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Improved carbon dioxide storage over clay-supported perhydroxylated glucodendrimer

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To the memory of the late Prof. Fritz Vögtle (March 8, 1939 – January 3, 2017)

Abstract. Low cost biosourced hybrid microporous adsorbents with improved affinity towards carbon dioxide (CO₂) were prepared through the incorporation of various amounts of glucosylated dendrimer into bentonite and montmorillonite-rich composite materials. Characterization by nitrogen adsorption-desorption isotherms, surface specific and pore size analyses (BET and BJH), thermogravimetric analysis (TGA), FTIR spectrophotometry, and X-ray diffraction (XRD) revealed changes in the interlayer spacing and textural structure of the materials. Thermal programmed desorption measurements (TPD) showed significant improvements of the retention capacity of CO₂ (CRC) and water (WRC). This was explained in terms of enhancement of both surface basicity and hydrophilic character due to the incorporation of terminal polyhydroxyl groups. The CRC was found to vary according to the previous saturation time with CO₂ and the carrier gas throughput. CO₂ was totally released upon temperature not exceeding 80°C or even at room temperature upon strong carrier gas stream, thus providing evidence that CO₂ capture involves almost exclusively physical interaction with the OH groups of the dendrimer. This result opens promising prospects for the reversible capture of carbon dioxide with easy release without thermal regeneration, more particularly when extending this concept to biosourced dendrimers.

Keywords: Hybrid materials; organoclay; dendrimer; clay; carbon dioxide; TPD.

Graphical abstract

Introduction

Reduction of greenhouse gas (GHG) emissions is one of today's major environmental concerns.^{1,2} For more than a decade, GHGs, including carbon dioxide (CO₂), have been identified as the main causes of observed global warming. CO₂ emissions by human activities still exceed the threshold of natural assimilation in carbon cycles. A fairly wide literature is now available in this regard. Due to the lack of viable solutions, a judicious strategy for our future resides in upstream redesigning the production and control processes involving CO₂ emissions.³

Given the acidic character of CO₂, its absorption in basic media constitutes one of the most practical avenues. Therefore, adsorbents with basic properties have been systematically used for this purpose.⁴ This feature has been largely exploited with amines, both in solution⁵ and in nanoporous materials,⁶ including polyamine dendrimers.⁷⁻¹² Supported amines can retain appreciable amounts of adsorbed CO₂ but require severe thermal treatment for their regeneration and the subsequent release of CO₂ due to the formation of stable carbamates. However, the reversible capture of this gas can be most effectively achieved when no thermal desorption is required. Among these, alkali and alkaline earth metal carbonates, alkali metal hydroxides, polyols in liquid phase, or supported on solid surfaces have been systematically explored.¹³ Supported alcohols showed lower but interesting affinity towards CO₂, involving instead, only weakly bonded carbonate-like associations that allow much easier gas release than carbamate-like bonding even at room temperature and under forced convection.¹⁴⁻¹⁵ Actually, the estimated binding energy between ethanol and CO₂ has been estimated at 0.84 kcal/mol^{16a} and the direct binding of cyclodextrin's OH group and CO₂ was further confirmed by CP/MAS ¹³C-NMR spectroscopy.^{16b}

Porous matrices displaying surface basicity such as layered double hydroxides (LDH) turned out to be effective CO₂ adsorbents, but non thermal regeneration can be achieved only through basicity attenuation by incorporating polyol dendrimers.¹⁶ Clay materials^{13,14,17-19} along with zeolites and analogous adsorbents²⁰⁻²³ are now the focus of growing interest due to both of their intrinsic and induced affinity towards CO₂.²⁴ The latter strongly correlates to the chemical composition, and can be improved either by purification for removing acidic impurities, if any, or insertion of organic moieties bearing several hydroxyl groups. However, unlike zeolites, clay minerals have lamellar structure than can be expanded by incorporating such organic species, cations (Na⁺, Ca²⁺, Mg⁺ and others), surfactants such as quaternary ammonium and others.²⁵⁻²⁷ For this purpose, and for objective reasons, the use of crude and unpurified clay materials would be an interesting route to further explore.

Bentonite is a low cost and widely available clay material that can exhibit interesting surface properties for various applications involving adsorption and catalysis without previous purification.²⁸⁻³¹ The presence of some components displaying low surface area and net negative charge are supposed to limit their potential applications as adsorbents and catalysts.^{28,32,33} However, even without previous

purification, judicious modification of bentonites may improve their adsorptive properties. In this regard, incorporation of organic dendritic moieties bearing high number of adequate surface chemical groups may considerably expand their porosity and specific adsorptive capacities.

Organo-clay materials functionalized with terminal amphoteric hydroxyl groups have been produced by inserting synthetic or various polyol dendrimers on clay minerals such as montmorillonite.^{13,14,17-19} Nevertheless, due to the hydrophilic nature of clay materials, uniform incorporation of hydrophobic polymers still remains a major challenge to be addressed, more particularly for high concentration or for high molecular weight entities. Interestingly however, dendrimeric architectures, particularly those made of a dense core and possessing a large number of surface OH groups at lower generation³⁴ such as glycodendrimers,³⁵⁻³⁸ may constitute a major improvement.

