Electronic Supplementary Information

Organic Functionalization of Mesopore Walls in Hierarchically Porous Zeolites

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1. Preparation of mesoporous-microporous hierarchical zeolites

Hierarchical zeolites were prepared by the addition of organosilane surfactants into the conventional synthesis composition of zeolite (ref. 11, 12).

A. MP-MFI

In a typical synthesis of MP-MFI sample, 4.01 g organosilane $[(CH_3O)_3SiC_3H_6N(CH_3)_2C_{16}H_{33}]Cl$ (52 wt% methanol solution), 2.66 g tetrapropylammonium bromide (TPABr), and 0.77 g NaOH were completely dissolved in 36.3 g H_2O. After the addition of 83.3 g diluted sodium silicate solution (Si/Na = 1.75; 6.83 wt% SiO_2), a solution containing 0.48 g sodium aluminate (53 wt% Al_2O_3, 43 wt% Na_2O; Riedel–deHaën) and 26.6 g of H_2O was added under stirring. Subsequently, 26 g of 10 wt% H_2SO_4 solution was added to the mixture under vigorous stirring. The final molar composition was 2.5 Al_2O_3/40 Na_2O/95 SiO_2/10 TPABr/26 H_2SO_4/9000 H_2O/5 organosilane. The mixture was crystallized under stirring at 140˚C for 5 days in a Teflon-coated stainless steel autoclave. The precipitated product was filtered by suction and washed with distilled water. The product was dried at 100˚C and calcined in air at 550˚C.

B. MP-BEA

Tetraethylammonium hydroxide (TEAOH, 35 wt% solution), sodium aluminate and NaOH were completely dissolved in H_2O and mixed with colloidal silica (Ludox TM-50, 50 wt% SiO_2). Then, an aqueous solution containing organosilane $[(CH_3O)_3SiC_3H_6N(CH_3)_2C_6H_{12}N(CH_3)_2\text{-}C_{16}H_{33}]BrCl$ (37.8 wt% methanol solution) was added to the resultant mixture under stirring. The final gel composition was 2.0 Al_2O_3/5 Na_2O/95 SiO_2/54 TEABr/4900 H_2O/5 organosilane. The synthesis gel was hydrothermally crystallized at 130˚C for 10 days under stirring. The precipitated product was filtered, washed with distilled water and dried at 100˚C. Dried product was calcined in air at 550˚C.

