

# Polyol–Clay Matrices with Improved Hydrophilic Character and Affinity towards CO<sub>2</sub> - Attempts to CO<sub>2</sub> Concentration at Room Temperature

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## ABSTRACT

Polyol-montmorillonite matrices were prepared by incorporating various OH-compounds via two procedures: *i.* a mere self-assembly of polyol dendrimers with clay dispersion in water; *ii.* a chemical grafting of Bis(2-hydroxyethyl)-aminopropyltriethoxysilane. Thermal programmed desorption analysis (TPD) revealed a significant improvement of the affinity towards CO<sub>2</sub> as compared to the starting clay mineral. This appears to be also due to the enhancement of the hydrophilic character. The major part of the adsorbed CO<sub>2</sub> can be released at 20–50°C from dry adsorbents, but at slightly higher temperature from hydrated matrices. The CO<sub>2</sub> retention capacity (CRC) was found to be strongly influenced by the operating conditions. CO<sub>2</sub> can be easily and completely released even at room temperature through forced convection in strong nitrogen stream or in dry and CO<sub>2</sub>-free media. In these experiments, the chemically modified clay mineral gave the highest CRC (54 µmol.g<sup>-1</sup>) at low N<sub>2</sub> flow rate for a specific surface area of only 44 m<sup>2</sup>.g<sup>-1</sup>. The adsorbent regeneration does not necessarily require heating, thereby opening new prospects for the reversible capture of gases using low-cost clay-based adsorbents.

**Keyword:** Silylated montmorillonite, 3-aminopropyltriethoxysilane, chemical grafting, TPD, CO<sub>2</sub> retention.

## 1. INTRODUCTION

A judicious strategy for reversibly capturing and concentrating carbon dioxide (CO<sub>2</sub>) resides in the synthesis of regenerable adsorbents that can act as respiratory systems. The latter should combine high CO<sub>2</sub> retention capacity (**CRC**) with weak retention strength. Optimum interactions with CO<sub>2</sub> would be an essential requirement to achieve high CO<sub>2</sub> uptakes with easy CO<sub>2</sub> desorption without heating [1,2]. Besides, the natural affinity of water towards CO<sub>2</sub> could contribute to these adsorptive properties. This can be partly achieved via the physical insertion of OH-compounds in clay porosity, but this resulted in low specific surface area and efficiency.

To overcome this shortcoming, a growing interest is now devoted to clay-based nanocomposites obtained through chemical grafting of organo-silane moieties [3,4] and to the features of the silylating agents to be grafted [5,6].

Notwithstanding that amine grafting has been intensively studied [7], the use of clay minerals as inorganic supports for preparing CO<sub>2</sub> adsorbents has been scarcely tackled. Attempts to modify montmorillonite under reflux conditions led to the insertion of a single silane molecules within the interlayer space. Ethanol/water mixtures enhance hydrolysis and polymerization of the silane molecules into siloxane bonds [8]. These two processes can occur even before clay pillaring, and lead to the formation of different sizes polymers. Among the latter, only those having appropriate size and configuration can be inserted into the clay interlayer space. At the edges and the structural defects of the montmorillonite layers, the terminal OH groups act as active sites for the silylation of organic moieties.

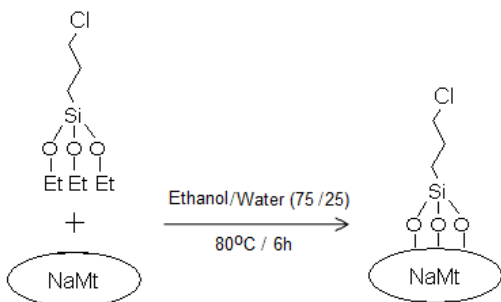
Two objectives were targeted in the present work, namely: *i.* to obtain hydrophilic matrices with high affinity towards CO<sub>2</sub> and easy regeneration without heating; *ii.* to demonstrate that medium strength interactions between the amphoteric character of alcohols and the amine basicity produce higher performances in the reversible capture of CO<sub>2</sub>. For this purpose, polyol-montmorillonite matrices were prepared by incorporating various OH-bearing derivatives via: *i.* a mere electrostatic self-assembly with a clay dispersion in water; *ii.* a chemical grafting of 3-diethanolamino-propyltriethoxysilane (3-diEtOH-APTS).

