

Partial Oxidation of Methane to Syngas over Plasma Treated Ni-Fe/La₂O₃ CatalystJian-guo Wang,^{†,††} Chang-jun Liu,^{*,†,††} