Addition of Al_2O_3 or Cr_2O_3 Promotes Metal Reduction in a CoO–NiO–MgO Solid Solution Catalyst for CH_4/H_2O Reforming

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Addition of Al_2O_3 or Cr_2O_3 promotes metal reduction in a CoO–NiO–MgO solid solution catalyst and provides great resistance to oxidative deactivation in steam reforming of methane.

The reforming of CH_4 with steam or CO_2 ($CH_4 + H_2O \rightleftarrows 3H_2 + CO$; $CH_4 + CO_2 \rightleftarrows 2H_2 + 2CO$) over supported metal catalysts is a well-established industrial process for generating synthesis gas. Because CH_4 reforming reactions are involved in gas-to-liquid technology and in the generation of fuel for fuel cells, the reactions have attracted attention. The major drawback of CH_4/H_2O reforming is deactivation of the catalyst due to carbon deposition. To overcome this drawback, researchers have investigated a number of transition-metal catalysts supported on various oxides.[1] NiO–MgO[2] and CoO–MgO[3] solid solution catalysts reduced at high temperature (>1073 K) exhibit long life and high resistance to carbon deposition during CH_4 reforming. However, these catalysts have the disadvantage that the reducibility of Ni and Co is poor. For example, the reduction degree of NiO is only 2.9% even after reduction at 1123 K for 0.5 h.[4] This poor reducibility results in low activity and poor stability of the catalysts at low temperature and high space velocity. However, catalyst activity under such conditions is crucial because the inlet temperature of an industrial reformer is less than 873 K, and the temperature is only gradually increased to 1123 K in the reactor.[1a]

The addition of noble metals is reported to promote the reduction of Ni in a NiO–MgO catalyst.[4] However, the use of even trace amounts of noble metals is not economical. Therefore, with the goal of improving the reducibility of a CoO–NiO–MgO catalyst, our research group has investigated the effects of oxides of various nonnoble elements (Cr, Mn, Fe, Cu, Sr, Zr, Sn, La, Ce, Pr, Nd, and Gd) on catalyst activity for CH_4/H_2O reforming at 2.1 MPa. We found that Cr_2O_3 and Al_2O_3 effectively increased the reducibility of the metals and retarded oxidative deactivation of the catalyst.

CoO–NiO/MgO catalyst (Co/Ni 3/1 (w/w), 10 wt % total) was prepared by wet impregnation of an aqueous $Ni(NO_3)_2 \cdot 6H_2O$ and $Co(NO_3)_3 \cdot 6H_2O$ solution with MgO (JRC-MGO500A), which had been precalcined at 1073 K for 5 h. The catalyst was dried at room temperature and at 343 K overnight and then calcined at 723 K for 5 h in flowing air.

CoO–NiO/MgO(Al) (1 wt % Al) and CoO–NiO/MgO(Cr) (1 wt % Cr) catalysts were prepared by wet impregnation of aqueous $Al(NO_3)_3 \cdot 9H_2O$ and $Cr(NO_3)_3 \cdot 9H_2O$ solutions, respectively, with CoO–NiO/MgO prepared as described above. The catalyst samples were dried at room temperature and at 343 K overnight and calcined at 723 K for 5 h in flowing air.

All the catalysts, hereafter referred to as CoO–NiO–MgO, CoO–NiO–MgO(Al), and CoO–NiO–MgO(Cr), were calcined at 1373 K for 5 h in static air. The resulting powders were pressed into pellets at 1.2 MPa for 3 min. The pellets were crushed and sieved to obtain grains with diameters between 250 and 500 µm. All the catalyst grains were reduced ex situ with H_2 at 1173 K for 20 h before the analysis described below.

A sample of each catalyst (100 mg) was loaded into a tubular Inconel reactor passivated with an aluminum diffusion coating. After reduction in situ with H_2 at 973 K for 1 h, the catalyst was cooled to 853 K, and the pressure was increased from 0.1 to 2.1 MPa. Then a CH_4/H_2O mixture (CH_4/H_2O 1/1.5 (mol/mol), space velocity (SV) 72000 h^{-1}) was passed over the catalyst. The reaction products were analyzed by gas chromatography with thermal conductivity detection. After the reaction was completed, the reactor was purged with Ar at the reaction temperature, and then the catalyst was cooled to room temperature and used for further analysis.