The aim of the present work resides in the synthesis and characterization of organo-clays from two different starting bentonites loaded with different amounts of a low generation dendrimer bearing 16 terminal hydroxyl groups. Toward this goal, a new tetrameric glucodendrimer (**4**) was built from a tetrapropargylated pentaerythritol derivative (**2**) that was linked to a glucosyl azide (**1**) using the well-established copper(I)-catalyzed azide-alkyne cycloaddition (CuAAC, “click chemistry”).^{39,40} The affinity of the composite materials towards carbon dioxide and hydrophilic character were discussed in terms of retention of CO₂ and water as determined by thermal programmed thermal desorption (TPD). The effects of clay purification, amount of incorporated dendritic polyol, and operating conditions during CO₂ adsorption were be thoroughly investigated.

Experimental

Synthetic procedures

All reagents were used as supplied without prior purification unless otherwise stated and obtained from Sigma-Aldrich. After work-up, the organic layers were dried over anhydrous Na₂SO₄. Evolution of reactions was monitored by analytical thin-layer chromatography using silica gel 60 F₂₅₄ precoated plates (E. Merck). The visualization of molecules was performed 1) by soaking in specific mixed acid (sulfuric acid/methanol/water: 5/45/45 v/v/v) and 2) by oxidizing solution of molybdate (prepared from 25 g of ammonium molybdate and 10 g of ceric sulfate dissolved in 900 ml of water and 100 mL of concentrated sulfuric acid, followed by heating to 300 °C. Purification by flash column chromatography was performed using silica gel from Silicycle Inc. (Qc, Canada) (60 Å, 40-63 µm) with the indicated eluent. The solvents employed for the chromatography were HPLC quality and were not distilled before use. They were evaporated under reduced pressure (rotary evaporator under vacuum generated by a system of glass filter pump). Optical rotations were measured with a JASCO P-1010 polarimeter. NMR spectra were recorded for solutions in CDCl₃ with a Bruker Avance III HD 600 MHz spectrometer. Proton and carbon chemical shifts are

reported in ppm (δ) relative to the signal of CDCl_3 (δ 7.27 and 77.23 ppm for ^1H - and ^{13}C , respectively). Coupling constants (J) are reported in Hertz (Hz), and the following abbreviations are used for signal multiplicities: singlet (s), doublet (d), doublet of doublets (dd), multiplet (m). Analysis and assignments were made by COSY (Correlated Spectroscopy) and HSQC (Heteronuclear Single Quantum Coherence) experiments. High-resolution mass spectra (HRMS) were measured with a LC-MS-TOF (Liquid Chromatography Mass Spectrometry Time of Flight, Agilent Technologies) in positive and/or negative electrospray mode by the analytical platform of UQAM. The known per-*O*-acetylated β -D-glucopyranosyl azide (**1**) was prepared under phase transfer catalysis following our published procedure⁴¹ and the physical properties fully agreed with published data. Tetra-*O*-propargyl pentaerythritol (**2**, tetrakis(2-propynyloxymethyl)methane) was also prepared following a published procedure with correct physical data.⁴²

Synthesis of glucodendrimer 4

Peracetylated glucodendrimer 3.

The procedure for the CuAAC click reaction between compound **1** and **2** follows our general synthetic protocol used when sugar azides are treated with a perpropargylated scaffold.^{42,43} Briefly, to a solution of glucopyranosyl azide **1** (932 mg, 2.50 mmol, 4.8 equiv.) and tetrapropargylated pentaerythritol **2** (150 mg, 0.52 mmol, 1.0 equiv.) in THF (6 mL) was added a solution of $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ (156 mg, 0.62 mmol, 1.2 equiv.) and sodium ascorbate (124 mg, 0.62 mmol, 1.2 equiv.) dissolved in H_2O (6 mL). The reaction mixture was stirred at 55 °C for 3 hours and at room temperature for 21 hours. The solvent was evaporated under vacuum and the residue was dissolved in EtOAc. The organic layer was washed with 5% aqueous EDTA solution (3x), water, and brine. The solvent was dried over Na_2SO_4 , filtered and removed under reduced pressure. The crude product was purified by silica gel column chromatography using a gradient of 1% to 3% of $\text{MeOH}/\text{CH}_2\text{Cl}_2$ to afford the desired glucodendrimer **3** as a white solid (750 mg, 0.42 mmol, 81%). R_f = 0.30, 95:5 CH_2Cl_2 -MeOH; ^1H NMR (CDCl_3) δ 8.02 (s, 4H, *H*-triazole), 6.04 (d, 4H, $J_{1,2}$ = 9.4 Hz, *H*-1), 5.59 (dd, 4H, $J_{2,3}$ = 9.4 Hz, *H*-2), 5.46 (dd, 1H, $J_{3,4}$ = 9.5 Hz, *H*-3), 5.40 (dd, 1H, $J_{4,5}$ = 9.5 Hz, *H*-4), 4.69-4.57 (m, 8H), 4.33 (dd, 4H, *H*-6a), 4.18 (dd, 4H, *H*-6b), 4.11 (dd, 4H, *H*-5), 3.51-3.40 (m, 8H), 2.10, 2.05, 2.04, 1.80 ppm (s, 48H, 4x12 CH_3); ^{13}C NMR (CDCl_3) δ 170.6, 170.0, 169.5, 168.8 (CO), 145.9, 121.6, 85.5 (C-1), 74.9, 72.9, 70.2, 69.0, 67.8, 64.8, 61.6, 45.2 (C_q), 20.6, 20.6, 20.6 ppm. ESI⁺-HRMS: $[\text{M}+\text{Na}]^+$ calcd for $\text{C}_{73}\text{H}_{96}\text{N}_{12}\text{O}_{40}\text{Na}$, 1803.57445; found, 1803.57058.

