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## CATALYTIC AND ADSORPTION PROPERTIES OF Al- AND Ti-MCM-41 SYNTHESIZED AT ROOM TEMPERATURE

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### Abstract

Aluminosilicate and titanosilicate MCM-41 were synthesized using a room temperature method. A preliminary catalytic evaluation was performed in the promotion of the 1-butene double bond isomerization, which was successful in probing differences in the acidity of the samples prepared.

*Keywords:* MCM-41, aluminosilicates, titanosilicates, 1-butene isomerization

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## INTRODUCTION

Since the discovery of MCM-41 [1,2], much interest has been devoted to metal containing samples [3], aluminium and titanium being very popular for acid and redox catalyzed reactions, respectively. The introduction of heteroatoms into the silica materials can be carried out either by a post-synthesis grafting of metal species onto the inner surface of the mesopores of a pure silica material, or by incorporation of metal during synthesis and is usually accompanied by a decrease in the regularity of the pore structure as compared with the pure silica grades of MCM-41. A variety of routes to prepare isomorphously substituted metal samples have been reported, the

most commonly used ones being based on a hydrothermal procedure using precursors containing other charge balancing inorganic cations. The introduction of protonic sites in these aluminosilicate materials usually requires a post-synthesis cationic exchange treatment of the calcined samples, which may cause disruption of the regular MCM-41 structure and an undesirable loss of framework aluminium. Alternative procedures have been reported to avoid this, which include the removal of the template by acidic alcohol solutions [4] and synthesis using primary amines as template [5], although in this latter case the resulting materials are similar to those known as HMS [6] as they exhibit only a single peak in the XRD pattern and therefore have a shorter range of hexagonal order compared with MCM-41 materials.

In the work presented in this paper, aluminosilicate MCM-41 samples were prepared by a method based on that developed for silica grades of MCM-41 [7], and later adapted to aluminosilicate materials [8]. It is carried out at room temperature, and uses cationic surfactants as templates and metal alcoxides and tetraethoxysilane as precursors. An analogous synthesis method is reported for the first time for the preparation of a titanosilicate MCM-41 sample. A titanium grafted MCM-41 sample was also prepared.

All the samples were catalytically evaluated on the model reaction of double bond position isomerization of 1-butene to 2-butenes. This is one of the most extensively used model reactions, which can proceed both through an acidic or a basic mechanism [9]. The *cis/trans* ratio of the 2-butene products expresses the effectiveness of the basic versus acidic catalytic pathways: values close to one correspond to the acidic mechanism, while values significantly higher than one are indicative of the basic process [9]. A reference sample of HNaY zeolite, with approximately 65 % of proton sites relative to the total cationic content, and Si/Al ratio of 2.6, was also tested on this model reaction.

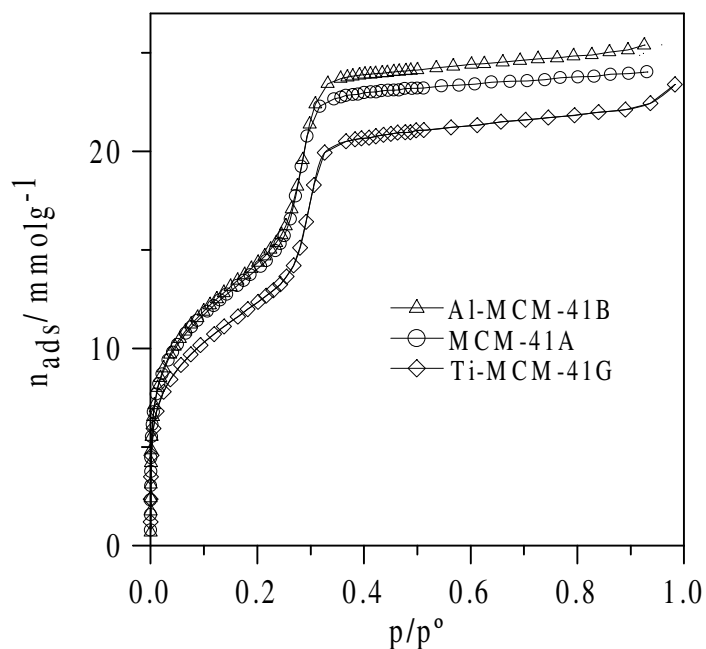
## EXPERIMENTAL

The pure silica MCM-41A and MCM-41B samples were prepared by a room temperature synthesis procedure [7] as described previously [10] using tetraethoxysilane, ammonia and *n*-hexadecyltrimethylammonium bromide in aqueous solution. Samples Al-MCM-41A, Al-MCM-41B and Ti-MCM-41 were prepared in a similar way but also including an appropriate volume of a solution of aluminium isopropoxide in propan-2-ol and a solution of titanium ethoxide in ethanol, following the procedure described in ref. [8] for aluminosilicate MCM. The suspensions were stirred for 1 h at room temperature and then the white products were filtered, washed with bidistilled water (except for sample MCM-41B which was washed with ethanol), dried at 343 K and finally calcined in air at 823 K (heating rate 3 K min<sup>-1</sup>) for 11 h. Sample Ti-MCM-41G was prepared

by grafting titanium on sample MCM-41B using the procedure described in ref [11].

