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ELECTRONIC SUPPORTING INFORMATION (ESI)

Introducing catalytic activity in helical nanostructures: Microwave assisted oxathioacetalisation catalysed by Al-containing helical mesoporous silicas

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Experimental

Materials characterisation

Porous texture was characterized by N_2 adsorption at 77 K in an AUTOSORB-6 apparatus. The samples were previously degassed for 5 h at 373 K at 5×10^{-5} bars. BET surface area estimated by using multipoint BET method using the adsorption data in the relative pressure (P/P_0) range of 0.05–0.30. The pore size distribution was calculated from the adsorption branch of the N_2 physisorption isotherms using the Barret-Joyner-Halenda (BJH) method. The mesoporous volume was checked out from the cumulative pore volume distribution curve.

The morphology of the mesoporous materials was investigated by transmission electron microscopy (TEM) using a JEM-2010 microscope (JEOL, 200 kV, 0.14 nm of resolution). Samples for TEM analysis were prepared by dipping a sonicated suspension of the sample in ethanol on a carbon-coated copper grid. The digital analysis of the TEM micrographs was performed using DigitalMicrographTM 3.6.1. by Gatan. SEM

analysis of all the samples, previously covered with gold, was carried out using a JM-6400 microscope (JEOL).

Small-angle powder X-ray diffraction (XRD) analysis was carried out with a Philips PW3040/00 diffractometer using a CuKα radiation (λ = 1.54056 Å), operating at 40 kV and 30mA, at a scanning velocity of 0.03°/min in the $0.7° < 2\Theta < 10°$ range.

Fourier Transform Infrared Spectroscopy (FTIR) analyses were performed on a Bruker IFS 66 spectrometer equipped with a DLaTGS detector. The spectra were taken with a 2 cm^{-1} resolution in a wavenumber range from 4000 to 400 cm^{-1}. FTIR analysis was recorded directly placing the solid sample in the ATR (golden gate) instrument.

Catalytic experiments

Commercial samples of Al-MCM-41 (Si/Al ratio 60) and Amberlyst 15 as well as H-Y (SiO_2/Al_2O_3 ratio 20) and H-ZSM-5 (SiO_2/Al_2O_3 ratio 30) were purchased from Sigma-Aldrich and Zeolyst Inc, respectively. All materials were tested in the catalytic experiments as purchased.

Microwave experiments were performed on a CEM DISCOVER microwave reactor with PC control and monitored by sampling aliquots of reaction mixture that were subsequently analysed by GC/GC-MS using an Agilent 6890N GC model equipped, with a 7683B series autosampler, fitted with a DB-5 capillary column and an FID detector. Experiments were conducted on a closed vessel (pressure controlled) under continuous stirring. The microwave method was generally power-controlled where the samples were irradiated with different power outputs (e.g. settings at maximum power, 300 W).

Response factors of the reaction products were determined with respect to the original carbonyl compounds from GC analysis using known compounds in calibration mixtures of specified compositions.

Characterization results

Al-HMM also mantains a 2-D hexagonal mesopore arragement, showing the three distinctive (100), (110), and (200) X-ray diffractions peaks characteristic of a p6mm mesopore structure.