Unprotected glucodendrimer 4.

Zemplén trans-esterification (NaOMe , MeOH) of peracetylated glucodendrimer **3** followed classical conditions.^{42,43} A solution of tetramer **3** (700 mg, 0.39 mmol, 1.0 equiv.) in 1 M solution of sodium methoxide in methanol (2 mL, pH 9) was stirred at room temperature until consumption of starting material. After 24 hours, the solution was neutralized by the addition of ion-exchange resin (Amberlite IR

120, H⁺), filtered, washed with MeOH, and the solvent was evaporated under reduced pressure to give **4** as white solid (395 mg, 0.35 mmol, 91%). ¹H NMR (D₂O) δ 8.02 (s, 4H, *H*-triazole), 5.75 (d, 4H, $J_{1,2}$ = 9.0 Hz, *H*-1), 4.53 (d, 8H), 4.01 (dd, 4H, $J_{2,3}$ = 9.3 Hz, *H*-2), 3.89 (dd, 4H, $J_{6a,5}$ = 12.4 Hz, $J_{6a,6b}$ = 1.5 Hz, *H*-6a), 3.81-3.70 (m, 12H), 3.68-3.59 (m, 4H), 3.38 ppm (s, 8H); ¹³C NMR (D₂O+acetone) δ 143.9, 123.8, 87.0 (C-1), 78.4, 75.5, 71.8, 68.5, 67.7, 62.9, 60.0, 44.0 ppm (C_q). ESI⁺-HRMS: [M+Na]⁺ calcd for C₄₁H₆₄N₁₂O₂₄Na, 1131.40486; found, 1131.40485.

Organo-bentonite preparation

The present research was achieved using bentonites as inorganic supports for the physical grafting of the dendrimer. A crude bentonite (Bent) with a silica / alumina ratio of 1.58 (w/w) was supplied by Sigma-Aldrich (MI, USA), and was previously purified into a 95% montmorillonite-rich material (NaMt) as already reported.^{13,14,17-19,45} For this purpose, 200 g bentonite was suspended in 2 L of 4M NaCl, stirred at 80°C for 6 hours in order to replace all cations by uniform sodium ions. The resulting solution was fractionated and subjected to several washes and sedimentation at room temperature in distilled water. Then, several centrifugations at 4000 rpm for 90 min and washing of the precipitate were carried out in distilled water to separate the montmorillonite from the other constituents of bentonite. Further, NaMt suspension was dialyzed through a cellulose membrane immersed for 4 days in distilled water repeatedly renewed 2 to 3 times per day under ultrasound exposure. Purification was then completed by ozonolysis for removing all possible organic impurities. This procedure was completed by drying in an oven at 80°C for 6 hours.

Both materials were loaded with different weight proportions of the polyhydroxylated dendrimer **4** to increase the retention capacity of CO₂ (CRC). In the case of bentonite, dendrimer incorporation was carried out without prior purification through mere impregnation with various amounts of aqueous solution of dendrimer **4** and slow drying at 60°C overnight with periodical mild stirring.

Dendrimer incorporation was carried out by mixing an aqueous solution of dendrimer (20 mL / mL) also stirred at room temperature, the volume of which corresponds to 25 mL of an aqueous solution containing 0.5 g of clay, previously stirred without heating for 2 hours. Various organoclays containing well determined amounts of dendrimer were prepared. For this purpose, we used percentage (w / w) of the dried mass of the clay. For intercalation of the dendrimer in Bent-A: 0.1%, 0.2%, 0.5% and 1% (w / w) of dendrimer **4** were introduced into the clay. For bentonite, the proportions 0.1% and 0.2% (w / w) dendrimer were used. The resulting solutions were stirred for 2 hours and dried overnight at 80 °C without stirring, before being gently crushed.⁴⁵

