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Bouhadjar Boukoussa, Aboubakr Hakiki, Nabil Bouazizi, Ana-Paola Beltrao-Nunes, Franck Launay, et al.. Mesoporous silica supported amine and amine-copper complex for CO₂ adsorption: Detailed reaction mechanism of hydrophilic character and CO₂ retention. *Journal of Molecular Structure*, 2019, 1191, pp.175-182. 10.1016/j.molstruc.2019.04.035 . hal-02164445

HAL Id: hal-02164445

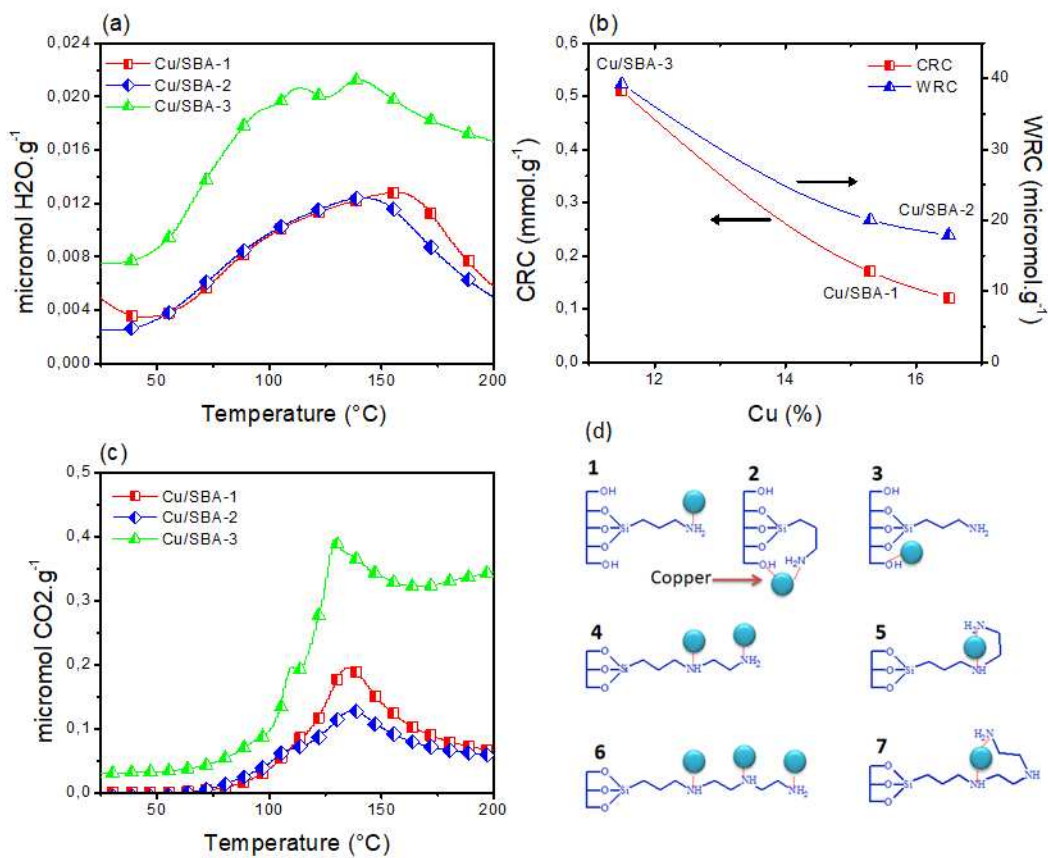
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Submitted on 6 Sep 2019

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Graphical abstract



Mesoporous silica supported amine and amine-copper complex for CO₂ adsorption: Detailed reaction mechanism of hydrophilic character and CO₂ retention

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Abstract

The mesoporous silica SBA-15 functionalized with various amines was prepared and then doped with copper (Cu^{++}). The modified materials were tested for the retention of CO_2 at room temperature using temperature-programmed desorption (CO_2 -TPD). Several parameters affecting the CO_2 retention capacity (CRC) were investigated such as effect of the nature of amine groups, repetitive adsorption-desorption cycles and dispersion of copper. CO_2 -TPD and H_2O -TPD were employed in order to correlate the hydrophilic character with the CO_2 retention capacity. The obtained results showed that amines-functionalized mesoporous materials containing their own moisture have good results towards the retention of CO_2 . Especially the triamine-functionalized SBA-15 has the greatest CRC value which results in the increase of the number of adsorption sites. The reuse of these solids in three adsorption/desorption cycles showed higher stability with a slight decrease in CRC. The dispersion of copper showed a progressive decrease in the CRC value. The correlation between the Cu% and the CRC shows that the value of the CRC decreases with increasing Cu% due to complexation of the adsorption sites (amines) by acid sites (copper).

Keywords : Mesoporous silica, Amine functionalized SBA-15, Temperature-programmed desorption, Carbon dioxide, Hydrophilic character.

1. Introduction:

Since the industrial revolution, the concentration of CO_2 in the atmosphere has been significantly increased leading thereafter to the increase of the average temperature of our planet. This rapid warming is due to the acceleration of the greenhouse effect which regulates the temperature on earth. This is linked to human activities causing significant CO_2 emissions. For the elimination of greenhouse gases, much attention has been paid to improving the activity of adsorbents for the capture of CO_2

particularly at lower temperatures [1-6]. Adsorption is the most suitable solution for the treatment of low levels of CO₂ concentration at low temperatures. To date, great efforts were made to obtain new materials that can improve the adsorption processes. In order to obtain a high affinity and adsorption capacity of CO₂, several materials have been tested such as clays [1-4], zeolites [7-10], mesoporous silicas [5, 11-13], activated carbon [14,15], polymers [16-18], MOFs [19,20], aerogels [21]...