The compositions of the calcined samples were determined by ICP after dissolution in hydrofluoric acid. Nitrogen adsorption isotherms at 77 K were determined on a CE Instruments Sorptomatic 1990, using helium and nitrogen of 99.999% purity.

Prior to the reaction, each sample was submitted to an in situ pre-treatment at 723 K, for 6 h, under a flow of dry nitrogen; the sample mass ranged from 0.100 to 0.200 g. The 1-butene isomerization was carried out in a fixed bed, vertical, down flow tubular reactor, with an on-line gas chromatograph, at 423 and 473 K. The reagent was diluted in nitrogen, with partial pressure of 0.1 atm, nitrogen flow of 3.6 L h<sup>-1</sup> and the total pressure was 1 atm. Periodically, a sample of the reactor effluent was analyzed in the gas chromatograph using a 50 m × 0.32 mm I.D. fused-silica PLOT Al<sub>2</sub>O<sub>3</sub> deactivated with KCl column.

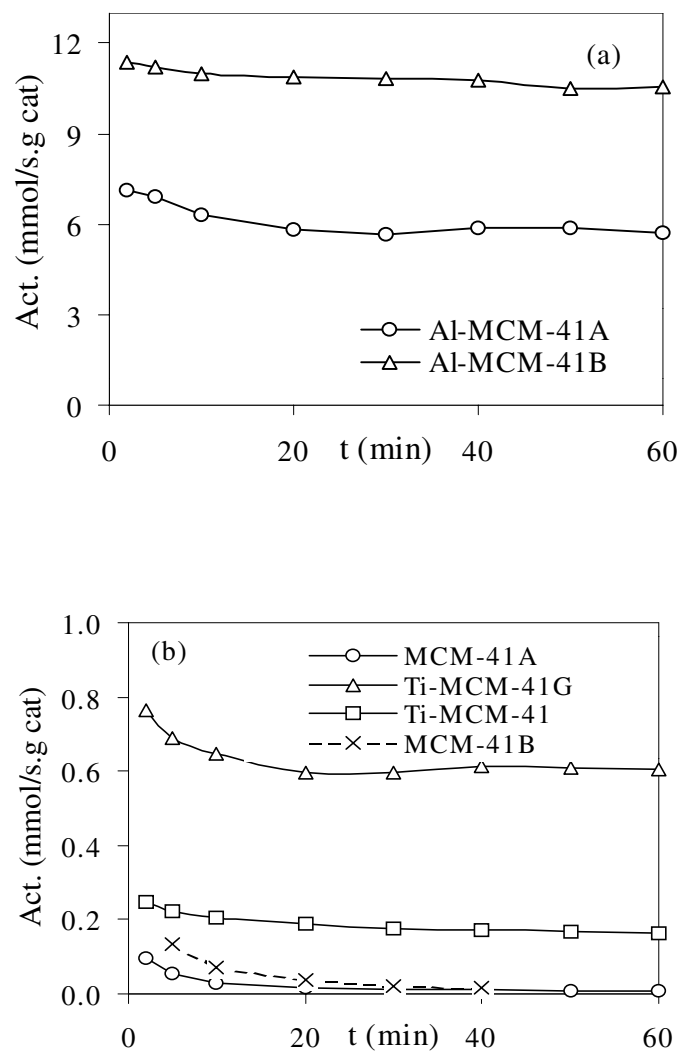


**Fig. 1.** Nitrogen adsorption isotherms determined at 77 K on samples Al-MCM-41B, MCM-41A and Ti-MCM-41G

## RESULTS AND DISCUSSION

All samples studied exhibited nitrogen isotherms typical of highly regular MCM-41 materials, being completely reversible and with well defined pore filling steps, as illustrated in Fig. 1 for three of the samples and where, for the sake of clarity, desorption points were omitted. The regularity was confirmed by the X-ray diffraction patterns, which showed, for all samples, at least three peaks at low angles indicative of a regular hexagonal array of the uniform pores characteristic of the MCM-41 structure. The steepness and reversibility of the steps in the isotherms are consistent with the presence of tubular pores of uniform size in each material, and the lack of hysteresis together with the low slope of the isotherms at high relative pressures, after pore filling is complete, are indicative of the absence of significant amounts of non-mesostructured material. These features are confirmed by the results of the  $\alpha_s$  analysis of the isotherms, as previously described [10], presented in Table 1, which show that all samples have, as desirable, low external surface areas ( $A_{\text{ext}}$ ), quite high pore volumes ( $V_p$ ) and total specific surface areas ( $A_s$ ), these values being calculated using  $0.808 \text{ g cm}^{-3}$  and  $0.162 \text{ nm}^2$  for the nitrogen density and cross sectional area, respectively. Only sample MCM-41B has a slightly higher external surface area, which indicates that the washing with ethanol had a somewhat disrupting effect in the structure.

