H_2 Production over Ni/γ-Al_2O_3 Catalyst Prepared by a Homogeneous Precipitation Method Using Urea for Direct Internal Reforming (DIR) in a Molten Carbonate Fuel Cell (MCFC)

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Ni/γ-Al_2O_3 catalysts (Ni content = 52 wt %) have been designed by a homogeneous precipitation method using urea as a precipitation agent for direct internal reforming in a molten carbonate fuel cell. Concentrations of precursor and urea have been systematically varied to develop highly active and KOH-resistant catalyst. Compared with the commercial catalyst, the developed catalyst exhibits strong stability against KOH as well as very high activity.

Recently, hydrogen energy has attracted significant interest. Commercially, H_2 is produced by steam reforming of methane (SRM), which is strongly endothermic.[1] It is known that the heat required for the endothermic SRM can be supplied by the electrochemical reaction in MCFC.[2–4]

Direct internal reforming (DIR) has several advantages such as the following. The overall efficiency of MCFC can be increased. The steam required for SRM is partially supplied by the electrochemical reaction in MCFC. The equilibrium CH_4 conversion in SRM is further driven forward due to consumption of H_2 by the electrochemical reaction in MCFC.[2–4]

However, catalyst deactivation occurs in DIR for MCFC owing to both liquid-phase pollution and vapor-phase pollution.[2–5] Liquid-phase pollution can be solved by installing a protective barrier in the pollutant pathway.[5,6] Vapor-phase pollution is mainly due to the poisoning by alkali originating from the molten carbonate electrolyte.[2–5] The effect is most pronounced for K and less for Li and Na.[2,5] Therefore, it is necessary to develop highly active and KOH-resistant catalysts for DIR in MCFC.

Al_2O_3-supported Ni catalysts have been used for the reforming reaction with methane.[7,8] The effect of alkali is stronger on less acidic supports due to the fact that the less acidic support has a looser bonding of alkali resulting in easier adsorption on the metal.[1] Based on a thorough literature survey, we have decided to select γ-Al_2O_3 as a support to selectively adsorb KOH, which will result in keeping Ni from being poisoned by KOH.

Ni/γ-Al_2O_3 (Ni = 52 wt %) catalysts were prepared by a homogeneous precipitation method.[9] $Ni(NO_3)_2 \cdot 6H_2O$ and $Al(NO_3)_3 \cdot 9H_2O$ were used as precursors. Urea was employed as a precipitation agent. The aging time was fixed at 24 h. The prepared catalysts were calcined at 400 °C for 6 h in air. Commercial Ni/γ-Al_2O_3 (Ni = 52 wt %) catalyst was employed as a reference catalyst for DIR in MCFC. The BET surface area was measured by N_2 adsorption at -196 °C using ASAP 2000 (Micromeritics). H_2 chemisorption was conducted in ASAP 2010 (Micromeritics). The calcined catalyst was reduced at 700 °C for 1 h in H_2 flow and analyzed at 50 °C. To see the effect of KOH on the catalytic activity, an appropriate amount of KOH was impregnated on the calcined catalysts followed by calcination at 650 °C for 6 h. Activity tests were carried out at 650 °C under atmospheric pressure in a fixed-bed microtubular quartz reactor. The catalyst charge was 5 mg and $MgAl_2O_4$ was used as a catalyst diluent. Prior to each catalytic measurement, the catalyst was reduced in 10% H_2/N_2 at 700 °C for 1 h. The feed $H_2O/CH_4/N_2$ ratio was fixed at 3/1/6. A gas hourly space velocity (GHSV) of 1512000 h^{-1} was used. The reformed gas was chilled, passed through a trap to condensate residual water, and then flowed to the on-line micro-gas chromatograph (Agilent 3000).

Table 1. Characteristics of supported Ni catalysts

Concentration/M		Surface area[a] /$m^2\ g^{-1}$	Dispersion[b] /%	Ni size[b] /nm
Precursor	Urea			
0.36	6.0	223	7.0	14
0.18	1.0	213	9.8	10
0.18	3.0	212	7.8	12
0.18	6.0	205	8.2	12
Reference	—	236	7.7	13

[a]Estimated from N_2 adsorption at -196 °C. [b]Estimated from H_2-chemisorption at 50 °C considering reduction degree.

Table 1 summarizes the BET surface area, Ni dispersion, and Ni crystallite size depending on the preparation conditions.

The catalyst prepared with the precursor concentration of 0.18 M and urea concentration of 1 M exhibits the highest Ni dispersion and the smallest Ni crystallite size. With increasing urea concentration, Ni dispersion decreases resulting in the increase of Ni crystallite size. This indicates that urea concentration plays a role in determining Ni dispersion.

Ni/γ-Al_2O_3 catalysts displayed in Table 1 were applied to SRM at 650 °C with a $H_2O/CH_4/N_2$ ratio of 3/1/6 and space velocity of 1512000 h^{-1}. The catalyst prepared with the precursor concentration of 0.36 M and urea concentration of 6 M showed 95% CH_4 conversion. The others exhibited equilibrium CH_4 conversion (97%) at the experimental conditions even though the GHSV is 500 times higher than the typical condition for SRM. All the catalysts were stable for more than 20 h without detectable catalyst deactivation.

Ni/γ-Al_2O_3 catalysts poisoned by 4 wt % K were also tested under the same experimental conditions. The reaction results for CH_4 conversion with time on stream are presented in Figure 1.