## 2. EXPERIMENTAL

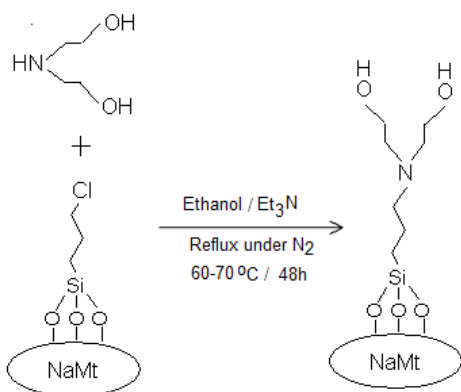
### 2. 1. Organoclay preparation

A commercial bentonite supplied by Aldrich was purified into a montmorillonite-rich material (NaMt) through repetitive settlings under ultrasound exposure, followed by ion-exchange and ozonation. OH-enriched organo-montmorillonites (NaMt-ROH) were prepared via two procedures. The first one involved a mere electrostatic self-assembly between a suspension of NaMt and an OH-compounds dispersion in aqueous media. For this purpose, various OH-compounds ranging from thioalcohols to polyol-amide dendrimers were employed. The second procedure implied a chemical grafting via the silylation of montmorillonite with 3-chloropropyl-triethoxysilane (3-CPTS). Thus, 3g CPTS were dissolved in 1000 mL of a 75:25 Vol. ethanol/water mixture under stirring at 80°C for 1h. The resulting solution was mixed with 10 g of NaMt under stirring, at 80°C for 6h (**Scheme 1**). The resulting

powder (NaMt-CPTS) was prone to chlorine substitution by diethanolamine under reflux at 60-70°C for 48 h (**Scheme 2**). The samples prepared are summarized in **Table 1**.



**Scheme 1.** Montmorillonite silylation



**Scheme 2.** Ethanol-amine grafting on NaMt-CPTS

The chemical grafting of Bis(2-hydroxyethyl)-aminopropyl-triethoxysilane ((2-HOEt)<sub>2</sub>APTS) was investigated through <sup>29</sup>Si-NMR and <sup>29</sup>Al-NMR (Varian Inova MS600 NMR spectrometer, at 119.192 MHz and 12.5 KHz spinning rate).

### 2.3. Adsorption-desorption tests

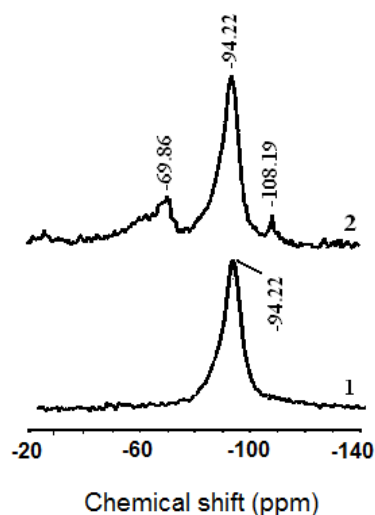
For the as-synthesized org-montmorillonites (particle size of 0.05 - 0.1 mm), the amounts of both desorbed water and CO<sub>2</sub> were assessed via thermal programmed desorption (TPD) between 20 and 200°C, using a Li-840A CO<sub>2</sub>/H<sub>2</sub>O Gas Analyzer. Each sample was dried in the TPD reactor under a nitrogen stream at 80-160°C for 1 hour, cooled down to 20°C, and then impregnated with pure or dry CO<sub>2</sub> as follows: **1.** in dynamic mode (with 0.615 mmol CO<sub>2</sub>.g<sup>-1</sup>) under 15mL.mn<sup>-1</sup> of nitrogen stream for qualitative plotting of the TPD patterns and estimation of the TPD peak; **2.** In static mode without nitrogen stream for accurate assessment of the **CRC** value. After saturation, the non-adsorbed CO<sub>2</sub> excess was evacuated by 1-15 mL.min<sup>-1</sup> of nitrogen stream until no CO<sub>2</sub> was detected. The saturation time was defined as the contact time of the organo-Mt sample at 20°C when impregnated with excess of pure dry CO<sub>2</sub> in static

conditions for 12 h, without nitrogen stream. The purge duration was defined as the time required to remove completely the unadsorbed CO<sub>2</sub> excess at 20°C under nitrogen stream. The **CRC** value was expressed in terms of μmol CO<sub>2</sub> desorbed per gram of dry adsorbent under 1-15 mL.min<sup>-1</sup> of nitrogen stream at a 5°C.min<sup>-1</sup> heating rate between 20°C and 80, 90 or 200°C, depending on the thermal stability limit, as determined by thermal analyses.

## 2. RESULTS AND DISCUSSION

### 3.1. Effect of the chemical grafting

Insights through <sup>29</sup>Si-NMR revealed that the chemical grafting of 3-diEtOH-APTS took place on the silanol groups of the edges of the clay mineral sheets (**Fig. 1**).