Characterization and thermal desorption measurements

The different organoclay samples prepared were characterized through X-ray diffractions (Siemens D5000 instrument, Co-K α at 1.7890Å), in the 2 θ range (2–50°). Nitrogen adsorption-desorption isotherms and BET calculations of the specific surface area (SSA) were performed on a Quantachrome device coupled with an Autosorb automated gas sorption system. Thus, samples of 100–150 mg were previously dried at 80°C for 24 h, degassed at 80°C for 16 h under a 10^{–4} Torr vacuum, and nitrogen adsorption was made at –195.7 °C. Thus, samples of 80–100 mg were previously dried at 140–150°C for 24 h, outgassed at 140 °C for 4 h under a 10^{–4} Torr vacuum and then subjected to nitrogen adsorption at –195.7°C. Thermal gravimetric analyses (TGA) were performed on a Seiko Instrument Inc., TG/TDA6200 thermal analyzer under air stream (100 mL·min^{–1}) and a heating of 5 °C·min^{–1}. The thermal stability and the amount of grafted species were assessed on the basis of the mass loss between 20°C and 800°C. Infrared spectra were recorded in ATR mode, using a KBr IR cell and Fourier Transform Infrared spectroscopy equipment (ThermoScientific, Nicolet 6700/Smart ATR). Differential Scanning Calorimeter (DSC) analyses were conducted on a Mettler Toledo TGA-SDTA851e, under a dry nitrogen stream of 20 mL·min^{–1} and heating rate of 5 °C·min^{–1}.

Thermal desorption measurements

The basicity of the OH-containing organo-Mts was assessed through thermal programmed desorption of carbon dioxide (CO₂-TPD), given the Lewis acid character of CO₂. This was achieved according to a procedure fully described elsewhere.^{46,47} Measurements were achieved using organo-Mts in the powder form with a particle size comprised between 0.05 and 0.1 mm in a temperature-programmed tubular oven, under various dry nitrogen stream (1 and 15 mL·min^{–1}) coupled to a CO₂-detector (Li-840A CO₂/H₂O Gas Analyzer). Prior to TPD measurements, each adsorbent powder was dried under nitrogen stream at 160 °C for 40 min, and then cooled to 20 °C. At this temperature, pure dry carbon dioxide was injected in the nitrogen stream till saturation of the adsorbent surface. The non-adsorbed CO₂ excess was evacuated under a nitrogen stream during at least 1 h, till no remaining CO₂ was detected at the TPD device outlet. In a second step, TPD measurements were performed between 20 °C and the upper temperature limit as estimated by TG–DTG measurements. The amount of desorbed CO₂ was detected and measured in real time, with a delay of 5 sec. At the end of the TPD process, temperature was maintained constant at 200 °C or 600 °C for 20 min in order to verify the influence of stronger desorption peaks on the TPD patterns. The CO₂ retention capacity (CRC) was expressed in terms of desorbed μ mol CO₂ per gram of dry clay material, i.e. the area described by the TPD pattern between 20° and 200°C. This upper temperature limit was determined by TG–DTG measurements, which revealed that the synthesized organo-Mts displayed thermal stability up to 240°C.

The retention capacity of CO₂ (CRC) and water (WRC) was assessed for all adsorbents by thermal programmed desorption of carbon dioxide (CO₂-TPD) according to a procedure fully described elsewhere.^{46,47} Prior to TPD, dynamic impregnation of the adsorbent was carried out with 200 mL of CO₂ at 20°C under a 15 mL·min⁻¹ dry nitrogen stream, followed by a purge under similar conditions for evacuating the non adsorbed CO₂ excess. TPD measurements were achieved under a 1 mL·min⁻¹ of dry nitrogen stream within a tubular oven coupled to a CO₂-detector (Li-840A CO₂/H₂O Gas Analyzer).^{14,48}

Results and discussion

Synthesis

The synthetic scheme leading to the tetraglucosylated dendrimer **4** is illustrated in Scheme 1. The simplicity of the procedure relied on the efficient of the multivalent CUAAC cycloaddition^{39,40, 42-44} between the known glucosyl azide **1**⁴¹ and tetrapropargylated pentaerythritol **2**⁴² to provide peracetylated dendritic intermediate **3** in 81% yield after purification by column chromatography. The structural integrity of the product was readily established by the complete disappearance of the characteristic acetylenic triplet of **2** at δ 2.40 ppm, a slight displacement of the four methylene protons next to the propargyl groups from δ 4.12 ppm to 4.63 ppm, together with the appearance of a sharp triazole signal at δ 8.02 ppm and integrating for four relative to the anomeric signals of the sugar residues appearing as a doublet ($J_{1,2}$ = 9.4 Hz) at δ 6.04 ppm. In addition, the complete absence of the azide frequency at ν 2100cm⁻¹ in the IR spectra of **3**, together with a distinct $[M+Na]^+$ of 1803.57 in the ESI-HRMS spectra, unequivocally established the structure of **3**. Removal of all 16 *O*-acetyl protecting groups of **3** using the classical Zemplén transesterification procedure (NaOMe, MeOH) uneventfully afforded glucodendrimer **4** in 91% yield as seen by the complete disappearance of all acetyl signals in ¹H-NMR spectra (see experimental). It is worth mentioning that this type of dendrimer build-up strategy, using “glyconanosynthons”^{34,38} and providing 16-surface OH functionalities at the G0 level, constitutes a distinctive advantage over other classical dendrimer syntheses using AB₂-type scaffolds and building blocks. This material was suitably incorporated within the clay matrices for the low-energy CO₂ “catch and release” strategy described below.

