MESOPOROUS SILICA MODIFIED WITH AMINE BY DOUBLE FUNCTIONALIZATION FOR CO₂ CAPTURE

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ABSTRACT: CO₂ adsorption on mesoporous silica modified with amine by double functionalization was studied. Microcalorimetry was used in order to investigate the influence on energetic sites and adsorption kinetic when amine density is increased by impregnation from previous grafted material. A microcalorimeter coupled to a manometric setup was used to evaluate the energy distribution of adsorption sites and calculate thermokinetic parameters from the differential enthalpy curves. CO₂ and N₂ adsorption equilibrium at 50 and 75 °C was measured using a magnetic suspension balance. Thus it was studied the impact of temperature increasing on adsorption capacity of the double functionalized material simulating post combustion conditions. The adsorption calorimetric study suggests a change in active sites distribution maybe complete ammonium carbamate formation as the amine density increases on MSG20I30 sample. Maximum thermokinetic parameter suggests that CO₂ diffusion resistance on the PEI impregnated sample is the kinetic limitation for MSG20I30.

KEYWORDS: silica; calorimetry; CO₂ adsorption; double functionalization.

1. INTRODUCTION

The emission of greenhouse gases distress governments, researchers and the population around the world because of their possible effects on the planet climate change. On November 2017 was held the COP23, in Germany, where were discussed strategies to reach the goals of the global action plan to combat global warming, keeping the increase of the world temperature below 2° Celsius degrees (COP23, 2017).

At this scenario, as large sources of greenhouse gases (GHG) are the burning of fossil fuels arising mainly from the energy production, industrial and transportation sectors (Waycarbon, 2017). Thus, preventive and remedial methods to deal with those emissions are been researched, among which stand out absorption, cryogenic and adsorption processes.

In this way, it is emphasized the research for more selective and efficient adsorbents, as in the case of porous supports functionalized with organic molecules that contains amino groups. Sanz et al (2013a) reported a sample that presents molar adsorption ratio of mol CO₂/ mol N up to 0.48, presenting a high efficiency of the incorporated amino groups for CO₂ adsorption, and showed as advantages the reduction of the toxic and corrosive potential, more stability in vacuum and temperature which leaves the regeneration process easier.

Among the processes utilized to incorporate organic molecules that contain amino groups on mesoporous silica supports are the grafting and the impregnation. The efficiency of the first one is related to the amount of OH surface groups and the amount of nitrogen that is actually placed in the structure, which, achieve lower values of nitrogen incorporated in the sample than on the impregnation process, however, this organic molecules are easily reachable by de CO₂ (Vilarrasa et al. 2014b). In the second method, the organic incorporation is higher. However these molecules are inside the narrow
pores of the samples. Due to the diffusional limitation, the amine groups are less reachable and they end up presenting lower molar ratio of CO$_2$/N impregnated (Sanz et al. 2013b).

Sanz et al. 2013a conducted researches combining both techniques, synthesizing grafted and impregnated samples which proved to be a promising study presenting, for a sample with a molar ratio CO$_2$/N of 0.45, adsorption capacities of 215mg of CO$_2$/g of sample, nearly 4.88 mmol of CO$_2$/g.

Thus, the goal of this study is to analyze the change of energy site distribution and kinetic mechanism by adsorption microcalorimetry of a mesoporous silica previously grafted with (3-Aminopropyl) triethoxysilane (APTES) and then impregnated with polyethyleneimine (PEI). The double functionalized sample will be study by gravimetric method (magnetic suspension balance) at temperatures close to post combustion scenario in order to know the improving of adsorption capacity at these conditions.

2. MATERIALS AND METHODS

2.1. Materials

For the impregnation was used a silica previously grafted with APTES named as MSG20, as well as water, methanol and molecular weight (800 MW) branched-polyethyleneimine (PEI) 50% m/v in water purchased from (Fluka Analytical, Switzerland). N$_2$, He (purity: 99.999 %) and CO$_2$ (purity: 99.98 %) were supplied by White Martins Praxair.