**Fig. 1.** Si<sup>29</sup> NMR spectra of 1. NaMt and 2. NaMt-SN(OH)<sub>2</sub>

Prior to silylation, NaMt displayed a single signal at -94.22 ppm (**Pattern 1**), assigned to the silicon in Si-O tetrahedral sheet of montmorillonite Q<sup>3</sup>[Si(OSi)<sub>3</sub>OM] (M stands for Al, Mg etc.) [7]. After grafting, two additional <sup>29</sup>Si signals at -69.86 and -108.19 ppm were attributed respectively to the hydrolyzed tridentate T<sup>3</sup>[Si(OSi)<sub>3</sub>R] (R = CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>NH<sub>2</sub>) and T<sup>4</sup>[Si(OSi)<sub>4</sub>]. This provides clear evidence of the formation of NaMt-O-Si-R bonds, i.e. the chemical grafting of Cl-PTS on the surface of NaMt. In contrast, no additional peak was observed by <sup>29</sup>Al-NMR, indicating that silylation of the aluminol groups of NaMt, if any, should have a minor contribution.

### 3.2. Affinity towards CO<sub>2</sub>

TPD measurements revealed significant changes in the CO<sub>2</sub>-TPD patterns of the prepared NaMt-ROH samples. The general tendency is that the mere presence of polyol-amine in the clay interlayer space induces a significant improvements of both the CRC values and moisture content as compared to the starting NaMt (**Table 1**).

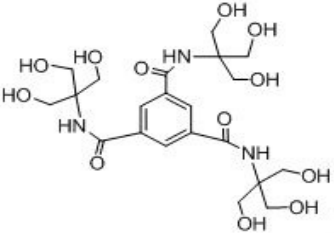
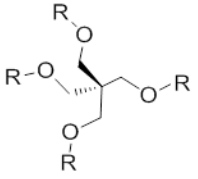
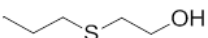
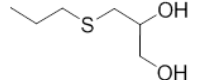
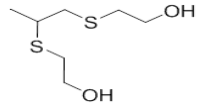
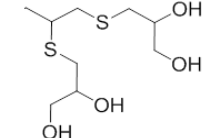
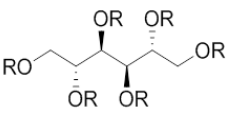
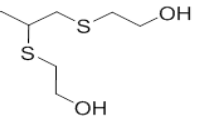
Adsorbent	Incorporated organic moiety	Loading grade (wt %)	CRC		Relative moisture content <sup>b</sup>
			$\mu\text{mol.g}^{-1}$	T(°C) <sup>a</sup>	
NaMt	None	0	8.3 26.8	90 200	1.0 22.1
NaMt-OSiRN(EtOH) <sub>2</sub>	Chemical grafting of (2-HOEt) <sub>2</sub> -APTS	0.3	54.1	80	6,8
NaMt-NHR(OH) <sub>3</sub>	Physical incorporation 	0.1	18.7	200	22.4
		0.2	12.5	200	13.7
		0.3	14.7	200	11.6
		0.5	14.1	200	20.6
		0.8	8.0	200	12.2
		1	10.9	200	15.0
		3	17.8	200	1.7
NaMt-SROH-1-4 	R = 	0.25 1	4.1 4.1	90 90	0.5 0.5
	R = 	0.25 1	6.5 2.4	90 90	0.4 0.5
	R = 	0.25 1	5.8 4.6	90 90	1.22 0.6
	R = 	0.25 1	1.8 1.8	90 90	0.5 0.6
NaMt-SROH-5 	R = 	0.25 1	3.4 8.7	90 90	0.7 0.9

Table 1. CO<sub>2</sub> retention capacity and relative moisture content of the NaMt-ROH samples prepared

<sup>a</sup> Upper temperature limit of the TPD range for assessing the CRC value and the moisture amount.

<sup>b</sup> The relative moisture content is the moisture content of the adsorbent reported to that of NaMt, taken as the reference.

NaMt-OSiRN(OH)<sub>2</sub> was by far the most effective adsorbent, affording CRC value of more than 54  $\mu\text{mol.g}^{-1}$  at desorption temperature not exceeding 80°C. This must be due not only to a high number of accessible OH groups grafted on the Si-OH sites located at the clay sheet edges, but also to the presence of nitrogen atoms in the structure of the grafted organic moiety. This is supposed to shift the polyol amphoteric character towards weak basicity.

