

A Stable and Active Nickel-based Catalyst for Carbon Dioxide Reforming of Methane to Synthesis Gas

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A novel Ni/La₂O₃ catalyst which exhibits high activity and excellent long-term stability for carbon dioxide reforming of methane to synthesis gas is developed.

Carbon dioxide reforming of methane produces synthesis gas with a low hydrogen-to-carbon monoxide ratio, which is desirable for the Fischer–Tropsch synthesis network.¹ This reaction also has very important environmental implications because both methane and carbon dioxide are greenhouse gases which may be converted into valuable feedstock. No established industrial technology for carbon dioxide reforming of methane to synthesis gas exists, in spite of the potentially attractive incentives for a large number of applications. A major problem inhibiting the industrial application of this process is catalyst deactivation, induced by carbon deposition *via* the Boudouard reaction ($2\text{CO} \rightarrow \text{C} + \text{CO}_2$) and/or methane cracking ($\text{CH}_4 \rightarrow \text{C} + 2\text{H}_2$), which are favourable under reaction conditions.^{2–4} In recent years, the process of carbon dioxide reforming of methane has received attention, and efforts have been focused on the development of catalysts which show high activity and are resistant to coking, thus displaying stable long-term operation. Nickel-based catalysts^{4–6} and supported noble metal catalysts (Rh, Ru, Ir, Pd and Pt)^{2,3,7,8} were found to give promising catalytic performance in terms of methane conversion and selectivity to synthesis gas. The catalysts based on noble metals are reported to be less sensitive to coking as compared to the nickel-based catalysts.^{3,9} However, considering the aspects of high cost and limited availability of noble metals, it is more practical, from the industrial standpoint, to develop an improved nickel-based catalyst which exhibits stable operation for a long period of time. This communication reports results obtained over a novel Ni/La₂O₃ catalyst which exhibits high activity and excellent stability for carbon dioxide reforming of methane to synthesis gas.

The supported Ni catalysts were prepared by the wet-impregnation method, using Ni(NO₃)₂ as the metal precursor. The water was evaporated under continuous stirring and the residue was dried at 383 K for 24 h. The dried residue was then ground and sieved and was heated at 773 K under N₂ flow for 2 h for complete decomposition of nickel nitrate. After this treatment, the catalyst was reduced at 773 K in H₂ flow for at least 5 h. The nickel dispersion was measured by H₂ chemisorption at room temperature. Before the measurement, the sample was further reduced at 1023 K in H₂ flow for 2 h. A nickel dispersion of 1, 0.5 and 3% was found for 17 mass% Ni supported on La₂O₃, CaO and γ -Al₂O₃ carriers, respectively. The Ni/La₂O₃ catalyst was characterized by XRD. It was shown that the fresh catalyst consists of metallic Ni crystallites and lanthanum oxide only.

Fig. 1 shows the alteration of the reaction rate over Ni/ γ -Al₂O₃, Ni/CaO and Ni/La₂O₃ catalysts as a function of time on stream obtained at 1023 K. The rates over Ni/ γ -Al₂O₃ and Ni/CaO are reduced continuously with reaction time, presumably due to accumulation of carbonaceous species on the catalyst surface. Although the initial rate over Ni/ γ -Al₂O₃ is higher than the respective one over Ni/CaO, probably due to the higher dispersion of the former catalyst, the deactivation rate over Ni/ γ -Al₂O₃ is also faster than that over Ni/CaO. In contrast, the rate over the Ni/La₂O₃ catalyst increases significantly with time on stream during the initial 2–5 h of reaction, and then tends to be invariable with time on stream during 100 h of reaction, showing an excellent stability. This leads to the suggestion that new catalytic sites, which are more

active and stable towards the reaction of CH₄–CO₂, are formed on the Ni/La₂O₃ catalyst surface, following exposure to the reaction mixture. The rate over the Ni/La₂O₃, at the stable level, is found to be approximately the same as the initial rate over the Ni/ γ -Al₂O₃. A study of the influence of contact time on the reaction rate indicates that conversions of methane and carbon dioxide increase rapidly as contact time increases from 0.002 to 0.07 g s ml⁻¹. Conversions approaching those expected at thermodynamic equilibrium are achieved at a contact time as low as *ca.* 0.06 g s ml⁻¹, which corresponds to a superficial contact time of *ca.* 0.02 s. In comparison, steam reforming of methane reactors, employing the commercial K-promoted Ni/ γ -Al₂O₃ catalyst, typically have superficial contact times of the order of 1 s.¹⁰ The low contact time (*ca.* 0.02 s) required to obtain the equilibrium conversion of carbon dioxide reforming of methane over the Ni/La₂O₃ catalyst indicates that the activity of the Ni/La₂O₃ catalyst is high enough for industrial operation.