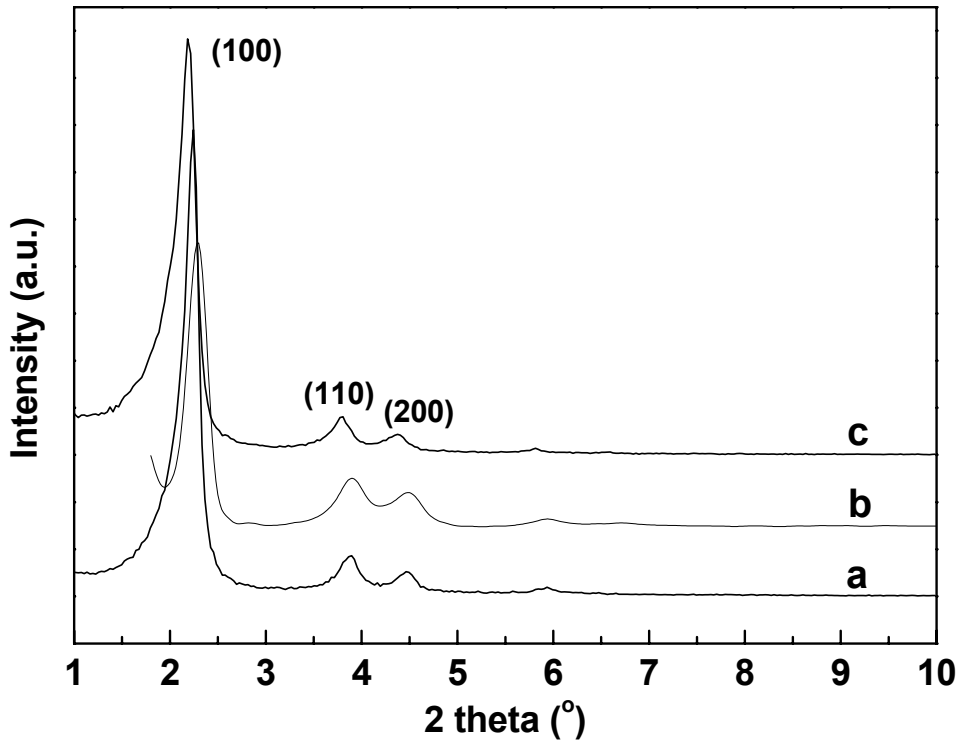

Figure 1. X-Ray diffraction patterns of samples with a nominal Si/Al ratio of the metal in each sample is (b) Al-HMM (Si/Al=190) and (c) Al-MCM (Si/Al=90). Spectra for (b) and (c) samples are shifted for clarity. Al-HMM (Si/Al molar ratio = 95 and Si/Al molar ratio= 190) as compared with the parent HMM material (a).

TEM images of Al-HMM (Si/Al=190) at different tilting angles confirmed the helical morphology of the material. Planes along the longitudinal axe of the rod were sequentially turned to be perpendicular to the beam, demostrating the spiral nature of the channels.