### 3.3. Hydrophilic character

In contrast, physical deposition of OH-compounds on the clay surface seems to generate much less accessible OH groups, most likely due to an aggregation of the organic

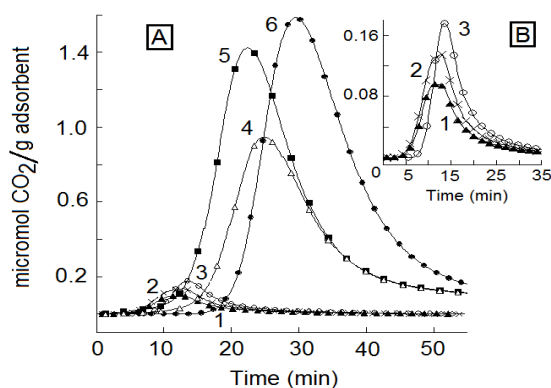
molecules into dense clusters [1,2]. For instance, NaMt-NHR(OH)<sub>3</sub> displayed almost similar CRC and moisture content as the starting material, while montmorillonite supported thio-alcohols (NaMt-SROH) turned out to be quite ineffective. They gave low CRC values of 1.8-8.7  $\mu\text{mol.g}^{-1}$  and lower moisture content as compared to the starting NaMt. This agrees with the fact that the amounts of water and CO<sub>2</sub> retained increase almost proportionally with the number of accessible OH groups of the incorporated organic moiety. This result confirms once again that when accessible, the OH groups display affinity towards both water and CO<sub>2</sub>, and act as adsorption sites.

The mere presence of sulfur atoms in the thio-alcohol dendrimer branches is expected to attenuate the hydrophilic

character of the OH groups. Their incorporation within the NaMt porosity produced the less effective adsorbents (NaMt-SROH) with the lowest CRC and moisture contents. The major part of the adsorbed CO<sub>2</sub> can be released at 20–50°C from dry adsorbents, but at slightly higher temperatures from hydrated matrices. This suggests that water also contributes to the retention of CO<sub>2</sub>.

### 3.3. CRC changes with operating conditions

Care should be taken when assessing the CRC value, because the adsorption-desorption equilibrium was found to be strongly influenced by the operating conditions (Fig. 2).



**Fig. 2.** TPD patterns for NaMt-S-N(OH)<sub>2</sub> between 20 and 80°C at different operating conditions. The latter are summarized for each curve in **Table 2**.

The highest CRC values were obtained with NaMt-OSiRN(EtOH)<sub>2</sub> at low N<sub>2</sub> flow rate (1 mL.min<sup>-1</sup>) during TPD measurements. This condition must prevent from diffusion hindrance, and seems to be an essential requirement for achieving high CRC values regardless to the impregnation mode (**Table 2**). Indeed, the CRC increased significantly from 3.7 to 54 μmol.g<sup>-1</sup> (curve 3 to 6) and from 3.8 to 46.8 μmol.g<sup>-1</sup> (curve 2 to 5) when performing TPD at low N<sub>2</sub> throughput. Even in dynamic conditions, the CRC reached 31.7 μmol.g<sup>-1</sup> (curve 4). However, the total removal of adsorbed CO<sub>2</sub> can be released even at room temperature through forced convection in a gas stream, or under static conditions in dry and CO<sub>2</sub>-free media, e.g. in the presence of KOH pills.

## CONCLUSION

The chemical grafting of 3-diEtOH-APTS produced effective adsorbents for the reversible capture of CO<sub>2</sub>. The latter was found to adsorb at room temperature, and higher amounts were retained in the presence of moisture. This indicates an effective contribution of water to the retention of CO<sub>2</sub>. In dry media, CO<sub>2</sub> can be released without heating under strong nitrogen stream. This causes the CRC to change according to the operating conditions. In these experiments, the chemically modified clay mineral gave the highest CO<sub>2</sub> uptake (54 μmol.g<sup>-1</sup>) at low N<sub>2</sub> flow rate for a specific surface area of only 44 m<sup>2</sup>.g<sup>-1</sup>. The relatively higher affinity of NaMt-OSiRN(OH)<sub>2</sub> towards CO<sub>2</sub> and water must be due to the presence of nitrogen atoms in the polyol structure. The adsorbent regeneration does not necessarily require heating, due to the weak base-like character.

Curve	Saturation conditions		Purge		TPD	
	Impregnation mode	N <sub>2</sub> flow rate (mL.min <sup>-1</sup> )	Duration (hours)	N <sub>2</sub> flow rate (mL.min <sup>-1</sup> ) <sup>d</sup>	N <sub>2</sub> flow rate (mL.min <sup>-1</sup> ) <sup>d</sup>	CRC (μmol/g) <sup>e</sup>
2	Static for 12 hours	0	1	15	15	3.8
3		0	3	1	15	3.7
5		0	1	15	1	46.8
6		0	3	1	1	54.1
1	Dynamic	15	1	15	15	2.3
4		15	1	15	1	31.7

Table 2. Effect of the operating condition on the CO<sub>2</sub> retention capacity (CRC) of NaMt-OSiRN(OH)<sub>2</sub>

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