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. Then, platinum modified carbon spheres were prepared by impregnation with an aqueous solution of H₂PtCl₆·6H₂O (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:40SiO₂:Al₂O₃:480H₂O at 140 °C for 72 h. The solid products were then treated through a two-step hydrothermal approach with the composition of Al₂O₃:SiO₂:H₂O = 1:120:650. Typically, sodium aluminate (50% Al₂O₃ and 38% Na₂O, 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/SiO₂ =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 (xPt-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 xPt@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\textsubscript{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 K\textalpha 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\textsubscript{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\textsubscript{2} flow (50 ml/min) and then purged under N\textsubscript{2} at the same temperature for 30 min.
A liquid mixture of C$_2$H$_5$OH/H$_2$O 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 ($X_{\text{EtOH}}$), and the selectivity ($S_i$) towards the products ($i = \text{H}_2, \text{CO}_2, \text{CO}, \text{CH}_4 \text{or CH}_3\text{CHO}$) (Eqs.(1-2)):

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

(1)

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S_i(\%) = \frac{\text{moles } P_i}{\sum \text{moles } P_i} \times 100
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(2)

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

References