Zeolites and Related Materials: Trends, Targets and Challenges
Proceedings of 4th International FEZA Conference
A. Gédéon, P. Massiani and F. Babonneau (Editors)

Amine modified, micro-mesoporous matrices for CO_2 retention: effect of occluded templates on performance

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Abstract

A new research area devoted to the exploration of different CO_2 capture technologies involves the use of novel adsorbents. The purpose of this study is to develop adsorbents which have a tailored surface functionality for improved CO_2 adsorption. We have synthesized two types of porous matrices: SBA-15 silica and MCM-22 zeolite. Different quantities of amine groups were incorporated into these ordered materials using post-synthesis impregnation. Our results show that high capacities were obtained using the impregnated samples. Occluded template and amino groups favor the adsorption on SBA-15, meanwhile the best results using MCM-22 were obtained impregnating the free-template samples. In these samples, approximately 90% of the CO_2 adsorption occurred almost instantaneously, and was removed just as rapidly at room temperature with an inert gas flow.

Keywords: CO_2 adsorbents, MCM-22, SBA-15.

1. Introduction

Industrial processes such as air separation, helium extraction, hydrogen production, etc. require CO_2 removal which is often found as an impurity. Additionally, an increase in the atmospheric CO_2 concentration has led to concerns regarding global warming [1]. As most of the CO_2 emissions are produced by stationary sources belonging to industrial energy production, the implementation of an efficient capture method for this contaminant would be of interest. Recent studies that investigate a series of technological processes to perform this capture are of increased interest in the development of new adsorbents. Among them, different types of zeolites and mesoporous solids have been proposed as selective adsorbents for CO_2 [2–5]. Additionally, an amine-based absorption technology has been established for over 60 years in the chemical and oil industries, for removal of acid gases from gas streams [6]. Consequently, the design of a new type of adsorbent is proposed for CO_2 retention. These materials should have a porous structure in which the interior has a basic organic compound which will help in the retention of CO_2 molecules. This should facilitate both physical and chemical adsorption. Specifically, the purpose of this work is to develop adsorbents presenting a tailored surface functionality for improved CO_2 adsorption at temperatures above 50°C. We have synthesized two types of porous matrices: SBA-15 silica (SBA-15) and MCM-22 zeolite (MCM-22). Different quantities of amine groups were incorporated into these ordered materials by post-synthesis impregnation, using

tetraethylenepentamine (TEPA) as the amine source. SBA-15 was selected as a support because of previous results reported by Yue et al. in [7], where an improved CO_2 adsorption capacity was obtained using non-template free samples. The reason for including the MCM-22 matrix in our studies is due to the fact that this ordered structure can be generated through the use of hexamethyleneimine (HMI) as a synthesis director.

2. Experimental

MCM-22 and SBA-15 were synthesized according to methodologies described in references [8] and [9] respectively. In order to get the template-free samples, the synthesized solids were calcined in air at 580°C for 6 h. The TEPA modified samples were prepared by a wet impregnation method, using ethanol as a solvent. In order to get different amine levels in the solids, two different amine/ethanol ratios were used and the impregnated samples were denoted as samples type 1 and 2. The amine content incorporated to each sample is detailed in Table 1. All as-synthesized (as), calcined (calc) and amine-containing samples (as-1, as-2, calc-1, calc-2) were analyzed by X-ray diffraction, N_2 adsorption/desorption and thermal gravimetric analysis.
The CO_2 adsorption and desorption were measured by thermal gravimetry, using a Shimadzu TGA-50 analyzer. The sample was preheated at 100°C in N_2 at a flow rate of 100 ml/min. Subsequently, CO_2 99.8% was introduced at a flow rate of 100 ml/min. The weight change of the adsorbent was followed to determine the adsorption/desorption performance at 75°C.

3. Results and Discussion

XRD patterns of samples SBA-15as and SBA-15calc, MCM-22as and MCM-22calc show the diffraction peaks ascribed to the corresponding structures. Nevertheless, the diffraction intensities diminished and small changes in the Bragg diffraction angles occur with the incorporation of the amine. TEM and SEM analyses obtained for samples before impregnation also indicate the morphologies and ordering usually ascribed for each one of these structures.

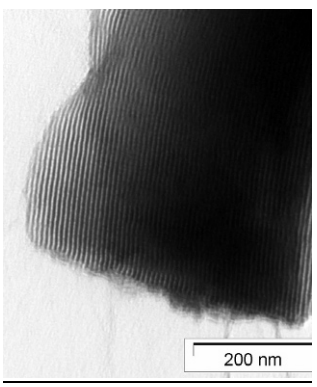

Figure 1. TEM micrograph of SBA-15calc sample.

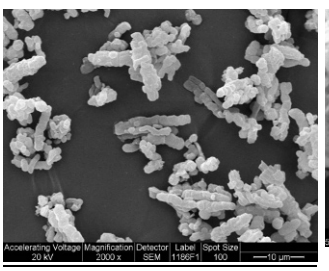

Figure 2. SEM micrograph of SBA-15calc sample.

