

SUPPORTING INFORMATION FOR

TEMPLATED SELF-ASSEMBLY OF ORDERED MESOPOROUS SILICA ON CLAY NANOTUBES

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Materials

Halloysite nanotubes (HNTs) were obtained from Sigma-Aldrich. The ordered mesoporous materials were synthesized via templating pathway using tetraethylorthosilicate (TEOS, 98 %) as a silica source, hexadecylamine, pluronic-123, and cetyltrimethylammonium bromide (all are from Sigma-Aldrich).

Synthesis procedure

The ordered micro-mesoporous materials were synthesized via templating pathway. Depending on silica type pluronic-123, hexadecylamine and cetyltrimethylammonium bromide were used to obtain SBA-15/HNT, HMS/HNT and MCM-41/HNT composite materials respectively (Fig. S1).

HNT were dispersed in water-alcohol template solution. The resulted mixture was stirred at room temperature for 1h. Following this, TEOS was added dropwise. The mixture was adjusted to pH 11 using 25 % $\text{NH}_3 \cdot \text{H}_2\text{O}$ and stirred for 4 h. Synthesized gels of the molar composition of template: $5\text{SiO}_2:775\text{H}_2\text{O}:75(\text{isopropyl alcohol}):1.95\text{HNT}$ was allowed to react at room temperature for 24 h and then treated hydrothermally at 90°C for 24 hours. The solid product was recovered by filtration, washed with the deionized water for three times to remove bromine totally. For dehydration the white solid was dried at 80-110°C for 4 h, the template was removed by calcination on air at 550°C for 4 h (heating rate 3 °C/min). The yields of SBA-15/HNT, HMS/PTE and MCM-41/PTE were 92, 89 и 90 % respectively.

Characterization

The isotherms of nitrogen adsorption/desorption were measured at 77 K with Micromeritics Gemini VII 2390t instrument. Before the measurements, the samples were degassed at 350 °C for 4 h. The specific surface area was calculated with the Brunauer–Emmett–Teller (BET) and Langmuir methods applied to in the range of relative pressures $P/P_0 = 0.05\text{--}0.30$. The pore volume and pore size distributions were determined from the adsorption branches of the isotherms based on the Barrett–Joyner–Halenda (BJH) model.

TEM microscopy studies of mesoporous supports and La-containing additives were carried out using a JEM-2100 JEOL microscope operating with a 100 kV accelerating voltage.

X-ray diffraction (XRD) data were obtained at room temperature on a Bruker D2 PHASER powder diffractometer in the $\theta\text{--}\theta$ geometry with X-ray generation at 30 kV and 10 mA using a copper anode ($\lambda(\text{CuK}\alpha) = 1.5418 \text{ \AA}$). Fig. S3. Diffraction patterns were recorded with sample rotation in the horizontal plane in the angle interval of 2θ of 1.5° to 8° using a step size of 0.05°

and 3 s per step. The diffraction patterns were processed using the Bruker software package diffrac.EVA. Identification of phases was carried out on the basis of ICDD.

The thermal stability of MCM-41/HNT composite was investigated at the temperature range of 600-1100 °C and 100 °C per step for 4 h treatment followed by low-temperature nitrogen adsorption/desorption measurements.

Mechanical stability: 0.5 g of MCM-41/HNT sample was compressed under different pressures using laboratory hydraulic press LabTech with press form. Taking into account the mass applied, diameter and thickness of the tablets the actual pressures were calculated. Following this, the textural properties of the test materials were measured by low-temperature nitrogen adsorption/desorption technique.

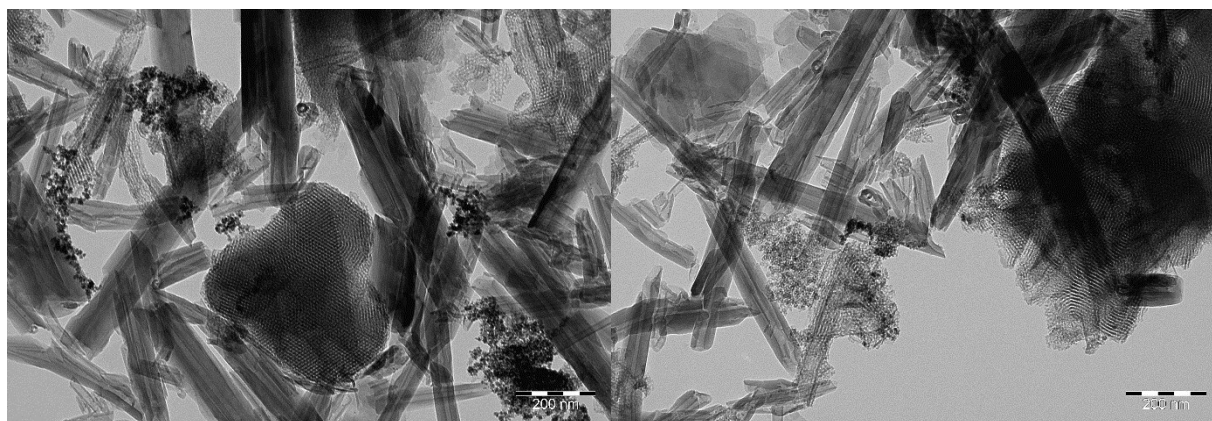


Figure S1. SBA-15/HNT.