The stability of the 17 mass% Ni/La₂O₃ catalyst at various temperatures was also investigated. The Ni/La₂O₃ catalyst was first treated in the CH₄–CO₂ mixture at 1023 K until the reaction rate reached the stable level (see Fig. 1). After this treatment, the reaction rates obtained at different temperatures were monitored as a function of time on stream (Fig. 2). It is shown that, following the treatment mentioned above, the resultant Ni/La₂O₃ catalyst is extremely stable, exhibiting no deactivation during 20 h of reaction at 823, 923 and 1023 K. These results are of significance since even supported noble metal catalysts, *e.g.* Rh catalyst, which has been reported to be one of the most stable catalysts for carbon dioxide reforming of methane^{2,3} still suffers carbon deposition and deactivation at reaction temperatures

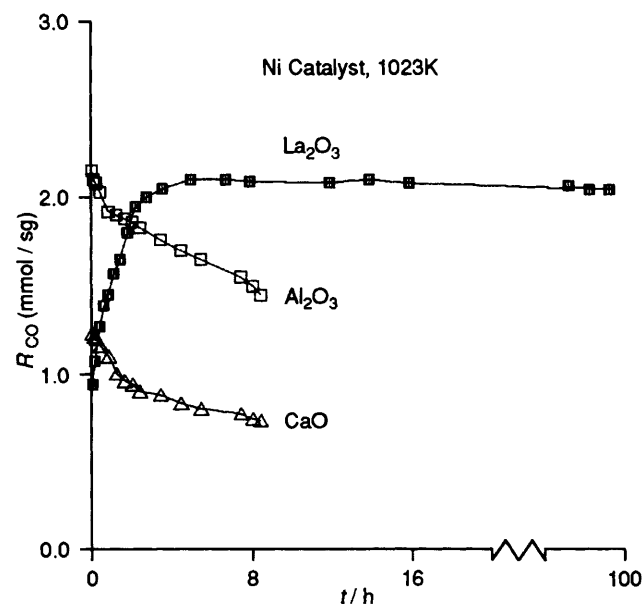


Fig. 1 Alteration of the reaction rate as a function of time on stream over 17 mass% Ni supported on La₂O₃, γ -Al₂O₃ and CaO carriers. Reaction conditions: $p_{\text{CH}_4} = 0.2$ bar, $p_{\text{tot}} = 1.0$ bar, CH₄–CO₂ = 1, $T = 1023$ K, M/F = 2×10^{-3} g s ml⁻¹.

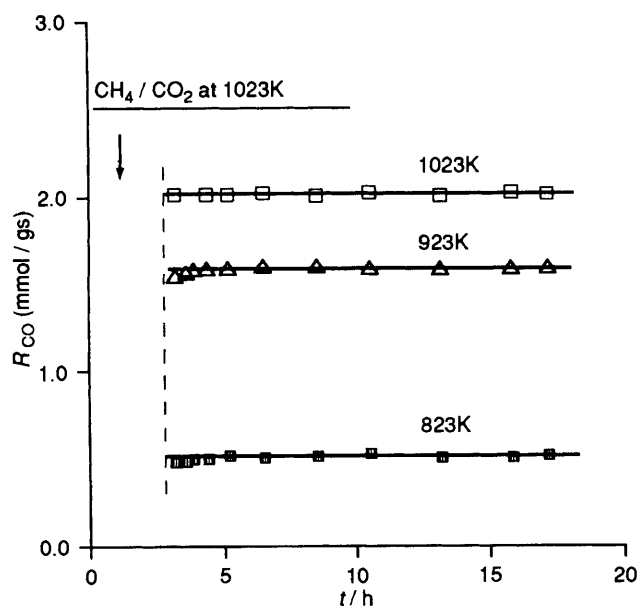


Fig. 2 Alteration of the reaction rate as a function of time on stream over 17 mass% Ni/La₂O₃ catalyst at reaction temperatures of 823, 923 and 1023 K. Reaction conditions: $p_{\text{CH}_4} = 0.2$ bar, $p_{\text{tot}} = 1.0$ bar, CH₄-CO₂ = 1, M/F = 2×10^{-3} g s ml⁻¹.

below 973 K. The absence of catalyst deactivation over the Ni/La₂O₃ catalyst over a wide temperature range (>823 K) suggests that a new type of nickel compound is formed on the surface, following the exposure of the catalyst to the reaction mixture for 2–5 h. The influence of Ni loading was investigated in the range of 3–17 mass%. The variation of the reaction rate as a function of time on stream over the catalysts with various Ni loadings was found to be similar to that shown in Fig. 1 for the 17 mass% Ni/La₂O₃ catalyst. However, reduction of the reaction rate after more than 20 h on stream was observed for the catalyst with low Ni loadings (<3 mass%), suggesting that the long-term stability of the catalyst is sensitive to metal loading.