2.2. Methods

Impregnation

MSG20 was used as bulk material. It was followed the wet impregnation method used by Xu et al, 2002. Then 0.40 g of PEI were stirred with 3.6 g of methanol for about 15 min. After that 0.45 g of MSG20 were added to the solution. It was maintained a proportion of 8 g of methanol per gram of MSG20.

The resultant slurry was continuously stirred for about 30 min and the solid was dried at room temperature overnight.

The as-prepared adsorbent was denoted as MSG20I30, where 30 represent the loading of PEI as weight percentage of the sample.

Chemical and textural characterization

The chemical composition of the samples or elemental analysis of carbon, hydrogen and nitrogen (C, O, N) was performed using a CHNS/O Analyzer 2400, Series II, from Perkin Elmer. The amine density was calculated using the equation 1.

\[
\phi_{\text{NH}_2} = \frac{N_cN_A}{A_{\text{BET}}10^{16}}
\]  

Where $\phi_{\text{NH}_2}$ is the amine density, $N_A$ is the Avogadro number, $N_c$ the nitrogen content (mol g$^{-1}$) and $A_{\text{BET}}$ is the surface area of the sample (m$^2$ g$^{-1}$).

Textural properties of silica samples were estimated using N$_2$ adsorption/desorption isotherms at -196 °C using an Autosorb iQ3 (Quantachrome Instruments, USA). MSG20 and MSG20I30 were outgassed at 120 °C under vacuum (10$^{-6}$ bar) during 4 hours. Specific surface area of all materials was calculated using Brunauer-Emmett-Teller ( BET) equation and micropore volume by Dubinin–Radushkevich (DR) model. Pore Size Distribution (PSD) of each sample was obtained using the BJH method on desorption branch. The total pore volume was calculated from the adsorption isotherm at P/P$_0$ = 0.985.

The identification of the crystalline phases of the mesoporous silica samples was performed by X-ray diffractometer model X’Celerator Pro MPD, with a detector X'Celerator operating in continuous scan conditions.

Thermogravimetric analyses (TGA) were carried out using as equipment model STA 409 CD/403/5/G SKIMMER (Netzsch, Germany) with a heating rate of 10 °C/min, under synthetic air flux (20 mL min$^{-1}$) with approximately 5.0 mg of sample. The temperature range for the TG analyses was from room temperature up to 800°C.

Microcalorimetric Experiments

Previously, the samples were outgassed (10$^{-3}$ mbar) at 120°C for 4 h. A Setaram C80 instrument (Setaram, France) was used. This setup is coupled to a manometric system. This is used to measure
the quantity of gas to be injected in the cell and obtain the adsorption enthalpy. As well as adsorbed amount in equilibrium under isothermal conditions. For each gas injection, the adsorption enthalpy was calculated using the so-called discontinuous procedure as described by Rouquerol et al. The integration of peaks was realized by Calisto® Software (v1.043 AKTS-Setaram).

This heat peak may provide not only thermodynamic but also kinetic information, as mentioned by Stošić and Auroux (2013). The kinetics of heat release during adsorption can be monitored by the change in the thermokinetic parameter \( \tau \). The calorimetric signal (D) decreases exponentially with time (t) after the maximum of each adsorption peak. Equation 3 shows the linearized form of this exponential decay, from which the thermokinetic parameter \( \tau \) may be estimated.

\[
\log D = \log D_m - \frac{t}{\tau}
\]  
Equation 2

Where, \( D \) and \( D_m \) represents the power signal and the maximum power signal (mW), \( t \) the time and \( \tau \) the parameter thermokinetic in seconds.

According to the model described by Cardona and Dumasic (1992) the curve of adsorption enthalpy in function of the CO\(_2\) uptake is adjusted as a polynomial (equation 5). If this polynomial is derivative, applying the equation 6 we would have the distribution of energetic sites in function of the adsorption enthalpy. Therefore, the energy distribution \( f(q) \) may be plotted for sites with similar energy, where \( n \) is the number of moles adsorbed in each of these sites and \( a_i \) are the polynomials coefficients. If we integrate this distribution in a given range of enthalpies, we can obtain the density of energy sites available to adsorption in this enthalpy range.

\[
\Delta h_{\text{diff}} = \frac{\Delta h_{\text{int}}}{dn} = \sum_{i=0}^{k} a_i n^i
\]  
Equation 5

\[
f(q) = -\frac{dn}{d\Delta h_{\text{diff}}} = -\frac{1}{\sum_{i=1}^{k} i a_i n^{i-1}}
\]  
Equation 6

### 3. RESULTS AND DISCUSSION

The N\(_2\) adsorption/desorption isotherms at -196°C are shown in Figure 1. All samples have a H2(b) type hysteresis (Thommes et al. 2015), which is associated with mesocellular silica foams (MSF) (Schmidt et al. 1999) leading to a shift of the hysteresis loop to a higher relative pressure. After the immobilization of PEI on MSG20, the total pore volume was reduced from 0.96 to 0.06 cm\(^3\) per gram of material (Table 1). The specific surface area was also dramatically reduced from 211 to 52, fact that is according to expectations for this sample where the PEI incorporated filled the pores, therefore the surface area micropore and total pore volume decreased. The Pore Size Distributions (PSD) for all samples in logarithmic scale (inset of Figure 1) show a bimodal distribution with a smaller pore size of ~1 nm (micropores) and larger pores with sizes around 7.8 nm confirming that our material remains mesoporous after the impregnation.

**Adsorption equilibrium**

A magnetic suspension balance was used to obtain equilibrium data of CO\(_2\) and N\(_2\) at 50 and 75°C for MSG20I30 sample.

Dual site Langmuir model was used to fit the experimental data for CO\(_2\) isotherms. For N\(_2\) experimental data was fitted using Langmuir model.

![Figure 1](Image)

**Figure 1** N\(_2\) isotherms and PSD’s at -196°C, open symbols belong to desorption step
Textural properties and content nitrogen $N_C$ results are summarized in Table 1. These findings indicate that amine groups have been effectively incorporated to the bulk MSG20. Textural properties decrease as content nitrogen increases.

Table 1 Textural properties calculated from $N_2$ isotherms and nitrogen content from elemental analysis

<table>
<thead>
<tr>
<th>Samples</th>
<th>$A_{BET}$ (m$^2$.g$^{-1}$)</th>
<th>Pore Vol (cm$^3$.g$^{-1}$)</th>
<th>Pore Size (nm)</th>
<th>Micro pore Vol (cm$^3$.g$^{-1}$)</th>
<th>$N_C$ (mmol.g$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>MSG20</td>
<td>211</td>
<td>0.96</td>
<td>7.80</td>
<td>0.056</td>
<td>1.76</td>
</tr>
<tr>
<td>MSG20I30</td>
<td>52</td>
<td>0.06</td>
<td>7.77</td>
<td>0.014</td>
<td>7.59</td>
</tr>
</tbody>
</table>

Figure 2 shows the X-Rays diffractogram for both samples. These are in contrast with a conventional SBA-15 sample. Conventional SBA-15 shows a typical XRD pattern of an ordered network of mesopores with (100), (110) and (200) reflections. It is typical of a hexagonal symmetry (Zhao et al. 1998). MSG20I30 does not present the reflections characteristics of SBA-15. Vilarrasa et al. 2014b and Liu et al. 2012 showed similar behaviors as characteristic of mesocellular foam structure (MSF). The presence of ammonium fluoride on the synthesis process could affect the hexagonal arrangement of the solid. It limits the growth of the mesochannels leading to shorter channels with low-range order. An increase in the pore size is caused by $\text{NH}_4\text{F}$ penetration into the hydrophobic core of the surfactant micelle, breaking up the honeycomb packing typical of the hydrothermal SBA-15. (Lettow et al. 2000) (Schmidt-Winkel et al. 2000).

X-ray results along with $N_2$ isotherm shape could indicate that our mesoporous material belongs to the mesocellular foam structure family. The results of the Thermogravimetric analysis (TGA) are shown in the Figure 3A. Figure 3B presents the derivate of the weight loss (DTGA) for MSG20 and MSG20I30.