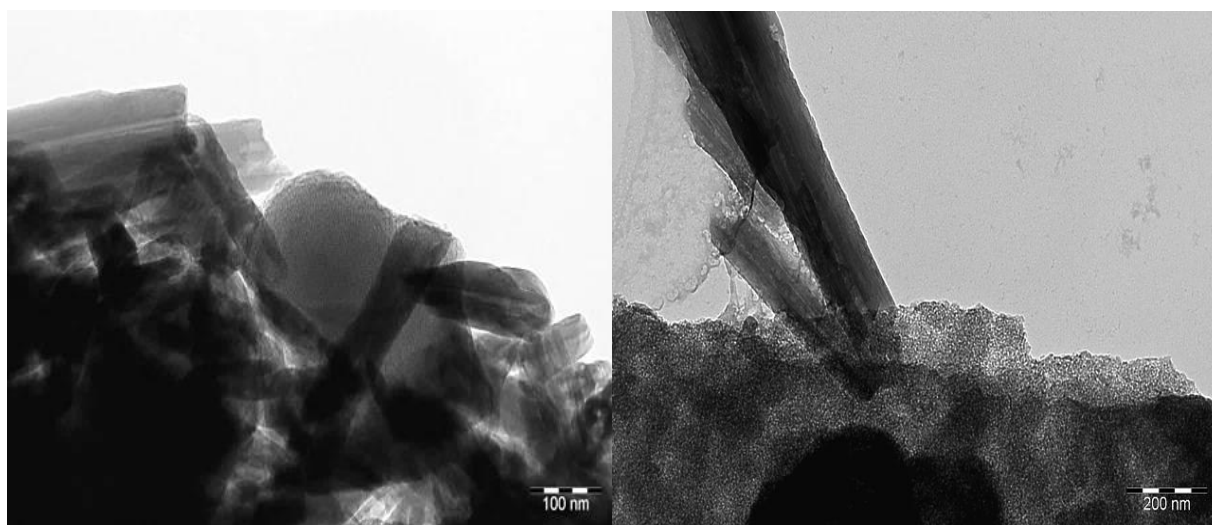


Figure S2. HMS/HNT.

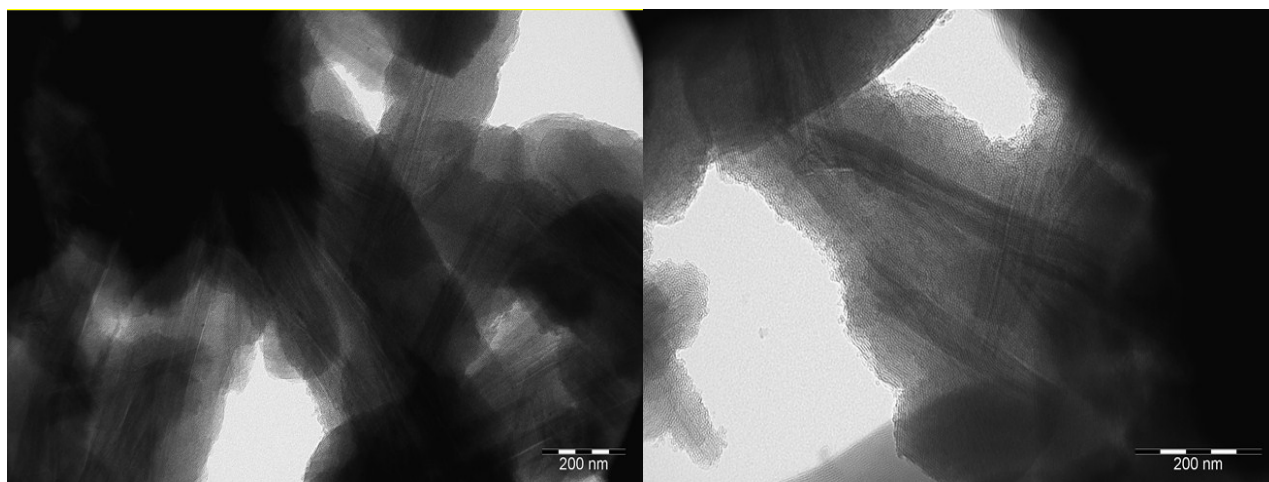


Figure S3. MCM-41/HNT.

