrance due to small interlayer spacing [5–7,9]. To overcome these constraints, possible improvements should consist in the preparation of highly porous organoclays via intercalation with dendrimers bearing high numbers of base sites weakly reactive towards CO_2 at ambient temperature.

Clays have already been intercalated with polymers for diverse purposes [10,11], but polyols insertion for CO_2 capture have scarcely been envisaged so far. Such organoclays will combine physicochemical features arising from both the clay support and organic moiety, i.e. (i) the exchangeable cation is responsible for most of the clay properties, more particularly the intrinsic base character [7,15]; (ii) since alcohols exhibit slightly higher basicity than water, the OH groups are expected to display amphoterical to weak base character, thanks to the lone electron pair on their oxygen atoms [13,16–18].

It is still unclear whether physical or chemical interactions are involved. This is why the present investigations were undertaken. For this purpose, a montmorillonite-rich material was intercalated by various amounts of polyol dendrimers, having base properties tailored according to the number of OH-groups grafted. Their performances in CO_2 retention were investigated through thermal programmed desorption, and compared to those of supported amines obtained by the same procedure.

2. Experimental

2.1. Organoclays preparation

A purified bentonite with a montmorillonite (Mt) content of ca. 88–90 wt.%, and quartz as the main impurity [19] was fully ion-

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exchanged with aqueous NaCl at 80 °C for 5–6 h into the NaMt form, and then washed, centrifuged, repeatedly dialyzed and dried overnight at 40 °C. CaMt and CuMt were also prepared according to the same procedure.

Further, mixtures of 2 g of NaMt with 1:1 mole ratio ethanol/water solutions containing various amounts of dendrimer were gently dried overnight (35 °C) till thorough solvent evaporation, so that the resulting organoclays contain 0.5, 1.0 and 3.0 wt.% of dendrimer. For comparison, beside a series of bulky hyperbranched H-20, H-30 and H-40 Boltorn polyol dendrimers, deriving from 2,2-bis (hydroxymethyl) propionic acid [20–22], with respective average numbers of OH groups of 12–15, 30 and 40–60, one used di-n-octylamine, mono- and di-n-butylamine as intercalating agents. Intercalation attempts were also performed with fully ion-exchanged CaMt and CuMt.

2.2. Characterization

Insights into the effects of intercalation were achieved through scanning electronic microscopy (Hitachi S-4300SE/N—VP-SEM instrument) and X-rays diffraction (Siemens D5000 instrument (CoK_α at 1.7890 Å, in the 2θ range 2–80°). Surface area measurements were performed on a Quantachrome Instrument, where samples of 250–400 mg were previously prone to outgasing at room temperature for 4 h and then to nitrogen adsorption at 77.30 K.

2.3. Thermal desorption measurements

Thermal programmed desorption of carbon dioxide (CO_2-TPD) was used to assess the interactions occurring between carbon dioxide and the sample. The latter were introduced in the TPD column and TPD measurements were performed between 20 and 550 °C according to a procedure fully described elsewhere [14]. Prior to TPD, each sample was dried under nitrogen stream at 140 °C for 3–4 h, and then cooled to 20 °C. At this temperature, pure dry CO_2 was injected in the nitrogen stream till saturation. Slow injection is required to avoid pore obstruction due to quick gas accumulation at the pore entry [9]. The non-adsorbed CO_2 excess was evacuated till no detection at the device outlet.

The CO_2 retention capacity (CRC) was defined in terms of mmol desorbed carbon dioxide per gram of dry clay, i.e. the area described by the TPD pattern between 20 and 100 °C. In this temperature range, adsorption is regarded as being totally reversible, inasmuch as the retained CO_2 can be easily and thoroughly desorbed.

3. Results and discussion

3.1. Interlamellar spacing upon clay intercalation

The build-up of the as-synthesized sandwich-like nanostructures has been demonstrated by X-rays diffraction (xrd). The NaMt sample shows sharp 0 0 1 xrd lines, corresponding to almost perfectly parallel clay sheets, a special feature of monoionic clay structures [15,23]. The interlayer spacing turned out to be a reliable index for clay exfoliation [24], inasmuch as the basal d_{001} spacing increased from ca. 10 up to almost identical values within the range 14.39–14.51 Å, after intercalation of NaMt by 0.5% of H-20, H-30 or H-40 dendrimers. Similar observations were made for 1% dendrimer loading. Here also, sharp 0 0 1 xrd lines were registered, providing a clear evidence of ordered structure with a face-to-face sheet arrangement, where the organoclay lamellae are aligned parallel (Fig. 1).

