SUPPORTING INFORMATION

Mesoporous MFI Zeolites by Microwave Induced Assembly between Sulfonic Acid Functionalized MFI Zeolite Nanoparticles and Alkyltrimethylammonium Cationic Surfactants

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Experimental section

Preparation of Mesoporous MFI Zeolites

The mesoporous ZSM-5 were synthesized as follow: ZSM-5 nano zeolites were prepared from a clear solution with the following molar composition: $1Al_2O_3$: $60SiO_2$: 11.5TPAOH: $1500H_2O$. In typical synthesis batch, 20.83 g Tetraethyl orthosilicate (TEOS, 98%; Aldrich), 19.08 g tetrapropylammonium hydroxide (TPAOH, 20~25%; TCI), 0.33 g aluminum isopropoxide (AIP; Aldrich) and 15 g distilled water were mixed homogeneously with stirring. The precursor solution was pre-crystallized under microwave irradiation (MW power of 600 W) at 120 ºC for 30 min followed by functionalization with MPTES (5 mol% with respect to the silica) under microwave at 120ºC for 1 h. The synthetic mixture is cooled to room temperature and 5 g H_2O_2 (30% in water) was added in order to oxidize thiol group for obtaining sulfonic acid funtionalized zeolite nanoparticles. The resultant solution was added to CTAB solution [1.78 g CTAB (5 mol% of silica) + 15 g deionized water] and stirred 3 hours. Finally, the mixture was subjected to microwave irradiation (MW power of 300-1200 W) at 165 ºC for 0.5-1.5 h [Meso-ZSM-5(SO_3H-CTAB)-MW], whearas in hydrothermal method the vessel was maintained at 165 ºC for 3 days [ZSM-5 (SO_3H-CTAB)-HT]. Crystallized products were filtered, washed with warm distilled water, dried at 90 ºC, and calcined in air at 550 ºC for 6 h for removing template and surfactant. Conventional microporous ZSM-5 [ZSM-5 (HT)] synthesized by hydrothermal treatment (165 ºC, 3 days) with the same molar composition: $1Al_2O_3$: $60SiO_2$: 11.5TPAOH: $1500H_2O$. For synthesizing mesoporous TS-1, analogues method was used with molar composition was $xTiO_2$: SiO_2: TPAOH: CTAB: H_2O = 1: 70: 114: 700: 2084 and in the case of synthesis of mesoporous S-1, x=0.

Characterization Methods

Mesoporous MFI zeolites were characterized by X-ray powder diffraction (XRD) using a Rigaku X-ray diffractometer with CuKα radiation (40 kv and 20 mA) over the range of $0.8 \leq 2\theta \leq 40$. N_2 adsorption and desorption isotherms were obtained at -196 °C on a micromeritics ASAP 2020 using static adsorption procedures. Samples were degassed at 300 °C and 10^{-6} Torr for the minimum of 12 h prior to analysis. BET surface areas were calculated from the liner part of the BET plot according to IUPAC recommendations. Pore size distribution was estimated from desorption branch of the isotherm by the method of BJH. Scanning electron microscopy (SEM) images were collected with a JEOL 630-F microscope. Transmission electron microscopy (TEM) images were obtained using a JEM-2100F instrument (JEOL). ^{29}Si-NMR spectra were recorded on a Bruker 600 MHz solid-state NMR spectrometer. A thermoanalyzer DSC200F3 was used for simultaneous thermal analysis combining thermaogravimetry and differential thermoanalysis (TG-DTA) at a heating rate of 10 °C min^{-1} in air. The zeta potential was determined by Otsuka Model ELS-Z at room temperature. Infrared spectra of Bronsted and Lewis acid site were determined by adsorption of pyridine and 2, 6-di-tert-butyl pyridine (2, 6-DTBPy) using a Nicolet Nexus 6700 FT-IR spectrometer with In-situ FT-IR cell. Spectra over the 4000–1400 cm^{-1} range were obtained by the co-addition of 64 scans with a resolution of 4 cm^{-1}. The samples were pretreated at 300 °C overnight under vacuum, pyridine or 2, 6-DTBPy was adsorbed at room temperature for 1 h. Spectra were collected after desorption at 150 °C for 1 h under high vacuum.

Catalytic reactions

Prior to the catalytic experiments each zeolite was activated at 450 °C for 90 min and then cooled down in a desiccator.