The amount of carbon deposition was quantified by temperature-programmed oxidation.[5] The amount of H_2 chemisorbed at 323 K (a measure of metal surface area) and the amount of O_2 absorbed at 1123 K (a measure of the total amounts of reduced Co and Ni) were determined by pulse methods.

Figure 1 shows CH_4 conversion versus time on stream for CoO–NiO–MgO and the catalysts containing additives. For all the catalysts, an induction period of 1–2 h was observed at the beginning of the tests. The induction period corresponded to the time required to replace the feed gas with the reactants in the cold trap (volume, ca. 110 mL) at a low linear velocity at 2.1 MPa. The activity of the CoO–NiO–MgO catalyst decreased with time, and the catalyst was completely inactive within 10 h.

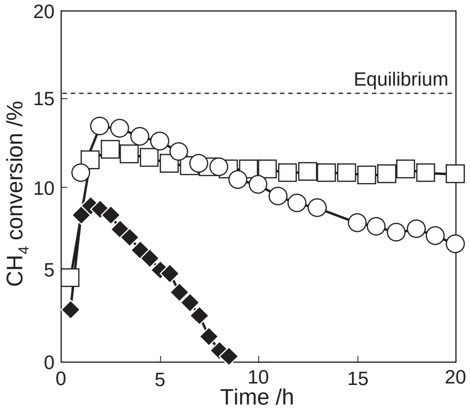


Figure 1. CH_4 conversion vs. time on stream for CH_4/H_2O reforming: CoO–NiO–MgO (◆), CoO–NiO–MgO(Al) (○), CoO–NiO–MgO(Cr) (□).

Table 1. O_2 absorption and H_2 chemisorption capacities, average metal particle size, and specific surface area of the catalysts

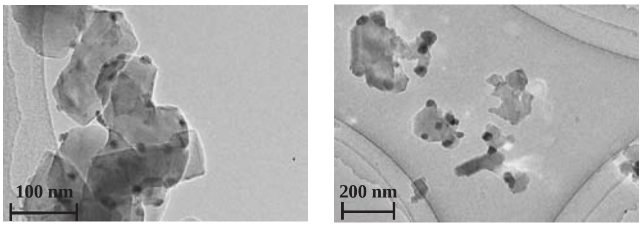
Catalyst	O_2 absorption[a] /µmol g^{-1}	H_2 chemisorption[b] /µmol g^{-1}	Particle size[c] /nm	BET /m^2 g^{-1}
CoO–NiO–MgO	74	0.7	13	14
CoO–NiO–MgO(Al)	588	5.7	37	19
CoO–NiO–MgO(Cr)	978	2.8	51	7

[a]Measured at 1123 K. [b]Measured at 323 K. [c]Measured by TEM.

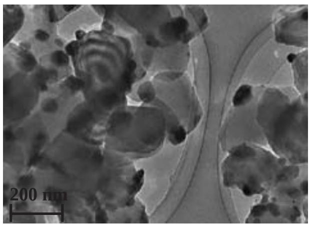
Because the amount of carbon deposited was negligible during the reaction (0.16 wt %), the deactivation was not ascribed to coking on active sites. Note that the catalyst turned from gray to beige during its deactivation. These results indicate that the metals on the supports were oxidized by H_2O in the feed gas;[4] that is, we ascribed the deactivation to oxidation of Co and Ni.