Scheme 1. Synthetic scheme leading to a tetraglucosylated pentaerythritol-based dendrimer (**4**) harboring 16-surface hydroxyl groups at the G0 level.

Structural changes upon dendrimer insertion

Comparison of the d_{001} basal spacing between bentonite (8.19 Å) and NaMt (9.72 Å) showed that purification into a montmorillonite-rich clay material induces a slight increase in the interlamellar space (Table 1). This can be explained in terms of substitution of all original cations by Na⁺ and removal of dense silica phases such as quartz and cristobalite.

Table 1. Structural characteristics of the organoclays.

Samples	Dendrimer loading (Wt %)	Denotation	d_{001} basal spacing (Å)	Specific surface area (m ² /g)
Bentonite	0	Bent	8.19	20.5
	0.1	Bent -0.1	8.33	33.7
	0.5	Bent -0.5	8.47	-
	1.0	Bent -1.0	8.47	23.4
NaMt	0	NaMt	9.72	
	0.1	NaMt -0.1	9.86	59.0
	0.5	NaMt -0.5	10.00	52.6
	1.0	NaMt -1.0	10.13	53.2

Dendrimer incorporation rather induced an increase in the interlamellar space almost proportionally to the amount of inserted organic moiety. This is supported by the increase in the d_{001} basal spacing for bentonites from 8.19 Å to 8.33 Å and then to 8.47 Å, when the amount of incorporated dendrimer increased from 0.1 and 0.5-1.0%, respectively (Fig. 3-a). For NaMt, the increase was from 9.72 Å to 10.13 Å. This is a special feature of organoclays.^{25,49} The higher d_{001} basal spacing registered for NaMt

and dendrimer-loaded derivatives indicated a more expanded lamellar structure, most likely due to the presence of monovalent Na^+ cations, known to induce no attractive interactions between two clay sheets. This is in agreement with the higher specific surface area (SSA) of NaMt ($59 \text{ m}^2\cdot\text{g}^{-1}$) as compared to bentonite ($20.5 \text{ m}^2\cdot\text{g}^{-1}$) (Table 1). Low dendrimer loading of 0.1 wt % was found to induce SSA improvement from 20.5 to $33.7 \text{ m}^2\cdot\text{g}^{-1}$, providing clear evidence of an interlamellar insertion of the dendritic moiety. Excessive dendrimer loading of 1.0 wt % produced a detrimental effect, since the SSA dropped down to 23.4 wt %, presumably due to enhanced OH-OH interactions that promoted dendrimer aggregation into clusters at the expense of the interlayer section.^{14,17-19}

Interestingly, unlike for bentonite, NaMt loading with dendrimer induced an SSA decay down to 52.6-53.2 $\text{m}^2\cdot\text{g}^{-1}$, presumably due to a structure compaction as a result of the sandwiching effect of the OH groups of the inserted dendrimer molecules. This effect seems to be attenuated by increasing the dendrimer loading up to 1.0 w %, most likely due the appearance of competitive interactions between the OH groups at the expense of OH-surface interactions.

FTIR insights revealed an increase in the stretching vibration band of the free OH groups between 3200 cm^{-1} and 3550 cm^{-1} with increasing amount of inserted dendrimers. This provided clear evidence of the incorporation of increasing number OH groups in the clay structure. In addition, the 3308 cm^{-1} band of the dendrimer was shifted to a higher frequency, i.e. 3440 cm^{-1} for organo-bentonites (org-Bent) and 3398 cm^{-1} for organo-montmorillonites (org-Mt). This indicated that at least a part of the dendrimer's OH groups were involved in interactions with the inorganic support (Fig. 1). The same phenomena were noticed for bentonite and NaMt and organically modified derivatives. This band increased with increasing dendrimer loading.

Fig. 1. FTIR spectra of crude bentonite with dendrimer-loaded derivatives (a) and NaMt with dendrimer-loaded derivatives (b) as compared to that of dendrimer 4. Both materials were intercalated with different amounts of dendrimer: 0.1% (w/w), 0.2% (w/w), 0.5% (w/w) and 1.0% (w/w).

The fact that this band was higher for org-Mt suggests weaker interactions of the OH groups with the inorganic surface, as supported by the slightly lower wavenumber (3398 versus 3400 cm^{-1}). It results that on NaMt, the dendrimer OH groups should be more accessible, most particularly for water molecules, thereby improving the hydrophilic character. This statement is in agreement with the lower amount of organophobic dense silica phases and with the higher intensity of the 3620 cm^{-1} band assigned to OH belonging to water molecules.

