Supporting Information

Ni@ZrO₂ Nanocomposite for Ethanol Steam Reforming: Enhanced Stability via Strong Metal-oxide Interaction

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1 Catalysts preparation

De-ionized water (18.0 MΩ) was used throughout our experiments and the apparatus was purchased from ULUPURE (Chengdu, China). Anhydrous ethanol (99.8 wt.%) and sodium dodecyl sulfate (SDS) were supplied by Sinopharm Chemical Reagent Co., Ltd. Analytical grade ZrOCl₂·8H₂O, NiCl₂·6H₂O, Ni(NO₃)₂·6H₂O, urea, polyethylene glycol (PEG, MW=20,000) and ammonia solution (25 wt.%) were purchased from Kermel Chemical Reagent (Tianjin, China). High purity gases of N₂ (99.999%), H₂ (99.999%), Ar (99.999%), He (99.999%), and 10%H₂-Ar were supplied by Sixon Gas (Suzhou, China).

NiO nanoparticles were prepared by a homogeneous precipitation method. Typically, NiCl₂·6H₂O, SDS, urea, and de-ionized water (18.0 MΩ) with a molar ratio of 1:2:30:60 were mixed, stirred at 313 K to yield a transparent solution and then kept at 353 K for 20 h. The water insoluble product was then filtered and washed with de-ionized water until no presence of chloride species followed by rinsing with ethanol for several times. The resultant solid was dried at 353 K for 12 h and calcined at 573 K for 4 h to yield brown powders.

For the preparation of nanocomposite Ni@ZrO₂ catalysts, the as-prepared NiO nanoparticles were dispersed in a ZrOCl₂ solution with the help of PEG (3wt%) and ultrasonication prior to the precipitation of zirconia precursor with an ammonia solution at a pH of 9.5. The resultant was then transferred into an autoclave and maintained at 413 K for 10 h. The product was then filtered, washed with de-ionized water (to remove the PEG and particularly the residual Cl⁻, which was tested by a AgNO₃ solution and confirmed by TDS tests) and subsequently with ethanol (for deep removal of the...
PEG and also the residual water) for several times, dried at 353 K for 12 h and calcined at 873 K for 4 h. The resultant powder was compressed and crushed into 20-40 mesh (0.42 ~ 0.85 mm).

For comparison, a conventional Ni/ZrO$_2$ catalyst was also prepared. Pure ZrO$_2$ was prepared in a similar way as the nanocomposite Ni@ZrO$_2$ catalyst but without the addition of NiO nanoparticles. Supported Ni/ZrO$_2$ catalyst was prepared by impregnating the as-prepared ZrO$_2$ powder with a Ni(NO$_3$)$_2$ solution followed by drying at 393 K for 12 h and calcination at 773 K for 4 h.

Metal loading of the catalyst was carefully adjusted to 15wt% ± 0.2wt% for both of the catalysts with confirmation by inductively coupled plasma optical emission spectrometry (ICP-OES).

2 Catalytic reactions

Ethanol steam reforming reaction was carried out at atmospheric pressure in a fixed-bed tubular quartz reactor (8 mm i.d., 300 mm long). For each catalytic assessment, 150 mg of catalyst diluted with quartz particles of the same diameter (5 times in volume to avoid adverse thermal effects) was charged and pretreated with a mixed reducing stream of H$_2$ (10 ml/min) and N$_2$ (40 ml/min) at 773 K for 1 h. Water and ethanol were premixed at a fixed molar ratio of 4:1 and fed into a vaporizer (423 K) by a HPLC pump (P230, Elite, China). An inert N$_2$ flow was also introduced into the vaporizer to help carrying the feed vapor into the reactor. Partial pressure of ethanol was maintained constant at 5% for all experiments. The reaction effluent was segregated into two streams for online analysis. The first stream was kept at 423 K and analyzed by a gas chromatography equipped with a Porapack Q column and a FID detector for possible organic species (e.g., methane, ethylene, ethane, acetaldehyde, ethanol, and acetone). The other stream passes through a condenser followed by a dryer, and was then analyzed by another gas chromatography equipped with a TDX-01 column and a TCD detector, using helium as carrier gas, for N$_2$ (also as internal standard) and the gaseous products (e.g., H$_2$, CO$_2$, CO, and CH$_4$).