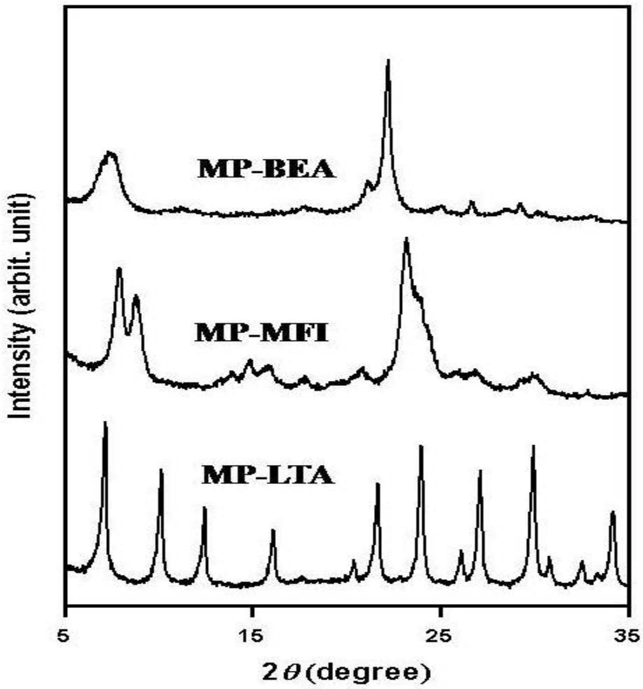
C. MP-LTA

Organosilane [$(CH_3O)_3SiC_3H_6N(CH_3)_2C_{16}H_{33}$]Cl (51.45 wt% methanol solution) was mixed with sodium metasilicate ($Na_2O_3Si \cdot 9H_2O$), sodium aluminate (53%Al_2O_3, 43%Na_2O), NaOH and H_2O to obtain the gel composition 100 SiO_2/250 Na_2O/75 Al_2O_3/14600 H_2O/5 organosilane. The synthesis gel was hydrothermally crystallized at 95˚C for 4 hours under stirring. The product was filtered and thoroughly washed with the distilled water. The product was dried at 100˚C and subsequently calcined in air at 550˚C.

2. Characterization of the materials

X-ray diffraction (XRD) patterns were recorded with a Rigaku Multiflex diffractometer equipped with Cu*Kα* radiation (40 kV, 40 mA). Nitrogen adsorption–desorption isotherms were measured at liquid nitrogen temperature (77 K) using Quantachrome Nova 2000 series analyzer. Before the measurements, all samples were degassed for 12 h at 300˚C. Pore size distribution was calculated by the Barrett–Joyner–Halenda (BJH) method using the adsorption branch. Thermogravimetric analysis (TGA) diagrams were recorded under air flow by using TGA Q500 (TA instruments) with 20 ˚C/min ramping rate. Elemental analyses (EA) were carried out using EA-110 (Thermo Finnigan, Italia). Analysis of Pd content was measured by inductively coupled plasma–atomic emission spectroscopy (ICP-AES) using OPTIMA 4300 DV (Perkin–Elmer).

<XRD patterns for hierarchical zeolites>



3. Synthesis of dichloro-β-oxoiminato-palladium-grafted hierarchical zeolites

After full dehydration at 450 ˚C, hierarchical zeolites (1.0 g) were refluxed for 12 h in 10 ml toluene solution containing β-oxoiminopropyltriethoxysilylane (1.5 g, 5 mmol). The product was filtered, washed with CH_2Cl_2 (10 mL) three times, and dried under vacuum at 80℃. 1 g of the resultant product was added into 4.5 mL $CHCl_3$ solution containing $Pd(CH_3CN)_2$ (0.1 g) and reacted for 6 h at 65 ˚C. The mixture was filtered, washed with $CHCl_3$ (10 mL × 3) and dried at 80 ˚C under vacuum. ICP analysis showed that 0.3 mmol of Pd was anchored on 1.0 g of MP-MFI zeolite.

4. Reaction condition for Sonogashira coupling reaction

Sonogashira reaction was carried out at 70 ˚C by using a glass vial equipped with a Teflon screw cap. Dichloro-β-oxoiminato-palladium-supported zeolite was added to a mixture of chlorobenzene (1.0 mmol), phenylacetylene (1.2 mmol), CuI (1 mol%), Na_2CO_3 (2.0 mmol) and solvent (H_2O/diemthylformamide = 0.7/0.7 in mL). The mole ratio between catalyst and chlorobenzene was 0.01. The reaction mixture was withdrawn periodically and analyzed by GC/GC-MS by using *n*-dodecane as an internal standard.

For measuring an isolation yield, final reaction mixture was filtered and washed with a H_2O-Et_2O mixture several times. The organic phase was separated, dried over $MgSO_4$, and then the solvent was evaporated under reduced pressure. The product was purified by column chromatography using silica gel. GC/GC-MS analyses were performed on an Agilent 6890N GC (He carrier gas, HP-5MS column, 30 m × 0.25 m × 0.25 µm) coupled to an Agilent 5975 Network Mass Selective Detector (electron impact ionization at 70 eV).

5. Hydrothermal stability test:

0.3 g of sample was dispersed in 20 mL aqueous solution containing 1.0 g Na_2CO_3, and heated at 90 ˚C for 24 h. After filtration and washing with water, the sample was dried at 80 ˚C under vacuum. The resultant powder was analyzed by N_2 adsorption-desorption measurement.