

THERMAL BEHAVIOUR OF NANOPOROUS COMPOSITES

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Abstract

The thermal behaviour of mesoporous composite materials prepared by pillaring of magadiite with silica was investigated. The composite samples were characterized by XRD, SEM, IR and BET methods. TG-DTG-DTA measurements have revealed their increased thermal and mechanical stability that may promote their application as catalysts in hydrocarbon reactions.

Keywords: mesoporous material, simultaneous TG-DTG-DTA, thermal and mechanical stability

Introduction

The poor mechanical, thermal and hydrothermal stabilities of MCM-41, MCM-48 (members of the M41S family of mesoporous silicate molecular sieves described by Mobil [1]), FSM-16 (hexagonal mesoporous silicate prepared by heat treatment of alkyl ammonium intercalated kanemite [2, 3]) and HMS (Hexagonal Mesoporous Silicate prepared by long-chain primary alkyl amines instead of ionic surfactants [4, 5]) materials are due to the easy hydrolysis of Si-O-Al or Si-O-Si bonds in their structures. These features have been the limiting factors in their application in hydrocarbon processes [6, 7].

Several suggestions were published to improve the thermal and mechanical characteristics of these types of mesoporous materials. These are as follows: (i) post synthesis treatment [8], (ii) treatment with trimethylchlorosilane [9, 10], (iii) development of new synthesis routes [11], (iv) pillaring layered structures to produce mesoporosity [12-14].

We attempted to apply a novel method for the preparation of mesoporous materials starting from magadiite by intercalation of silicate tubes, similar to the building blocks of MCM-41, between the magadiite layers [15]. In this work we report on the thermal behaviour of this novel composite material in comparison with the parent MCM-41 and magadiite.

Experimental

Preparation procedure

Magadiite, MCM-41 and their aluminium containing derivatives ($\text{Si}/\text{Al}=40$) were prepared by the hydrothermal synthesis described by Schwieger *et al.* [16], Schramm *et al.* [17], Pál Borbély *et al.* [18], and Ellenstad *et al.* [19].

The synthesis procedure for the new mesoporous materials from magadiite is as follows. A given amount of hexadecyl-trimethylammoniumbromide (HTA) was mixed with an appropriate amount of magadiite and was stirred for 1 day. Then, sodium silicate and sulfuric acid were combined with the detergent-swollen magadiite at room temperature. Stirring was continued for 1 h. The solution pH was adjusted to 10 with sulfuric acid and the gel was crystallized for 6 days under static autogeneous conditions at 373 K. After filtering and washing with distilled water the cake was dried at 373 K and then calcined at 773 K for 10 h to burn the template off. Another preparation method was also used to prepare aluminium containing composite from the detergent-swollen magadiite. The Al-MCM-41 synthesis procedure described by Schmidt *et al.* was followed; the aluminium source was aluminium sulfate [19].

Characterization

Samples have been characterized by physical-chemical methods like X-ray diffraction, BET, IR spectroscopy using the KBr matrix technique, scanning and transmission electron microscopy (SEM, TEM), acidity measurements using pyridine as a probe [20].

The thermal behaviour of the samples was investigated by means of a Derivatograph-Q type (MOM, Budapest) instrument, using generally 10 K min^{-1} heating rate in the 300–1300 K temperature range. Samples were placed on a multi-plate sample holder made of platinum.

For the mechanical stability test pellets were pressed from the powders using a pressure tool with 63 or 159 MPa pressures. The pellets were crushed and investigated by XRD.

Results and discussion

The gel compositions ($\alpha = \text{SiO}_2$ (mol in MCM-41)/ SiO_2 (mol in magadiite)), BET areas and interlayer distances of the samples before and after calcination are listed in Table 1.

Magadiite has a 1.55 nm interlayer distance, while in its pillared derivative the layers are propped apart. The distance between the layers, 4.02 nm, surpassed the value measured for MCM-41 (3.94 nm). This means that even MCM-41 tubes may be accommodated in-between the magadiite layers.

The relative intensities of the reflections for samples pressed with different pressures into pellets are seen in Fig. 1. Data reveal that the composite material exhibits much higher mechanical stability than MCM-41. This behaviour can be explained

by assuming a structure where the elementary tubes of MCM-41 are enclosed between the magadiite layers.

Table 1 Physical characteristics of the samples

No.	Sample	As synthesized	Calcined form	
		XRD/ $d_{100}(\text{nm})$	XRD/ $d_{100}(\text{nm})$	BET/ $\text{m}^2 \text{g}^{-1}$
1	Na-Si-magadiite	1.551	1.551	38.7
2	Na-Al-magadiite	1.551	1.551	42.3
3	HTA-magadiite	2.945	—	50
4	Si-MCM-41/Si-magadiite $\alpha=0.25$	3.224	3.110	113
5	Si-MCM-41/Si-magadiite $\alpha=0.5$	4.016	3.841	204
6	Si-MCM-41/Si-magadiite $\alpha=1$	4.016	3.841	408
7	Si-MCM-41/Si-magadiite $\alpha=2$	4.016	3.841	770
8	Si-MCM-41/Si-magadiite $\alpha=4$	4.209	3.841	592
9	Si-MCM-41/Al-magadiite $\alpha=2$	4.016	3.841	856.3
10	Al-MCM-41/Si-magadiite $\alpha=2$	4.177	4.067	753.1
11	Al-MCM-41/Al-magadiite $\alpha=2$	4.237	4.021	782.0
12	Si-MCM-41	3.944	3.944	1169.2
13	Al-MCM-41	4.032	4.059	931.5