On the other hand, significant differences can be seen in the results of the catalytic studies shown in Fig. 2. While the pure silica samples present practically no catalytic activity ( $\approx 0.1 \text{ mmol s}^{-1}\text{g}^{-1}$ , at 473 K), the incorporation of very small amounts of aluminium lead to a considerable increase in the catalytic activity, which is higher for the sample with more aluminium ( $\approx 11.4 \text{ mmol s}^{-1}\text{g}^{-1}$ , at 423 K) and is probably associated with the appearance of surface Brønsted acid sites. In fact, the observed selectivities, expressed in a cis/trans 2-butene ratio close to one, are indicative of the acid mechanism. It should be noted that this was achieved without any significant alterations in the pore structure, only a small increase in the pore size being observed, and it appears that the structure was even improved, as the pore volumes and total surface are slightly higher in comparison with the pure silica sample MCM-41A. As the formation of extraframework aluminium usually results in a loss of quality in the pore structure, our results suggest that the aluminium in our samples must be incorporated in the framework leading to the formation of Brønsted acid sites. However, further work on solid-state NMR is required to clarify if this is indeed the case.



**Fig. 2.** Catalytic activities, as a function of time on stream, for the aluminium MCM-41 samples at 423 K (a) and for the pure silica and titanium modified MCM-41 samples at 473 K (b)

**Table 1**

Results of the characterization of the MCM-41 samples

Sample	Composition Si/(Al or Ti)	$A_s$ ( $m^2g^{-1}$ )	$A_{ext}$ ( $m^2g^{-1}$ )	$V_p$ ( $cm^3g^{-1}$ )	$D_p(H)$ (nm)
MCM-41A	-	1092	26	0.801	3.00
Al-MCM-41A	>211*	1117	24	0.845	3.09
Al-MCM-41B	138	1107	44	0.822	3.09
Ti-MCM-41	84	1055	56	0.794	3.18
Ti-MCM-41G	24	962	55	0.709	3.13
MCM-41B	-	1042	95	0.790	3.34

\*the nominal composition of the gel was Si/Al=840

Our results are in accordance with those obtained previously on HMS type materials [5], in the sense that Brønsted acid sites are introduced into the samples during synthesis, without the need of post-synthesis ion-exchange treatment. Therefore, this type of site may have been generated by the decomposition of the ammonium surfactant during the calcination step. On the other hand, the synthesis procedure used in our present study allowed us to obtain samples with the MCM-41 structure. It is interesting also to note that in a previous detailed study on hydrothermally synthesized aluminosilicate MCM-41 samples [12] no Lewis or Brønsted acid sites were detected for a sample with a Si/Al of 266.

Nevertheless, the acid strength of the Al-MCM-41(A and B) is lower than that of the reference HNaY zeolite, which presents a mild acid character: the only products formed with the mesoporous materials were *cis*- and *trans*-2-butene, while many other products were observed with the zeolite, including C<sub>3</sub> and C<sub>5</sub> branched and linear products; in this case, a more demanding reactional process was effective, consisting in the dimerisation of the reagent 1-butene, isomerization and cracking of the C<sub>8</sub> dimer, *etc.*

With regard to the titanium containing samples, it can be seen from Fig. 2 that, as expected, they show a much lower catalytic activity than the aluminosilicate samples but also, and more importantly, that there are some notable differences between the two samples. The quite low activity obtained for the sample Ti-MCM-41, similar to the corresponding pure silica MCM-41A, and the presence of some activity by the titanium grafted Ti-MCM-41G, which undoubtedly contains only titanium on the surface of the pores, suggests that in the former sample the titanium substituted silicon in the framework. These results are consistent with previous findings on Ti-HMS [13] for which

Brønsted acid sites were only observed for samples which had higher coordination Ti sites, probably due to titania nanodomains. It can be speculated that the very low acidity of our room temperature synthesized sample may be an advantage for its use as a redox catalyst, as it has been noticed that the amount of Brønsted sites can influence the selectivity and activity towards some redox catalyzed reactions [13, 14].

## CONCLUSIONS

The results presented in this study show that the room temperature synthesis method used is an adequate method for obtaining aluminium containing MCM-41 materials with highly uniform pore structure and enough acidity to catalyse the reaction of 1-butene double bond isomerization at 423 K. The catalytic results obtained with the Al containing MCM-41 samples suggest that it will be worthwhile to extend this study to other acid catalyzed reactions. A considerable increase in the catalytic activity is observed by increasing the amount of aluminium incorporated but without a significant loss of the quality of the pore structure. Because no charge balancing cations are present in the synthesis, the introduction of catalytic acid sites is achieved directly during the calcination step by decomposition of the surfactant, without the need of a post-synthesis ion-exchange treatment, which is usually needed for hydrothermally synthesized materials.

It was also found that the same catalytic reaction was successful in probing differences in acidity of titanium containing MCM-41 prepared by using different synthesis procedures. Although both methods lead to highly regular MCM-41 materials, it was found that the sample where titania was grafted on the surface of silica based MCM-41 exhibited some acidity, while the incorporation of titanium during the room temperature synthesis lead to a material which presented practically no catalytic activity for the tested model reaction.

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