TGA study of the thermal stability of bentonite (Fig. 2) showed two major mass losses, the first one around 100°C attributed to dehydration and the second, of lower intensity, at ca. 450°C assigned to dehydroxylation. Interestingly, increasing dendrimer loading in org-Bent samples induced a significant decrease of water loss (Fig. 2-a), which accounted for a significant decay of the hydrophilic character. A weak mass decrease of less than 1% between 200° and 380°C accounted for the dendrimer decomposition. No mass loss was noticed between 120°C and 200°C , providing evidence of the appreciable thermal stability of the organoclays up to 200°C . This is an essential requirement for accurate TPD measurements within this thermal stability threshold.

Fig. 2. DTG patterns of of crude bentonite with dendrimer-loaded derivative (a) and NaMt with dendrimer-loaded derivatives (b). Both materials were intercalated with different amounts of dendrimer: 0.1% (w/w), 0.2% (w/w), 0.5% (w/w) and 1.0% (w/w).

Intrinsic properties of the clay support

Blank tests performed on unmodified clay samples showed almost similar TPD profiles for bentonite and NaMt. Both materials displayed intrinsic affinity towards CO_2 , with a single TPD desorption peak around 65°C within the temperature range $20\text{--}200^\circ\text{C}$ (Fig. 3), the latter accounted for its weak basicity

strength. A slight increase of the amount of desorbed CO_2 beyond 160°C was noticed only for bentonite. This was attributed to its stronger basicity, most likely due to the presence of native alkaline-earth carbonates. This is a special feature of bentonite, which is supported by the presence of carbon and calcium in the chemical composition before purification. Repetitive dehydration did not alter such basicity strength, which appears to be recovered after each saturation with CO_2 and even enhanced by increasing retention driving force induced by higher amounts of impregnating CO_2 (Fig. 4).

Fig. 3. Repetitive CO_2 -TPD patterns of crude bentonite (a) and NaMt (b) after three successive CO_2 adsorption-desorption cycles under similar operating conditions, but without rehydration.

Fig. 4. Effect of the amount of injected CO_2 on TPD profiles for dehydrated bentonite. These experiments were performed after dynamic impregnation with: 1) 70, 2) 150 and 3) 300 mL of dry CO_2 per 40 mg clay samples at 20°C under a $15\text{ mL}\cdot\text{min}^{-1}$ of dry nitrogen stream, respectively. 4) Another attempt was run after static saturation with excess CO_2 overnight without a nitrogen stream. Both types of experiments were followed by a purge under similar conditions and TPD with $1\text{ mL}\cdot\text{min}^{-1}$ of dry nitrogen stream.

Here, the intrinsic affinity towards CO_2 seems to strongly correlates to the moisture content in this temperature range.¹⁵ The weak basicity corresponding to desorption temperature in the range 40-120°C totally disappeared upon dehydration, regardless of the amount of injected CO_2 used for saturation. However, it is worth mentioning that the stronger basicity corresponding to desorption temperature exceeding 160°C still persisted even after multiple CO_2 adsorption-thermal desorption cycles which did not seem to be altered by dehydration. The H_2O -TPD patterns showed almost similar profiles with a single desorption peak within the same temperature range (Fig. 5). This suggests that the adsorbed moisture is responsible for such a CO_2 retention through weak basicity. This is well argued by the fact that decreasing moisture content in both materials after repetitive TPD without rehydration induced decay in the amount of desorbed CO_2 .

Fig. 5. Repetitive H_2O -TPD patterns of crude bentonite (a) and NaMt (b) after three successive CO_2 adsorption-desorption cycles under similar operating conditions, but without rehydration.

Similar behavior was observed for NaMt, which clearly demonstrates that water contributed to the surface properties by inducing weak basicity on the inorganic support. The similar behavior of bentonite and NaMt clearly validates that purification can be avoided, at least regarding the intrinsic affinity towards CO_2 and hydrophilic character. The increase of the amount of desorbed CO_2 beyond 120°C accounted for a stronger basicity, most likely due to the electrons pair of the lattice oxygen atoms belonging to the clay mineral structure. However, this relatively strong basicity should play a significant role within the temperature range 20-200°C imposed by stability considerations. The fact that increasing amount of injected CO_2 raised the shape of the TPD profile indicates that the retention capacity must be strongly dependent on the saturation conditions. This result is of great importance, because it clearly illustrates that CO_2 adsorption is controlled by slow gas diffusion inside the clay interlayer space.

Effect of dendrimer incorporation

Dendrimer insertion was found to revitalize the weak basicity even by injecting dry CO₂ on dry organoclay materials. This is well illustrated by the appearance of a bump in the TPD profiles of both clay materials between 40 and 160°C (Fig. 6). Here, such basicity must be attributed to the OH groups belonging to the polyol dendrimer. This effect appears to be more pronounced on bentonite. Inasmuch as higher amount of desorbed CO₂ were registered by comparison to dendrimer-loaded NaMt.

