Short communication

CO$_2$ reforming of methane over coke-resistant Ni–Co/Si$_3$N$_4$ catalyst prepared via reactions between silicon nitride and metal halides

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ABSTRACT

A series of Ni–Co/Si$_3$N$_4$ catalysts with different Ni/Co ratios were prepared via reactions between commercial silicon nitride (Si$_3$N$_4$) and metal halides (i.e., NiCl$_2$ and CoF$_3$) at high temperature (930 °C). By using X-ray diffraction and electron microscopy, it was shown that this method of catalyst preparation leads to formation of bimetallic Ni–Co nanoparticles encapsulated by a SiN$_x$ layer (Ni–Co@SiN$_x$) on supporting Si$_3$N$_4$ material. The 4.0Ni–3.6Co/Si$_3$N$_4$ catalyst was highlighted by showing highly stable catalysis for stoichiometric CO$_2$ reforming of methane under widely varied reaction conditions, and was found completely free of coke formation after CRM reaction for 100 h.

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1. Introduction

Syngas production from reforming of methane is a key step in industry for converting natural gas into synthetic fuels and other chemicals. Carbon dioxide reforming of methane (CRM) is attractive because it produces syngas with a lower H$_2$/CO ratio (theoretically be unity for stoichiometric CRM reaction), which is preferentially used as feedstock for Fischer–Tropsch synthesis of long-chain hydrocarbons as well as for hydroformylation and carbonylation reactions. The interest to CRM is further spurred in recent years with the utilization of unconventional natural gas resources (e.g., coal-bed gas and biogas) that generally contain large quantities of CO$_2$ [1,2].

Noble metals (i.e., Rh, Pt, Ru and Pd) as well as Ni and Co are active for catalyzing CRM reaction. Considering the cost and availability about noble metals, supported Ni-based catalysts are the choices for industrial practice and attract the most research interest. However, the deactivation of Ni-based catalysts, mainly caused by carbon deposition (or coke formation), constitutes the greatest obstacle for industrial applications [1,3]. Extensive efforts have been made to improve the stability and coke-resistance of Ni-based CRM catalysts by kinetically inhibiting carbon deposition under conditions that coke formation is favored by thermodynamics. Strategies developed to minimize coke formation include controlling ensemble size of Ni on surface [4], reducing Ni particle size [5,6], and promoting catalyst with redox or basic metal oxides to facilitate coke volatilization [7]. Several Ni-based catalysts showing excellent coke-resistant capability and catalytic performance for CRM have been developed, i.e., nanocomposite Ni/ZrO$_2$ catalysts consisting of comparably sized Ni-metal (10–15 nm) and ZrO$_2$ (7–25 nm) nanocrystals [8], and Ni/MgO catalysts reduced from NiO–MgO solid solution [6,9]. In recent years, bimetallic Ni–Co catalysts with similar Ni and Co loadings were found to show stable activity for CRM reaction [10–13]. However, coke formation was still observed over these stable catalysts, hinting that at least to some extent the problem of carbon deposition could not be avoided.

Si$_3$N$_4$, being a material with good mechanical properties and basic surface, has been used to support Ni, and the Ni/Si$_3$N$_4$ catalysts were found to show high activity and stability for stoichiometric CRM reaction, but the formation of coke was clearly evidenced with TEM and TG analysis [14]. Herein, we report a novel method for preparing coke-resistant bimetallic Ni–Co/Si$_3$N$_4$ catalysts by making use of reactions between metal halides (i.e., NiCl$_2$ and CoF$_3$) and basic Si$_3$N$_4$. A series of Ni–Co/Si$_3$N$_4$ catalysts with different Ni/Co ratios were prepared. Under widely varied CRM reaction conditions, the Ni–Co/Si$_3$N$_4$ catalyst with appropriate Ni/Co ratio exhibited stable activity with completely suppression of coke formation during a reaction time up to 100 h. A possible explanation for this excellent catalytic performance is presented based on kinetic studies and catalyst characterization.

2. Experimental

A suitable amount of anhydrous NiCl$_2$ (Stream) and CoF$_3$ (Alfa) was mixed carefully with Si$_3$N$_4$ (Beijing DK nano technology Co. LTD) in a mortar. The mixture was then heated in N$_2$ flow from room temperature to 930 °C with a ramp of 5 °C/min, followed by an isothermal period of

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1 h to obtain mNi–nCo/Si$_3$N$_4$, where "m" and "n" denote the weight percentage (wt.%) of Ni and Co, respectively, according to ICP-OES measurement. The catalytic reaction was conducted in a vertical fixed-bed U-shape quartz reactor (i.d. 8 mm) under atmospheric pressure. Details of catalyst characterization and reaction test are available in the Supplementary material.