The alkylation reactions were carried out with mesitylene (16 mmol), benzyl alcohol (4 mmol) and Catalysts (50 mg) in a 25 mL single-necked flask, the mixture was stirred at room temperature until became homogeneous phase then increasing the temperature to 100 °C under mechanical stirring 15 min. Dodecane was used as internal standard. The course of the reaction was followed by analyzing the reaction mixture periodically using a gas chromatograph (HP 6890) equipped with a flame ionization detector (FID) and a capillary column (HP 5% silicone gum). The products were also identified by GC/MS. The molecular dimension of the product was estimated and the energy minimized conformation of product was drawn by using Chem3D Ultra 10.0.

Table S1 Textural properties of various MFI ZSM-5.

Catalyst	S_{BET} (m^2/g)	S_{Mic} (m^2/g)	S_{Ext} (m^2/g)	V_{Total} (cm^3/g)	V_{Mic} (cm^3/g)	V_{Meso} (cm^3/g)
Meso ZSM-5 (SO_3H-CTAB)-MW	529	129	400	0.81	0.06	0.75
Meso ZSM-5 (CTAB)-MW	500	110	390	0.40	0.05	0.35
ZSM-5 (SO_3H-CTAB)-HT	388	162	226	0.30	0.09	0.21
ZSM-5 (HT)	348	203	145	0.23	0.12	0.11

Table S2 Textural properties of Meso ZSM-5 (SO_3H-CTAB)-MW depending on various microwave power and irradiation time.

Catalyst	S_{BET} (m^2/g)	S_{Mic} (m^2/g)	S_{Ext} (m^2/g)	V_{Total} (cm^3/g)	V_{Mic} (cm^3/g)	V_{Meso} (cm^3/g)
Meso ZSM-5 (300 W-1.5 h)	466	135	331	0.41	0.07	0.34
Meso ZSM-5 (600 W-0.5 h)	520	144	376	0.55	0.08	0.47
Meso ZSM-5 (600 W-1.0 h)	519	117	402	0.57	0.06	0.51
Meso ZSM-5 (600 W-1.5 h)	529	129	400	0.81	0.06	0.75
Meso ZSM-5 (1200 W-1.5 h)	580	92	488	0.93	0.03	0.90

Table S3 Zeta potential of sulfonic acid functionalizaed mesoporous ZSM-5 and non-functionalized mesoporous ZSM-5.

Zeta potential (mV)	Nanozeolites	Sulfonic acid functionalized nanozeolites	CTAB Solution	Assembled nanozeolites with cationic CTAB
Meso ZSM-5 (SO_3H-CTAB)-MW	-9.6	-21.2	39.1	24.4
Meso ZSM-5 (CTAB)-MW		-		37.3

Zeta potential is one of the main forces that mediate interparticle interactions. As the present study focus on the ionic interaction between sulfonic acid functionalized MFI zeolite nanoparticles and alkyltrimethylammonium cationic surfactants, zeta potential can be regarded as an important measurement to elucidate such interactions. The zeta potential measurements can be conceptualized in the following manner.

1. Higher the zeta potential value for a system in cationic and anionic assemblies can be regarded as weak interaction.
2. Lower zeta potential value for a system in cationic and anionic assemblies can be regarded as strong interaction.

a) Biotechnology and bioengineering 2003, 83, 149.
b) European Journal of Pharmaceutics and Biopharmaceutics 2006, 62, 267.
c) Drug development and industrial pharmacy 2002, 28, 207.

The zeta potential of nanozeolites, sulfonic acid functionalized nanozeolites, CTAB solution and assembled sulfonic acid functionalized nanozeolites or non functionalized nanozeolites with cationic CTAB were measured.

Fig. S1 Low and wide angle XRD patterns of Meso TS-1 (SO_3H-CTAB)-MW and Meso S-1 (SO_3H-CTAB)-MW.