Fig. 6. CO₂-TPD patterns of bentonite (a) and NaMt (b) before and after dendrimer insertion. Dynamic impregnation with 1.5 mL CO₂/g for 40 mg clay mineral at 20 °C in a 15 mL·min⁻¹ of dry nitrogen stream, followed by a purge and TPD under 1 mL·min⁻¹ of dry nitrogen stream.

a. 1) Bent-0.2; 2) Bent-0.5; 3) Bent-1.0; 4) Bent-0.1; 5) Bent.

b. 1) NaMt; 2) NaMt-0.1; 3) NaMt-0.2

Interestingly, intermediate dendrimer loading of 0.2 wt% for organo-bentonites and of 0.1 wt% for organo-NaMt produced the highest amount of desorbed CO₂. Such a phenomenon was already reported¹⁷⁻¹⁹ and was explained in terms of dendrimer aggregation, through H-bridges and/or hydrophobic interactions for excessive dendrimer loadings. This rather suggests that moderate contents in dendrimer favor OH-clay interactions that promote dendrimer dispersion and intercalation in the interlayer space. This agrees with their higher specific surface area as compared to higher loadings (Table 1). Nevertheless, this contrasts with the higher specific surface areas of organo-bentonites as compared to their NaMt derivatives. This paradox cannot be explained only in terms of structure porosity, because the dispersion level of the dendrimer and the non-uniform CO₂ retention strength on the accessible clay surface should play a much more significant role. In this regard, deeper insights are required for comparing the effect of nitrogen throughput during the purge step on two organo-bentonites having two different dendrimer loadings, namely 0.1 and 0.2 wt%. These two factors are supposed to strongly depend on CO₂ retention strength and diffusion inside the clay porosity.

CO₂ adsorption strength

The first assessment of the weak basicity was previously estimated by thermal desorption temperature, which was found not to exceed 80°C, regardless of the dendrimer loading. The CO₂ retention strength can also be estimated by exposing CO₂-saturated samples to strong carrier gas stream during the purge. Indeed, decreasing nitrogen throughput for the purge of the excess non-adsorbed gas was found to improve the CO₂ uptake. A first overview of the results obtained for two different dendrimer loadings revealed that increasing nitrogen throughput purge induced a significant depletion of the amount of desorbed CO₂ (Fig. 7).

Fig. 7. CO₂-TPD patterns of Bent-0.1 under different nitrogen throughputs for:
a: impregnation with CO₂: 1) 1 mL·min⁻¹; 2) 5 mL·min⁻¹; 3) 10 mL·min⁻¹; 4) 15 mL·min⁻¹.
b: Thermal programmed desorption: 1) 1 mL·min⁻¹; 2) 3 mL·min⁻¹; 3) 5 mL·min⁻¹; 4) 10 mL·min⁻¹.
 All these TPD patterns were performed after dynamic impregnation with 100 mL CO₂/g for 40 mg clay mineral sample for 60 min at 20 °C under different N₂ streams.

This can be explained in terms of an improvement of forced convection upon strong carrier gas stream, in agreement with previous data.^{13,14,16-19,45,47} The OH groups brought by the dendrimer insertion are known to display amphoteric character that promotes weak interaction with CO₂ similar to that induced by water molecules. This interaction is supposed to be so weak, that full CO₂ release can be achieved through strong nitrogen stream only even at room temperature, provided that the forced convection was maintained for a sufficiently long time. That is why accurate assessment of the CO₂ retention capacity (CRC) is strongly dependent on the operating conditions during adsorption, purge, and desorption.

It is worth mentioning that the amount of CO₂ desorbed from Bent-dendrimer **4** composite 0.1% (Fig. 7-a) is almost twice as high to that registered with Bent-dendrimer **4** nanocomposite 0.2% (Fig. 7-b). This must be due to different specific surface areas of the organo-bentonites and to different dispersion level of the incorporated dendrimer. When extending the saturation time of the adsorbent by

the CO₂ excess (100 mL CO₂/g for 40 mg clay mineral sample) from 20 to 60 min, an increase in the amount of desorbed gas was noticed, but only up to a certain level (Fig. 8).

Fig. 8. CO₂-TPD patterns of Bent-0.2 after different contact times with CO₂ (impregnation): 1) 60 min; 2) 30 min; 3) 90 min; 4) 120 min; 5) 20 min. Static impregnation with 100 mL CO₂/g for 40 mg clay mineral sample at 20°C in a 15 mL·min⁻¹ of dry nitrogen stream, followed by a purge and TPD under 1 mL·min⁻¹ of dry nitrogen stream.

Here, CO₂ retention appears to be proportional to the driving force involving the excess CO₂ and prolonged contact time, but must be controlled by slow diffusion. Surprisingly, longer saturation time of 90 and 120 min produced a detrimental effect, most likely due to the fact that excessive contact time resulted in CO₂ condensation that obstructed pore entries and hindered diffusion. Therefore, here also, this factor should be taken into account when assessing the CRC.

