

HYDROGEN PRODUCTION THROUGH CATALYSIS

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Introduction

Hydrogen production has been the focus of increased interest due to its role as the primary fuel for low-temperature fuel cells such as Proton Exchange Membrane (PEM) fuel cells. Catalytic processes play a major role in the production of hydrogen, whether the starting material is a hydrocarbon (methane, gasoline), a coal gas, or an alcohol. We have been studying several catalytic systems to be used in hydrogen production, including those that can be used for ethanol, methanol, liquefied petroleum gas, and coal gas. In this communication, two examples will be presented from our recent work focusing on catalytic steam reforming (SR) of hydrocarbons and water-gas shift (WGS) reactions.

Results and discussion

Steam reforming of lower alkanes

Steam reforming of methane is usually performed at high temperatures over Ni-based catalysts. When these catalysts are used with higher hydrocarbons, however, coke formation becomes a major concern. In this work, steam-reforming of non-methane lower hydrocarbons has been studied over lanthanide promoted Ni/Al₂O₃ catalysts. Sol-gel Ni/Al₂O₃ catalysts promoted with La, Ce, and Yb were prepared by a modified sol-gel technique. Metal nitrates and aluminum tri-*sec*-butoxide (ATB) were used as precursors. Ethanol was used as a solvent.

The function of lanthanide promotion has been studied in detail with various characterization techniques. Alkane steam reforming was carried out in a fix bed flow reactor at 500 °C at atmospheric pressure. Prior to the reaction, catalysts were reduced *in situ* at 600 °C. As shown in Fig. 1, the presence of lanthanide elements (Ce or Yb) in sol-gel Ni/Al₂O₃ catalysts improves steam reforming activity and stability significantly.

Temperature-programmed Oxidation (TPO) profiles of carbon deposited on 20%Ni/Al₂O₃ and 20%Ni-2%Ce/Al₂O₃ catalysts after 20 h propane steam reforming at 500 °C, H₂O/C = 1.3 are shown in Fig. 2. A low-temperature peak at 360 °C could be assigned to surface carbon deposited on Ni particle surface, which is highly reactive and easily oxidized. A larger peak at 640 °C could be due to the bulk carbon (filament or extruded carbon, Fig. 3), which needs to migrate to Ni surface for reactions.

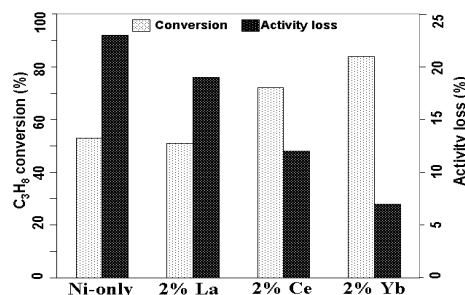


Fig. 1 Effect of lanthanide promotion on 20wt% Ni/Al₂O₃ catalysts for propane steam reforming.

Although the temperatures at which the CO₂ is eluted from the surface are identical for the two catalysts, the amount of CO₂ evolution from the oxidation of carbon deposited on 20% Ni/Al₂O₃ catalyst is much higher compared to Ce-promoted catalyst. The amount of carbon deposited on the catalyst is reduced by approximately 90% upon cerium promotion (Fig. 2-inset).

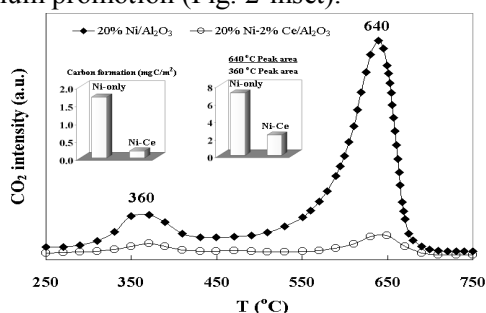


Fig. 2 TPO profiles of post-reaction 20% Ni/Al₂O₃ and 20% Ni-2% Ce/Al₂O₃ catalysts.

Fig. 3 shows the TEM images for post-reaction 20% Ni/Al₂O₃ and 20% Ni-2% Ce/Al₂O₃ catalysts. Over Ni-only catalyst, the carbon filaments were observed with the diameter of about 50 nm, which is roughly the same as that of the Ni particle at the tip of the carbon filament. In contrast to carbon filaments formed on unpromoted catalyst, "Extruded" carbon on post-reaction Ni-Ce catalyst is observed. Nickel particle still remains on alumina support surface. This indicates that cerium inhibits coke deposition and carbon filament formation. X-ray diffraction studies have shown an increase in the lattice parameter of Ni, suggesting that cerium could be embedded in the nickel lattice, thus inhibiting carbon dissolution through nickel and reducing carbon diffusion through nickel particles.

