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CO_2 reforming of methane over modified Ni/ZrO_2 catalysts[†]

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CO_2 reforming of methane was performed over two series of modified Ni/ZrO_2 catalysts having high nickel contents. One is the modification of zirconia with lanthanum-, cerium- or manganese-oxide. Among them, $Ni/La–ZrO_2$ exhibited the highest activity and good stability, whereas $Ni/Ce–ZrO_2$ and $Ni/Mn–ZrO_2$ gave low carbon formation during the reaction. The other modified catalysts were prepared by adding basic oxides to the nickel side. $Ni–Mg/ZrO_2$ exhibited the best activity and stability, wherein a magnesium promoter is attributed to increasing the dispersion of nickel and enhancing the interaction between CO_2 and the catalyst during the CO_2 reforming. Copyright © 2001 John Wiley & Sons, Ltd.

Keywords: CO_2 reforming; Ni/ZrO_2; support modification; alkaline-earth metal oxides; promoters

INTRODUCTION

As a massive utilization of CO_2 into useful chemicals production, CO_2 reforming of methane has received increasing attention.[1–4] This reaction produces synthesis gas having a low H_2/CO ratio, which is applicable to Fischer–Tropsch synthesis and oxo-synthesis. Considerable effort has been devoted to the development of high-performance catalysts for CO_2 reforming.[1–7] It has been observed that the nature of the support and promoter to be adopted for the reforming catalyst affects greatly the catalytic performance in CO_2 reforming.[1] As a result of new application of a zirconia support for CO_2 reforming, Lercher *et al.*[5] have recently reported the development of a new Pt/ZrO_2 catalyst with excellent performance. However, they have failed to apply Ni/ZrO_2 catalyst with high nickel loading to the same reaction due to a serious plug of the reactor by coke. In contrast, we have successfully performed CO_2 reforming on Ni/ZrO_2 catalysts with more than 10 wt% nickel loading in spite of giving rise to a large amount of carbon deposition.[6] Despite its high activity, the modification of the catalyst system is necessarily required for much improvement of the catalyst stability.

Here, we investigate nickel-based catalysts using zirconia as a support for CO_2 reforming, wherein the support was modified by lanthanum-, cerium- or manganese-oxide and nickel species were also modified by some basic oxides in order to figure out the effect of the modification to Ni/ZrO_2 catalyst.

EXPERIMENTAL

The modification of the zirconia support was carried out by the sol-gel method using a mixture of zirconyl chloride and the corresponding foreign metal salt of lanthanum-, cerium- or manganese-oxide. The atomic ratio of zirconium to each promoter is 5:1. Nickel catalysts loaded on these modified supports were prepared by impregnation with the solution of metal nitrates (the molar ratio of nickel to each alkaline-earth metal promoter is 1:1). The catalyst samples were calcined at 773 K for 4 h in air.

Activity tests were carried out under atmospheric pressure at 1023 K using 50 mg of catalyst mixed with 250 mg of quartz sand (reactant gas: 20 vol.%

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CH_4–20 vol.% CO_2–60 vol.% N_2; flow rate: 50 cm^3 min^{-1}). The catalyst was reduced in 5% H_2–N_2 with 20 cm^3 min^{-1} at 973 K for 2 h before the reaction. During the reaction, the carbon balance of each catalytic run was confirmed to be more than 97%.

Thermogravimetric analysis (TGA) was performed on an Intelligent Gravimetric Analyzer. The sample was pre-reduced at 973 K for 2 h, purged with helium for 20 min, and then cooled to room temperature. Afterwards, temperature-programmed surface reaction (TPSR) was performed using 20 vol.% CH_4–20 vol.% CO_2–60 vol.% He (50 cm^3 min^{-1}) at a heating rate 5 K min^{-1}. The catalysts were further characterized by extended X-ray absorption fine structure (EXAFS), as described in detail elsewhere.[7]

RESULTS AND DISCUSSION

In our previous work, it was reported that Ni/ZrO_2 catalyst with high nickel loading exhibits not only high activity but also good catalyst stability for 30 h towards CO_2 reforming of methane.[6] In that case the carbon species initially deposited on the catalyst within a few minutes played a role as an active reaction intermediate to react with CO_2. Despite its high activity, the modification of the catalyst system is necessarily required for much improvement of the catalyst stability. This study, therefore, is focused on finding out a good modifier to the zirconia support and a good promoter to nickel in order to improve catalyst stability.