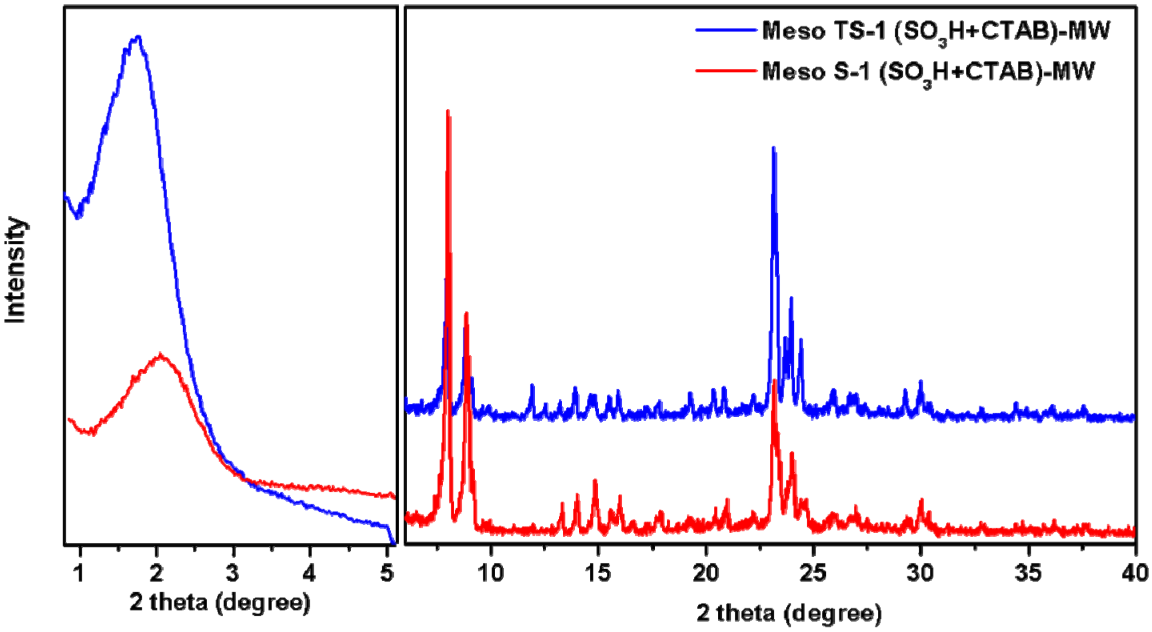


Fig. S2 Low and wide angle XRD patterns of Meso ZSM-5 (SO_3H-CTAB)-MW synthesized with various length of cationic surfactant.

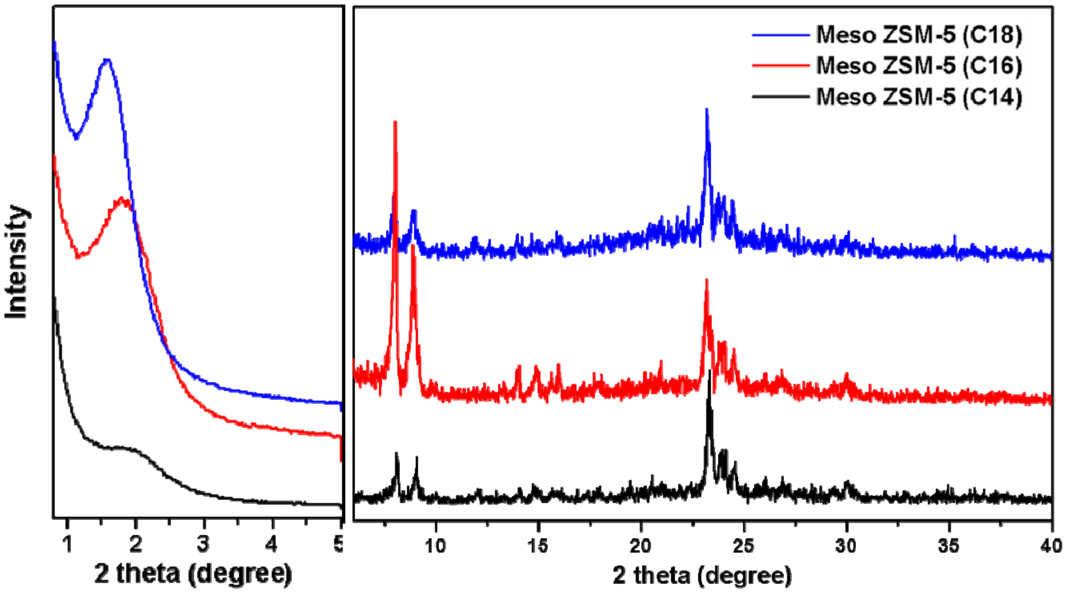
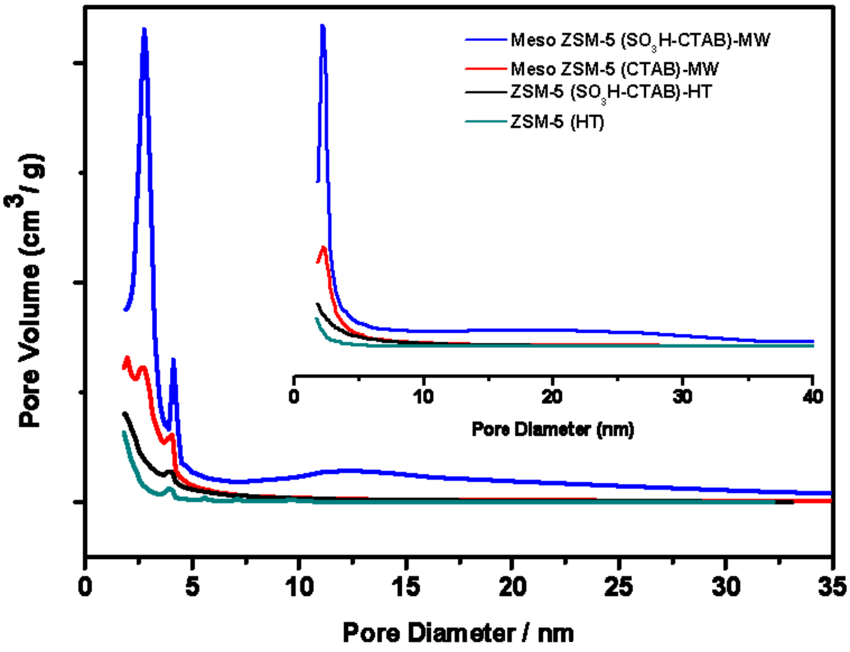