In the meantime, the surface area increased from 49–52 m^2/g (NaMt) to 179, 191 and 197 m^2/g for NaMt loaded by H-20, H-30 and H-40 dendrimers, respectively (Table 1). These relatively close

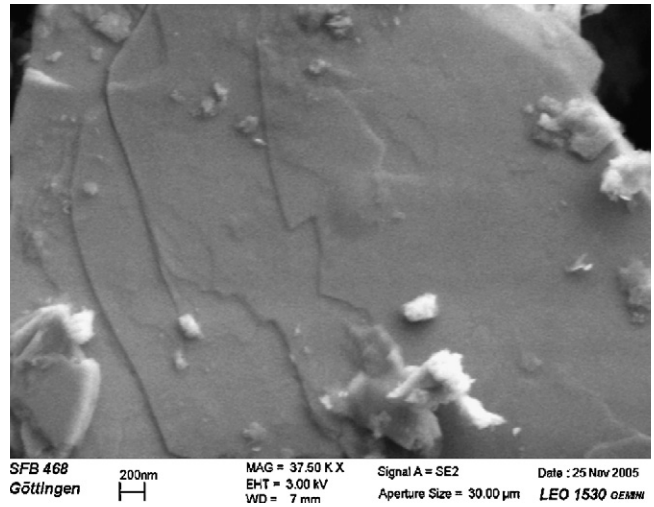

Fig. 1. Micrograph of face-to-face lamellae arrangement. NaMt—0.5 wt.% dendrimer H-20.

values reveal a negligible role of the dendrimer molecular weight at least for low dendrimer loadings. Micro- and mesoporosity were also improved, inasmuch as the proportion of micro and mesopores (pore diameter < 100 Å) increased from ca. 60% to almost 80%. Therefore, as long no dendrimer clusters form, the surface area seems to be generated by the snarl porosity of a thin dendrimer layer, flattened, sprawled and perfectly sandwiched between the clay sheets.

Taking into account that CO_2 is a linear molecule smaller than that of nitrogen, with a kinetic diameter of 3.4 Å, internal diffusion should not be greatly influenced by porosity, inasmuch as more that 96% of the total pore is attributed to pores with diameter exceeding 5 Å. In clay structures, the surface area is the key-parameter that determines the number of accessible adsorption sites.

In agreement with previous data [10,11], raising dendrimer content up to 3 wt.% alters such a structure, since higher d_{001} spacing (20–30 Å) and broader 0 0 1 lines were registered. This results in scattered structures with a wide variety of clay lamellae orientations (Fig. 2), presumably due to possible change in the shape of the dendrimer molecules [25], and/or their tendency to aggregate into dense clusters. Nonetheless, because dendrimers are hydrophobic, and clay minerals are rather hydrophilic [26], full exfoliation of the clay platelets by mere melt-intercalation is difficult to achieve [27], more particularly for high loading levels.

Unlike NaMt, where H-20 and H-30 dendrimers produced high clay exfoliation, CaMt and CuMt did not undergo intercalation by any dendrimer, as supported by the face-to-face arrangement of the CaMt clay lamellae (Fig. 3). The sharp 0 0 1 line and almost unchanged basal d_{001} spacing (12.3 and 13.6 Å) along with the surface area (49–52 m^2/g) obtained after intercalation attempts suggest a strong sandwiching effect, a special feature of bivalent cations that prevents clay lamellae from spreading in the presence of organic molecules, unless compatibilizing agents [28] are used.

3.2. Effect of clay intercalation upon the TPD profile

Insertion of H-20 dendrimer induced change in the CO_2-TPD pattern of the starting NaMt support. In the investigated range, the desorption peak shifted from ca. 50–55 °C for NaMt to approximately 40 °C for NaMtH-20. All polyol-based organoclays display almost similar TPD patterns for similar loading grades, with a maximum desorption temperature laying around 35–45 °C (Fig. 4).

This precise indicator of the strength of the interaction occurring between CO_2 and the adsorption sites provides clear evidence that

Table 1
Effect of dendrimer content upon the organoclay capacity of CO_2 retention (CRC).

Clay sample	Dendrimer inserted		Surface area (m^2/g)[a]	Pore data						
	Name	Amount (wt.%)		Size distribution[b] (pore volume%)				Predominant pore radius (Å)	Pore volume (mL/g)	CRC[c]
				<5 Å	5–10 Å	10–100 Å	>200 Å			
NaMt	None	0	49–52	–	20–40	15–20	15–20	109	0.0647	0.685
CaMt	None	0	37–38	–				–	–	0.097
CuMt	None	0	–	–				–	–	0.053
NaMtH-20-1	Boltorn H-20	0.5	178–180	1–2	4–7	65–70	5–8	23.2	0.2947	0.417
NaMtH-20-2	Boltorn H-20	1	–	–				–	–	0.793
NaMtH-20-3	Boltorn H-20	3	–	–				–	–	0.950
NaMtH-30-1	Boltorn H-30	0.5	190–192	1.5–2	6–9	60–65	7–9	21.2	0.2871	0.970
NaMtH-30-2	Boltorn H-30	1	–	–				–	–	1.376
NaMtH-30-3	Boltorn H-30	3	165–175	–				–	–	1.230
NaMtH-40-1	Boltorn H-40	0.5	195–197	3–4	15–20	45–55	9–10	23.11–28.3	0.3022	1.457
NaMtH-40-2	Boltorn H-40	1	160–165	–				–	–	2.716
NaMtH-40-3	Boltorn H-40	3	137–142	–				–	–	0.750
NaMt-$BuNH_2$	n-Butylamine	0.5	–	–				–	–	1.528
NaMt-diBuNH	Di(n-butyl)amine	0.5	–	–				–	–	1.987
NaMt-diOctNH	Di(n-octyl)amine	0.5	–	–				–	–	1.534

[a] Triplicates were measured, but only the two closest values were taken into account.
[b] The pore size (diameter) distribution was estimated in percent of the total pore volume with a relative error of 5%.
[c] The CO_2 retention capacity (CRC) is expressed in terms of mmol CO_2 desorbed/g dry clay in the temperature range 20–100 °C.

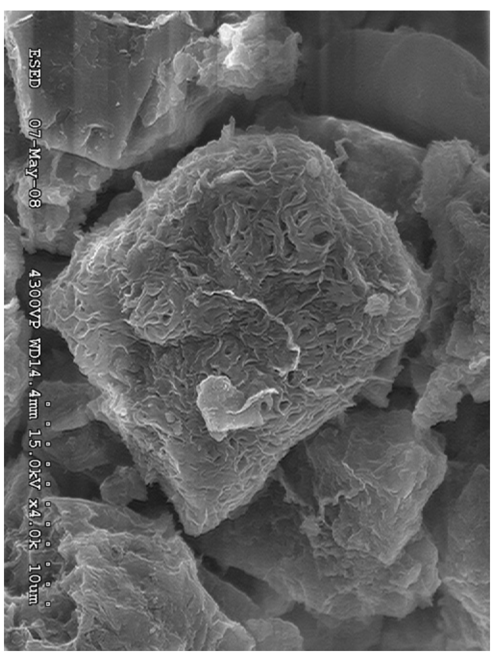

Fig. 2. Micrograph of highly exfoliated organoclay. NaMt–3 wt.% dendrimer H-20.

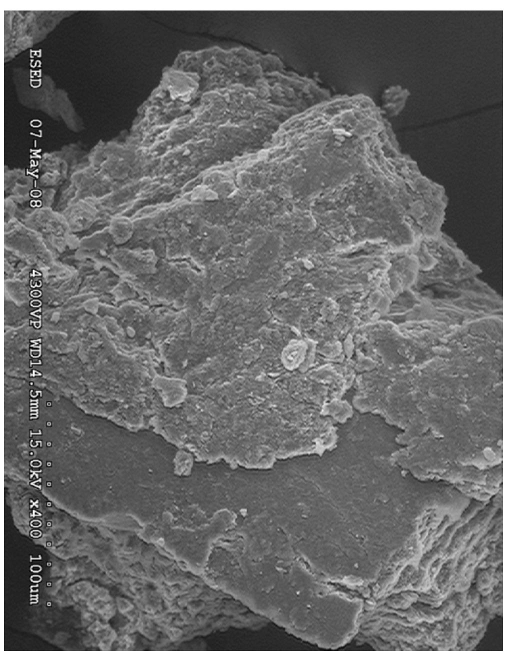

Fig. 3. Micrograph of face-to-face lamellae arrangement for CaMt contacted with dendrimer H-20.