Among the materials suitable for adsorption of CO₂, there are mesoporous silicas (such as SBA-15, MCM-48 and MCM-41) which have interesting physico-chemical properties [5, 11, 22-28]. They are useful for a large number of applications mainly due to their high surface areas and large pore sizes. Their surfaces containing silanol groups are the key factors of these ranges of materials; it is easily possible to functionalize them by different organic molecules to improve their performance through the CO₂ adsorption. The interactions between carbon dioxide and the surface of the materials differ according to the nature of the functionalized molecules or immobilized metals on the surface of the materials [28-32].

In our previously published work we have shown that the dispersion of OH-rich molecules (such as glycerol, polyol ...) have physical interactions towards carbon dioxide leading thereafter to the low CO₂ retention capacity (CRC) [1-4]. Among the advantages of these materials, the adsorption/desorption process takes place at low temperatures (reversible capture of CO₂) [1-4]. The presence of water molecules (material containing its own moisture) on the surface is a very important parameter that contributes significantly to the retention of CO₂ [1-4]. It should also be noted that the CO₂ retention capacity is related to the OH group's content, their number and the hydrophilic nature of the modified material [1-4].

Ouargli-Saker et al showed that the modification of the surface of the mesoporous silica by metals-NPs (such as Cu, Fe and Pd) can modify the adsorption behavior of CO₂ [28]. Significant CRC values were obtained due to different interactions between CO₂ and metals-NPs giving the formation of carbonate or carbonate associated with metals-NPs. However, no reproducibility was observed during the repetitive adsorption-desorption cycles leading subsequently to a decrease in CRC value due to the presence of chemical processes between the metals-NPs and surface of mesoporous silica. The same remarks were observed during the dispersion of conductive polymer polyaniline on the surface of the SBA-15 [11].

In recent years, amine-functionalized materials have attracted considerable interest, especially in the capture of carbon dioxide [30-32]. These hybrid materials are capable to adsorb the CO₂ at lower pressure [30-32]; they exhibit high selectivity and affinity towards carbon dioxide [30-32]. The adsorption kinetics for these kinds of materials is fast, their energy costs are quite low and their adsorption behaviors in the presence of moisture are efficient [33]. Generally, the interactions between amine-functionalized materials and carbon dioxide were described by chemisorption mechanism. In dry conditions, the amines react with CO₂ to form carbamate, while in the presence of moisture leads to the formation of hydrogen carbonates [34].

By examining the literature, it is found that very few studies have been published on CO₂ adsorption assisted by TPD analysis. Based on this technique, several questions can be answered such as: (1) the adsorption and desorption behavior of CO₂ in dry and wet conditions, (2) determination of the number of adsorption sites and their strengths, (3) effect of hydration and dehydration on CRC, (4) effect of anchoring a transition metal on CRC, (5) effect of repetitive cycles on CRC and hydrophilic character

The main objective of this work is to study the adsorption of CO₂ on the mesoporous silica SBA-15 functionalized by mono-, di- and tri-amines and their counterparts anchored by copper. The adsorption behavior of CO₂ was investigated by temperature-programmed desorption, which is an effective method to characterize surface of amine-functionalized material providing important information on the surface chemistry. The CO₂ retention capacity (CRC) and the hydrophilic character of the modified mesoporous materials were determined by CO₂-and H₂O-TPD, respectively. The affinity towards CO₂ and the retention force of CO₂ were discussed in terms of the distribution of CO₂ and desorption heat respectively.

2. Experimental

2.1. Preparation of adsorbents

The mesoporous silica SBA-15 was prepared hydrothermally using TEOS as a silica source, P123 as a structuring agent. The preparation method was well described in our previously published work [5, 11, 25, 27]. The calcined mesoporous silica SBA-15 has been functionalized by different aminosilanes according to the method described in the literature [5, 27]. Briefly 0.6 g of SBA-15 was dispersed in a solution containing 150 ml of toluene and 3 g of aminosilane, the mixture was refluxed at 60 °C for 24 hours. The final product was filtered washed with toluene and ethanol and then dried at 60 °C overnight. The aminosilanes used in this study are (3-Aminopropyl) triethoxysilane, N-(3-trimethoxysilylpropyl) ethylenediamine and N-(3-trimethoxysilylpropyl) diethylenetriamine and the solids obtained were named SBA-1, SBA-2 and SBA-3 respectively. While the unmodified parent material SBA-15 was named SBA-0.

According to the literature, the functionalized materials were treated in a 100 mL of solution containing $\text{Cu}(\text{NO}_3)_2$ (1M) [5]. The mixture was stirred at room temperature for 2h. The obtained products were filtered several times washed with distilled water and dried at 60 °C overnight. The obtained samples were named according to the nature of the functionalized materials used as Cu/SBA-1, Cu/SBA-2 and Cu/SBA-3.

2.2. Samples characterization

The XRD powder diffraction of functionalized and doped samples were analyzed by Bruker AXS D-8 diffractometer with Cu-K α radiation ($\lambda=1.5418 \text{ \AA}$) in the 2θ range of 0.5–4° and 5–50°. The FTIR spectra of obtained samples were collected on a BRUKER ALPHA Platinum-ATR in the range of 500–4000 cm^{-1} . SEM images for copper containing amine-functionalized materials were observed by (FESEM), Ultra 55 Zeiss and equipped by EDX Brucker Quantax model.

