

Supporting Information

Synthesis of a hierarchically macro-/mesoporous zeolite based on a micro-emulsion mechanism

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Section □: Synthesis of other materials and catalytic reaction

Hp-ZSM(x): synthesized with the steam assisted crystallization approach similar to that for Hp-ZSM, under the same total solvent volume (17 ml) of ethanol and water but different different ethanol/water ratio. Here 'x' refers to the ethanol volume added, and x = 17 ml; 13 ml; 10 ml, 7 ml, 4 ml and 0 ml, meaning six parallel experiments under these volumes of ethanol added under total solvent volume of 17 ml. The sample Hp-ZSM (10) here is Hp-ZSM in the main text.

Hp-ZSM (50 h): hydrothermally treated Hp-ZSM in boiling water at 100 °C (reflux) for 50 h for stability tests.

Meso-ZSM-5: synthesized with the steam assisted crystallization approach similar to that for Hp-ZSM (0) but using NaOH (0.9 ml, 0.5 mol/L aqueous solution) to adjust pH value. Other conditions are the same as for Hp-ZSM.

Conventional ZSM-5: synthesized by using a traditional hydrothermal method

under the same ratio of Si/Al as Hp-ZSM (0), in which the above zeolite sols was added NaOH (0.9 ml, 0.5 mol/L aqueous solution) to adjust pH value, and then was directly hydrothermally heated at 150 °C for 72 h.

Conventional Al-MCM-41: synthesized by using a hydrothermal method under the same ratio of Si/Al was: 0.078 g NaAlO₂ was dissolved in CTAB aqueous solution (1 g CTAB with 35.71 g distilled water), then, 6.2 ml TEOS was added. After stirred for 2 h, the mixture was hydrothermally treated at 110 °C for 72 h.

H Hp-ZSM; HZSM-5; Hmeso-ZSM-5; HAl-MCM-41: synthesized following published conventional methods* by NH₄⁺ ions exchanging in a 1 M NH₄NO₃ solution at 353 K for 10 h, using a liquid/solid ratio of 100 ml per gram of catalyst. Then, the materials were separated from the solution by filtration and thoroughly washed. The procedure was repeated three times to complete the Na⁺ ion exchange. Subsequently, the ion-exchanged materials were dried and calcined at 550 °C for 5 h to produce the acidic catalysts.

Catalytic activity testing: a certain amount of lauric acid and ethanol to form totally 5 ml mixture with the molar ratio between lauric acid and ethanol at 1:12. Then, 0.1 g Hp-ZSM was added into the mixture. The reaction was carried out under atmosphere refluxing (351 ± 2 K). The yield of ethyl laurate was determined periodically by using GC-MS (Agilent, 6890/5973N).

* Tanate Danuthai, Siriporn Jongpatiwut, Thirasak Rirksomboon, Somchai Osuwan, Daniel E. Resasco, Conversion of methylesters to hydrocarbons over an H-ZSM5 zeolite catalyst, *Applied Catalysis A: General*, **2009**, *361*, 99-105.

