Poster

CO_2 ADSORPTION BY AMINE MODIFIED MESOPOROUS SILICA MATERIALS: SYNTHESIS OPTIMIZATION

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CO_2 is one of the greenhouse gases whose increasing concentration in the atmosphere is proposed to have direct linkage to global warming. Large-scale separation of CO2 by liquid phase alkylamines is the most widely developed commercial technology. However, the use of liquid amines has several disavantages: high energy consumptions, a difficult solvent regeneration, equipment corrosion or problems with viscosity flow. Separation processes based on solid sorbents are an alternative to overcome some of these limitations [1].

The family of mesoporous materials called M41S (MCM-41, MCM-48 and MCM-50) is a subject of growing interest since they were discovered by Mobil researchers in 1992 [2]. These materials are the result of the ordering of micelles formed when a silica and surfactant solution is under proper conditions. In the case of MCM-48, the micelles are ordered in hexagonal arrays, MCM-48 has a three-dimensional cubic structure and MCM-50 has an unstable lamellar structure.

The characteristic properties of these materials are: i) a very narrow pore size distribution in the mesoporous region, typically between 2 and 4 nm, ii) a high specific surface area (1000-1500 m^2/g), iii) a highly ordered structure and iv) an active surface chemistry that allows an easy modification of the properties of these solids. All of them make these materials very attractive for numerous applications such as catalysis, separations, and encapsulation of molecules.

The aim of this work is the surface modification of the MCM-48 [3] by silane coupling agents in order to improve the separations. In this work we report the MCM-48 modification with 3-aminopropyl tri-etoxisilane (APTS), in which the amino groups will react with CO_2 as follows:

$$2\,(R\text{-}NH_2) + CO_2 \leftrightarrow R\text{-}NH\text{-}COO^- + {}^+H_3N\text{-}R$$

In order to locate the organic groups inside the pores of MCM-48 two different functionalization strategies have been carried out:

Method A, in which the modification is carried out in the calcined material to obtain fully functionalized pores; and Method B, that is made in the as synthesised with surfactant agent occluding mesopores to get partially functionalized pores, after functionalization the surfactant is extracted.

To optimise the reaction different variables are studied: Time of reaction, temperature of reaction and APTS concentration.

Figure 1 shows the X-ray diffractograms for MCM-48 powder as synthesized, calcined and functionalized by means of method A and B. As can be seen, structure of MCM-48 remains after both functionalization methods. Method A give rise to a displacement to higher 2θ angles in comparison to the calcined sample because of the reduction of the pore diameter produced by the APTS molecules.

CO_2 adsorption isotherms at 298 K for MCM-48 powder unmodified and functionalized by method A and B are presented in Figure 2. The sample modified with method A adsorbed a higher amount of CO_2 than the one with method B. This behavior can be explained by the higher amount of amine groups that could react with CO_2 molecules present in sample A. This was confirmed by means of elemental analysis: Sample modified by method A had 2.24 mmol NH_2/g while the one modified with method B had 1.85 mmol NH_2/g since the pores are occluded with surfactant during the reaction with APTS. Furthermore, the amount of NH_2 obtained by elemental analysis is in good agreement with the weight loss observed in TGA experiments.

The Method A sample shows a good adsorption compare to literature [1]

References:

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Figures:

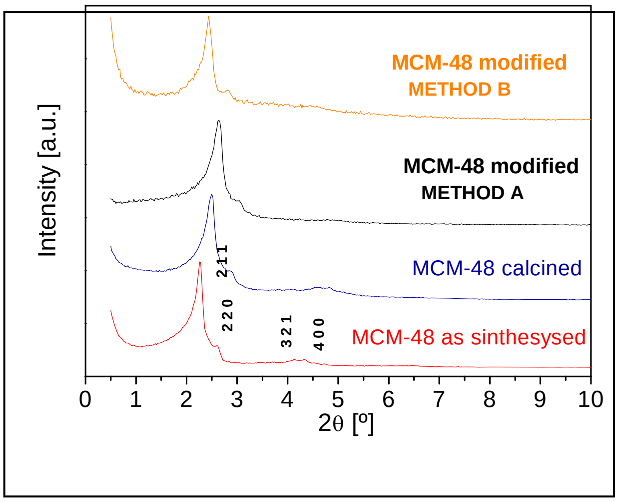

Fig. 1. X-ray diffractograms of MCM-48 powder as synthesized, calcined and modified by methods A and B.

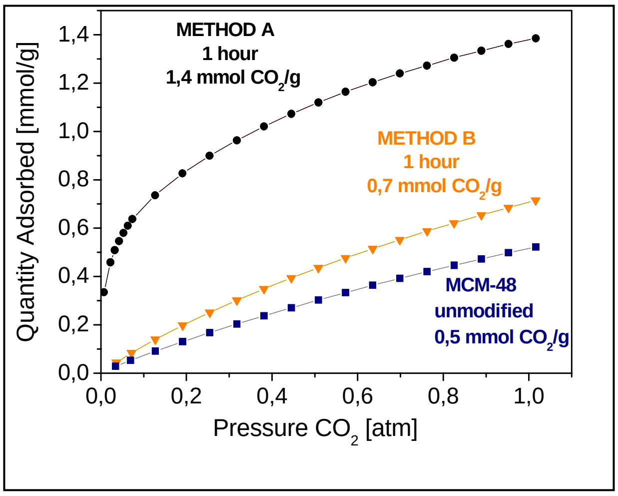

Fig. 2. CO_2 adsorption isotherms at 298 K of MCM-48 powder without modification and modificated by methods A and B