A new 3D mesoporous carbon replicated from commercial silica as a catalyst support for direct conversion of cellulose into ethylene glycol

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Supplemental Materials

1. Catalyst preparation

CMK-3 and MC were synthesized by nanocasting method as reported previously (Chem. Mater. 2006, 18, 5153). In detail, 1 g of SBA-15 or commercial silica was impregnated with 1.25 g of sucrose, 0.14 g of concentrated H₂SO₄, and 5 g H₂O, and the resultant mixture was left at ambient temperature overnight, and dried at 373K for 6 h and 443 K for 6 h. The above impregnation procedure was repeated once again with 80 % amount of the sucrose and concentrated sulfuric acid that was used in the first impregnation. The final solid was carbonized at 1173 K in N₂ for 6 h. The silica was removed by 4 wt% HF etching for 3 times. After filtration, washing, and drying at 383 K overnight, the CMK-3 or MC was obtained.

Tungsten carbides were prepared by the carbothermal hydrogen reduction (CHR) according to our previous paper (Angew. Chem. Int. Ed., 2008, 47, 8510). In a typical preparation, 1.0 g of the carbon support was impregnated with an aqueous solution containing 0.588 g of ammonium metatungstate (AMT), followed by drying at 393 K. The sample was then carburized in a H₂ flow under a three-stage heating ramp: from room temperature to 823 K at 10 K/min, and then to 1173 K at 1 K/min and holding at that temperature for 1 h. Prior to exposure to air, the as-prepared carbide catalysts were passivated in a flow of 1% O₂/N₂ for 12 h at room temperature. The resulting samples are denoted as WC_x/MC, WC_x/CMK-3, and WC_x/AC, respectively. The Ni-doped tungsten carbides were prepared by impregnating 1.0 g of the carbon support with an aqueous solution containing 0.588 g of AMT and 0.157 g of nickel

nitrate, followed by carbothermal hydrogen reduction at 1023 K. The resulting samples have 2% of nickel nominal weight loading and denoted as 2%Ni-WC_x/MC, 2%Ni-WC_x/CMK-3, and 2%Ni-WC_x/AC, respectively.

2. Characterization methods

Nitrogen adsorption-desorption measurements were performed at 77 K with a Micromeritics ASAP2010 instrument. Prior to the measurements, the samples were degassed at 523 K for 5 h. The specific surface areas were calculated with BET equation and the average pore diameters were estimated with desorption branches based on BJH model.

X-ray diffraction (XRD) patterns were collected on a PW3040/60 X' Pert PRO (PANalytical) diffractometer equipped with a Cu K_{α} radiation source ($\lambda = 0.15432$ nm), operating at 40 kV and 40 mA. A continuous mode was used for collecting data at a scanning speed of 5°/min.

TEM images were obtained on a Tecnai G^2 Spirit FEI Transmission Electron Microscope and a JEOL 2000EX electronic micoroscope operating at 120 kV. A few droplets of a suspension of one sample in ethanol were put on a micro-grid carbon polymer supported on a copper grid. Scanning electron microscopy (SEM) experiments were performed with a FEI Quanata 200F electron microscope operating at 20 kV.

Thermogravimetric analysis (TGA) was carried out using a Setaram Setsys 16/18 analyzer (France) from 298 K to 1273 K in an air flow of 25 ml/min with a heating rate of 10 K/min.

3. Reaction tests

Cellulose (Merck, microcrystalline) catalytic conversion was carried out in a stainless-steel autoclave (Parr Instrument Company, 300 ml) typically at 6 MPa H₂ pressure (measured at RT) and at 518 K for 30 minutes. For each reaction, 1.0 g cellulose, 0.30 g catalyst and 100 mL water were put into the reactor, and stirred at rate of 1000 r/minute. After the reaction, the liquid-phase products were analyzed by HPLC and ESI-MS. Cellulose conversions were determined by the change of cellulose weight before and after the reaction. The yield of polyols was calculated by the equation: yield (%) = (weight of polyol in the products)/ (weight of cellulose put into the reactor) ×100%.

4. Results



Figure S1. Nitrogen adsorption-desorption isotherms and corresponding pore size distributions of SiO₂, SBA-15, MC and CMK-3.



Figure S2. TEM images of (A) SiO_2 , (B) SBA-15, (C) MC and (D) CMK-3, and SEM images of (E) SiO_2 and (F) MC.



Figure S3. TEM images of the catalysts after the third run. (A) WCx/MC, (B) WCx/CMK-3, and (C) WCx/AC.



Figure S4. XRD patterns of (A) WCx/MC, (B) WCx/CMK-3, and (C) WCx/AC catalysts before and after recycling tests, and (D) Ni-doped tungsten carbides.

catalysts	W content (wt%)
fresh WCx/MC catalyst	42
WCx/MC-after 2 nd run	34
WCx/MC-after 3 rd run	34
WCx/MC-after 4 th run	34
fresh WCx/CMK-3 catalyst	40
WCx/CMK-3-after 2 nd run	34
WCx/CMK-3-after 3 rd run	31
WCx/CMK-3-after 4 th run	27
fresh WCx/AC catalyst	32
WCx/AC-after 2 nd run	21
WCx/AC-after 3 rd run	14
WCx/AC-after 4 th run	12

Table S1 The W content of WCx/MC, WCx/CMK-3, and WCx/AC catalysts before and after recycling tests, determined by TG-DTA.