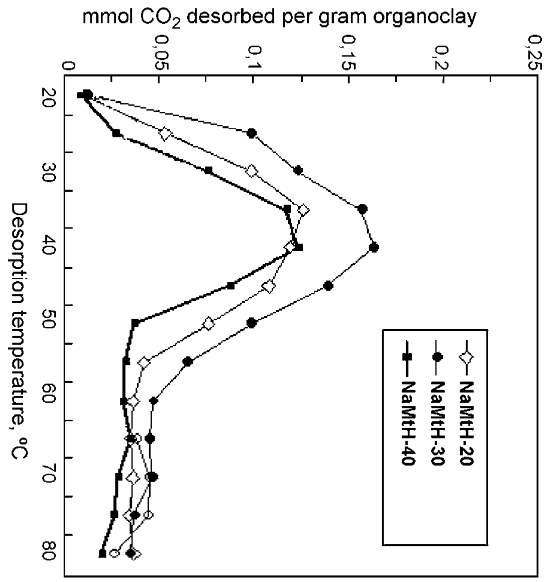

Fig. 4. Effect of the dendrimer inserted (all organoclays contain 3 wt.% of incorporated organic moieties).

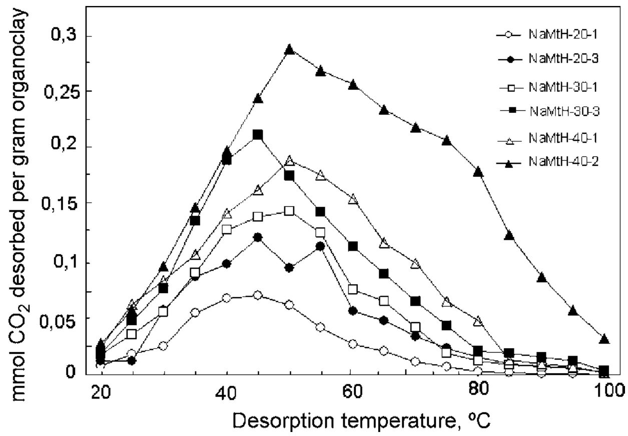

Fig. 5. Effect of dendrimer content on the TPD profile.

polyol-based organoclays release more easily CO_2 than the starting support. The amount of desorbed CO_2, defined as being the area under the TPD profile, increases in the following sequence: NaMtH-30 > NaMtH-20 > NaMtH-40. This sequence supposes an increasing number of OH groups, which seems to play a key-role, being correlated to both the content and size of the polyol moiety (Fig. 5).

Increasing the dendrimer content, and consequently the amount of OH groups supposed to be grafted on the polyol molecule, induced an increase in the TPD area (Fig. 6). However, NaMtH-40-3 does not obey this general tendency, and the decay of the surface area up to 137–142 m^2/g for high loading grade (Table 1) suggests a hypothetical formation of dense clusters with small number of accessible OH groups.

3.3. Capacity of retention of CO_2 (CRC)

TPD measurements between 20 and 550 °C show that supported amines retain ca. 10–15 times more CO_2 than polyol organoclays. The stronger basicity of amines may promote the formation of carbamic acid ($H_2NC(O)OH$), more stable than carbonic acid generated between polyols and CO_2. This makes polyols to be easier to regenerate, inasmuch as CO_2 almost completely desorbs at 150 °C, while less than 20% of the adsorbed CO_2 can be released from amines (Fig. 6).

Accurate assessment of the CO_2 retention capacity (CRC) requires conditions of totally reversible sorption over polyols. For this purpose, a special interest was focused towards the range 20–100 °C, where the CRC value was estimated by the area under the TPD pattern. As compared to CuMt (0.053) and CaMt (0.097), NaMt displays higher CRC (0.685) (Table 1).This is consistent with the lowest polarizing effect of Na^+ cations [14]. For this reason, a special interest was devoted to NaMt as base support for further clay intercalation with dendrimers.