Ethanol conversion ($X_{\text{ethanol}}$) and selectivity of different products ($S_i$) were calculated as follow:

$$X_{\text{ethanol}} = \frac{F_{\text{ethanol, in}} - F_{\text{ethanol, out}}}{F_{\text{ethanol, in}}} \times 100\%$$

$$S_i = \frac{F_i}{\sum F_i} \times 100\%$$

wherein, $F_{\text{ethanol, in/out}}$ is the molar flow rate of ethanol at the inlet/outlet of the reactor respectively; $F_i$ represents the molar flow rate of different possible products $i$ (e.g., H$_2$, CO$_2$, CO, CH$_4$, ethylene, ethane, acetaldehyde, and acetone) at the reactor outlet.

3 Characterization
Elemental analysis of catalysts was performed on an ICP-OES (Varian Vista-MPX) at a high frequency emission power of 1.5 kW and a plasma airflow of 15.0 L/min. The samples were dissolved separately in nitrate solution by microwave digestion (Anton Parr) before tests.

Nitrogen adsorption–desorption isotherms were obtained at 77 K with Micromeritics TriStar 3000. The specific surface area was calculated from the isotherms using the BET method. The average pore diameters and cumulative volume of pores were obtained by the BJH method from the desorption regimes of the isotherms. Before adsorption–desorption measurements, all samples were outgassed under vacuum at 573 K for 4 h.

X-ray powder diffraction (XRD) patterns were recorded by a Rigaku D/MAX-3B powder X-ray diffractometer using the Cu Kα radiation, over a 2θ range of 20–80° with a step size of 0.02° at a scanning speed of 5°/min. The phase identification was made by comparing to the Joint Committee on Powder Diffraction Standards (JCPDS).

Hydrogen temperature-programmed reduction (H₂-TPR) was conducted on a Micromeritics Autochem II 2920 instrument. In a typical experiment, 50 mg of catalyst sample was pretreated by Ar (30 ml/min) at 673 K for 0.5 h and cooled to 323 K after the pre-treatment. The sample was then heated at a rate of 10 K/min to 1173 K in a reducing gas flow of 10%H₂-Ar (30 ml/min) while the TCD signal was recorded continuously. To check the reducibility of the nickel catalysts, 27.7 mg of Ni(NO₃)₂·6H₂O corresponding to 7.1 mg NiO in 50 mg of NiO/ZrO₂ sample was also decomposed in situ at 673 K for 0.5 h at a rate of 5 K/min followed by temperature-programmed reduction at the same conditions. Hydrogen consumption of the NiO (decomposed in situ from nickel nitrate) and Ni/ZrO₂ were calculated as 78.9 cm³/g and 46.8 cm³/g, which were in good agreement with the expected value of 77.0 cm³/g and 48.1 cm³/g, respectively. For the Ni@ZrO₂ sample, the calculated hydrogen consumption was 40.0 cm³/g based on H₂-TPR results and increased to 47.1 cm³/g when the reduction was kept at 773 K for 1 h.

Hydrogen pulse chemisorption was conducted on the same apparatus as H₂-TPR experiments. 100 mg of the catalyst sample was reduced in the same reducing gas flow at 773 K for 1 h after pretreatment at 673 K in Ar for 0.5 h. After flushing with Ar flow (30 ml/min, 0.5 h) at the reduction temperature, the sample was cooled down to 323 K under Ar. H₂ pulses were then injected at the temperature until the eluted peak area of consecutive pulses was constant. The active surface area was calculated from the volume of H₂ adsorbed by assuming a H/Ni stoichiometry of 1 and a surface area of 6.5 × 10⁻²⁰ m² per Ni atom.

Morphology of reduced nickel catalyst (773 K/1 h) was observed through a transmission electron microscope (TEM, Tecnai G2 F20) equipped with an energy dispersion X-ray spectrometer (EDX) and a high angle annular dark field detector (HAADF) operated at an accelerating voltage of 200 kV. The sample powder was dispersed in ethanol by ultrasonication; drops of the suspension were applied onto a copper grid-supported transparent carbon foil and dried in air.
Carbon deposition analysis was carried out using a thermal analysis system (STA449F3, NETZSCH Corp.). The experiments were performed in a flow of air (50 ml/min) with a heating rate of 10 K/min and a final temperature of 1073 K.
4 Physico-chemical properties of nickel catalysts

Fig. S1 TEM images of (a) NiO and (b) Ni/ZrO₂ catalyst. (c) Particle size distribution of NiO obtained from its TEM images. (d) EDX result for the selected area in red circle in (b).
Fig. S2 (a) XRD patterns, (b) TG curves, and (c,d) TEM images of nickel catalysts after activity tests at 873 K for 50 h.