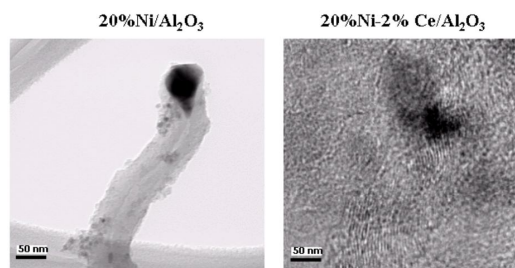


Fig. 3 TEM images of post-reaction 20% Ni/Al₂O₃ and 20% Ni-2% Ce/Al₂O₃ catalysts.

Water-gas shift reaction

The water-gas shift reaction is of central significance to produce high-purity hydrogen. Generally, the high-temperature water-gas shift reaction (HTS) is conducted on Fe-Cr catalysts. However, these catalytic systems possess many drawbacks such as low activity at low temperatures and harmful effect of Cr⁶⁺ on human health. Thus, development of chromium-free catalytic systems which has high activity is necessary.

Chromium-free iron-based catalysts promoted with first row transition metals for WGS have been developed with three synthesis methods. The effect of synthesis variables and methods on the catalyst structure was investigated.

Fe-based catalysts promoted by first row transition metals were prepared for high-temperature water gas shift reaction. The steady-state reaction experiments were performed using a fixed-bed flow reactor at 400 °C, CO/H₂O/N₂ = 1/1/8. Prior to the reaction, catalysts were reduced *in situ* at 350 °C for 2 h. The catalytic activity is defined as moles of CO converted per moles of Fe present per hour.

It is believed that the function of chromium in commercial HTS formulations is to stabilize magnetite from sintering, thus enhancing the activity and stability of iron catalysts. Our reaction results showed that the presence of Mn and Ga caused a decrease in WGS activity whereas the addition of Al in Fe catalysts improved WGS activity. Further characterization indicated that Al could be a potential chromium replacement. When Cu was used as a structural promoter, Fe-Al-Cu catalyst was seen not only to match the activity of Fe-Cr catalyst (as a representative of commercial HTS catalysts), but to surpass it.

When the catalysts were characterized with X-ray diffraction, it was seen that the incorporation of Al led to smaller crystalline size of the hematite phase (Fig 4). The particle sizes calculated using the line broadening of the (104) diffraction line and applying the Scherrer equation, showed that the average particle size went from 47 nm for Fe-only

catalyst to 31 nm for Fe-Al catalyst when they were both calcined at 450°C.

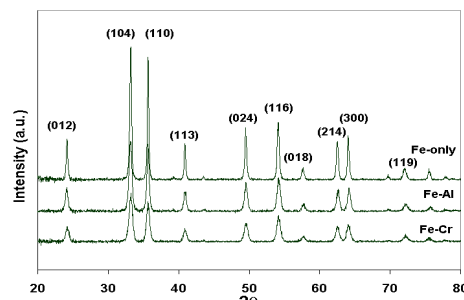


Fig. 4 X-ray diffraction patterns of calcined catalysts

When a sol-gel technique was used for catalyst preparation, a significant improvement was observed in the catalytic activity. X-ray photoelectron spectroscopy showed that the sol-gel technique allowed the Cu to be very uniformly distributed in the magnetite matrix. Temperature-programmed reduction patterns of different catalysts indicated that, with the addition of promoters, the reduction feature that represents transition from hematite to magnetite phase shifts to lower temperatures. This effect is very pronounced for Cu-promoted catalyst. The catalyst that was prepared by a coprecipitation-impregnation method showed two reduction features, corresponding to the reduction of Cu⁺² to Cu⁰ and the reduction of hematite to magnetite, the catalyst which was prepared by the sol-gel technique showed only one reduction feature, suggesting that Cu no longer exists as a separate phase, but is now a part of the iron oxide matrix. The incorporation of Cu species into magnetite lattice can, in turn, modify the electronic properties of Fe-based catalysts, resulting in a significant improvement of WGS performance.

Conclusions

These studies show that it is possible to affect the activity and stability of the catalysts that are used in hydrogen production by incorporation of promoters or modification of the synthesis techniques. The detailed structural and surface characterization of the catalysts provides valuable insight into the role of the promoters and the effect of the synthesis parameters and allows "fine-tuning" of the catalyst performance.