

Supporting Information

Ordered mesoporous carbons as highly active catalysts for hydrogen production by CH₄ decomposition

Experimental

Materials and chemical preparation

SBA-15 was synthesized using tetraethylorthosilicate [TEOS, Si(OC₂H₅)₄, ≥ 98%], as silica source, and poly(ethyleneglycol)-block-poly(propyleneglycol)-blockpoly(ethyleneglycol) [PEO₂₀PPO₇₀PEO₂₀, Pluronic P-123], as non-ionic surfactant. Both reactants were obtained from Aldrich and used as received.

In a typical synthesis, a reaction mixture was prepared having a chemical composition as follows: 4 g Pluronic P123 : 0.041 mol TEOS : 6.67 mol H₂O : 0.24 mol HCl. After 6 hours at 40°C under stirring, the white suspension was hydrothermally treated at 90 °C for 3 days. The solid product was filtered, dried and calcined at 550°C for 6 hours under static air.

CMK-type materials were synthesized by nano-replication technique, using SBA-15 as hard-template, furfuryl alcohol [FA, Acros Organics 99%] as carbon precursor, oxalic acid [OA, Acros Organics 98%] as polymerization catalyst and trimethylbenzene [TMB, Aldrich 98%] as solvent. No further purification was applied for any chemical product.

For the synthesis of CMK-samples, oxalic acid and furfuryl alcohol (0.006 g OA/1.5 mL FA) were first dissolved in TMB. The volumetric proportion FA/TMB was 50% for CMK-5 carbon while no TMB was added for CMK-3 synthesis. The solution was then infiltrated into the SBA-15 pores by wetness impregnation technique at room temperature. After the polymerization treatment at 50°C and 90°C for 1 and 2 days, respectively, the composite was calcined under inert atmosphere using the following program: a) 150 °C for 3 h; b) heating to 300 °C at 1 °C/min c) heating to 850 °C at 5

°C/min and d) isothermal for 3 h. The silica template was subsequently removed from the composite by dissolution with 1 M NaOH in ethanol-water mixture. The black powders were filtrated and thoroughly washed with water, ethanol, diluted HNO₃ solution and acetone. Finally, the solids were dried at 90°C overnight.

Characterization

Nitrogen adsorption-desorption isotherms were measured at 77 K using a Micromeritics Tristar 3000 sorptometer. Samples were previously degassed at 200 °C under inert gas flow. Brunauer–Emmet–Teller (BET) equation and Barret–Joyner–Halenda (BJH) model were applied for surface area and pore size distribution determinations, respectively.

TEM images were obtained using a Philips Technai 20 Transmission Electron Microscope, operating with a tungsten filament working at 200 kV. Microscopic chemical composition of samples was determined by EDX technique coupled to the microscope.

Powder X-ray diffraction (XRD) patterns were obtained using a Philips X'PERT MPD diffractometer operating with Cu K α radiation.

Reaction tests

Catalytic activity tests of carbons towards hydrogen production via methane decomposition were performed on a simultaneous DSC-TGA apparatus (SDT 2960, TA instruments) at atmospheric pressure. In a typical reaction a given amount of carbon catalyst, between 2 and 15 mg, was loaded into a ceramic pan. The amount of each carbon catalyst was selected taking into account the expected duration of the experiment, the volume available in the ceramic pan and the carbon density. Every catalyst was dried under nitrogen flow prior to the reaction. Thus, for the temperature programmed reactions, the loaded catalyst was dried at 250 °C and cooled down to 50 °C under 100 ml min⁻¹ of N₂ flow. Thereafter, the gas flow was changed to 100 ml min⁻¹ of 10 % CH₄/Ar and, at the same time, the catalytic system was subjected to a heating ramp of 10 °C min⁻¹ up to 1100 °C. For isothermal reactions, after the aforementioned

drying and cooling down steps, the catalytic system was heated up to 1000 °C under the nitrogen flow. Once the target temperature was reached, the gas flow was changed to 100 ml min⁻¹ of the reactive mixture (10 % CH₄/Ar). During all reactions, methane is passed in a great excess compared to the catalyst amount, leading to overall conversions in the range of 1.5 to 3.5 %.