The activity and stability of the CoO–NiO–MgO catalyst were improved drastically by the addition of Al_2O_3 and Cr_2O_3. CH_4 conversion over the CoO–NiO–MgO(Al) catalyst decreased gradually, whereas the CoO–NiO–MgO(Cr) catalyst maintained high CH_4 conversions for 20 h. Note that influence of loading of Al_2O_3 on CoO–MgO was investigated. However, further addition (2.5% and 5.0% Al) did not improve catalytic stability. To clarify influence of the additives on the catalyst properties, we measured H_2 chemisorption at 323 K and O_2 absorption at 1123 K after in situ reduction at 973 K, which followed ex situ reduction at 1173 K (Table 1). O_2 absorption on the CoO–NiO–MgO catalyst was determined to be 74 µmol g^{-1}. If we assume that Ni and Co were oxidized to NiO and CoO, respectively, the O_2 absorption value indicates that 9% of the Ni and Co included in the catalyst was oxidized by the O_2 pulse. In contrast, larger amounts ($\geq$588 µmol g^{-1}) of O_2 were absorbed on the CoO–NiO–MgO catalysts containing Al_2O_3 and Cr_2O_3. However, some of the O_2 absorption on the catalysts may have been due to oxidation of the additives. Consequently, we assumed that oxidation of the additives, that is, oxidation of Cr^0 to Cr^{3+} and Al^0 to Al^{3+}, contributed to the increased oxygen consumption, in order to calculate minimum reduction degree of Ni and Co. By subtracting the contribution of additive oxidation, we estimated the total reduction degrees of Ni and Co for the CoO–NiO–MgO(Cr) and CoO–NiO–MgO(Al) catalysts to be at least 99 and 36%, respectively. Thus, we demonstrated that the addition of Al_2O_3 and Cr_2O_3 drastically increased the reduction degrees of Ni and Co. Furthermore, these results indicate that the addition of Cr_2O_3 improved reduction of Ni and Co greatly, which provided excellent stability to the catalyst (Figure 1).

The CoO–NiO–MgO catalyst chemisorbed 0.7 µmol g^{-1} of H_2. If one hydrogen atom was adsorbed on each metal atom, this value corresponds to only 0.1% of the Co and Ni atoms included in the catalyst. As reported previously, low reduction degrees of Ni and Co result in low metal surface areas.[4] The H_2 chemisorbed on the catalyst was increased fourfold and eightfold by the addition of Cr_2O_3 and Al_2O_3, respectively. Therefore, we concluded that the additives promoted the reduction of Co and Ni and that the modified catalysts had higher metal surface areas. Note that such effect of Cr_2O_3 was reported in a patent, although it seems that the loading of Ni, i.e., more than 30 wt %, was too much to work as reforming catalyst.[6] The high metal surface areas contributed to the consumption of H_2O, and the oxidation of Co and Ni by excess H_2O must have been retarded.



(a) CoO–NiO–MgO (b) CoO–NiO–MgO(Al)



(c) CoO–NiO–MgO(Cr)

Figure 2. Transmission electron micrographs of the catalysts after ex situ reduction with H_2 at 1173 K.

Transmission electron microscopy measurements were made to compare metal particle size formed by ex situ reduction at 1173 K (Figure 2 and Table 1). The metal particle size was increased by the addition of Al_2O_3 and Cr_2O_3, and this size increase was due to the increase in the reduction degrees of Co and Ni. Formation of larger particles is known to confer resistance to oxidation by H_2O in the CH_4/H_2O mixture.[7]

To summarize, we demonstrated that the addition of Al_2O_3 or Cr_2O_3 to CoO–NiO–MgO drastically promoted the reduction of Co and Ni in a H_2 stream. The promotion of reduction led to increases in the metal surface area. In addition, the aggregation of the reduced metal was promoted, and relatively large metal particles were formed. The modified catalysts showed high and stable activity for H_2O reforming of CH_4 at 2.1 MPa. Note also that we have already shown that the CoO–NiO–MgO(Al) and CoO–NiO–MgO(Cr) catalysts show stable activity under practical reaction conditions for the generation of synthesis gas with a H_2/CO ratio of 2 (2.1 MPa, $CH_4/H_2O/CO_2 = 1/1/0.5$, 1123 K, 20 h) (see Figure S1)[5] with only minor coking (<0.1 wt %). Thus, we expect these catalysts to be highly useful industrial catalysts.

References and Notes

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