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An optimum NiO content in the CO_2 reforming of CH_4 with NiO / MgO solid solution catalysts

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Reduced NiO/MgO, with a NiO content in the range 9.2–28.6 wt%, was found to be a highly effective catalyst for the CO_2 reforming of CH_4 to CO and H_2 (at 790°C, atmospheric pressure and a space velocity of 60000 $cm^3 g^{-1} h^{-1}$). For smaller or higher NiO contents, the yield was smaller, being negligible for 4.9 wt%. In contrast to the other reforming catalysts, the new catalyst has high stability, since in the optimum NiO range the CO yield remained unchanged at 95% for 120 h without any carbon deposition. The formation of a solid solution between NiO and MgO, which was demonstrated by both X-ray diffraction and temperature-programmed reduction, is most likely responsible for the high selectivity and stability in a large range of compositions of NiO/MgO.

Keywords: Ni; Mg; CH_4; CO_2 reforming

1. Introduction

Synthesis gas is an important feedstock for the methanol and the Fischer–Tropsch syntheses, reason for which the conversion of CH_4 to the synthesis gas CO/H_2 is of industrial significance. So far, three routes have been suggested to achieve such a conversion: (i) steam reforming of CH_4; (ii) catalytic partial oxidation of methane; and (iii) CO_2 reforming of CH_4.

The steam reforming of methane constitutes, for the time being, the dominant commercial method for the production of synthesis gas [1,2]. This reaction has, however, poor selectivity for CO and a high H_2/CO ratio, unsuitable for the methanol and the Fischer–Tropsch syntheses. Although the catalytic partial oxidation of CH_4 has high activity and selectivity [3–6], the process cannot be easily controlled because of the generation of hot spots in the catalyst [7]. The CO_2 reforming of CH_4 provides a high CO selectivity, more suitable H_2/CO ratios, and converts both CH_4 and CO_2, which are greenhouse gases, into valuable feedstocks [8–14]. For this reason, the latter reaction attracted increasing attention. However, no commercial catalyst is yet available for this reaction, because the generation of carbon when the conventional reforming catalysts, such as Ni/Al_2O_3, are employed results in the rapid deactivation of the catalyst. We reported in a recent paper [15] that the formation of carbon over Ni could be suppressed when a reduced NiO/MgO solid solution catalyst with a NiO/MgO weight ratio of 20/100 was used. In addition, the catalyst had high stability and yields. The scope of the present paper is to emphasize the existence of a large range of NiO/MgO compositions for which the yields have optimum, large, values.

2. Experimental

The catalysts were prepared by impregnating MgO (or, for comparison purposes, Al_2O_3) with an aqueous solution of nickel nitrate, then drying at room temperature in air and finally calcining at 800°C in air for 1.5 h. The reduction of the catalysts was carried out in H_2 (20 ml/min) at 500°C for 14 h; this was followed by an increase in temperature to 790°C at a rate of 20°C/min also in H_2 (20 ml/min). The stoichiometric CO_2-reforming reaction was carried out at atmospheric pressure, 790°C and a space velocity of 60000 $cm^3\ g^{-1}\ h^{-1}$ over a number of prereduced NiO/MgO catalysts. Samples of 0.020 g of catalyst held on quartz wool located in a quartz tube (2 mm inside diameter) were employed. The yield of CO is defined as the ratio (in the product) CO (mol)/[CO (mol) + CO_2 (mol) + CH_4 (mol)] × 100% and the yield of H_2 as: CH_4 conversion (%) × H_2 (mol)/[H_2(mol) + H_2O (mol)] in the product. The catalysts have been examined by X-ray diffraction (XRD) both before and after reaction. Temperature-programmed reduction (TPR) experiments were also performed by heating the samples from room temperature to 800°C, at a rate of 17 K/min, in a 4% H_2/Ar gas flow rate of 47 ml/min through a quartz tube of 2 mm inside diameter.

3. Results and discussion

It was found that the reduced NiO/MgO catalysts can provide maximum yields of CO and H_2 of over 95 and 91% (fig. 1), respectively, for NiO contents between 9.2 and 28.6 wt%. The yields are higher than those previously reported for other catalysts [8–14]. The reduced catalyst had no activity for a NiO content of 4.8 wt%.