CO₂ adsorption capacity

The affinity towards CO₂ is herein expressed in terms retention capacity (CRC), which was defined as the area of the TPD pattern within the temperature range considered. The latter was found to increase with increasing amount of impregnating CO₂, which exerts a significant driving force on CO₂ adsorption. For instance, the CRC of bentonite was of 0.058 μmol·g⁻¹ for 1.75 mL CO₂/mg adsorbent and of 0.636 μmol·g⁻¹ for 7.5 mL·mg⁻¹ (Table 2).

Table 2. Effect of varying operating conditions on CO₂ retention capacity of organo-bentonites

Contact time with CO ₂ (hours)	Dendrimer loading (wt %)	CO ₂ /ads (mL·mg ⁻¹)	TPD N ₂ stream (mL·min ⁻¹)	Purge N ₂ stream (mL·min ⁻¹)	CRC (mmol·g ⁻¹)
12	0.0	1.75	15	1	0.058
12		3.75	15	1	0.188
12		7.5	15	1	0.636

12	0.1	2.5	15	1	1.500
12		2.5	15	5	0.937
12		2.5	15	10	0.806
12		2.5	15	15	0.620
12	0.2	2.5	15	1	0.165
12		1.25	15	5	0.152
12		1.25	15	1	0.307
0.33		2.5	15	1	0.276
0.50		2.5	15	1	0.512
1.0		2.5	15	1	0.576
1.5		2.5	15	1	0.317
12	0.5	2.5	15	1	0.114

** Impregnation with 100 mL of CO₂ at different time and followed by purge and TPD at 1 mL·min⁻¹ of dry stream nitrogen between 20 and 200°C.

The CO₂ /adsorbent vol/wt ratio was calculated by dividing the volume of dry CO₂ injected for impregnation by the mass of the dry adsorbent samples, which was of 40 mg.

The different CRC values were measured through TPD runs performed between 20 and 200°C with 40 mg dry adsorbent. The impregnation time was defined as being the duration required for contacting the dry adsorbent sample with a certain amount of dry CO₂. Saturation is an impregnation of the adsorbent with an excess CO₂ under similar conditions for a certain contact time, usually overnight.

Low dendrimer loading of only 0.1 wt % gave higher CRC of 1.5 mmol·g⁻¹, even with lower amount of impregnating CO₂ of 2.5 mL·mg⁻¹. This CRC value dramatically dropped to 0.620 mmol·g⁻¹ when raising the nitrogen stream from 1 to 15 mL·min⁻¹, or to 0.276-0.576 mmol·g⁻¹ when shortening the contact time with CO₂ to 0.33-1.5 hours and increasing the dendrimer content up to 0.1 wt %. Thus, it clearly appears that the operating conditions greatly influenced the adsorption on such materials. In some cases, even prolonged contact time of high dendrimer contents produced detrimental effect on the CRC. The most plausible explanation resides in that quick multilayer CO₂ adsorption on the external surface of the clay particle reduced the diffusion inside the intraparticle volume. This is a special feature of fast gas condensation on microporous materials.^{13,14,18,19,21,22,45} Dendrimer incorporation induced a significant improvement of the CRC, but large dendrimer contents (0.5 wt % and 1wt %) exhibited detrimental effects, presumably due to a decay of porosity.^{17-19,45} Here, all the operating parameters were expected to act not only through their individual effect, but also via interactions between them. Deeper insights are still needed to further investigate this behavior.

Conclusions

In the present work, the incorporation of polyol dendrimer into the clay induced marked improvements of the surface basicity and hydrophilic character by raising the surface density of the OH groups. The latter were found to induce only weak basicity, and to promote no competitive interactions with both CO₂ and water molecules. Moisture content also contributes to CO₂ retention within the temperature range 20-200°C in both native and dendrimer-loaded clay materials. Dehydration turned out to be detrimental for the weak basicity of the unmodified clay materials, but showed a much lower effect on dendrimer-loaded composites. Both native and montmorillonite-rich materials displayed similar

behavior, thereby providing evidence that clay purification is not necessary, since the dense phase impurities exhibited negligible interactions with CO₂ and water. Up to a certain level, dendrimer content played a beneficial role by improving the affinity towards CO₂ and water. Excessive loadings of organic moiety beyond 0.2 wt % produced a decay of both properties. Within the temperature range 20-200°C, the dendrimer-loaded clay showed stability and the CO₂ retention capacity (CRC) was found to depend only on the operating conditions for adsorption, purge, and thermal desorption. Given the weak basicity of the organo-bentonites, CO₂ was found to desorb even at room temperature upon strong nitrogen stream during the purge step. This result is of great importance, because it provides evidence that CO₂ capture involves mainly physical condensation and that thermal regeneration of the adsorbent is not needed. The basicity and hydrophilic character of our biosourced polyol dendrimers with higher number of hydroxyl groups should be interesting to explore. Research is still in progress toward this goal together with exploring the detail factors involved in other atmospheric pollutants such as NO_x and SO_x for instance.

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