

SYNTHESIS, CHARACTERIZATION AND CO₂ ADSORPTION-DESORPTION OF MCM-48 AND MCM-41 MOLECULAR SIEVES

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Objectives

Preparation by grafting of functionalized MCM41 and MCM48 molecular sieves. MCM41 molecular sieve was prepared by the method developed by Beck et al. [1] and MCM48 was synthesized according to the procedure developed by Ortiz et al. [2]. 3-aminopropyl-triethoxy silane (APTES) was used as functionalization agent.

The modified silica were characterized by powder X-ray diffraction analysis (XRD), infrared spectroscopy (FT-IR) and nitrogen adsorption-desorption experiments.

Adsorption-desorption of CO₂ and the influence of temperature for CO₂ adsorption on amino-functionalized mesoporous materials was performed by using temperature programmed desorption – TPD method

Experimental

Sample preparation:

MCM41 preparation method: 1g of MCM41 was dissolved in 50 mL toluene and stirred for an hour. After that an excess of 3.39 mmol of APTES was added and refluxed overnight. Resulted white solid was removed from solvent by filtration washed with toluene and distilled water and dried for 8h under reduced pressure at 80 °C.

MCM48 preparation method: a solution containing 2.6 g of CTAB, 120 mL H₂O, 50 mL of ethanol and 12 mL NH₄OH were added to 3.4 g of TEOS. This solution was stirred for at room temperature overnight. Resulted white solid was removed from solvent by filtration washed with toluene and distilled water and dried for 8h under reduced pressure at 80 °C.

Functionalization of the mesoporous silicas:

0.5 g of prepared molecular sieve, MCM41 or MCM48, was added to a mixture containing 50 mL of toluene and 0.79 mL of 3-aminopropyl-triethoxy silane. The reaction mixture was vigorously stirred under reflux temperature for 24h. The obtained solutions were decanted and the resulted solids were washed several time with ethanol. Further the solids were dried out in an oven at 80°C for 4h and then were annealed at 540°C for 9h. The resulted functionalized molecular sieves were denoted as MCM41 sil and MCM48 sil respectively.

Sample characterization:

FT-IR: Jasco 430 spectrometer in the 4000–400 cm⁻¹ range, using KBr pellets.

XRD: XD 8 Advanced Bruker diffractometer using the Cu K_α radiation, phase composition.

BET: Nova 2000 Quantachrome instrument series, N₂(g) adsorption-desorption technique.

TA: TGA/SDTA 851-LF 1100 Mettler apparatus.

Thermal Analysis and TPD method

The samples with mass of about 20 mg were placed in alumina crucible of 150 μL. The measurements were performed in dynamic air atmosphere with the flow rate of 50 mL min⁻¹, in the temperature range of 25–650 °C with a heating rate of 10 °C min⁻¹. The thermal analysis system was coupled with a Pfeiffer–Vacuum–Thermo Star mass spectrometer by silica capillary at temperature of 200 °C. Adsorption measurements were carried out using the same thermogravimetric analyzer connected to a gas delivery manifold. High-purity CO₂ and 30%CO₂ in N₂ at 1 atm. was used for the adsorption runs, and N₂ was used as a regenerating purge gas for CO₂ desorption.

Each sample was pretreated in flowing N₂ at 150 °C, then cooled to the desired adsorption temperature (40÷80°C), and exposed to 30% CO₂/N₂ (70 mL/min⁻¹) for 120 min.