3. Results and discussion

A series of mNi–nCo/Si$_3$N$_4$ catalysts with different Ni/Co ratios and nominal total metal loadings of 10 wt.% were prepared by adjusting the NiCl$_2$/CoF$_3$ ratio in the precursor mixtures (NiCl$_2$, CoF$_3$ and Si$_3$N$_4$). The NiCl$_2$/CoF$_3$ ratio in the mixture (or nominal Ni/Co ratio) strongly affected the deposition efficiency of Ni and Co: both the actual loadings of Ni and Co in the mNi–nCo/Si$_3$N$_4$ catalyst decreased with increasing nominal Ni/Co ratio (Table S1). The NiCl$_2$/CoF$_3$ ratio in the precursor mixtures also strongly affected the distribution and size of Ni/Co particles on Si$_3$N$_4$ surface. Transmission electron microscopy (TEM) images of both the monometallic catalysts as well as those of the 0.8Ni–8.8Co/Si$_3$N$_4$ and 2.4Ni–0.2Co/Si$_3$N4 catalyst showed the presence of very large metal aggregates (>100 nm) (Fig. S1). When the Ni and Co loadings are getting closer, the metal particles become smaller and distribute more homogeneously on the Si$_3$N$_4$ surface (Fig. 1a–c). Homogeneously distributed particles of sizes of 10.1 ± 2.2 nm were clearly observed on the 4.0Ni–3.6Co/Si$_3$N$_4$ catalyst with comparable Ni and Co loadings (Fig. 1b). These observations indicate that the reactions between NiCl$_2$/CoF$_3$ and Si$_3$N$_4$ did accomplish the deposition of Ni and Co on Si$_3$N$_4$. However, the reactions appear quite complex, which await further investigation.

The XRD patterns of these reduced mNi–nCo/Si$_3$N$_4$ samples are presented in Fig. 1d. The XRD pattern of 1.7Ni/Si$_3$N$_4$ shows a peak at 44.46° characteristics of diffraction due to Ni (111), while that of 10.9Co/Si$_3$N$_4$ shows a peak at 44.19° characteristics of diffraction due to Co (111). All the bimetallic mNi–nCo/Si$_3$N$_4$ show one diffraction peak between that

of Ni (111) and Co (111), and a systematic shift of the diffraction from that of Ni (111) to Co (111) was observed with decreasing Ni/Co ratio (Fig. 1d). Similar phenomena have been reported for Ni–Co/TiO$_2$ catalysts with varying Ni/Co ratios, suggesting the formation of Ni–Co alloy in these reduced catalysts [10]. Interestingly, an amorphous shell encapsulating the metal particles can be distinguished for these catalysts (inserts, Fig. 1a–c). The particles on the 4.0Ni–3.6Co/Si$_3$N$_4$ catalyst were further analyzed with energy dispersive spectroscopy (EDS) during STEM measurement (Fig. 1e). Fig. 1f presents the EDS line scan profiles of a representing particle (insert of Fig. 1e). The signals of N, Si, Ni and Co show similar trends as the particle was scanned from bottom to up, which would suggest a core–shell structure that a bimetallic Ni–Co particle is encapsulated by an amorphous SiN$_x$ shell (Ni–Co@SiN$_x$ structure). Note that such core–shell structures were not observed on Ni/Si$_3$N$_4$ catalyst prepared by wet impregnation Si$_3$N$_4$ with nickel nitrate aqueous solution [14].

To investigate the performance of mNi–nCo/Si$_3$N$_4$ catalysts for CRM reaction, the inter- and intra-particle mass and heat transfer limitations were first eliminated by testing the most active one, 4.0Ni–3.6Co/Si$_3$N$_4$ catalyst, with different dilute (SiC)/catalyst ratios and pellets sizes (Fig. S2). Fig. 2 shows CH$_4$ conversion of CRM reaction at 700°C as a function of time on stream under strictly kinetic regime, which would enable a sensitive evaluation of catalyst activity and stability. The 4.0Ni–3.6Co/Si$_3$N$_4$ catalyst showed an induction period of around 20 h and then produced a stable CH$_4$ conversion of ca. 10%. The 2.6Ni–5.1Co/Si$_3$N$_4$ showed a higher initial CH$_4$ conversion (12%), but deactivated continuously to ca 7.0% after 50 h reaction. A slight deactivation could also be noticed on 2.9Ni–0.8Co/Si$_3$N$_4$ catalyst (CH$_4$ conversion decreased from 5.1 to 4.8%). The other catalysts with higher or lower Ni/Co ratios deactivated quickly within 10 h whereas the monometallic Ni catalyst showed only negligible CH$_4$ conversion.