Fig. S3 Pore size distribution of various MFI ZSM-5.



The pore size distributions (PSDs) from desorption branch of isotherm resulted in tri-model pore system including large amounts of uniform pores (2.7 nm) due to the surfactant micelle structure, medium mesopores (4.1 nm) and large mesopores (12.4 nm) (Fig. 2). Whereas the measurements from adsorption branch of isotherm (Fig. S3 Insert figure) was contrary depicting absence of medium pore (4.1 nm) indicating bi-model nature. This difference in calculation of PSDs from adsorption and desorption branch were attributed to tensile strength effect indicated by forced closure due to sudden drop in the volume adsorbed along the desorption branch in the p/p^0 range 0.41–0.48 which were in consonance with earlier reports (Microporous and Mesoporous Materials 60 (2003) 1–17).

Fig. S4 TEM image of Meso ZSM-5 (SO_3H-CTAB)-MW.

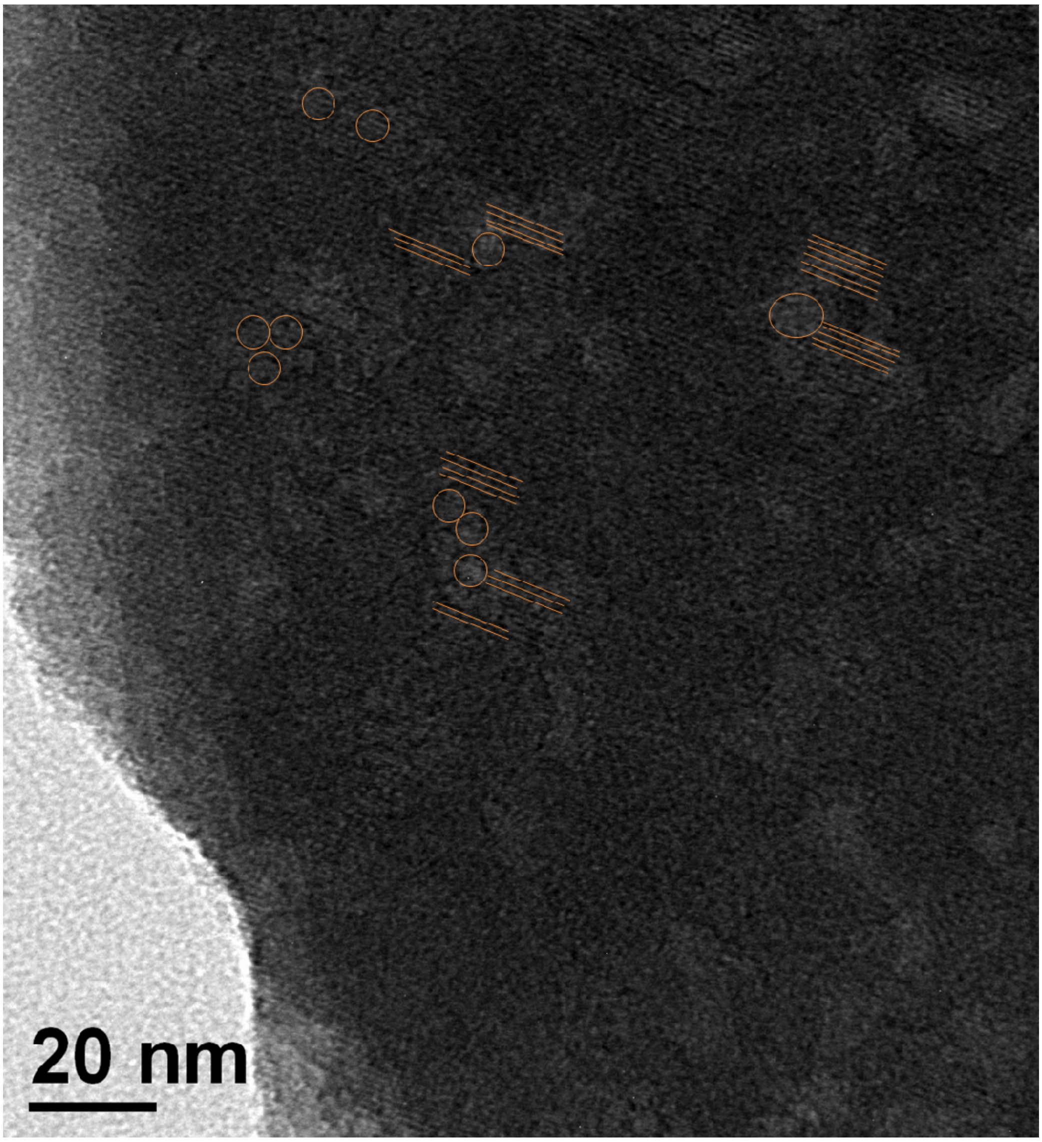


Fig. S5 Low and wide angle XRD patterns of Meso ZSM-5 (SO_3H-CTAB)-MW synthesized by various microwave power.

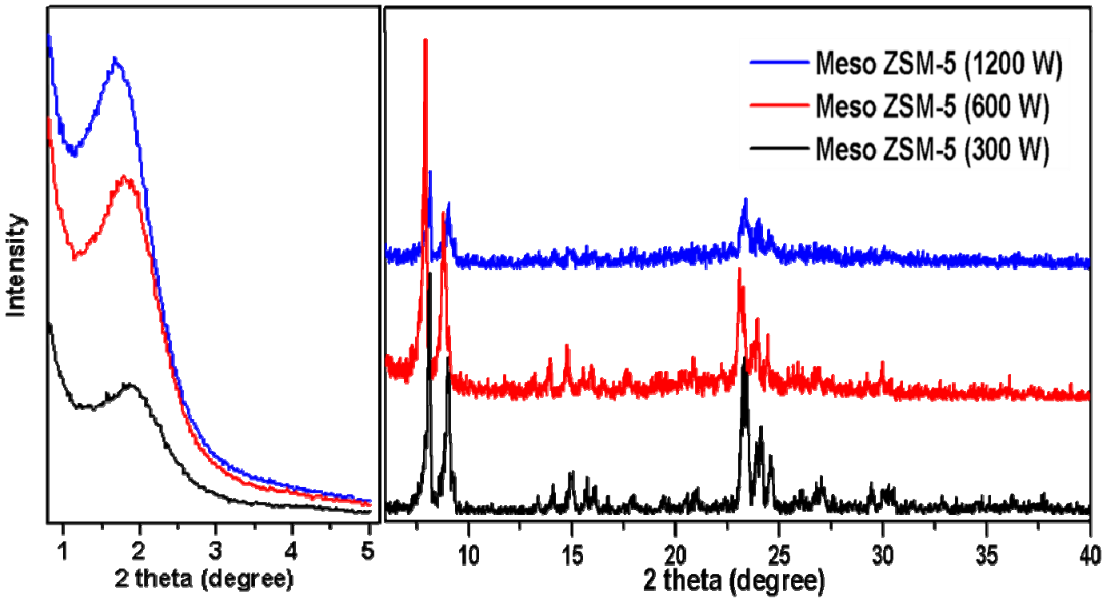


Fig. S6 Low and wide angle XRD patterns of Meso ZSM-5 (SO_3H-CTAB)-MW synthesized by various microwave irradiation time.