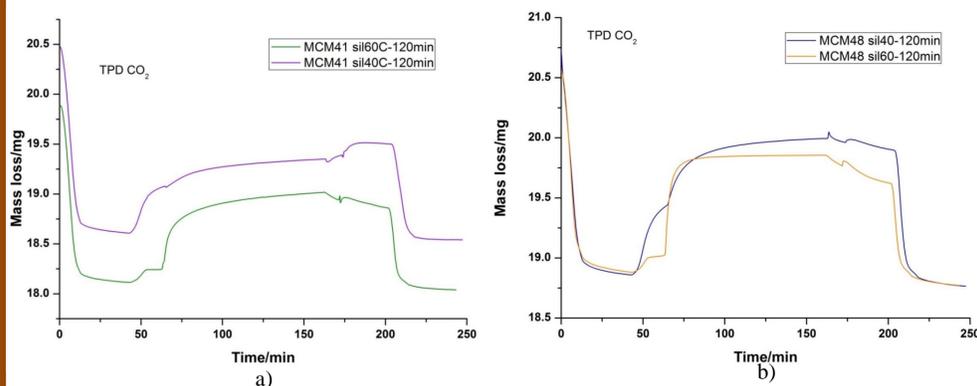


Fig. 8. CO₂ adsorption-desorption steps of functionalized samples MCM41 sil (a) and MCM48 sil (b) with isotherms at 40 and 60 °C.

Conclusions

- X-ray diffraction analysis confirms the presence of hexagonal structure in case of MCM41 and the cubic structure in case of MCM48 as synthesized molecular sieves.
- The present bands at 1641–1385 cm⁻¹ on the IR spectra of both MCM41 sil and MCM48 sil were assigned to N–H stretching vibrations and N–H bending vibrations, respectively, providing evidence of the successful grafting of amine on the surface of the molecular sieves.
- The isotherms are type 4 and also present a condensation step in the relative pressure range of 0.2-0.3 which is correlated with capillary condensation in the channels of the mesoporous sieve.
- From the obtained results it can be observed that the optimal temperature for CO₂ adsorption-desorption by TPD is 60 °C.

Results and Discussions

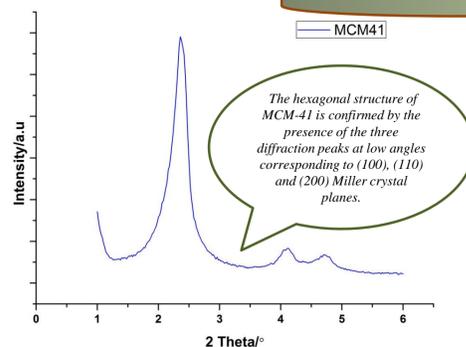


Fig. 1. XRD spectra of MCM41 composite.

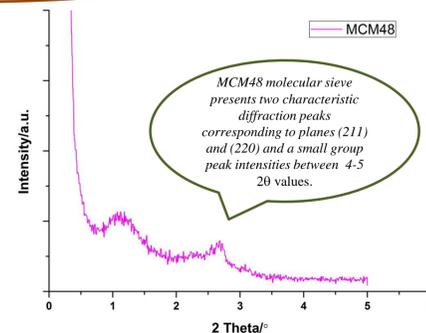


Fig. 2. XRD spectra of MCM48 composite.

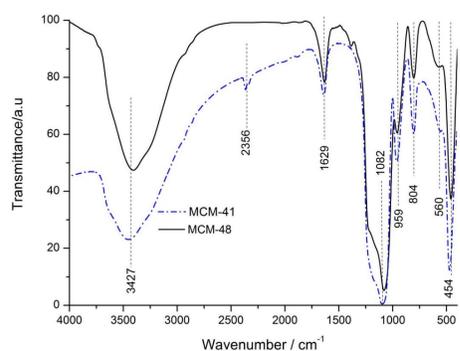


Fig. 3. FT-IR spectra of MCM41 and MCM48 composites.

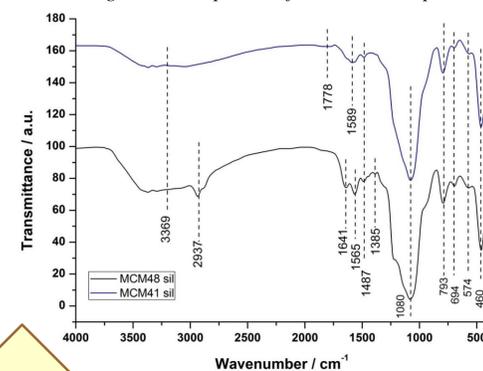


Fig. 4. FT-IR spectra of MCM41 sil and MCM48 sil composites.