2.3. Temperature-programmed desorption (CO_2 - and H_2O -TPD)

The CO_2 retention capacity (CRC) and hydrophilic character were determined by thermal programmed desorption of CO_2 and water (CO_2 -TPD and H_2O -TPD). Approximately 20–50 mg of adsorbent was introduced in a tubular glass reactor made (2mm internal diameter) and a dry nitrogen flow rate (5 mL min^{-1}) was triggered. The quantities of water and adsorbed CO_2 were measured using a Li-840A unit $\text{CO}_2/\text{H}_2\text{O}$ gas analyzer. The measurement of CO_2 by TPD gives three kinds of data: (1) the number of adsorption sites were determined by the CO_2 retention capacity (CRC); (2) the distribution of sites were determined by peak area ratios; (3) the adsorption site strengths were determined by the temperature of the desorption peak. The evaluation of the CRC value was taken after a static saturation mode, the evacuation of the

excess of CO₂ not adsorbed was conducted by a flow of nitrogen of 15 ml min⁻¹. The TPD measurements were made between 200 °C for the modified materials and 550 °C for the SBA-15 (parent material) at a heating rate of 5 °C min⁻¹ and a nitrogen flow rate of 15 ml min⁻¹ (mode dynamic).

3. Results and discussion

3.1. Materials Characterization

3.1.1. Structural properties

The XRD patterns recorded between $2\theta = 0.5-4^\circ$ of SBA-15 (parent material), amine-functionalized-SBA-15 and their counterparts modified by copper are shown in figure 1S. As shown in figure 1S the XRD patterns are typical of 2D hexagonal (p6mm) phase. A very intense peak associated with two peaks of lower intensity were obtained which are attributed to the three diffraction peaks of the (100), (110) and (200) planes. These indexed planes are detectable on the XRD patterns of all the functionalized materials, which indicate a good organization of structure. However, for the case of the materials doped with copper there was the disappearance of some peaks may be due to the filling and recovery of the surface by copper. We also note that there was the displacement of peak (100) at low angles for all amine-functionalized materials. This confirms that the amine groups were well functionalized in the inner surface of the SBA-15 leading subsequently inflating the lattice parameter a_0 (see Table 1). While for the doped materials, the lattice parameter is substantially unchanged. The XRD diffraction patterns at high angles ($5 \leq 2\theta \leq 50$) for copper-modified materials were investigated in order to determine the nature of the copper in the support. According to the figure 2S, we note that there was the formation of new peaks

suggesting the formation of different forms of amine-copper complex, which are different compared to the salt $\text{Cu}(\text{NO}_3)_2$.

3.1.2. FTIR spectra

Figure 1 shows the infrared spectra of SBA-15 and its modified counterparts. All materials with or without modification have several characteristic absorption bands corresponding to the mesoporous silica materials [11, 25]. A broad symmetrical absorption band at 3400 cm^{-1} is attributed to isolated silanol groups, this band is present in all samples, and it increases during the modification of the surface by the amine-copper complexes. The only explanation related in the hydration potential of these copper-containing mesoporous materials with the water molecules. The shoulder at 3600 cm^{-1} is attributed to the hydrogen bonds of the Si-OH hydroxyl groups with the O-Si groups of the silica walls (Si-OHO-Si). A wide band in the range $3680\text{--}3000\text{ cm}^{-1}$ corresponds to the elongation vibrations of the OH groups of the physisorbed water. The vibration band of the terminal OH groups attached to a silicon atom is located at 3500 cm^{-1} [35]. Mesoporous silica also exhibits asymmetric and symmetrical elongation vibrations of Si-O-Si at $1200\text{--}1070\text{ cm}^{-1}$ and 800 cm^{-1} , respectively. The band at 500 cm^{-1} is attributed to Si-O stretching vibrations and the band at 561 cm^{-1} is a criterion for the formation of an ordered network [36].

New weak bands were obtained at $1500\text{--}2000\text{ cm}^{-1}$ for all materials containing amines or amine-copper complex which are assigned to C-H bands containing in aminosilanes. The band located at $1645\text{--}1622\text{ cm}^{-1}$ is attributed to deformations vibrations of physisorbed water, nitrate species can overlap with this bands and also with Si-O-Si groups at $900\text{--}1000\text{ cm}^{-1}$ [37-40]. The modified materials have weak bands between $2933\text{--}2809\text{ cm}^{-1}$ due to elongation bands of $-\text{CH}_3$ and $-\text{CH}_2$ containing in aminosilanes. The bands at 3544 and 1514 cm^{-1} corresponds to the NH vibration

overlapped by a wide band of adsorbed water. All bands of materials containing amine-copper complex were displaced from their starting materials (functionalized materials), confirming that the copper was complexed by amines. According to the vibration modes of Cu/SBA-1, Cu/SBA-2 and Cu/SBA-3 it is found that these samples have different bands compared to the salt $\text{Cu}(\text{NO}_3)_2$, confirming that the copper species Cu^{++} have been complexed by the amine groups and not deposited in the form of salt. These results are in agreement with those obtained by the XRD analysis.