Section III Supplemental Figures and Table

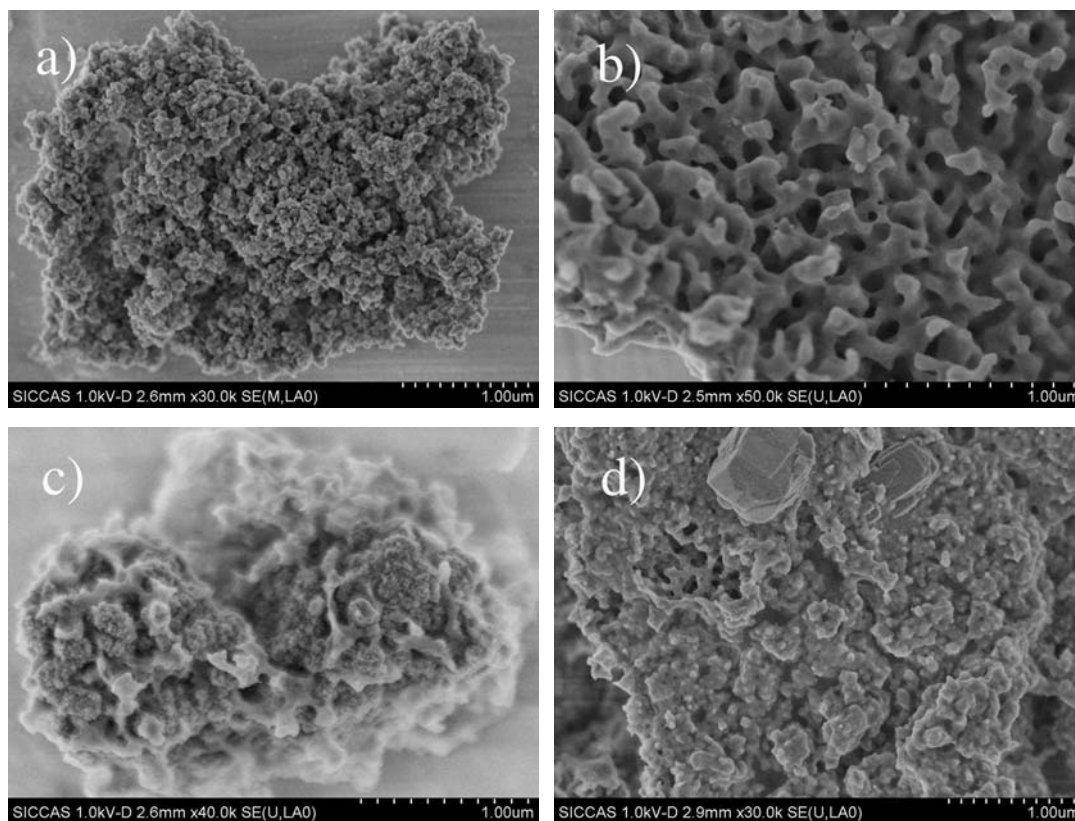


Figure S1 Representative SEM images of hierarchical zeolites prepared by adding different volumes of ethanol: a) Hp-ZSM (17); b) Hp-ZSM (13); c) Hp-ZSM (7); d) Hp-ZSM (4).

* Hp-ZSM (0) was not characterized here, which showed amorphous framework according to corresponding XRD patterns.