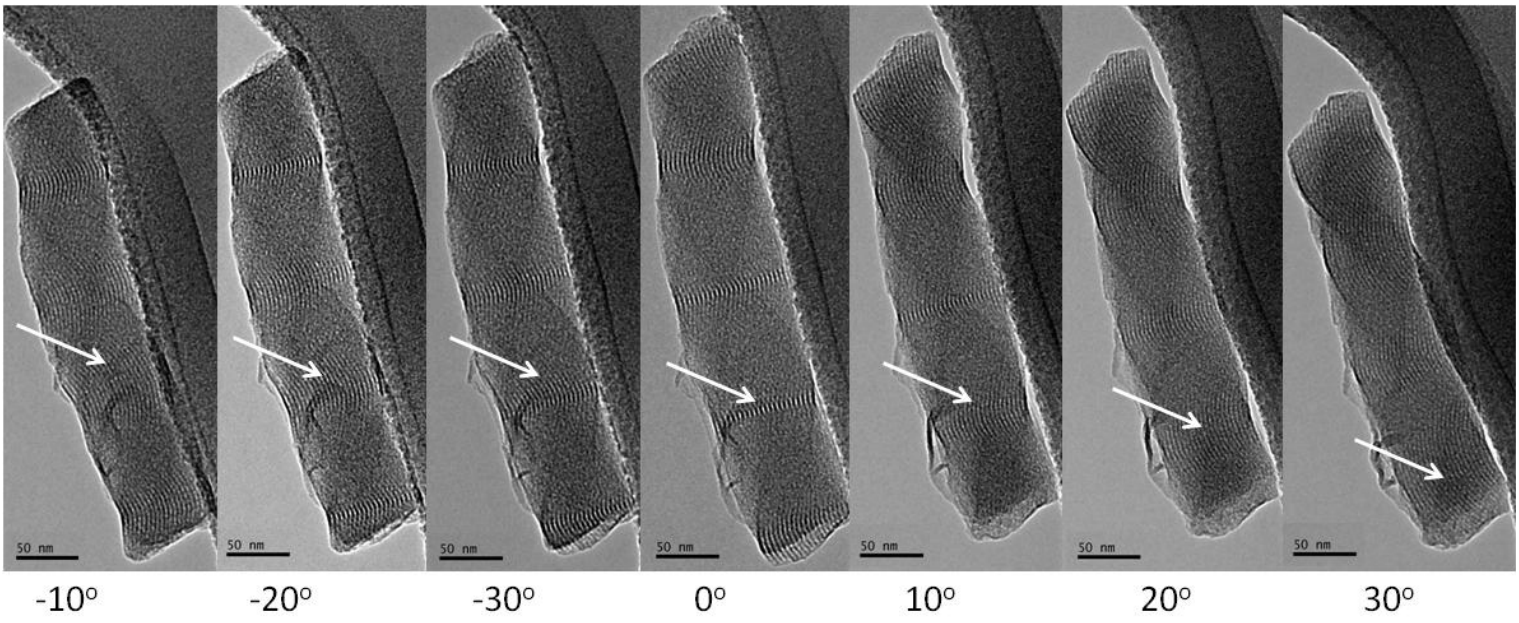

Figure 2. TEM images of Al-HMM (Si/Al=190) sample taken at the tilt angles indicated. The tilt axis is parallel to the rod axis.

The SEM analysis of these mesoporous silica materials confirms the helicoidal morphology of the rods, as evidence by the SEM micrograph shown in Figure 3, corresponding to the Al-HMM (Si/Al=190) sample.

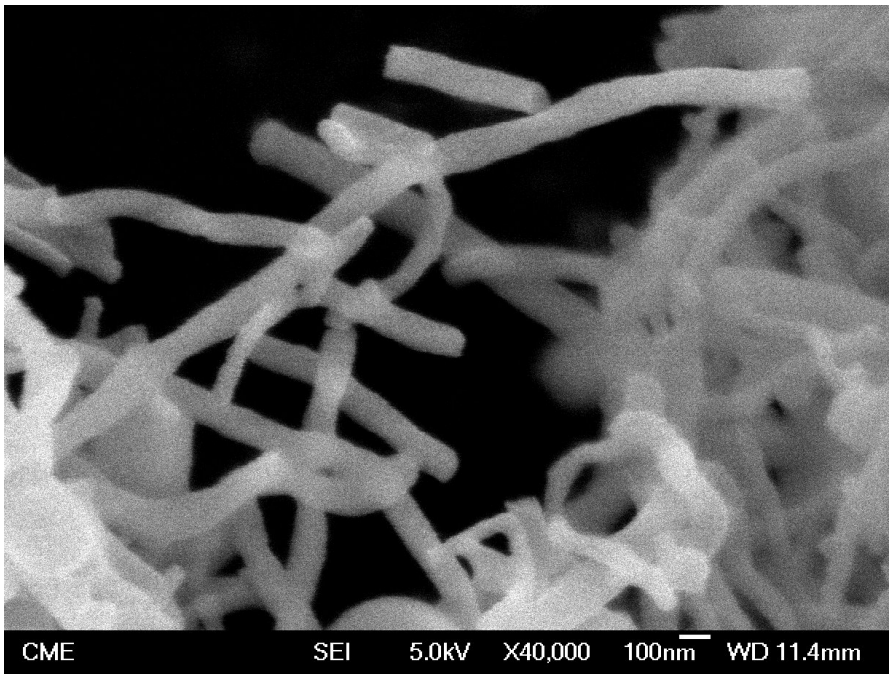

Figure 3. SEM image of Al-HMM (Si/Al=190) sample .