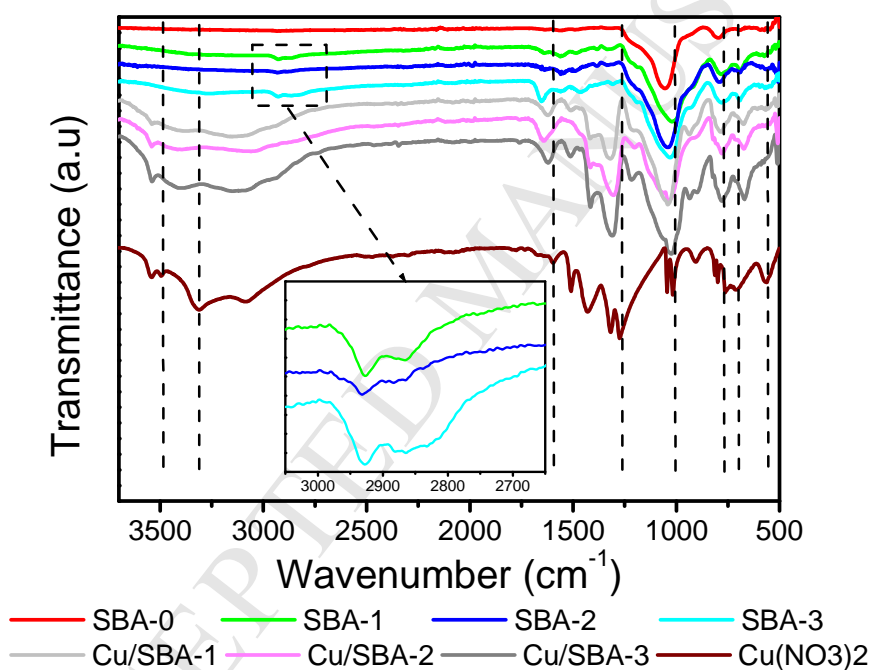


Figure.1. FTIR spectra of SBA-15 and its modified counterparts

3.1.3. SEM images

The morphology of SBA-15 containing amine-copper complex was observed by scanning electron microscopy (SEM). Figure 2 shows the SEM images of Cu/SBA-1, Cu/SBA-2 and Cu/SBA-3. All samples have the same morphology in the form of elongated aggregates of average 600 nm. At a high magnification the morphology of

the primary particles which constitute these aggregates have a rod shape. This also confirms that the morphology of SBA-15 was modified after treatment with amines and copper (case of Cu/SBA-1 and Cu/SBA-2), while the morphology of Cu/SBA-3 is almost similar to the pure mesoporous silica SBA-15. This is probably due to the higher percentage of copper containing Cu/SBA-1 and Cu/SBA-2, the filling of the inner surface with an excess of copper leads essentially to the formation of copper clusters in the outer surface, whereas the lower percentage of copper leads only to dispersion in the inner surface (case of Cu/SBA-3).

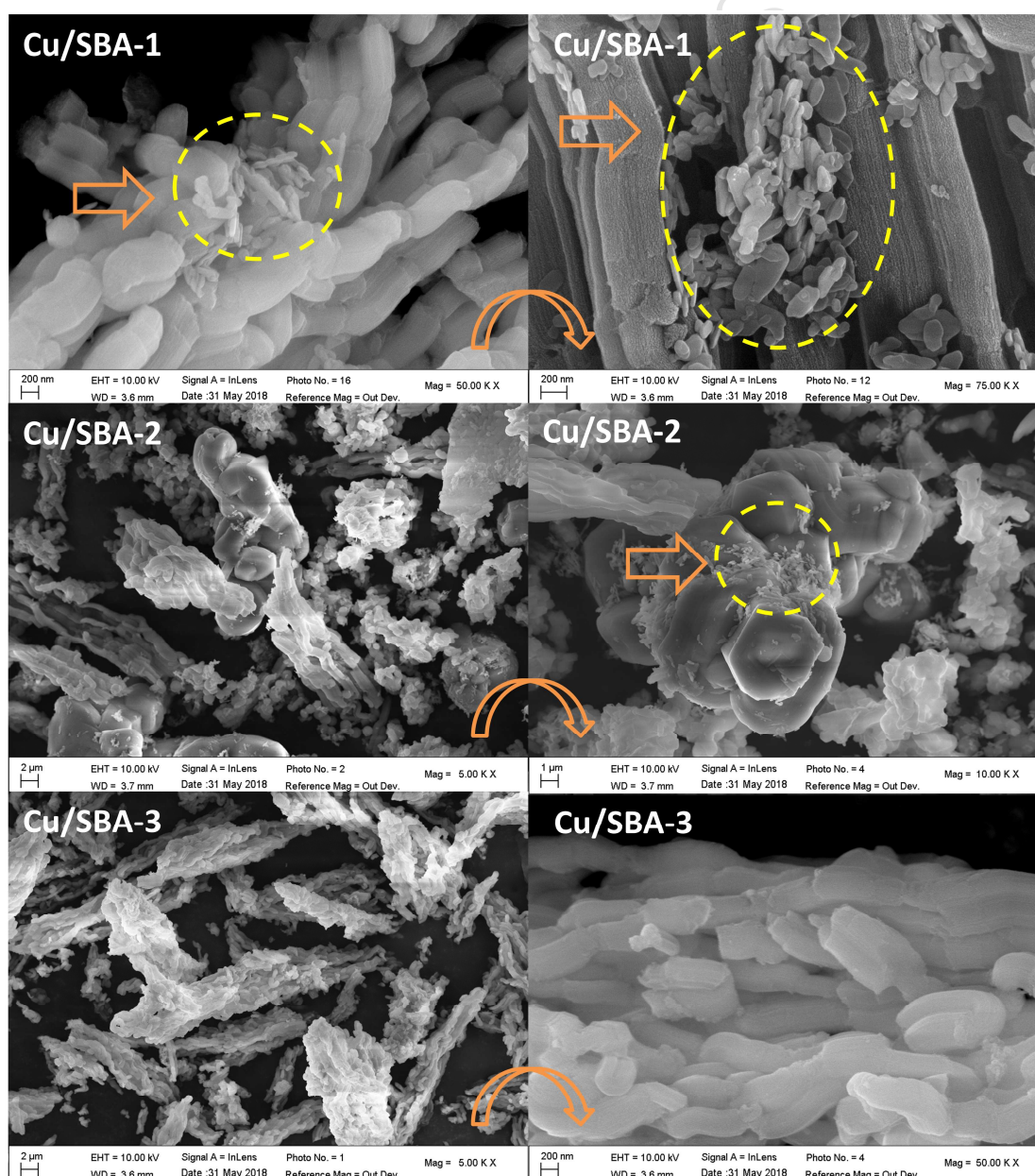


Figure.2. SEM images of Cu/SBA-1, Cu/SBA-2 and Cu/SBA-3.