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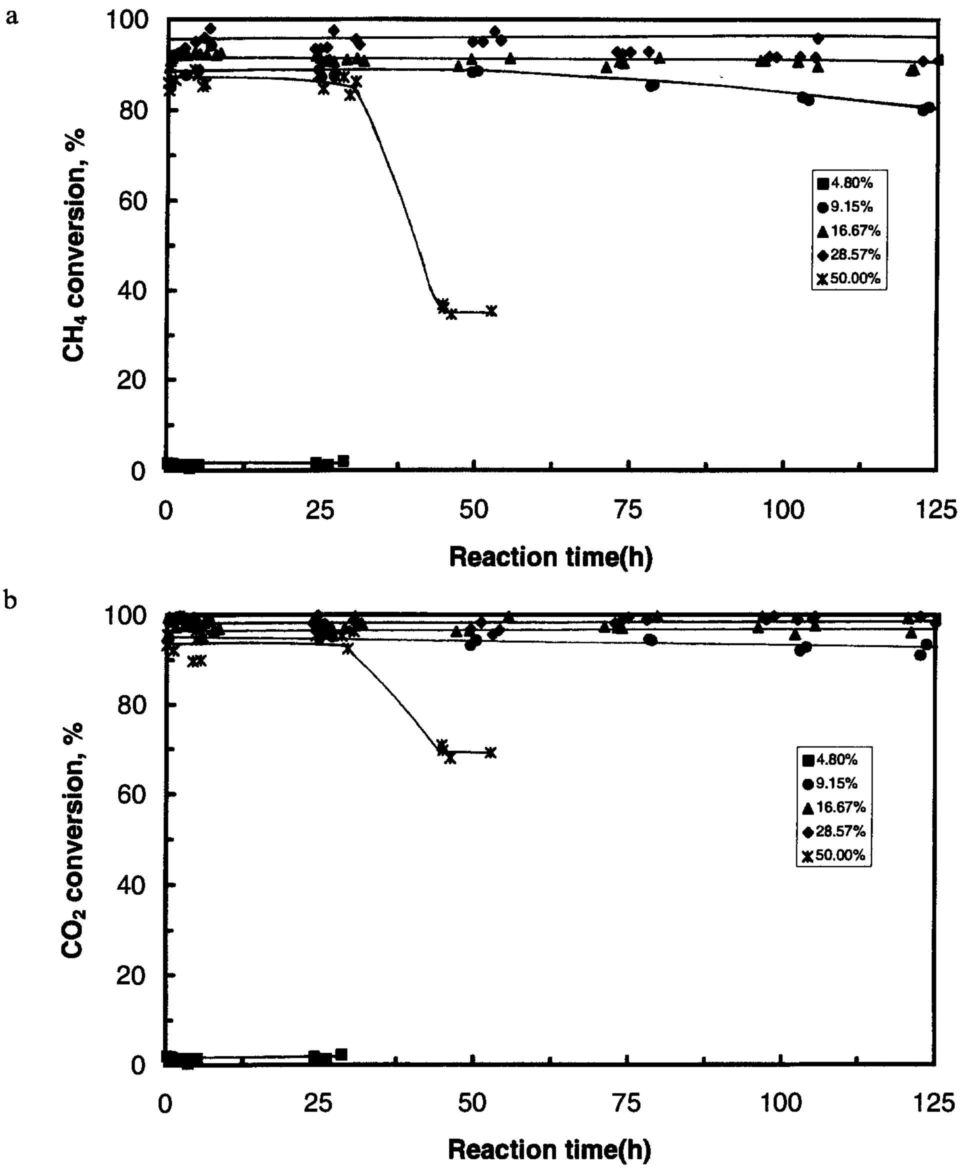

Fig. 1. (a) CH_4 conversion for reduced NiO/MgO catalysts. (b) CO_2 conversion for reduced NiO/MgO catalysts. (c) CO yield for reduced NiO/MgO catalysts. (d) H_2 yield for reduced NiO/MgO catalysts.

When the content of NiO in NiO/MgO catalysts was in the optimum range of 9.2 to 28.6 wt%, the CO yield of the catalysts hardly changed in 120 h (fig. 1) because the latter catalysts inhibit carbon formation. Indeed, while the reduced NiO/Al_2O_3 catalysts became black after a few hours, the reduced NiO/MgO catalysts maintained their initial color for NiO contents between 4.8 and 28.6 wt%. However, the catalyst with a NiO content of 50 wt% became black after about 50 h. At the higher NiO content of 50 wt%, the yield of CO decreased, from 91 to 53% after 40 h. Let us also note that, on the reduced 16.7% NiO/Al_2O_3 catalyst, carbon deposition occurred quickly, resulting in the decrease of the feed gas space velocity and the plugging of the reactor. For the unreduced NiO/MgO catalysts, the activities were also dependent on the NiO content. At 16.7 wt% NiO, the catalyst had hardly any activity, while at 28.6 wt%, the CO yield increased from 3 to 89% in about 20 h, remaining at the latter value for the remaining duration of the experiment (fig. 2).