In order to explore the nature of the new type of nickel compound at the stable level, the influence of various pretreatments, including heating under flows of O₂, air, H₂, CO₂ and CH₄ at 1023 K for 1–5 h, on the performance of the Ni/La₂O₃ catalyst was investigated. It was observed that, regardless of what kind of pretreatment was applied, the initial reaction rate was always lower than the reaction rate at the stable level. Although the pretreatment affects the initial rate to a significant extent, it does not influence significantly the value of the reaction rate at the stable level. These results imply that there exists a strong tendency of the Ni/La₂O₃ catalyst to form a stable surface structure under working reaction conditions. It can also be deduced that none of the pretreatments described

above result in an initial surface state which is analogous to the stable surface state. It is interesting to observe that when the catalyst is exposed to H₂ (or O₂) at 1023 K, following the establishment of the stable surface state, evolution of CH₄ (or CO₂) is observed. Consequently, the stable surface structure is altered or destroyed upon exposure to O₂ or H₂. However, the stable surface structure is found to be essentially retrievable after several hours of reaction. These results imply that carbon itself may constitute an imperative component contained in the stable surface structure. This is also in agreement with the observation of increased weight of the used catalyst, as compared to that of the fresh catalyst. It is recalled^{11,12} that the carbonaceous sites formed during the reaction of oxydehydrogenation of ethylbenzene to styrene are catalytically active, their formation promoting the reaction rate. Similarly, it appears that the carbon originating from the CH₄-CO₂ mixture on the Ni/La₂O₃ catalyst may also be active, promoting the reaction *via* the participation of itself, or by its interaction with a component migrated from the La₂O₃ carrier (*e.g.* LaO_x species). La₂O₃ is known to be capable of migrating onto the supported metal crystallites under reducing atmospheres at elevated temperatures.¹³

In summary, the present findings reveal that Ni/La₂O₃ catalysts exhibit high activity and excellent long term stability for carbon dioxide reforming of methane to synthesis gas. Preliminary results show that a new type of Ni compound, containing a carbon component, is formed on the Ni/La₂O₃ surface, following exposure to the reaction mixture (CH₄-CO₂) for 2–5 h. The carbon originating from the CH₄-CO₂ mixture on the Ni/La₂O₃ catalyst may play a role leading to enhancement of the reaction rate.

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References

- 1 D. L. Trimm, *Catal. Rev. Sci. Eng.*, 1977, **16**, 155.
- 2 J. T. Richardson and J. A. Paripatyadar, *Appl. Catal.*, 1990, **61**, 293.
- 3 A. T. Ashcroft, A. K. Cheetman, M. C. H. Green and P. D. F. Vernon, *Nature*, 1991, **352**, 225.
- 4 T. Sodesawa, A. Dobashi and F. Nozaki, *React. Kinet. Catal. Lett.*, 1979, **12**, 107.
- 5 A. M. Gadalla and B. Bower, *Chem. Eng. Sci.*, 1988, **43**, 3049.
- 6 A. M. Gadalla and M. E. Sommer, *Chem. Eng. Sci.*, 1989, **44**, 2825.
- 7 A. Erdohelyi, J. Cserenyi and F. Solymosi, *J. Catal.*, 1993, **141**, 287.
- 8 J. R. Rostrop-Nielsen and J.-H. Bak Hasen, *J. Catal.*, 1993, **144**, 38.
- 9 J. R. Rostrop-Nielsen, *Stud. Surf. Sci. Catal.*, 1988, **36**, 73.
- 10 *Catalyst Handbook*, ed. M. V. Twigg, Wolfe, London, 1989.
- 11 G. E. Vrieland and P. G. Menon, *Appl. Catal.*, 1991, **77**, 1.
- 12 A. E. Lisovskii and C. Aharoni, *Catal. Rev. Sci. Eng.*, 1994, **36**, 25.
- 13 T. H. Fleisch, R. F. Hicks and A. T. Bell, *J. Catal.*, 1984, **87**, 398.