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Supplementary material

Organotemplate-free synthesis of hollow Beta zeolite supported Pt-based catalysts for the low-temperature ethanol steam reforming

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2. Experimental section

2.1 Catalyst preparation

The carbon spheres were fabricated according to literature indicated.[1] Then, platinum modified carbon spheres were prepared by impregnation with an aqueous solution of $H_2PtCl_6{\cdot}6H_2O$ (Aldrich, 99.99%) to obtain the desired loading (0.5, 1 and 2 wt.%). This solution was stirred for 12 h and dried at 100 °C overnight. Afterwards, a LbL technique was performed with nano-Beta seeds of 50 nm, which was synthesized from a mixture with the molar composition of $8TEAOH{:}40SiO_2{:}Al_2O_3{:}480H_2O$ at 140 °C for 72 h. The solid products were then treated through a two-step hydrothermal approach with the composition of $Al_2O_3{:}SiO_2{:}H_2O$ = 1:120:650. Typically, sodium aluminate (50% Al_2O_3 and 38% Na_2O, Kermel) was dissolved in distilled water, then tetraethylorthosilicate (TEOS, Aldrich) was added to the above solution. After stirring the mixture for 2 h, an appropriate amount of modified carbon spheres (related to C/SiO_2 =30 wt.%) was added. The mixture was then transferred into a teflon-lined autoclave and crystallized at 140 °C for 5 days. The resulting product (*x*Pt-C@HBS) was separated by centrifugation and washed with distilled water for three times. To remove the carbon spheres, the samples were calcined in air at 500 °C for 10 h with a rate of 1 °C/min, the hollow zeolite samples are denoted as *x*Pt@HBS, where *x* represented the nominal Pt loading (wt.%).

2.2 Catalyst characterization

The crystalline structure of catalysts was analyzed by X-ray diffraction (XRD) spectra, with a Rigaku D/max-2500 diffractometer equipped (40 kV, 100 mA), provided with a Cu cathode, with a scanning rate 1 °/min.

BET surface areas were measured at -196 °C with a Micromeritics ASAP-2020 instrument. Before the N_2 adsorption, all of the catalysts were outgassed at 300 °C for 24 h. The surface area was calculated by the Brunauer-Emmett-Teller (BET) method, and the micropore surface area and pore volume were calculated using the t-plot approach.

X-ray photoelectron spectroscopy (XPS) was performed with a V.G. Scientific ESCALAB250 using Al Kα radiation (1486.6 eV, 150 W). The recorded spectra was fitted by a least square procedure to a product of Gaussian-Lorentzian function.

Crystal morphology and size of samples were observed with a scanning electron microscope (SEM, SU-1500, Hitachi). Transmission electron microscopy (TEM) was used to study the crystal structure of the catalysts (JEM 1011, operating at 100 kV).

The elemental analysis of samples was carried out on a Perkin Elmer OPTIMA 2000DV ICP Optical Emission Spectrometer.

2.3 Catalytic performance testing

Ethanol steam reforming was performed in a fixed-bed micro-reactor at the atmospheric pressure. 0.5 g of catalyst (40-60 mesh) diluted with 4 times of inactive SiO_2 was settled between two quartz wool layers in the reactor. Before reaction, the fresh catalysts were reduced in situ at 300 °C for 2 h under a H_2 flow (50 ml/min) and then purged under N_2 at the same temperature for 30 min.

A liquid mixture of C_2H_5OH/H_2O molar ratio 1:6 (0.07 mL/min, WHSV: 7.35 h^{-1}) was fed by a micro-liquid pump to vaporized at 150 °C and carried into the reactor using N_2 as carrier. The effluent of the reactor was analyzed on-line by a GC 950 gas chromatograph using two TDX-01 packed columns, a TCD and a FID. For the separation and quantification of the liquid products, another gas chromatography (GC-9890B) with a Porapak Q capillary column connected to a FID detector was applied. The results were expressed through the conversion of ethanol (X_{EtOH}), and the selectivity (S_i) towards the products (i = H_2, CO_2, CO, CH_4 or CH_3CHO) (Eqs.(1-2)):

$$X_{EtOH}(\%) = \frac{(\text{moles EtOH}_{in} - \text{moles EtOH}_{out})}{\text{moles EtOH}_{in}} \times 100 \quad (1)$$

$$S_i(\%) = \frac{\text{moles } P_i}{\sum_{i=1}^{n} \text{moles } P_i} \times 100 \quad (2)$$

where P_i is the molar amount of different components in the products.

References

[1] X. Sun, Y. Li, Angew. Chem.-Int. Ed. 43(2004) 3827-3831.