

Modulated formation of Metal–Organic Frameworks by Oriented Growth over Mesoporous Silica

Zahra Karimi^a, Ali Morsali^{*a}

^a Department of Chemistry, Tarbiat Modares University, 14115-175, Tehran, Iran.

E-mail address: morsali_a@modares.ac.ir

DOI: 10.1039/b000000x

General Experimental Procedures

All materials are of commercial reagent grade and are purchased from Merck Company. P123 (poly (ethylene oxide)–poly (propylene oxide)–poly (ethylene oxide) (EO20–PO70–EO20)) is purchased from Aldrich Company.

MOF-5. Control sample of MOF-5 bulk crystals is prepared according to literature.¹ The original procedure is slightly modified but reactants molar ratio is not altered. Zinc nitrate hexahydrate (Zn(NO₃)₂·6H₂O) is first dehydrated at 80 °C under vacuum for 12h to give Zn(NO₃)₂·0.86H₂O (calculated based on weight change). Terephthalic acid (BDC), (0.08 g, 0.5 mmol), is then reacted as organic linker with the dehydrated zinc nitrate, (0.29 g, 1 mmol) as metal precursor, in N,N-dimethylformamide (DMF) solvent (9.5 g, 130 mmol) and the system is refluxed at 120 °C for 24 h. After cooling, the supernatant is removed and crystals are collected, washed with DMF, and immersed in fresh chloroform overnight. The chloroform is changed three times and the final product is vacuum dried at 120 °C overnight. The resulting crystals are stored in desiccator to avoid water adsorption.

SBA-15 mesoporous silica. Synthesis of SBA-15 is conducted according to literature.² Pluronic P123 (M_w= 5800, EO₂₀PO₇₀EO₂₀) is used as a template, and the silica source is TEOS, which is added drop wise to an acidic P123 aqueous solution and then stirred at 40 °C for 24 h at 600 rpm. The reaction mixture is acidified by adding HCl aqueous solution. The molar ratio of the reaction mixture is 1 TEOS: 0.0168 P123: 5.8 HCl: 155 H₂O. The powder is recovered by filtration and dried overnight to give as-synthesized SBA-15. To remove the surfactant template, further calcination is carried out at 600 °C for 6 h (labeled as SBA-15).

SBA-15/CH₃. As-synthesized SBA-15 (2.0 g) is dispersed in dry toluene (160 mL) under N₂ flow at 80 °C and trimethylchlorosilane (TMCS) is then added. The mixture is filtered after 24h of stirring and washed with toluene several times. The resulting precipitate is dried under vacuum at 80 °C for 10 h. The surfactant template is removed by solvent extraction via ethanol refluxing for 5 days. Thus, passivated SBA-15 with the external surface capped with -Si(CH₃)₃ groups (labeled as SBA-C) is obtained.

Designation of MOF/SBA Composites. To study composition-structure relationship, different concentration of SBA-15

mesoporous silica (1-10 wt%) is introduced into the system, along with the chemical precursors of MOF-5, to synthesize MOF/mesoporous silica composites.

Preparation of the composites based on mesoporous silica and MOF-5 is performed by the suspension of varying amounts of SBA mesoporous silica (1, 3, 5, 10 wt%, the wt% of the silica additive is calculated based on the amount of metal precursor) in dehydrated zinc nitrate solution in DMF. Well-dissolved DMF solution of BDC is then added to the mixture to complete the MOF-5 precursors. The resulting suspensions are subsequently refluxed at 120 °C for 24 h and subjected to the same steps as described for the MOF-5 control sample. The resulting solid product is then centrifuged, washed several times with DMF and ethanol and vacuum dried at 80 °C overnight. After solvent exchange with chloroform, the final composite products are vacuum dried at 90 °C for 24h. The composites are referred to as MS/n with n = 1, 2, 3, and 4 for the different SBA contents (1, 3, 5, and 10 wt%, respectively).