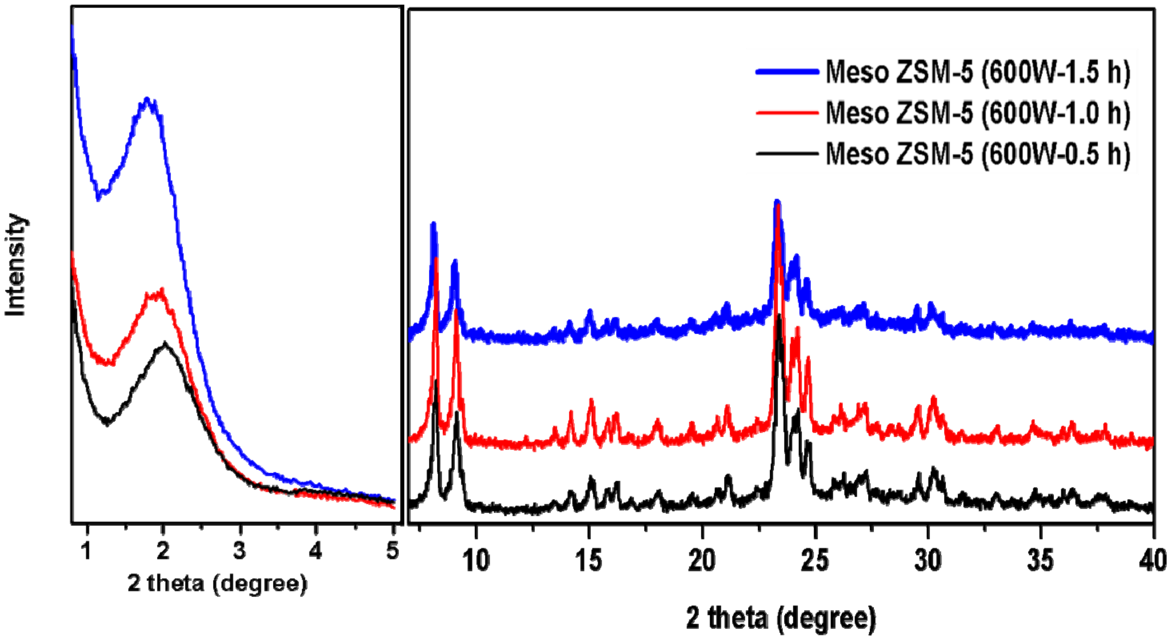


Fig. S7 SEM images for (a) ZSM-5 (SO_3H-CTAB)-HT, (b) Meso ZSM-5 (300 W), (c) Meso ZSM-5 (600 W-0.5 h), (d) Meso ZSM-5 (600 W-1.0 h), (e) Meso ZSM-5 (600 W-1.5 h), (f) Meso ZSM-5 (1200 W).