3.1.4. EDX analysis

The EDX spectra of Cu/SBA-1, Cu/SBA-2 and Cu/SBA-3 are shown in figure 3S. This figure clearly shows that these solids are mainly constituted by silicon and oxygen, which are the principal constituents of the mesoporous silica SBA-15, while the carbon and nitrogen are the main constituents of aminosilanes. In all samples we note the presence of copper with different percentages; this confirms that the copper has been well dispersed on the surface of these materials. The percentages of copper determined by EDX analysis are shown in the blue histogram. In all cases the Cu/SBA-2 sample has the highest copper percentage in which increases in the following sequence Cu/SBA-3 < Cu/SBA-1 < Cu/SBA-2. We find that the diamine-containing SBA-15 (Cu/SBA-2) has a very good affinity for Cu⁺⁺ compared to the mono-amine. This is due to the presence of several amine sites that can attract Cu⁺⁺ species. However, a strong decrease in percentage of copper was obtained by the triamine-containing SBA-15; this is probably linked to the blocking of the pores by a large molecule (N-(3-trimethoxysilylpropyl) diethylenetriamine) leading subsequently a weak diffusion of Cu⁺⁺ species within the pores of the SBA-15.

3.2. CO₂ adsorption–desorption tests

3.2.1. Correlation between hydrophilic character and CO₂ retention capacity (CRC)

The CO₂- and H₂O-TPD profiles of parent material (SBA-0) and its amine-modified counterparts are shown in the figure 3. The H₂O-TPD profile of SBA-0 shows an intense peak centered at 150 °C due to the dehydration of physically adsorbed water (figure 3a). In this case, the possible explanation arises from hydrogen and/or van der waals interactions between the silanol groups and the water molecules. After the

functionalization of the mesoporous silica by aminosilanes (figure 3 b-d) the H₂O-TPD profiles were improved compared to the parent material (SBA-0). These profiles indicate the presence of two peaks confirming the existence of two different hydrophilic sites. The peaks located at low temperatures are due to several interactions between the water molecules and non-functionalized silanol groups. While the peaks located at higher temperatures are due to the interactions between water molecules and amines-containing mesoporous silica. In all cases, the functionalization of the amines induces a significant improvement in the hydrophilic character expressed in terms of the amount of water desorbed thermally, more particularly for the sample containing triamine (SBA-3) suggesting that the sample containing more amine groups provides multiple interactions with water molecules. The water retention capacity (WRC) increases in the following sequence SBA-0 < SBA-1 < SBA-2 < SBA-3 (see figure 4).

As shown in the CO₂-TPD profile, the mesoporous silica SBA-0 exhibits an intrinsic affinity towards carbon dioxide before functionalization with aminosilanes (figure 3a). The CO₂-TPD profile of SBA-0 showed the existence of different peaks, the weak, medium and strong peaks located at 100 °C, 180 °C 320-500 °C respectively, which arise from the interaction of CO₂ with free silanol, water molecules and the oxygen of the framework. The CO₂-TPD profiles of amine-functionalized materials showed higher intensities compared to the parent material SBA-0 (figure 3 b-d). All these materials have a similar CO₂-TPD profile (figure 3 b, c and d). The general trend is that CO₂ desorption even starts at 50-60 °C, and that all CO₂ is desorbed at 160 °C. The nature of aminosilane used has a positive effect on the adsorbed amount of CO₂. The intensity of desorption peak increases with the increasing the number of nitrogen containing each aminosilane leading subsequently to the increase in the

number of accessible adsorption sites. Preliminary remarks indicated that higher CRC values were obtained with triamine-functionalized mesoporous silica SBA-3. This sequence corresponds to the higher number of adsorption sites compared to the other materials, and also to the higher water content that contributes to a significant way for retention of CO₂ (figure 4).