The XRD patterns (fig. 3) reveal very similar structures for NiO/MgO and MgO, indicating that NiO and MgO form a solid solution. The XRD of the reduced 50 wt% NiO/MgO catalyst showed after reaction the presence of Ni besides the NiO/MgO solid solution phase; in the 16.7 wt% NiO/MgO catalyst, only small amounts of Ni phase could be identified after reaction.

As shown in fig. 4, there is one peak at 350°C in the TPR of NiO. In contrast, there is a small peak in the 50 wt% NiO/MgO catalyst and no obvious peak in the 16.7 wt% NiO/MgO. This indicates that NiO and MgO form indeed a solid solution.

In some investigations [8,11], it was concluded that it is impossible to avoid carbon formation for CO_2/CH_4

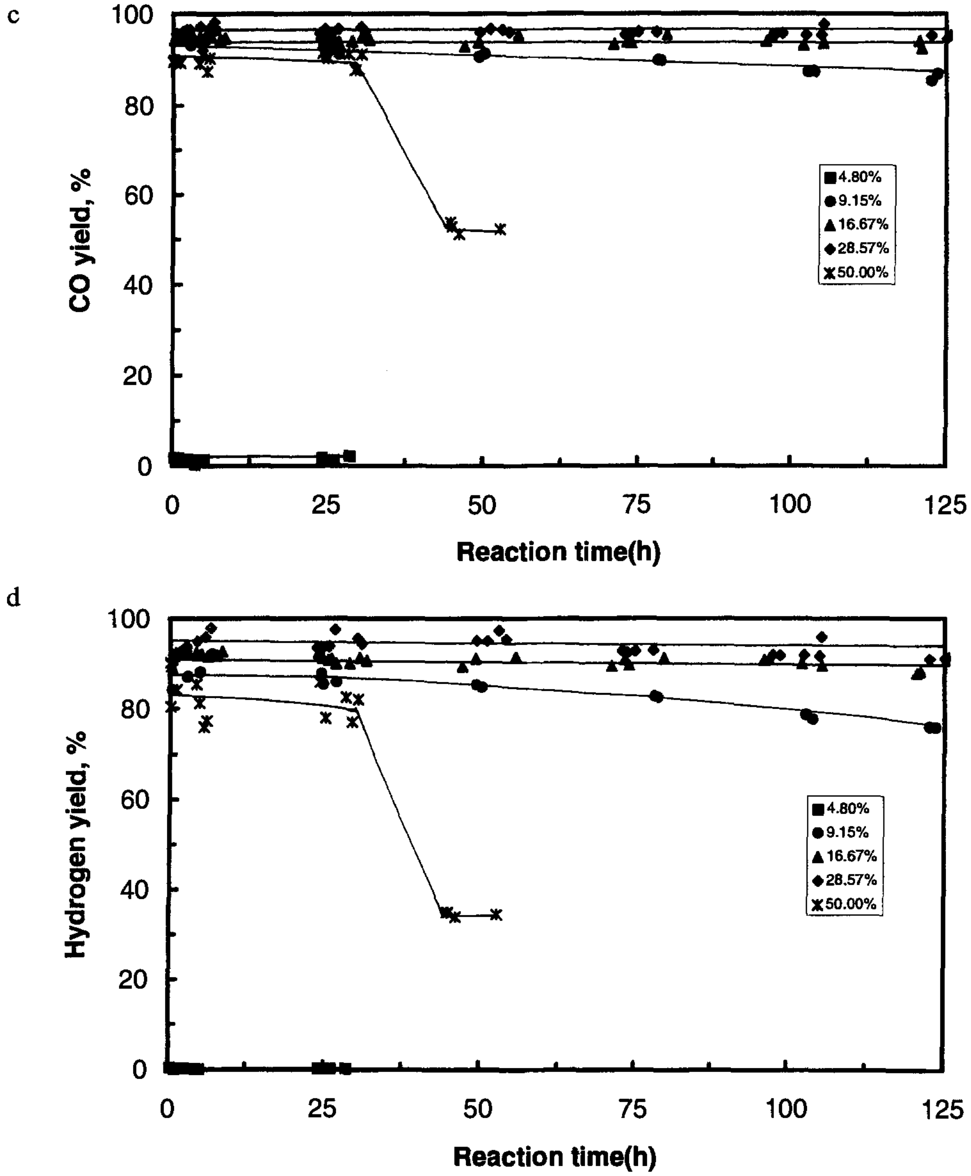

Fig. 1. (Continued.)