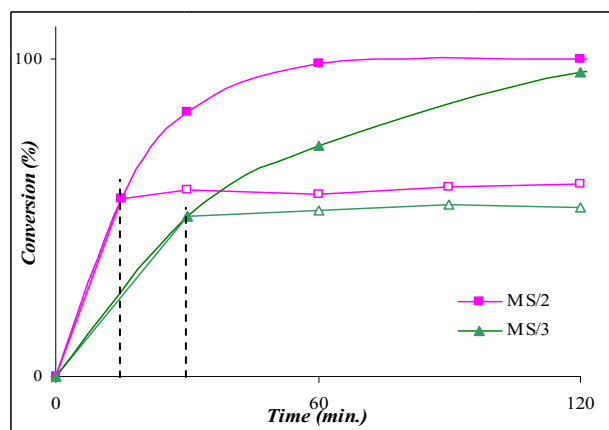
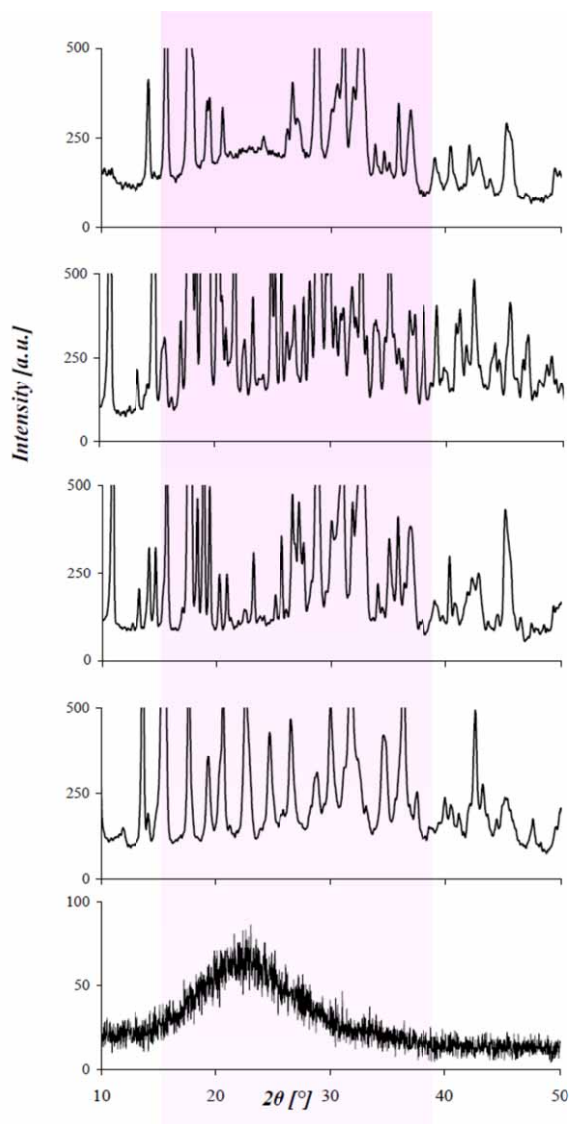
The same procedure is followed grow of MOF-5 crystals over passivated mesoporous silica. For the purpose, 3 wt% SBA-C is inserted to into MOF-5 precursor solution. The resulting composite is labeled as MS/C.

Instrumentations. Characterization of the synthesized organic-inorganic porous materials is performed by different conventional techniques. X-ray powder diffraction (XRD) data are acquired on a Philips X-Pert diffractometer using Cu K α radiation. TEM images are acquired using Loe 912AB Microscope operating at 120 kV and FE-SEM images are captured on Philips XL-300 instrument. Surface area and porosity are measured on NOVA 2200E Quantachrome instrument.

Catalytic experiments. Friedel–Crafts alkylation of toluene with benzyl bromide is studied using both the control MOF-5 and newly prepared MS/n composites as catalyst. Reactions are performed in a magnetically stirred round bottom flask fitted with a reflux condenser. Catalytic reactions are carried out under atmospheric pressure at 100 °C with toluene (18.66 mmol), benzyl bromide (6.22 mmol), catalyst (0.012 g), and n-dodecane (0.74 ml) as internal standard. Reaction coordinates is monitored by withdrawing aliquots from the reaction mixture at different time intervals. The samples are quenched using aqueous Na₂CO₃ solution (1%, 1ml) and the organic components are extracted with dichloromethane. Gas chromatography, GC-HP5890 chromatogram are applied to keep the track of reaction.

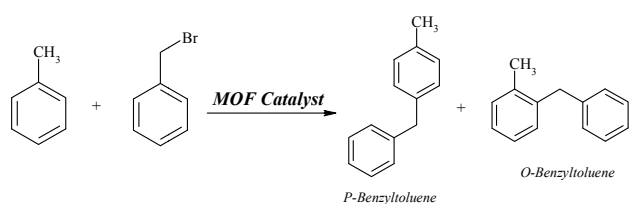
S1- XRD results of SBA-15 and comparison between composites

The following figure shows the wide angle XRD plot. For SBA-15, there is a broad reflection peak (15° to 35°) associated with the (101) silica planes. The broad reflection peak of silica is always present in the MS/n composites. This broad peak becomes much stronger when the content of SBA-15 is increased. Presence of the reflection of silica attests the successful formation of a hybrid structure of metal-organic framework and mesoporous silica.



1. J. Hafizovic, M. Bjørgen, U. Olsbye, P. D. C. Dietzel, S. Bordiga, C. Prestipino, C. Lamberti and K. P. Lillerud, *J. Am. Chem. Soc.*, 2007, **129**, 3612-3620.
2. D. Zhao, J. Feng, Q. Huo, N. Melosh, G. H. Fredrickson, B. F. Chmelka and G. D. Stucky, *Science*, 1998, **279**, 548-552.

S2- Friedel-Crafts alkylation of toluene with benzyl bromide in presence of MOF catalyst.



S3- Leaching test.

The test is performed for MS/2 and MS/3 as a model for the other systems. To assess heterogeneity of systems, the catalysts are filtered after 30 minutes of reaction and the filtrate is allowed to react further. Results reveal that the liquor does not react further and hence, Leaching test indicated no contribution from homogeneous catalysis.