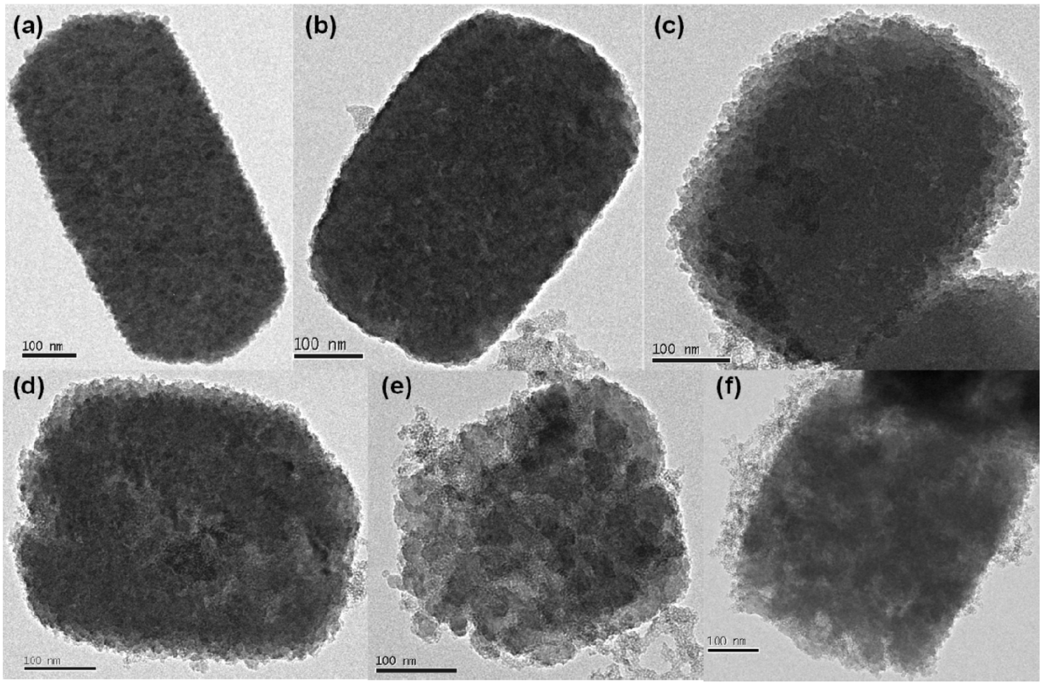


Fig. S8 FT-IR spectra of after adsorption of (A) Pyridine and (B) DTBPy on Meso ZSM-5 (SO_3H-CTAB)-MW and