molar ratios of 1 : 1 on nickel based catalysts, such as Ni/Al_2O_3. The sulphur passivation, commercialized in steam reforming (the SPARG process), can inhibit to a certain extent carbon formation by blocking some of the active sites [16]; however, it reduces also the catalytic activity. Even though the noble metal catalysts can suppress efficiently the carbon deposition in the carbon dioxide reforming [8,11,17], they are expensive. For this reason, the presently proposed reduced NiO/MgO solid solution catalysts may have commercial value.

As shown in fig. 1, the reduced NiO/MgO catalysts activate very well both CH_4 and CO_2 and have rather high stability. The unexpected stability of the reduced NiO/MgO catalysts is most likely due to the almost identical crystal structures of NiO and MgO. Both NiO and MgO have a face-centered cubic structure with almost the same lattice parameters and bond distances [18]. For this reason, MgO and NiO can form solid solutions. This was demonstrated both by the XRD results, which showed that NiO/MgO forms a single phase, and by the absence of a peak in the TPR results. The formation of NiO/MgO solutions has the following consequences [15]: (i) Only a small amount of NiO is reduced to Ni which segregates as small particles over the surface of the support. Because of the small amount, little sintering occurs. This is why NiO/MgO catalysts have rather high stability in a large range of NiO contents. Since NiO does not form solutions with Al_2O_3, it is more easily reduced and the relatively large amount of Ni sinters generating relatively large particles. (ii) Because there are strong interactions between the small Ni particles which are present on the reduced NiO/MgO catalyst and MgO, the donor ability of Ni is decreased. The bonding of the CO molecule to a transition metal atom such as Ni involves the donation of the lone electron pair of the carbon atom to vacant d orbitals of the metal atom

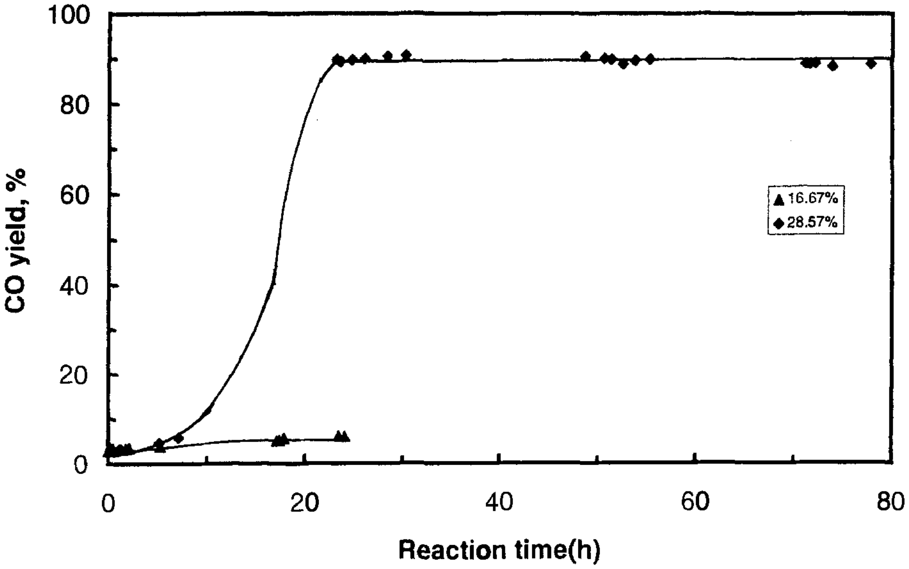

Fig. 2. CO yield for unreduced NiO/MgO catalysts.

and the back donation of electrons from the filled d orbitals of the metal to the vacant antibonding π^* orbitals of the CO molecule [19]. This weakens the CO bond, thus stimulating the CO decomposition. The donor ability of Ni and, consequently, the ability for disproportionation of CO are, however, decreased by the strong interactions between the small Ni particles and MgO. At high NiO contents (50 wt%), a larger amount of NiO is reduced. As a result, the sintering is intensified and the Ni particles become large and behave like bulk materials. Therefore, the strong interactions, which are responsible for the decrease of the donor ability, are absent and the deactivation, via the Boudouard reaction, of the catalyst is intensified. At low NiO contents (4.8 wt%), a too small amount of Ni is generated, and, hence, the activity is negligible.