TGA showed a first weight loss for MSG20I30 sample before 100°C, presumably CO$_2$ adsorbed and moisture. The PEI began to decompose above 160 °C (point 2 in the DTGA) and a sharp weight loss appeared at 205 °C up to ~650 °C. When the temperature was increased above 220 °C, the rate of weight loss decreased. Point 3 in DTGA indicates that a different decomposition process took place. It could be related with the APTES when comparing with MSG20 DTGA. At 650 °C, the amine grafted was completely decomposed and removed as volatiles. The organic content in MSG20I30 was calculated to be about ~31 wt % (loss weight from 150 up to 750°C), in agreement with the designed PEI loading. However, the starting sample (MSG20) has an organic content around 10%, indicating that there is loss of PEI during the impregnation process. For MSG20I30 ~150°C would be the maximum operating temperature to avoid the decomposition of the material. Its temperature is lower than MSG20, where the maximum of operation is ~250°C.
Figure 3 A) TGA for MSG20 and MSG20I30  B) DTGA for both materials.

Figure 4 shows the adsorption microcalorimetric curves of our samples at 25°C under anhydrous conditions. The samples show a decrease in the differential enthalpy with increasing CO₂ uptake, which suggests that the materials have a heterogeneous surface according to the classification proposed by Llewellyn et al. (2000).

Both curves show the initial enthalpy values of ~-110/-120 kJmol⁻¹ at low coverage. Thus we can consider that this high enthalpy value is due to the interaction of CO₂ with grafted amines. Namely, the chemisorption of CO₂ on amine pairs to form propyl ammonium carbamate species has an adsorption enthalpy of ~-90kJmol⁻¹ (Alkhabbaz et al. 2014).

Although the enthalpy at low coverage is similar, it is perceptible that there is a change of energy sites with the addition of PEI.

For the better appreciation of the change of adsorption mechanism on the double functionalized solid, Figure 5 presents the distribution of active sites to adsorption of CO₂ on the samples. Peaks in the distribution represent sites accumulation with the same energy of adsorption. In the case of chemisorption these represent intermediate products formed as soon as the CO₂ pressure increases.

The energy distribution (figure 5) showed four signals for MSG20. Two corresponding to low enthalpies maybe belong to physisorption on the pores showed in the PSD (Figure 1). The other two are present at enthalpies higher or close to -
The propyl 810 ty increases, in contrast with the cause irreversibly bound 0I30 reaches 2.2 m diffusion would perhaps be materials 2.4 r max, (2012) for ma max, (Silyl propyl) carbamate formation is suppressed energy consumption be va cuum. For this reason, MSG20I30 could be an interesting CO2 capture adsorbent with respect to energy consumption because irreversibly bound (silyl propyl) carbamate formation is suppressed. MSG20I30 distribution has not this peak. Although diffusional resistances are increased as is mentioned by Bollini et al. (2012) for materials with high amine density affecting the kinetic.

Table 3 summarizes amine density on samples, as well as the adsorption sites and the maximum thermokinetic parameter in each case. For both solids, the active sites with strength lower than ~40 kJ mol⁻¹ do not vary significantly as the amine density increases, in contrast with the chemisorption sites (strength higher than ~40 kJ mol⁻¹), which consistently increase for higher amine loadings.

The values of the maximum thermokinetic parameter (τₘₐₓ) are also presented in Table 3. The MSG20 sample showed τₘₐₓ at ~43 kJmol⁻¹, this value provides additional evidence that the adsorption mechanism is essentially due to carbamic acid formation by hydrogen bonds (Aziz et al. 2012).

For MSG20I30, τₘₐₓ is 1274 seconds and correspond at -34 kJmol⁻¹. This suggests diffusional resistances that have been observed for highly PEI loaded materials. (Bollini et al. 2012) The enthalpy is lower than grafted sample because ammonium carbamate forms quickly and the formation of other subproducts is apparently suppressed, thus diffusion would perhaps be limiting kinetically the adsorption for MSG20I30 sample. For MSG20I30 the maximum thermokinetic parameter at ~-34kJmol⁻¹ is related to physisorption. It provides additional evidence that the adsorption mechanism is essentially due to physisorption on this sample (diffusional resistances).