ZSM-5 (SO_3H-CTAB)-HT.

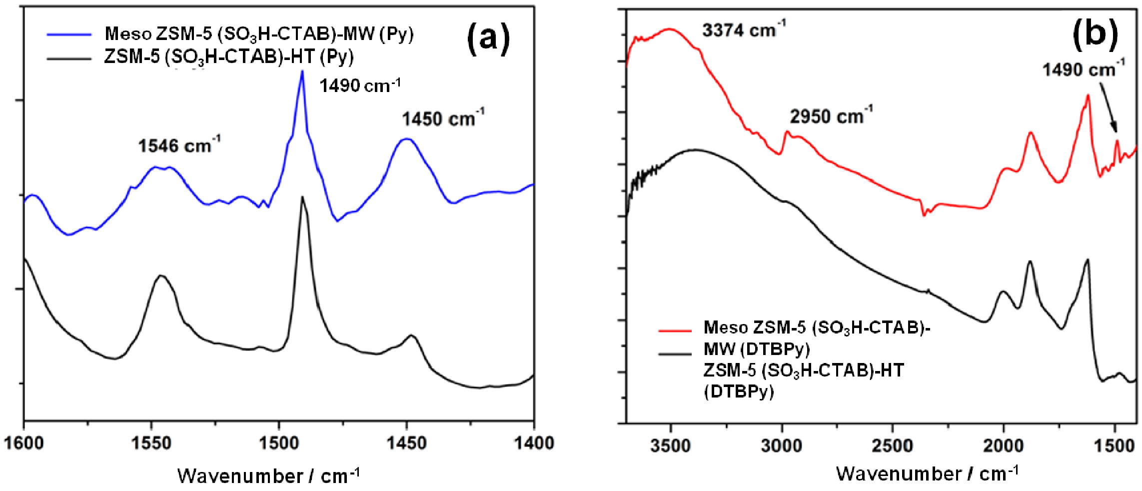
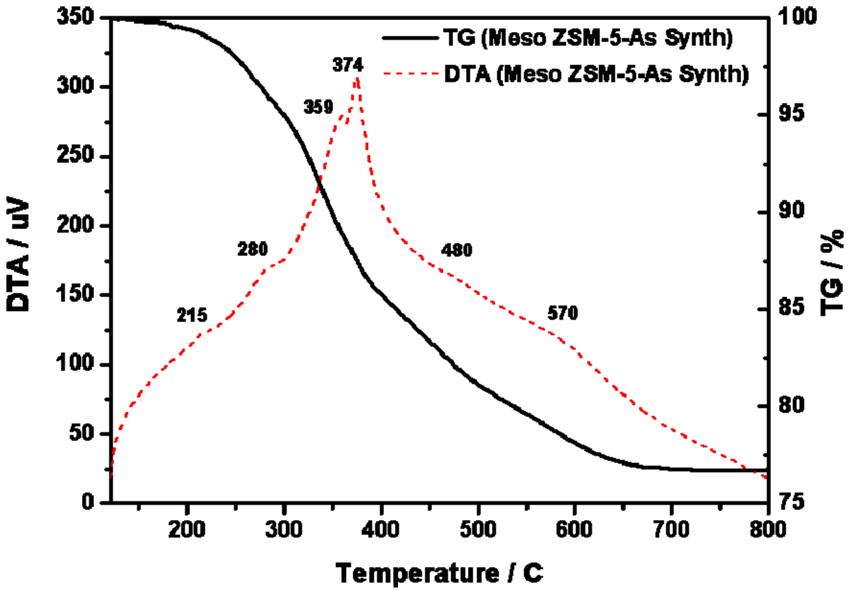
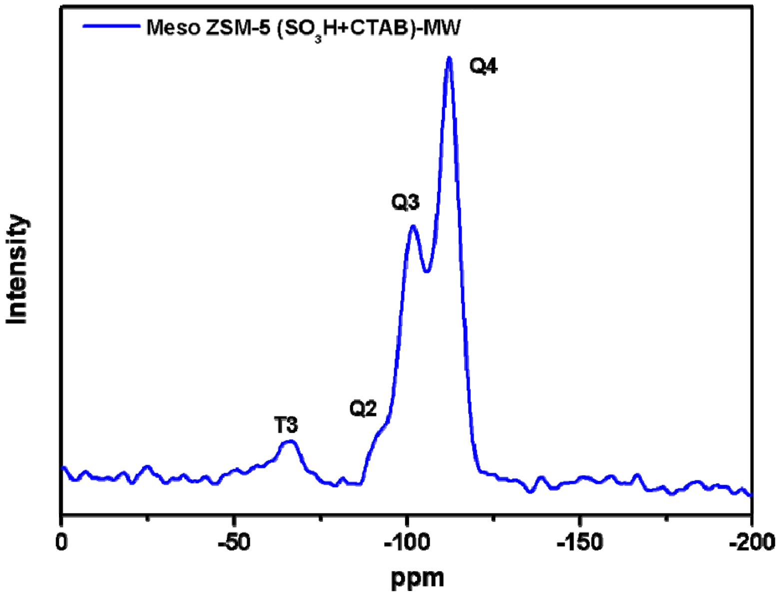