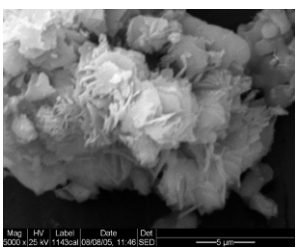

Figure 3. SEM micrograph of MCM-22calc sample

Figure 1 is a TEM micrograph of SBA-15calc sample, showing the hexagonal arrangement of the cylindrical channels. Fig. 2 shows the particles morphology obtained by SEM, where the typical cylinders of SBA-15 silica can be observed. In the case of MCM-22-calc sample, SEM analysis indicates the presence of layered particles, 2-15 μm in size (Fig. 3).

Table 1. BET surface area, pore volume and CO_2 adsorption capacity for the different synthesized samples.

Sample	Description	% amine (wt/wt)	Pore Volume (ml/g)	BET area (m^2/g)	Adsorption (g/g)x100
M1	SBA-15calc	-	0.65	645	0.96
M2	SBA-15calc-1	46.48	0.04	22.48	3.99
M3	SBA-15calc-2	63.52	0.00	4.62	3.16
M5	MCM-22calc	-	0.22	390	2.49
M6	MCM-22calc-1	36.40	0.01	4.37	5.51
M7	MCM-22calc-2	54.12	0.00	1.8	10.29
M4	MCM-22as	-	0.11	26.34	0.24
M12	MCM-22as-1	37.86	0.01	11.64	4.15
M8	MCM-22as-2	53.33	0.00	3.45	7.64
M9	SBA-15as	-	0.02	25.1	0.24
M11	SBA-15as-1	48.56	0.02	20.8	7.07
M10	SBA-15as-2	63.55	0.00	9.1	11.94

Table 1 lists the BET surface area, pore volume and CO_2 adsorption capacity for the different synthesized samples. With increasing amine loading, the pore volume decreased and the N_2 adsorption was restricted. This lowers the corresponding BET area values obtained. It should be taken into account that the pore volume values and BET areas were obtained using nitrogen as an adsorbate, a molecule which is larger than CO_2.

Considering samples based on zeolite matrices, for the calcined sample presenting free pores (MCM-22cal), a low value for the CO_2 adsorption capacity was observed. For MCM-22as, a sample containing the HMI template, adsorption capacity values are also very low. The imine located inside the pores does not produce any improvement in the extent of adsorption. On the contrary, impregnation with TEPA increases the adsorption noticeably. In this case, higher effectiveness in samples impregnated after being calcined, reaching values of 102.9 mg CO_2/g (MCM-22cal-2), were obtained. The adsorption in this case is favored by TEPA impregnation performed on template-free pores. This effect is clearly seen in Fig.4a, where the thermogravimetric scanning curves for CO_2 adsorption on MCM-22 calc samples are shown. It can be observed that the weight of the MCM-22cal-2 noticeably increases at very short times.

For samples with the SBA-15 structure, the SBA-15as sample has pores filled with the PEP-PPE-PEP template, of polymeric nature. This solid presented a relatively low adsorption capacity without TEPA impregnation. This capacity increased noticeably as the amine load was increased. According to Yue et al [7], it could be inferred that the polymeric template is suitable as an additional surface for the amine to locate. The highest adsorption value was obtained for this sample without calcination and with the higher amine load used (SBA-15as-2). Results were similar to those obtained with MCM-22cal-2 sample, and the thermogravimetric scanning curves for CO_2 adsorption on SBA-15as samples are shown in Fig.4b.

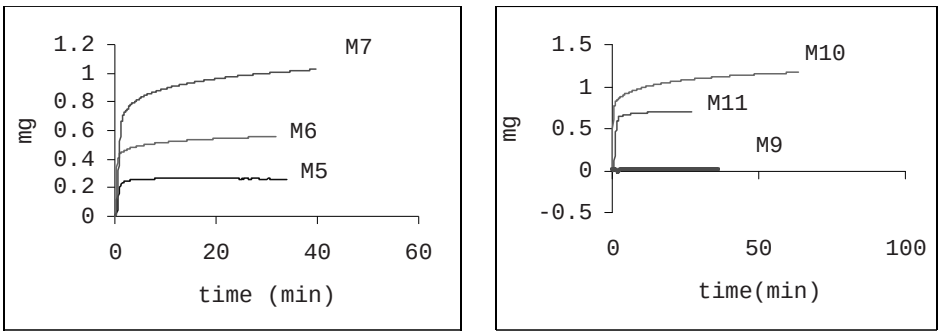

Figure 4. Thermogravimetric scanning curves for CO_2 adsorption on MCM-22calc samples (a) and SBA-15as samples (b).

4. Conclusion

The CO_2 adsorption capacities of prepared samples significantly improved with the incorporation of the amine. Adsorption measurements showed materials having a CO_2 capacity varying from 4 to 120 mg/g at 75°C, depending on the amine content. In these samples, approximately 90% of the adsorption of CO_2 occurred almost instantaneously. The presence of templates inside the pores produces different effects on the adsorption capacity, depending on the matrix structure. Adsorbents based on MCM-22 materials seem to be promising for CO_2 selective adsorption. Compared with conventional and novel SBA-15 adsorbents [7, 10], high capacities were obtained using free-template MCM-22 samples. Adsorption capacities obtained are significantly higher, similar to those achieved with adsorbents of last generation [10].

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