Instead of confirming catalyst stability for a longer reaction time, in this work we examined catalyst stability according to high-temperature aging under reaction conditions as an easier way for a rather shorter time. Catalytic activities of Ni/ZrO_2 and Ni/modified-ZrO_2 catalysts before and after reaction test at 1123 K for 10 h in CO_2 reforming are compared in Fig. 1. It is clear that lanthanum oxide modification to zirconia enhances the catalytic activity compared with that of Ni/ZrO_2, whereas Ni/Ce–ZrO_2 and Ni/Mn–ZrO_2 exhibit lower activities than Ni/ZrO_2. Their activities decrease in the following order: Ni/La–ZrO_2 > Ni/ZrO_2 > Ni/Ce–ZrO_2 > Ni/Mn–ZrO_2. The catalyst stability towards thermal aging was the best on Ni/La–ZrO_2, and was the worst on Ni/ZrO_2. As illustrated in Fig. 2, TGA results reveal that the amount of carbon formed on the catalysts during the TPSR is of the same order as their catalytic activities towards CH_4 conversion as well as CO_2 conversion in the CO_2 reforming, indicating that a high degree of carbon formation results from the high reactivities towards both reactants, though these results were not obtained at reaction temperature. Thus Ni/La–ZrO_2, which exhibits the

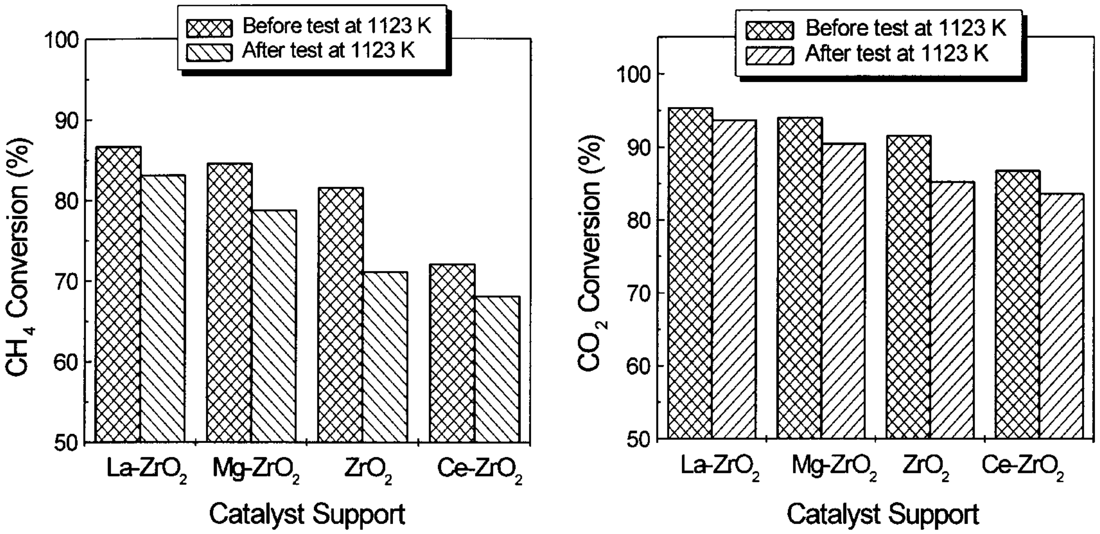

Figure 1 Comparison of methane conversion measured at 1023 K before and after the test at 1123 K over catalysts of Ni/ZrO_2 and Ni/modified-ZrO_2 catalysts with 13.2 wt% nickel loading. Reaction conditions: *W/F*, 0.06 g s ml^{-1}; time-on-stream for each set of data, 10 h.

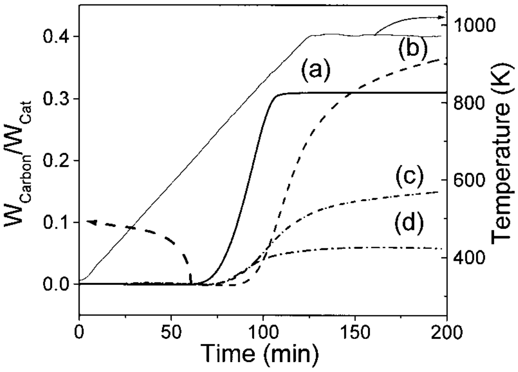

Figure 2 TGA results of TPSR in CH_4–CO_2–He over Ni/ZrO_2 and Ni/modified-ZrO_2 catalysts with 13.2 wt% nickel loading: (a) Ni/ZrO_2, (b) Ni/La–ZrO_2, (c) Ni/Ce–ZrO_2, and (d) Ni/Mn–ZrO_2. Analysis conditions: sample weight, *ca* 10 mg, 20 vol.% CH_4–20 vol.% CO_2–60 vol.% He; flow rate, 50 cm^3 min^{-1}; heating rate, 5 K min^{-1}.

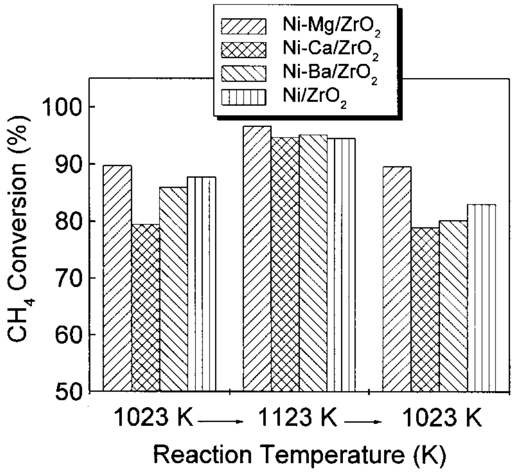

Figure 3 Methane conversion over alkaline earth metal-promoted Ni/ZrO_2 catalysts with 10.0 wt% nickel loading. Reaction conditions: *W/F*, 0.06 g s ml^{-1}; time-on-stream for each set of data, 10 h.

highest activity, gives larger carbon deposition than on Ni/ZrO_2, whereas Ni/Ce–ZrO_2 shows the least carbon deposition. The addition of cerium- and manganese-oxides to zirconia diminishes the carbon deposition greatly during the reaction. These results are consistent with the previous studies of cerium- and manganese-modified Ni/Al_2O_3 catalysts.[8,9] As demonstrated in Ni/ZrO_2 catalysts,[6] the carbon species formed initially on other zirconia-based nickel catalysts may also play a role as one of reaction intermediates. It is likely that the activities and the degree of carbon formation of supported nickel catalysts are strongly affected by the interaction of nickel sites and the support, which can be greatly modified by promoters to be added. However, the degree of carbon deposition appears not to be directly connected with catalyst stability, at least under the given conditions here.

The promotion of lanthanum in Ni/La–ZrO_2 may reveal that CO_2 interacts with La_2O_3 to form carbonate, which scavenges carbon from nickel, thus restoring the nickel particles to their original state, as in Ni/La_2O_3, as proposed by Zhang and Verykios.[4] These results demonstrate that among the applied modifiers only La_2O_3 could improve the catalytic properties by enhancing CO_2 activation to react with the active carbon intermediate. On the other hand, the lesser amounts of coke on Ni/Ce–ZrO_2 and Ni/Mn–ZrO_2 catalysts might be ascribed to the high concentration of labile oxygen species arising from CO_2 interaction with the modified supports.[8,10]

Figure 3 compares activities of modified Ni/ZrO_2 catalysts with alkaline-earth metal oxides as a promoter of metallic nickel. This modification was investigated for neutralizing residual surface acid sites of the Ni/ZrO_2 catalyst and enhancing the interaction of the catalyst surface with CO_2. At 1023 K, Ni–Mg/ZrO_2 yields the highest activity and the others show lower activities than Ni/ZrO_2 (Fig. 3). However, at 1123 K all modified Ni/ZrO_2 catalysts exhibit similar activities to Ni/ZrO_2, which means an insensitivity to the presence of a promoter due to high reaction temperature. When the activity is measured again at 1023 K after 1123 K test, Ni–Ca/ZrO_2 and Ni–Mg/ZrO_2 present excellent stability. On the other hand, Ni/ZrO_2 and Ni–Ba/ZrO_2 give poor stability.