It is clear that urea concentration is a key parameter to prepare highly KOH-resistant catalysts by a homogeneous preparation method. The catalyst prepared with the urea concentration of 1 M showed about 80% CH_4 conversion. With increasing the urea concentration up to 6 M in the synthesis of catalyst using a homogeneous precipitation method, Ni/γ-Al_2O_3 catalysts be-

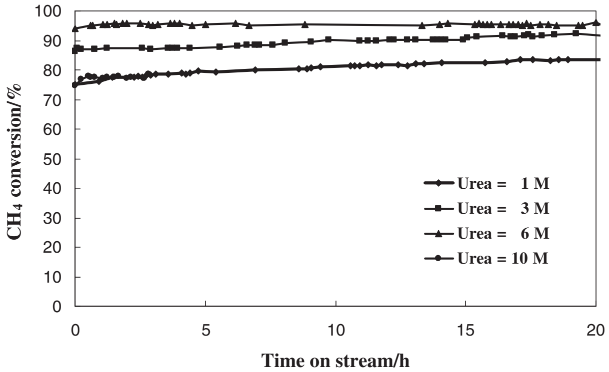

Figure 1. The effect of urea concentration on Ni/γ-Al_2O_3 catalysts synthesized by a homogeneous precipitation method (KOH poisoning: 4 wt % K, $H_2O/CH_4/N_2 = 3/1/6$, $T = 650$ °C, GHSV $= 1512000\,h^{-1}$).

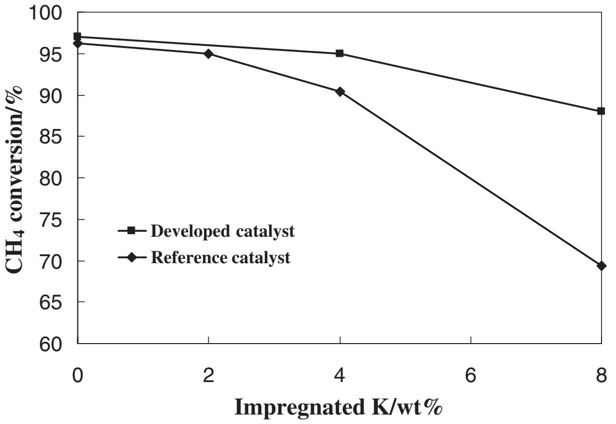

Figure 2. Comparison results between the developed catalyst and the reference catalyst ($H_2O/CH_4/N_2 = 3/1/6$, $T = 650$ °C, GHSV $= 1512000\,h^{-1}$).

came highly KOH-resistant catalysts for DIR in MCFC. As a result, the catalyst prepared with the urea concentration of 6 M exhibited 95% CH_4 conversion, which is slightly lower than equilibrium CH_4 conversion. On the other hand, the catalyst prepared with the urea concentration of 10 M showed 80% CH_4 conversion. Therefore, it has been confirmed that the preparation condition in a homogeneous precipitation method is very important to prepare highly KOH-resistant catalysts for DIR in MCFC. According to the above results, the catalyst prepared with the precursor concentration of 0.18 M and urea concentration of 6 M exhibited the optimum catalytic activity both in the form of fresh catalyst and in the form of the catalyst poisoned by KOH.

To compare the developed catalyst, which was prepared with the precursor concentration of 0.18 M and urea concentration of 6 M, and the reference catalyst, both catalysts were poisoned by an appropriate amount of KOH and applied to SRM under the same experimental conditions (Figure 2). When both catalysts were poisoned by 4 wt % K, the developed catalyst showed 95% CH_4 conversion, which is 5% higher than that of the reference catalyst. With the poisoning by 8 wt % K, the developed catalyst exhibited 88% CH_4 conversion, which is 18% higher than that of the reference catalyst. Therefore, it has been confirmed that the developed catalyst is strongly KOH resistant, when poisoned by high content of KOH.

The fact that the Ni/γ-Al_2O_3 catalyst prepared with the precursor concentration of 0.18 M and urea concentration of 6 M exhibited strong resistance against KOH poisoning can be explained as follows: First, KOH is selectively adsorbed on the acidic γ-Al_2O_3 support, resulting in keeping Ni from being poisoned by KOH. By using a homogeneous precipitation method, nanosized NiO was dispersed uniformly on the γ-Al_2O_3 support. Nanosized Ni crystallite size was maintained during the calcination process followed by the reduction process. Therefore, when the catalyst was poisoned by KOH, the support could effectively prevent KOH from poisoning Ni surface. Second, this catalyst has optimum nanosized Ni dispersion. It is most likely that the catalyst prepared with the precursor concentration of 0.36 M and urea concentration of 6 M showed relatively low CH_4 conversion (95%) in the form of fresh catalyst compared with other catalysts due to the lowest Ni dispersion in Table 1. On the other hand, when the catalyst prepared with the precursor concentration of 0.18 M and urea concentration of 1 M was poisoned by 4 wt % K, the CH_4 conversion was 80% even though this catalyst shows the highest Ni dispersion in Table 1. This is possibly due to the sintering of Ni crystallite by KOH poisoning. It was reported that the presence of alkali did not enhance the sintering of Ni crystals when Ni crystallite size is bigger than 200 nm.[2] It has also been reported that the catalyst deactivation by alkali is likely to have been caused by enhanced Ni crystallite growth when Ni crystallite size is relatively small.[3] The latter is plausible because the prepared catalysts have Ni crystallite size ranging from 10 to 14 nm. Thus, it has been speculated that optimum Ni dispersion exists to have strong resistance against KOH poisoning.

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