The FT-IR spectra of MCM41 is evidenced by the peaks located at the following wavenumber: the peak at 1082 cm⁻¹ corresponds to stretching vibration of the Si–O–Si bond; the peak present around 804 cm⁻¹ can be assigned to Si–O–Si stretching vibrations; and a peak is found at 454 cm⁻¹ corresponding to banding vibration. After modification with APTES, the MCM41 still retained its siliceous structure, but some additional bands are observed at 694 cm⁻¹, a weak peak which is due to the bending of N–H bonds and the symmetrical –NH₃⁺ bending at 1589 cm⁻¹, indicating the existence of amine groups; the small band present around 1487 cm⁻¹ attributed to –NH₃⁺ stretching vibration in the case of MCM41 sil.

The FT-IR spectra of MCM48 presents a broad present at 3427 cm⁻¹ that can be assigned to free hydroxyl groups located on the surface. After the MCM48 surface reactions with APTES, the IR bands characteristic for hydroxyl groups became smaller, indicating that a large part of the surface hydroxyl groups reacted with the functionalized agent. Bands present at 2937 cm⁻¹ are due to CH stretching in CH₂CH₂CH₂NH₂ groups.

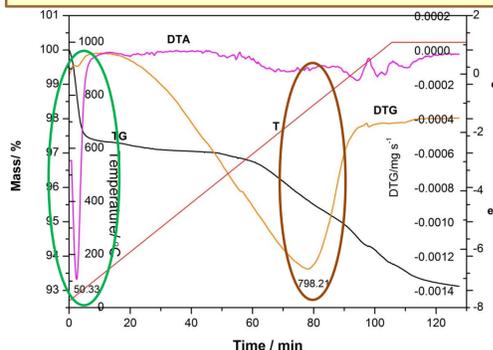


Fig. 5. TG-DTG-DTA curves of MCM48 composite.

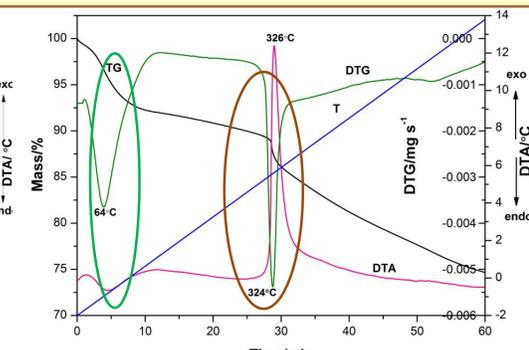


Fig. 6. TG-DTG-DTA curves of MCM41 sil composite.

The mass loss in the temperature range 25 – 100 °C was attributed to desorption of water residing within the pores and the water H-bonded to surface silanol groups (Fig. 4 and Fig. 6). Following steps of mass loss in case of MCM48: from 100 to 300 °C surfactant decomposition, from 300 to 520 °C residual surfactant decomposition and silanol condensation and from 520 to 800°C residual silanol condensation take place. The mass loss in the range 300 – 500 °C (Fig. 6) was attributed to the decomposition of the grafted organic functional group.

Table 1. Textural properties of the studied materials

No.	Sample	Specific surface area (m ² /g)	Pore volume BJH _{Des} (cc/g)	Average pore diameter BJH _{Des} (nm)
1.	MCM41	1299.7	0.695	3.30
2.	MCM41 sil	655.8	0.611	3.25
3.	MCM48	1466.059	0.802	3.48

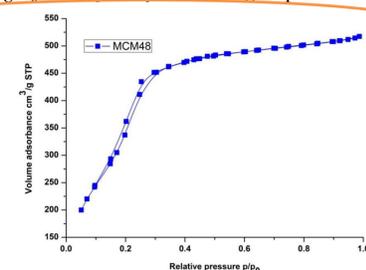


Fig. 7. Nitrogen adsorption-desorption isotherms of MCM48 molecular sieve