

Supporting Information

On the Origin of Reactivity of Steam Reforming of Ethylene Glycol on Supported Ni Catalysts

Shuirong Li, Chengxi Zhang, Peng Zhang, Gaowei Wu, Xinbin Ma and Jinlong Gong*

Key Laboratory for Green Chemical Technology of Ministry of Education, School of Chemical Engineering and Technology, Tianjin University, Tianjin 300072, PR China

Email: jlgong@tju.edu.cn

1 Catalysts preparation

Nickel catalysts were prepared by impregnation method with a metal loading of 15wt%. The support oxides, MgO, CeO₂, and ZrO₂, were prepared by calcination of the corresponding nitrates at 923 K for 2 h. Commercial γ -Al₂O₃ (particles, 20~40 mesh) was also pretreated in static air at 923 K for 2 h before use. The impregnation was conducted at ambient temperature with an excess of ethanol solution of nickel nitrate for the oxides. After impregnation, the catalysts were dried in air (373 K, 12 h) and calcined at 773 K for 2 h.

2 Catalytic reactions

Catalytic test of ethylene glycol steam reforming was conducted in a fixed-bed quartz flow reactor (8 mm i.d., 300 mm length) under atmospheric pressure. Catalyst samples (200 mg, grain size of 0.38-0.83 mm) were mixed with inert diluter (quartz particles) with a 1:5 volume ratio. Prior to the reaction, the catalyst was reduced with 10% H₂/N₂ (50 mL min⁻¹) at 973 K (for Ni/ γ -Al₂O₃ and Ni/MgO) or 773 K (for Ni/CeO₂ and Ni/ZrO₂) for 2 h. Aqueous solution of ethylene glycol was fed employing an HPLC pump (P230, Elite, China) into a vaporizer (473 K) and mixed with a nitrogen stream before purged into the reactor. The effluent was analyzed on-line by a gas chromatography (Agilent 6820) equipped with FID and TCD detectors.

Ethylene glycol conversion (X_{EG}), hydrogen yield (Y_{H_2}), and selectivity of carbonaceous compounds (S_j) were calculated as follow:

$$X_{EG} = \frac{F_{EG,in} - F_{EG,out}}{F_{EG,in}} \times 100\%$$
$$Y_{H_2} = \frac{F_{H_2}}{(F_{EG,in} - F_{EG,out}) \times 5} \times 100\%$$

$$S_j = \frac{\gamma_j F_j}{(F_{EG,in} - F_{EG,out}) \times 2} \times 100\%$$

Where, $F_{EG,in/out}$ is the molar flow rate of ethylene glycol at the inlet/outlet of the reactor respectively, F_{H_2} and F_j represents the molar flow rate of H_2 and carbonaceous specie j at the reactor outlet, γ_j is the number of C atoms in the molecular formula of carbonaceous specie j .

3 Characterization

Nitrogen adsorption–desorption isotherms were determined at 77 K on a Micromeritics TriStar 3000 and all samples were outgassed under vacuum at 573 K for 4 h before measurement. The specific surface areas were calculated by the BET method and the pore size distributions were calculated from the desorption branch of the isotherm by BJH model.

XRD patterns were recorded by a Rigaku D/MAX-3B powder X-ray diffractometer using the Cu K α radiation ($\lambda = 0.15418$ nm), over a 2θ range of 15–85 ° with a step of 0.02 ° at a scanning speed of 8 ° min⁻¹. The phase identification was made by comparing to the Joint Committee on Powder Diffraction Standards (JCPDS).

Hydrogen temperature-programmed reduction (H_2 -TPR), temperature-programmed desorption of ammonia (NH_3 -TPD) and O_2 volumetric chemisorption were conducted on a Micromeritics Autochem 2920 instrument. In a typical experiment, 100 mg of catalyst sample was mounted on a quartz wool plug in a U-shaped quartz sample tube. Before the measurements, the sample was pretreated by Ar (30 mL min⁻¹) at 673 K for 1 h and cooled to 323 K. H_2 -TPR was carried out in a flow of 10% H_2 -Ar (30 mL min⁻¹) from 323 K to 1123 K at a heating rate of 10 K min⁻¹ while the TCD signal was recorded continuously.

For the NH_3 -TPD experiments, upon *in situ* reduction at the conditions same as catalytic activity tests, the sample was saturated with NH_3 by flowing 10% NH_3 -He at 393 K for 30 min, flushed with pure helium (30 mL min⁻¹) for 1 h before desorption analysis. NH_3 -TPD analysis was carried out with a ramp of 10 K min⁻¹ from 393 K to 1073 K in a He flow of 30 mL min⁻¹. A QIC-20 mass spectrum was connected to the chemisorption analyzer to trace the signal of NH_3 ($m/z = 17$), N_2 ($m/z = 28$), and H_2 ($m/z = 2$) in real time.

For the O_2 volumetric chemisorption, the measurements were carried out at 673 K and a fixed volume of 1.076 mL of either H_2 or O_2 was introduced through a pulse injection valve. The sample was first reduced by a series of H_2 pulses until a maximum

reduction of the sample, and then oxidized by a series of O₂ pulses until saturation. This procedure of H₂ pulses followed by O₂ pulses was repeated again to calculate the oxygen storage capacity (OSC) of the sample based on the O₂ uptake. Since NiO_x species in the catalysts can be partially reduced at 673 K as indicated in the H₂-TPR profiles of these catalysts (Fig. 1B), the direct measurement over reduced nickel catalysts could produce misleading results. The corresponding oxides were chosen as samples to be tested in the O₂ volumetric chemisorption.