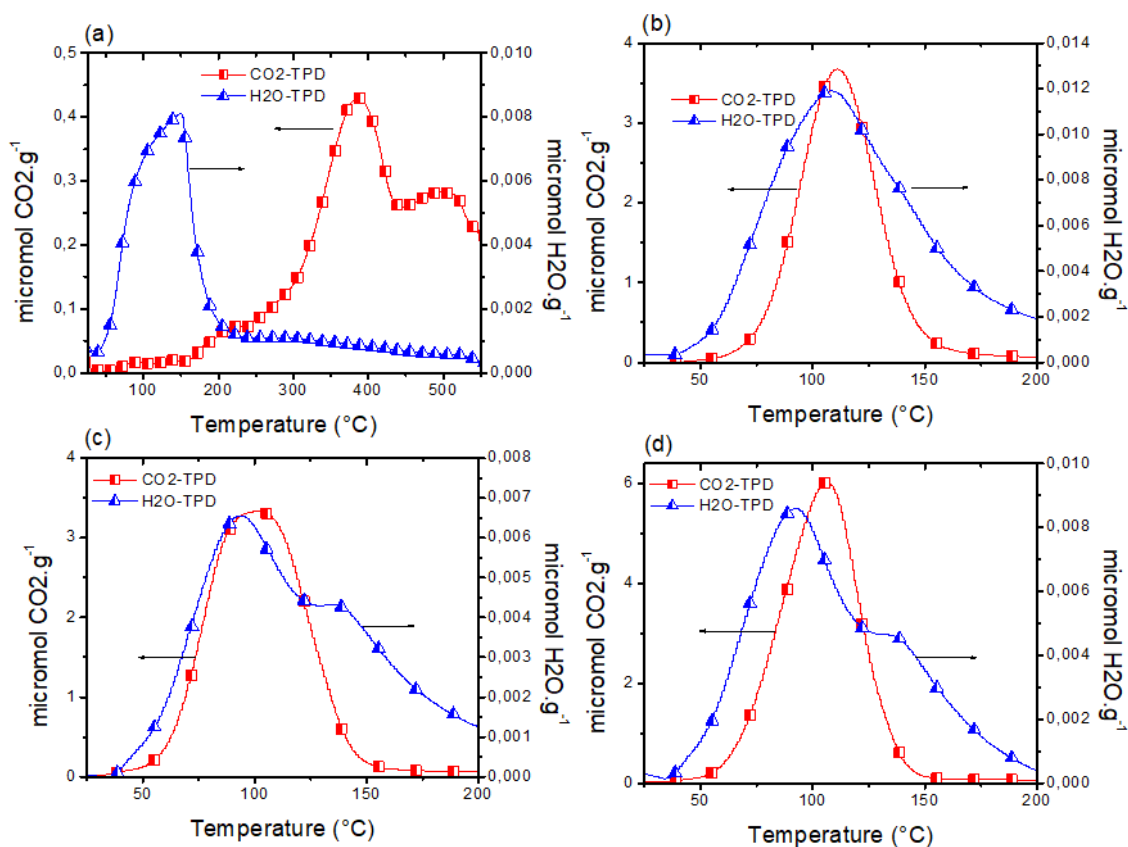


Figure 3. CO₂- and H₂O-TPD profiles of parent material SBA-0 and its amine-modified counterparts, a) SBA-0, b) SBA-1, c) SBA-2 and d) SBA-3.

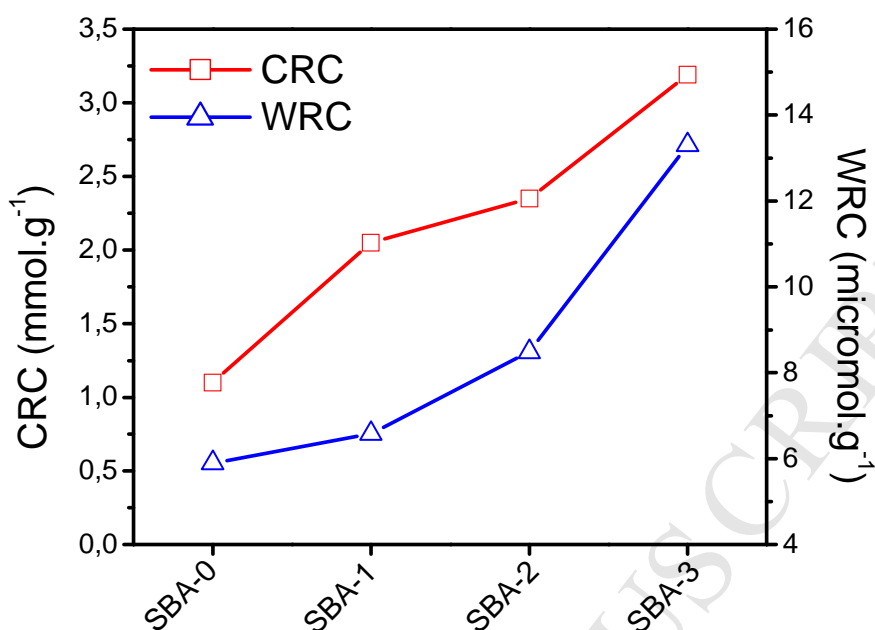


Figure.4. Correlation between the hydrophilic character and CO₂ retention capacity (CRC)

3.2.2. Effect of repetitive adsorption-desorption cycles

CO₂-TPD profiles of repetitive adsorption-desorption cycles of SBA-0 and its amine-modified counterparts are shown in figure 5. It is clearly indicated that the intensity of the CO₂-TPD profile for the parent material (SBA-0) was decreased progressively after the third cycle (figure 5 a), which is strongly related to the progressive decrease of the adsorption sites after water dehydration process; this confirms the contribution of water molecules in the retention of CO₂. The CO₂-TPD profiles of amine-functionalized materials showed higher stability during the third cycle with a slight decrease in the intensity of each sample (figure 5 b, c and d) which subsequently led to a slight decrease in the value of CRC (figure 4S). This is probably due to the elimination of water molecules that contribute slightly to CO₂ retention. It is clearly indicated that after the third adsorption-desorption cycle the peaks of the CO₂-TPD profiles were shifted to the highest temperatures. This is conclusive evidence which

confirms that the hydrogen carbonates formed in wet conditions easily release CO₂ at low temperatures, while carbamates obtained through interactions between amines and CO₂ in dry conditions release CO₂ at higher temperatures.