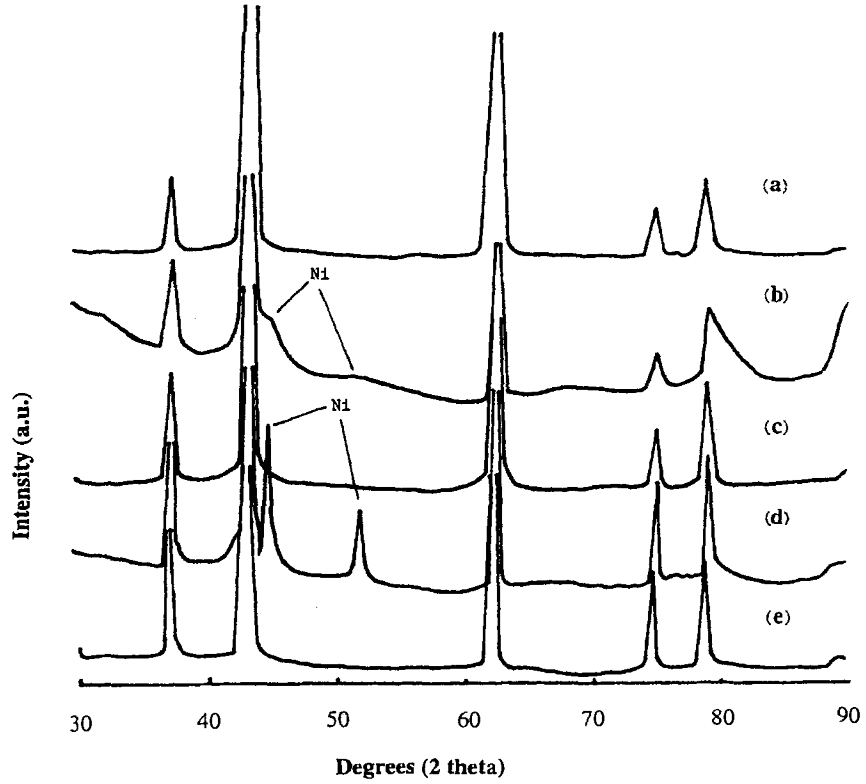

Fig. 3. X-ray powder diffraction patterns of (a) calcined MgO, (b) 16.7 wt% NiO/MgO catalyst (after reaction), (c) 16.7 wt% NiO/MgO catalyst (before reduction), (d) 50% NiO/MgO catalyst (after reaction), and (e) 50% NiO/MgO catalyst (before reduction).

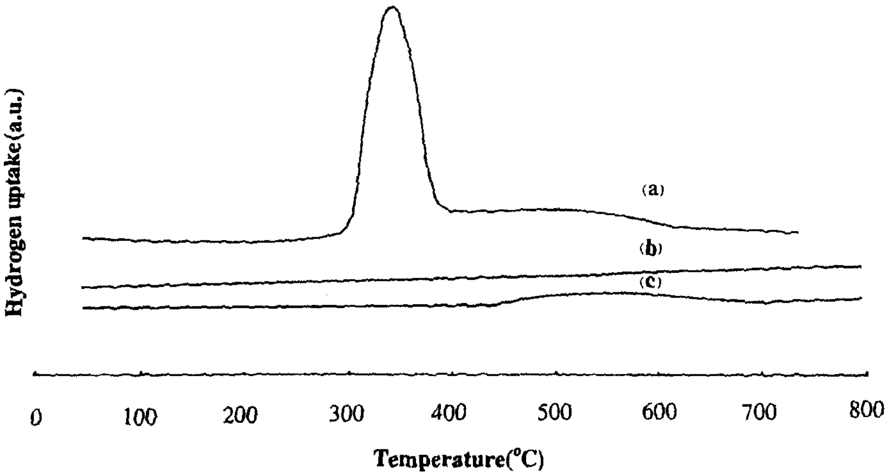

Fig. 4. TPR profiles of (a) NiO, (b) 16.7 wt% NiO/MgO catalyst and (c) 50 wt% NiO/MgO catalyst.

From the above results, one can conclude that the NiO/MgO solid solution might be an appropriate industrial catalyst for the CO_2 reforming of CH_4. In addition, solid solution catalysts may have applications to other catalytic reactions.

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