The 4.0Ni–3.6Co/Si$_3$N$_4$ catalyst after reaction for 50 h was characterized using TEM (Fig. 1g). The core–shell structures were retained on the Si$_3$N$_4$ surface, but the size of bimetallic Ni–Co particles increased from
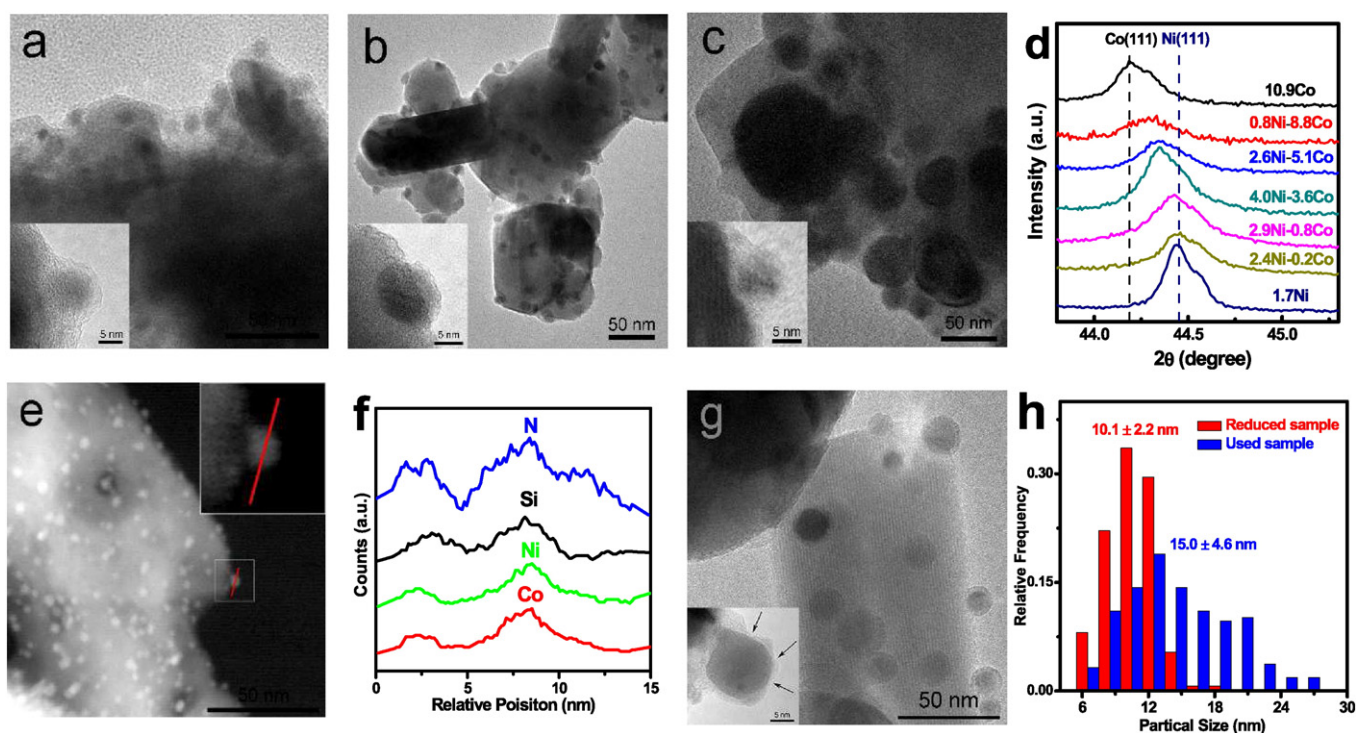

Fig. 1. TEM images of (a) 2.9Ni–0.8Co/Si$_3$N$_4$, (b) 4.0Ni–3.6Co/Si$_3$N$_4$, (c) 2.6Ni–5.1Co/Si$_3$N$_4$; (d) XRD patterns of reduced mNi–nCo/Si$_3$N$_4$ catalysts; (e) STEM image of 4.0Ni–3.6Co/Si$_3$N$_4$, the insert shows a particle analyzed with EDX line scan (represented with a red line) from bottom to up; (f) EDS line scan profiles for the particle in the insert of (e); (g) TEM image of the used 4.0Ni–3.6Co/Si$_3$N$_4$ catalyst after reaction for 50 h, arrows in (g) indicate pores in the shell; (h) particle size distribution of the reduced and used 4.0Ni–3.6Co/Si$_3$N$_4$ catalyst.

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