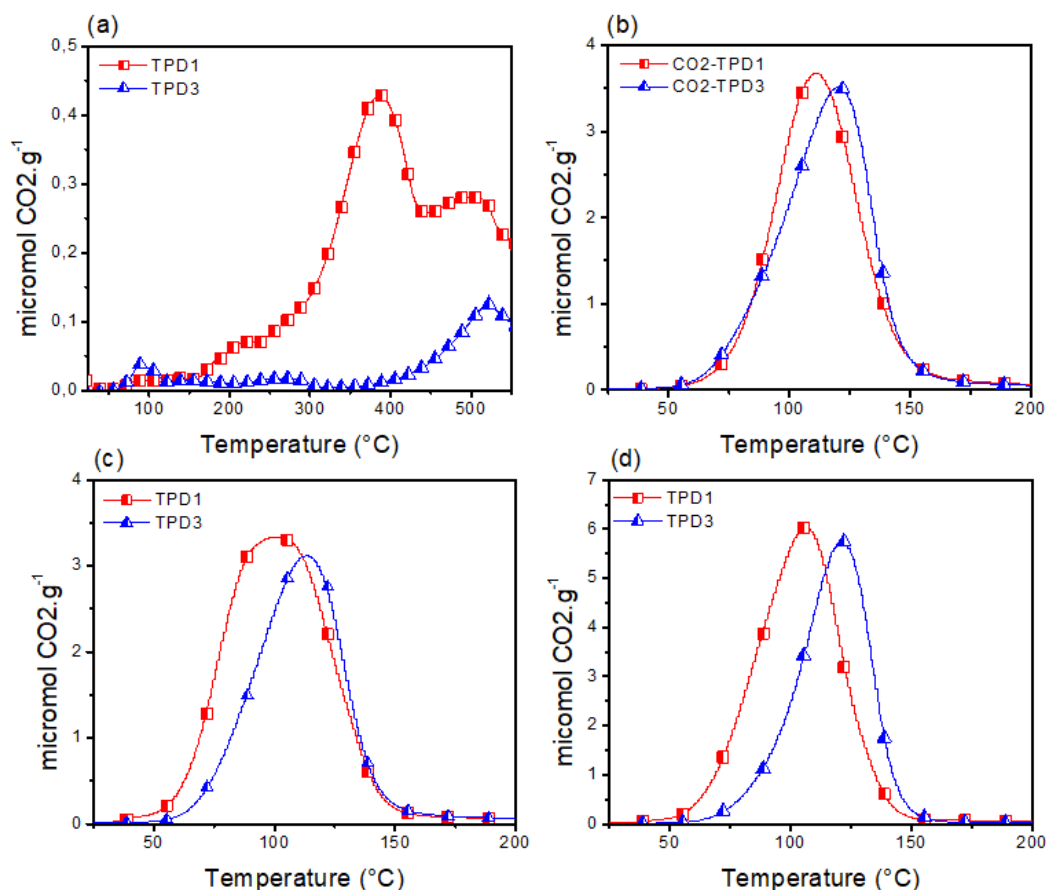


Figure.5. CO₂- and H₂O-TPD profiles of SBA-0, SBA-1, SBA-2 and SBA-3 obtained after the third adsorption-desorption cycles, a) SBA-0, b) SBA-1, c) SBA-2 and d) SBA-3.

3.2.3. Effect of copper anchoring on CRC and WRC

The H₂O-TPD profiles of different materials doped with copper are shown in figure 6a. The H₂O-TPD profiles and their intensities are different compared to undoped materials, confirming that the mechanism of water adsorption is different compared to the amine-functionalized-materials. This affinity via the water molecules is probably related to the hydration potential of the copper species. The Cu/SBA-3 material

exhibits the most intense profile that corresponds to the higher WRC value (figure 6b). The water retention capacity (WRC) increases in the following order Cu/SBA-2 < Cu/SBA-1 < Cu/SBA-3. This coincides with the percentage of copper; the low percentage of Cu generates a higher value of WRC. The only explanation resides in the formation of copper aggregates for materials containing a higher percentage of Cu which limits the diffusion of water molecules in the inner surface. These results are consistent with scanning electron microscopy analysis.

The intensity of the CO₂-TPD profiles was gradually decreased after the doping of amine-functionalized mesoporous silica by copper (figure 6c). The CO₂ desorption starts at 80 °C confirming that the interaction between the materials and the CO₂ molecules follows a different mechanism compared to undoped materials. This decrease in intensity and CRC is related to the saturation of the adsorption sites by Cu⁺⁺, which is considered as acidic sites. The coordination of Cu⁺⁺ with amines-functionalized SBA-15 occurs by several interactions between Cu⁺⁺, amines or non-functionalized silanol groups Si-OH [41].

It is noted that the CRC value increases with decreasing acid sites (the percentage of copper). For these materials the hydrophilic character plays a very important role in the retention of CO₂ because the most important value of CRC was obtained by the Cu/SBA-3 material which exhibits great hydrophilicity (higher value of WRC) (figure 6b).