Since it exhibited the best activity and stability, Ni–Mg/ZrO_2 catalyst was further characterized by X-ray diffraction (XRD) and EXAFS in order to recognize the function of MgO in the reaction. From XRD patterns of Ni–Mg/ZrO_2 samples, it was observed that a stable solid solution of NiO and MgO was formed, which is similar to that in the Ni/MgO system.[1,2] The reacted catalysts, which were reduced before reaction, contained no characteristic peaks of Ni^0 crystallites. These results demonstrate that nickel species could be isolated by MgO and hence become highly dispersed on the surface. These dispersed Ni^0 species and NiO phases on Ni–Mg/ZrO_2 samples were also identified by EXAFS by using nickel foil and nickel oxide as references (Fig. 4). The characteristic peak

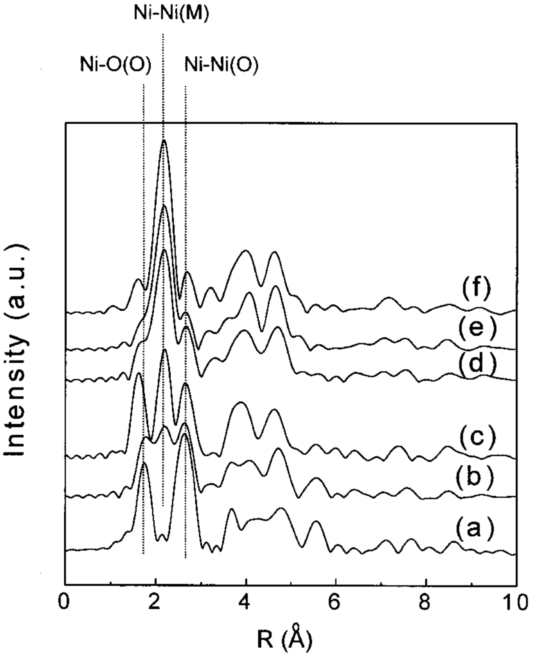

Figure 4 Fourier transformed EXAFS spectra of 10 wt% Ni–Mg/ZrO_2 catalysts without phase correction: (a) calcined sample, (b) reduced sample, and the sample after the CO_2 reforming reaction at 1023 K for (c) 1 h and (d) 4 h, and at 1123 K for (e) 1 h and (f) 4 h. Notation: Ni—O(O), the first coordination shell of NiO; Ni—Ni(O), the second coordination shell of NiO; Ni—Ni(M), the first coordination shell of metallic nickel.

of Ni^0 is observed to exist together with NiO on the reduced sample. On prolonging the reaction time at 1023 K or increasing the reaction temperature to 1123 K, the characteristic peak intensities of Ni^0 in terms of nickel–nickel amplitude increase significantly while the intensities of nickel–oxygen amplitude responsible for NiO species decrease. These results indicate that the remaining NiO species even after pre-reduction are continuously reduced to produce new Ni^0 species during the reaction, which may result in a high activity and good stability. The amount of carbon deposited on Ni–Mg/ZrO_2 catalyst was much less than that formed on Ni/ZrO_2 catalyst. Supplementary EXAFS results showed that, after CO_2 treatment at reaction temperature, the sample used could be restored to the original state of the calcined sample. This shows the high reactivity of CO_2 towards the reduced sample as well as the deposited carbon. Therefore, the promotion effect of MgO on Ni–Mg/ZrO_2 is suggested as not only isolating nickel species *via* the formation of solid solution, but also enhancing CO_2 activation to produce active oxygen species to react with the carbon deposited on nickel sites.

CONCLUSION

By introducing lanthanum oxide into zirconia and magnesium oxide into nickel, the activity of Ni/ZrO_2 catalyst for CO_2 reforming of methane was improved and a better catalyst stability was achieved. It is revealed that a stable interaction phase of NiO and MgO is formed on Ni–Mg/ZrO_2 catalyst, which results in a highly dispersed state of nickel species with an increased interaction between CO_2 and the catalyst.

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