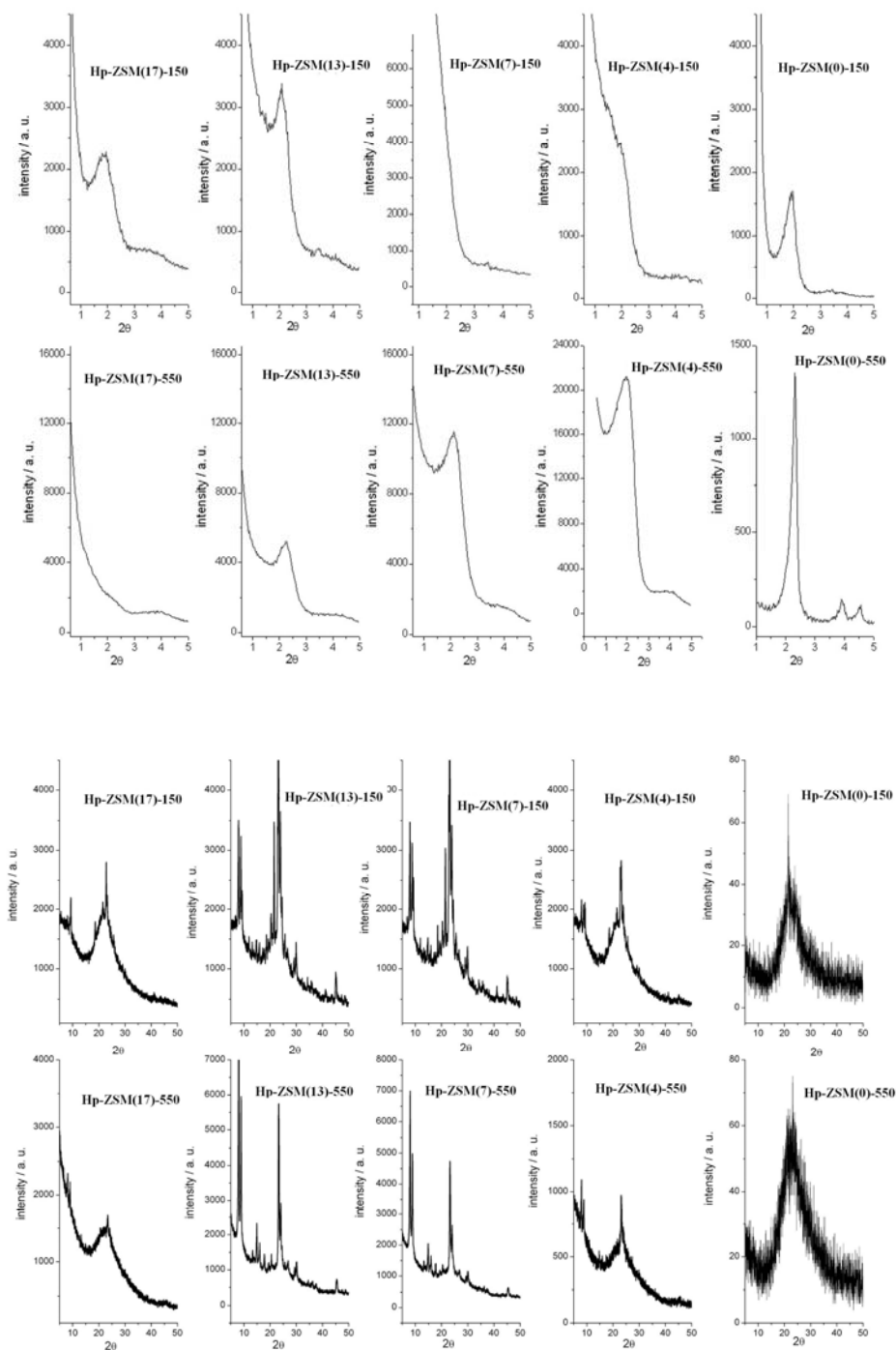


Figure S2 Small and wide angle XRD patterns of as-steamed samples, named as Hp-ZSM (x)-150, in row 1 and 3; and those for calcined samples, named as Hp-ZSM (x)-550, in row 2 and 4, respectively, under different volumes of ethanol added.

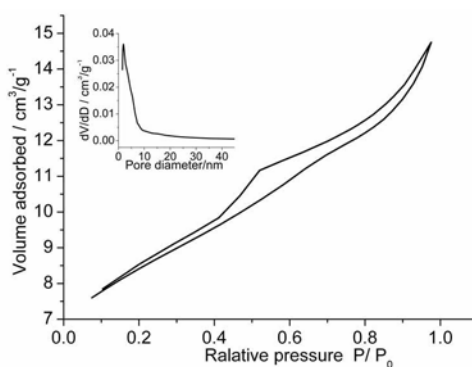


Figure S3 N₂ adsorption-desorption isotherms and corresponding pore size distribution of Hp-ZSM (50 h).

Table S1 Textural properties of the relative materials.

sample	S_{BET} (m^2g^{-1})	S_{micro} (m^2g^{-1})	$S_{\text{external/meso}}$ (m^2g^{-1})	V_{micro} (cm^3g^{-1})	$V_{\text{external/meso}}$ (cm^3g^{-1})	$D_{\text{peak pore}}$ (nm)
Al-MCM-41	962.6	-	962.6	-	0.72	2.4
meso-ZSM-5	373.6	189	184.6	0.098	0.23	2.0
ZSM-5	261.4	196.3	65.1	0.103	0.03	-

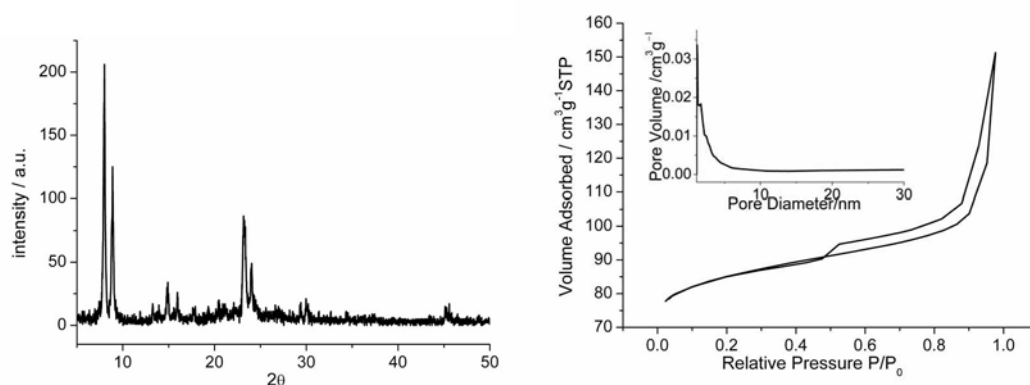


Figure S4 Textural properties of ZSM-5.