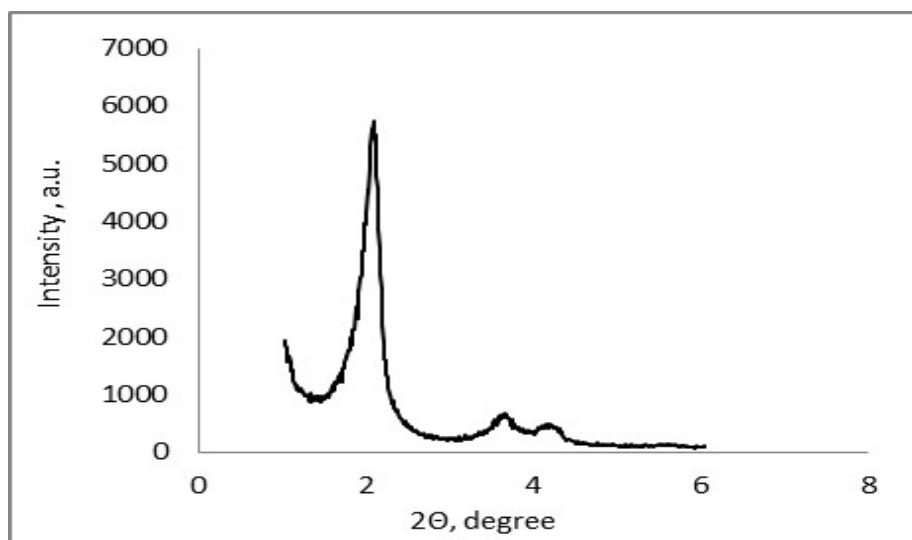


Figure S4. Low-angle patterns of MCM-41/halloysite.

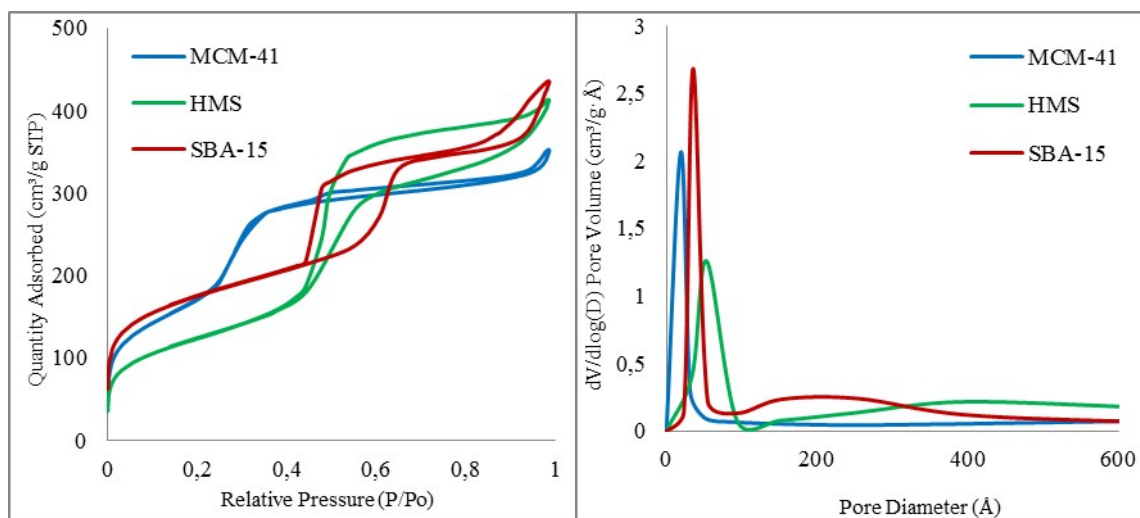


Figure S5. Nitrogen adsorption/desorption isotherms and pore size distribution of materials synthesized.

Table S1. Textural properties of MCM-41/HNT composite after thermal treatment

Temperature, °C	Surface area, m ² /g		Pore Volume, cm ³ /g	Pore Diameter, Å
	BET	Langmuir		
600	620	858	0.54	24
700	606	842	0.52	24
800	552	585	0.49	24
900	546	807	0.39	24
1000	445	617	0.33	29
1100	115	154	0.11	83

Table S2. Textural properties of MCM-41/HNT composite after mechanical treatment

Pressure, MPa	Surface area, m ² /g		Pore Volume, cm ³ /g	Pore Diameter, Å
	BET	Langmuir		
0.1	620	858	0.54	24
100	592	778	0.54	24
200	561	718	0.53	25
300	555	709	0.54	26
500	520	680	0.48	26

Table S3. Comparative activity of the additives and e-cat in the desulfurization of the liquid products of the cracking of VGO

Sample	Gasoline, wt%	LCO, wt%	HCO, wt%	Coke, wt%	Total sulfur in liquid products, ppm	Δ ^a , %
La-MCM-41/HNT- Al ₂ O ₃	44	22	12	5	9132	25
e-cat	45	21	11	6	12120	-