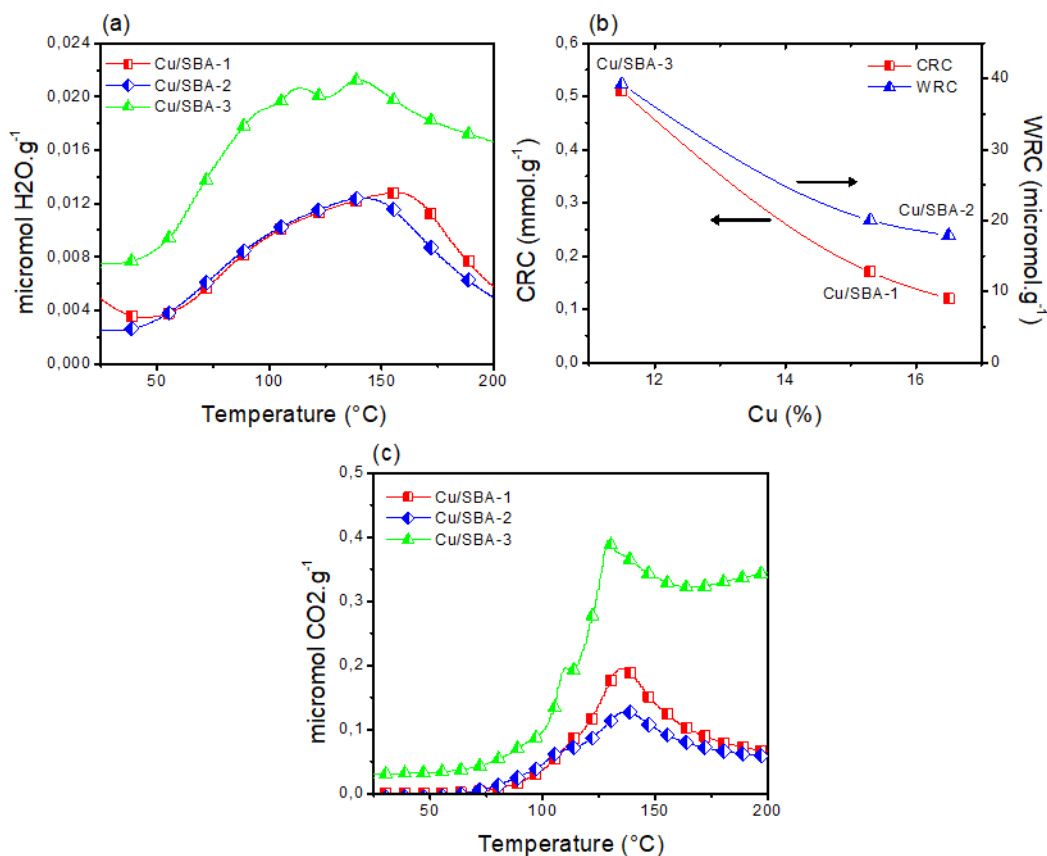


Figure.6. (a) H₂O-TPD profiles of materials doped by copper, (b) Correlation between percentage of copper, CRC and WRC, (c) CO₂-TPD profiles of materials doped by copper and (d) mechanism of interaction between amines-functionalized SBA-15 and copper.

2.3.4. Comparative study:

Table 1 shows a comparative study between different materials via the CO₂ retention capacity obtained by the same conditions using Temperature-programmed desorption. As shown in the table 1, the structure of the mesoporous silica and the nature of the dispersed zero-charge metal significantly affect the CRC value. High capacities were obtained during the first use MNPs-containing SBA-15 or SBA-15 [28]. The possible explanation resides in the formation of carbonates and/or carbonate associations with the metal nanoparticles, and also some traces of metal oxides and oxygen atoms of the surrounding network can contribute to the retention of CO₂. However, a sharp

decrease in CRC was recorded during the third adsorption-desorption cycle due to the presence of chemical processes between the MNPs and the surface of mesoporous silica [28]. The use of modified clays showed low CRC values, probably due to their lower surfaces compared to mesoporous materials [42]. The nanocomposite Pani/SBA-15(30) showed a low CRC value compared to the amine-functionalized SBA-15 [11]. The reaction of CO₂ with tertiary amines such as polyaniline occurs with a lower reactivity to CO₂ compared to primary and secondary amines. In all the cases studied, the amine functionalized SBA-15 showed the highest values of CRC even after reuse, confirming their stability during CO₂ adsorption-desorption cycles.

Table1. Comparison of CO₂ retention capacities (CRC) on different adsorbents

Samples	Adsorption method	CRC₁ (mmol.g⁻¹)	CRC₃ (mmol.g⁻¹)	References
Fe-SBA16	TPD	2.88	0.57	[28]
Fe-SBA15	TPD	2.38	0.67	[28]
Pd-SBA16	TPD	2.04	0.71	[28]
Pd-SBA15	TPD	2.00	2.36	[28]
Cu-SBA16	TPD	2.54	0.44	[28]
Cu-SBA15	TPD	3.24	0.51	[28]
NaMt	TPD	0.19	//	[42]
NaMt-Pd	TPD	0.24	//	[42]
NaMt-Fe	TPD	0.36	//	[42]
NaMt-Cu	TPD	0.31	//	[42]
Acid-bentonite	TPD	0.26	//	[43]
Pani/SBA-15(30%)	TPD	0.22	0.03	[11]
SBA-1	TPD	2.05	1.95	This work

SBA-2	TPD	2.35	2.06	This work
SBA-3	TPD	3.19	3.04	This work
Cu/SBA-1	TPD	0.51	//	This work
Cu/SBA-2	TPD	0.17	//	This work
Cu/SBA-3	TPD	0.12	//	This work

Conclusions

The mesoporous silica SBA-15 functionalized by mono, di and tri-amines was well prepared and then modified by copper. The XRD analysis showed the inflation structure of SBA-15 after functionalization by aminosilanes. The modification of amines-functionalized SBA-15 by copper species showed the appearance of a new phase probably due to the formation of an amine-copper complex. The SEM images showed a typical SBA-15 morphology with another phase corresponding to the copper species. The EDX analysis of the copper-doped samples showed that the percentage of copper increases according to the following sequence Cu/SBA-2 > Cu/SBA-1 > Cu/SBA-3. The Cu/SBA-3 sample showed the lowest amount of copper probably due to pore blockage by the large aminosilane molecules. The application of SBA-15 functionalized by mono-, di- and tri-amine in the CO₂ retention showed interesting results. The best CO₂ retention capacity (CRC) was obtained by the material containing more amine sites (tri-amine) in the wet state. The application of materials containing their own moisture showed the highest values of CRC compared to dehydrated materials suggesting the participation of water molecules in CO₂ retention. The CO₂ has been easily released in humid conditions. While in the dry state the release of CO₂ requires higher temperatures. The repetitive CO₂ adsorption-desorption cycles of amine-functionalized SBA-15 have shown a good stability with a

slight decrease in CRC during the third cycle. The anchoring of copper on these materials have shown a progressive decrease of the CRC compared to the undoped samples due to the fixation of the acidic sites, and the CRC value increases with decreasing the percentage of copper (decrease of number of acid sites). These results are of great interest because it is possible to prepare bi-functional materials containing acid-base sites and their proportions can be easily modified by dispersing of some percentages of copper.

Compliance with ethical standards

Conflict of interest: The authors declare that they have no conflict of interest.

Acknowledgement

This work was supported by grants from MDEIE-FQRNT (2011-GZ-138312) and FODAR-UQ-2015 (QC. Canada) to A.A and R.R

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Highlight

- Mesoporous silica SBA-15 was functionalized with various amines then doped with copper.
- New functional SBA-15 high CO₂ retention capacity.
- The effect of amines nature on CO₂ adsorptions were investigated
- Mesoporous silica provided a good reusability