Fig. S9 TG-DTA curve of as synthesized Meso ZSM-5 (SO_3H-CTAB)-MW.



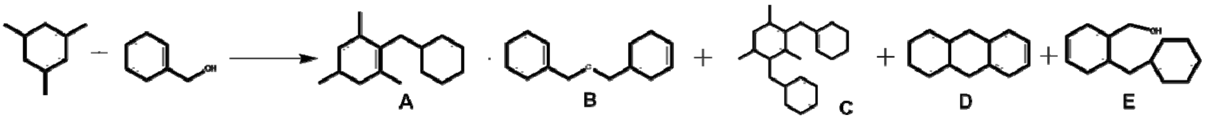
TG-DTA analysis was performed in order to verify the presence of sulfonic acid functional group as shown in the Fig. 8. As synthesized Meso ZSM-5 (SO_3H+CTAB)-MW samples have the first weight loss in the region of 210-280 °C which due to decomposition of surfactants (CTAB). Weight loss at 359 °C attributed to the loss of organo sulfur fragment due to the decomposition of 3-mercapto propyl groups on the zeolite particle surfaces. Weight loss at 374 °C was due to decomposition of zeolite template (TPAOH). In high temperature region, the two intensive peaks are observed around 480, and 570 °C corresponds to the decomposition of alkyl sulfonic groups.

Fig. S10 ^{29}Si-NMR spectra of as synthesized Meso ZSM-5 (SO_3H-CTAB)-MW.



The attachment of organo functional moieties (MPTES) was confirmed by ^{29}Si MAS NMR. The appearance of T3 at -66 ppm structural units illustrated the formation of Si–C bonds in the frameworks and thus the effective incorporation of organic groups. This also suggested the silanation on the external surface of nano zeolite.

Scheme S1 Alkylation of mesitylene with benzyl alcohol over Meso ZSM-5 (SO$_3$H-CTAB)-MW and ZSM-5 (SO$_3$H-CTAB)-HT.



The influence of mesoporosity was easily demonstrated by the results of alkylation reaction. Meso ZSM-5 (SO$_3$H-CTAB)-MW gave almost four fold higher conversion compared with ZSM-5 (SO$_3$H-CTAB)-HT. Even the selectivity for benzylated mesitylene product (A) was 2 times higher. Whereas the conversion of bezyl alcohols remains higher in both the cases, however the higher conversion in case of ZSM-5 (SO$_3$H-CTAB)-HT contributes to formation of dehydration product dibenzyl ether which mainly formed by the reaction onto external surface due to diffusion limitation. These significant differences in catalytic activity inferred the benzylation of mesitylene inside the mesopores of ZSM-5 (SO$_3$H-CTAB)-MW. Other products such as C, D and E which produced by the external surface active site were observed with similar selectivity in both catalysts.