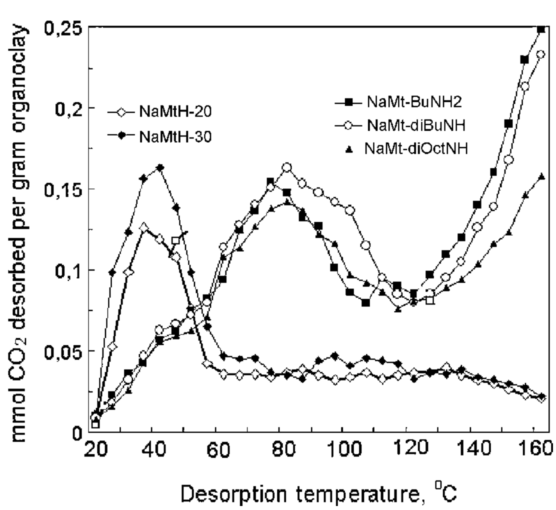

Fig. 6. Effect of the organic moiety (0.5 wt.%) upon the CO_2 retention capacity.

The general tendency is that polyol organoclays display lower CRC (0.417–1.457) than supported amines (1.528–1.987). The increasing CRC sequence from NaMtH-20-1 (0.417) to NaMtH-40-2 (2.716) must be due to raising number of OH groups supposed to be grafted on the organoclay. Nevertheless, excessive loading (3 wt.%) with bulky dendrimers (NaMtH-30-3 and NaMtH-40-3) affects the CRC (1.23 and 0.75, respectively), most likely due to a decrease in the number of accessible OH groups, as well argued by the surface area decay from 191 to 170 m^2/g for NaMtH-30, and from 183–184 to ca. 140 m^2/g for NaMtH-40.

Deeper insights into the CRC values reveal that CO_2 does not adsorb stoichiometrically, inasmuch as the area of the TPD pattern for NaMtH-20-2 is not necessarily twice higher than for NaMtH-20-1. In addition, larger amounts of CO_2 than expected by stoichiometry adsorb on the organoclays. Unlike the one-to-one association between CO_2 and gaseous alcohols reported by some authors [16], our results suggest that at least two CO_2 molecules are simultaneously retained by each OH group, in agreement with other data [17].

Thus, stacks of CO_2 molecules weakly bound to each other may form in a kind of bulk supercritical phase. This assertion does not agree with the chemical reaction of CO_2 with alcohols and oxygenated compounds stated by some authors [16]. The easiness of the consecutive CO_2 desorption upon a slight heating suggests rather the occurrence of only weak physical interactions. By analogy with alcohols in the gas phase, these interactions must be of Lewis acid–base (L-AB) type, and proceed via hydrogen bonds and/or an electron donor–acceptor (EDA) complex [17]. Nevertheless, the EDA complex cannot be responsible of the CO_2 adsorption, because it forms only through preferential orientation of the carbon atom of an approaching CO_2 molecule (acceptor) along the direction of the electron pair of the oxygen atom on an OH group (donor). Subsequently, the EDA population must be relatively rare [17].

Therefore, the non-stoichiometric adsorption of CO_2 can be explained only in terms of hydrogen bonds, and formation of CO_2 multilayers around the adsorption sites [13]. This finding is of a great interest, inasmuch as alcohol and even ethers or any oxygenated organic compounds can reversibly retain CO_2 [9]. Nonetheless, saturation at the pore entry can cause quick formation of CO_2 multilayers without layer completion and then pore obstruction [13]. This is why care should be taken for accurate CRC measurements by slowly injecting CO_2 to favor gas penetration during adsorption.

4. Conclusion

Montmorillonite intercalation by polyol dendrimers provides expanded microporous materials with improved surface properties arising from both the inorganic support and organic moiety. The clay behavior towards intercalation is strongly dependent of the exchangeable cation and the dendritic moiety. Thermal programmed desorption of carbon dioxide demonstrated that polyol-Mt organoclays display optimal base properties for the reversible retention of CO_2. A judicious compromise between highest adsorption capacities promoted by increasing number of OH groups and lowest desorption temperatures makes polyol organoclays to be suitable for easier regeneration with lower energy consumption, as compared to supported amines. Each OH group displays a sufficiently weak basicity to exert only physical interaction towards more than one CO_2 molecule, and the amounts of retained CO_2 are larger than those predicted by stoichiometry. Reduction of other greenhouse gases by varying the chemical functions of the organic moiety could also be envisaged, opening, thereby, new prospects in valorizing clay materials in low-cost depollution technologies.

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