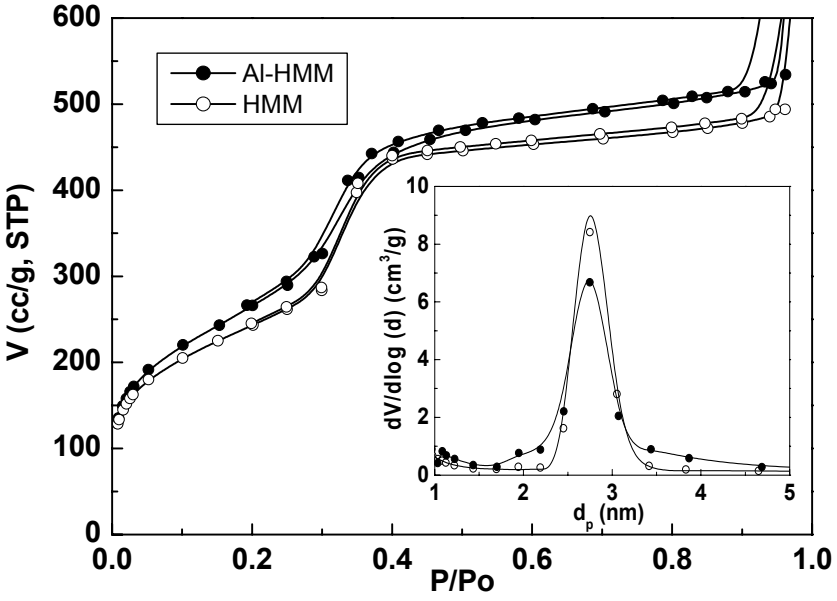

Figure 4. Representative nitrogen adsorption isotherms and their corresponding pore size distribution of Al-HMM (filled circles, Si/Al ratio=95) as compared with the parent helical material HMM (hollow circles).

For those materials with Al on their structures, infrared spectra showed a shift of the band at ca. 1040 cm–1 towards higher wavenumbers. This is consistent with the metal incorporation into lattice positions of the helical silica materials.

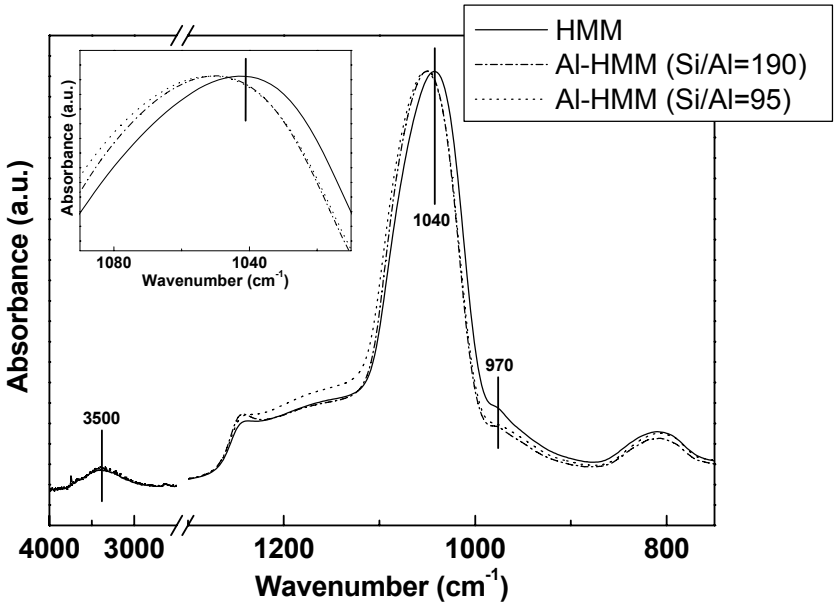

Figure 5. FTIR spectra of Al-HMM (Si/Al molar ratio = 190 and 95) as compared with the parent HMM material.

Al-HMM were also highly reusable under the investigated reaction conditions, preserving over 90% of their initial activity after 4 uses. For the reuses, the quantities of samples were doubled to ensure enough quantity of catalyst to be reused 4 times (there is some catalyst loss in every cycle)

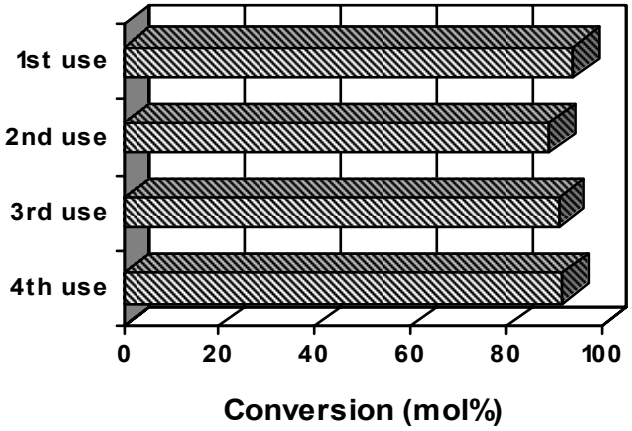

Figure 6. Reuses of the Al-HMM (Si/Al=95) catalyst. Reaction conditions: 10 mmol cyclohexanone, 20 mmol 2-mercaptoethanol, 0.1 g catalyst, microwaves, 300 W, 2 min, 70ºC (maximum temperature achieved).