Simultaneous TG-DTG-DTA measurements showed that the amount of water released from the samples was higher for those containing aluminium than for the aluminium-free materials. This feature is due to the more hydrophilic character of the aluminium containing samples. Figure 2 shows the DTG curves for the aluminium-

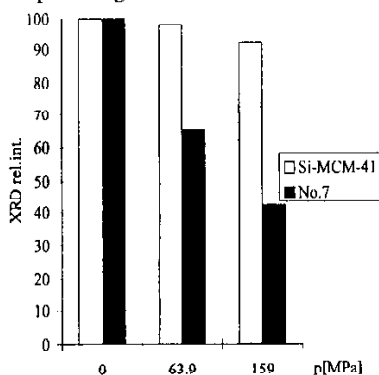


Fig. 1 Comparison of the mechanical stabilities of the aluminium-free composite and the Si-MCM-41 sample

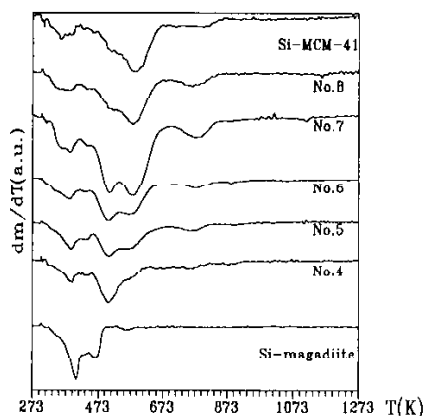


Fig. 2 DTG profiles of samples of different compositions

free materials. It is seen that the shape of the curves related to the composite materials is in between those of MCM 41 and magadiite. The DTG curves for samples with low magadiite content do not, while for those of high magadiite contents do have an indication of high temperature mass loss. We assumed that these high temperature peaks are due to the sealing between magadiite SiOH and that of MCM 41. The higher the MCM-41 content of the composite the more pronounced this peak is. This observation is in accordance with those obtained with ^{29}Si MAS NMR and IR spectroscopy [15, 20]. The mass losses divided into several temperature groups are listed in Table 2. As the last column of the table shows the mass loss decreases with increasing the magadiite content of the composite. The highest (51.5 mg/100 mg) and the lowest (18.3 mg/100 mg) belongs to MCM-41 and magadiite, respectively. From these values the loose structure of MCM-41, its high water and SiOH contents and thereby its structural instability can be concluded.

Table 2 Summary of TG-DTG-DTA measurements: percentage mass losses in various temperature ranges for the aluminium-free samples

Sample	α value	$T_{\text{range}}/\text{K}$				Total mass loss/%
		273-433	433-533	533-673	673-1273	
Si-MCM-41	-	7.9	10.8	24.1	8.7	51.5
Composite	4	6.6	10.6	19.2	9.0	45.4
Composite	2	7.1	12.1	18.5	9.6	46.3
Composite	1	7.2	11.0	13.6	7.9	39.7
Composite	1/2	6.9	8.9	9.4	3.1	28.3
Composite	1/4	5.9	10.9	7.5	5.8	30.1
Si-magadiite	-	10.1	5.0	1.2	2.0	18.3

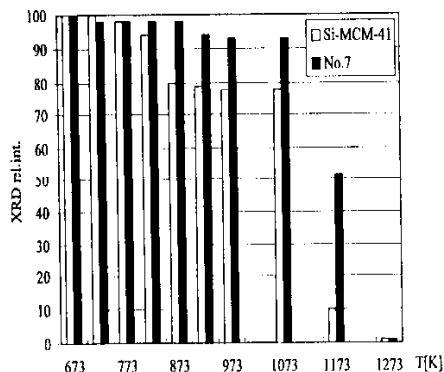


Fig. 3 Comparison of the thermal stabilities of the aluminium-free composite and the Si-MCM-41 sample

In order to compare the thermal stability of the composite material to that of MCM-41 the following experiments were carried out. Portions of both samples were heated to increasing temperatures for 1 h. After cooling back to room temperature under nitrogen, XRD patterns were recorded. From the diffractograms the intensity ratios of the first reflections were calculated and compared. These values are shown in Fig. 3. It is clear that crystal destruction of the composite takes place after treatment at a temperature higher than that for MCM-41. Heating at 1273 K transformed both samples to amorphous material.

Conclusions

A silicate composite material was prepared by synthesizing MCM-41 in the presence of magadiite.

Substantial improvement of the thermal and mechanical stability for the mesoporous composite was achieved. This feature is explained on the basis of the composite structure.

The composite materials may be used as catalysts or catalyst supports.

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