<table>
<thead>
<tr>
<th>Samples</th>
<th>Ø_NH₂ molec⁻²</th>
<th>Energy sites μmol CO₂ g⁻¹</th>
<th>Thermokinetic Parameter</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>&lt;40 kJ mol⁻¹</td>
<td>&gt;40 kJ mol⁻¹</td>
<td>τₘₐₓ s</td>
</tr>
<tr>
<td>MSG20</td>
<td>5.02</td>
<td>190</td>
<td>573</td>
</tr>
<tr>
<td>MSG20I30</td>
<td>87.91</td>
<td>240</td>
<td>1113</td>
</tr>
</tbody>
</table>

CO₂ and N₂ adsorption isotherms were measured for double functionalized material at 50 and 75°C. The isotherms are shown in Figure 6 and 7.

Figure 6 CO₂ isotherms for MSG20I30
As expected, CO₂ adsorption is enhanced with the increase of temperature, particularly at low pressures. For MSG20I30 sample, CO₂ uptake is higher at 75°C. This is a typical behavior of chemisorption process so that MSG20I30 reaches
at 75°C the higher adsorbed concentrations for CO$_2$. This behavior of PEI-impregnated on mesoporous materials, such as MCM-41 or KIT-6 was explained in other works (Son et al. 2008) where the increase of CO$_2$ adsorption capacity with temperature was attributed to an expansion of PEI aggregates within the pores when temperature is changed. Thus, at low temperature, PEI is disposed inside the channels, only the external active sites of PEI being accessible to CO$_2$ molecules. On the contrary, at higher temperatures PEI expands occupying all the available space in the pores, thus becoming more accessible to CO$_2$ (Xu et al. 2002). On the other hand, kinetic effects could be considered as an explication. When the temperature increases the kinetics and mobility of CO$_2$ is higher and it is easier to enter in the inaccessible regions at lower temperatures (Sanz et al. 2010). The result of this is the increase of CO$_2$ uptake with temperature and this reflects into the parameters of the model where for MSG20I30 $q_{m1}$ and $b_1$ are higher at 75°C than 50°C summarized in Table 4. This fact has an important impact in the selectivity. The correlation coefficient shows that the model adjusts well the experimental data.

Table 4 Model parameters for MSG20I30 at 50 °C and 75° C.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>CO$_2$</th>
<th>N$_2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$q_{m1}$, mmolCO$_2$ g$^{-1}$</td>
<td>2.13</td>
<td>2.66</td>
</tr>
<tr>
<td>$b_1$, bar$^{-1}$</td>
<td>14.00</td>
<td>15.70</td>
</tr>
<tr>
<td>$q_{m2}$, mmolCO$_2$ g$^{-1}$</td>
<td>1.02</td>
<td>1.06</td>
</tr>
<tr>
<td>$b_2$, bar$^{-1}$</td>
<td>0.13</td>
<td>0.11</td>
</tr>
<tr>
<td>$R^2$</td>
<td>0.9939</td>
<td>0.9970</td>
</tr>
</tbody>
</table>

4. CONCLUSION

Mesoporous silica double functionalized was obtained from previous grafted material. MSG20I30 sample shows a change in the way to adsorb CO$_2$. While CO$_2$ forms carbamate, carabamic acid and syllyl propyl carbamate when is chemisorbed on grafted silica, it forms only ammonium carbamate on MSG20I30 sample. This maybe improves the reversibility to work in cycles. However, maximum thermokinetic parameter shows that adsorption kinetic was affected. The parameter increased in contrast with the start material. Its correspondent enthalpy suggests that physical effects restrict the rate of adsorption. This limiting would be CO$_2$ diffusional resistance inside PEI impregnated on MSG20I30 sample. Materials double functionalized have high thermic stability to be used at high temperatures (up to 150°C) as demand post combustion scenarios. Dynamic and reversibility studies should be carry out on this material, in order to study the performance at cyclic process.

5 REFERENCES

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