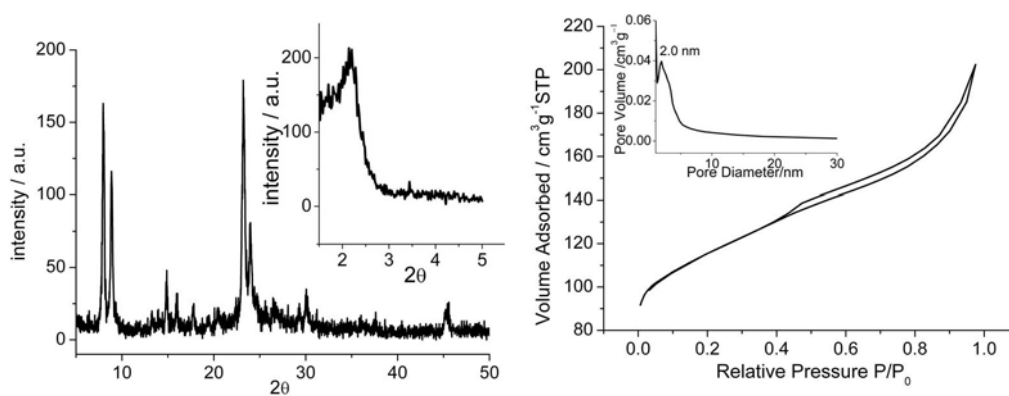


Figure S5 Textural properties of meso-ZSM-5.

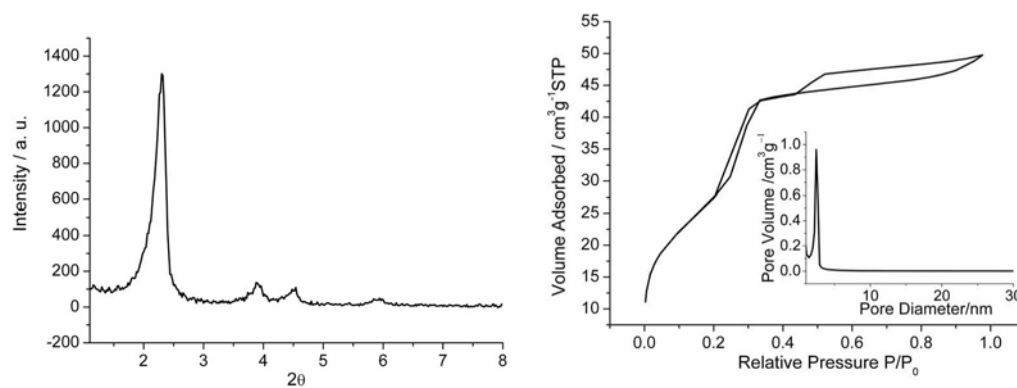
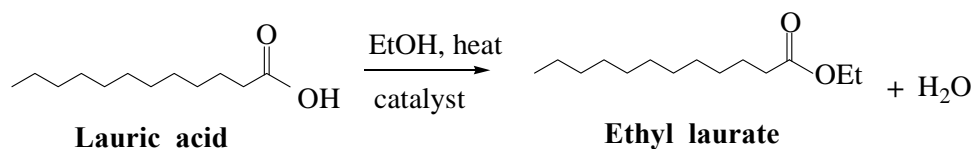


Figure S6 Textural properties of MCM-41.



Scheme S1 Reaction of esterification of lauric acid with ethanol to produce ethyl laurate.

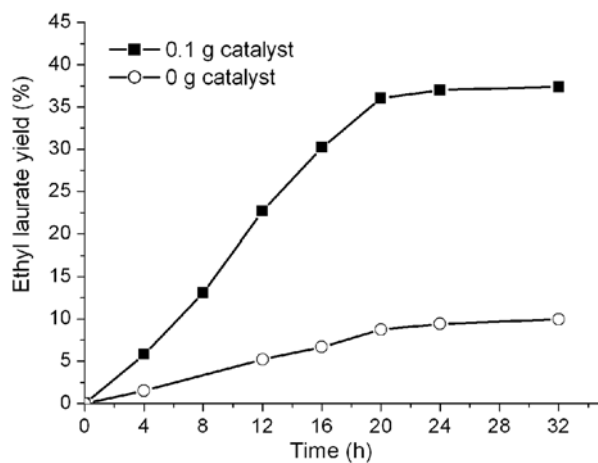


Figure S7 Esterification of lauric acid with ethanol to produce ethyl laurate.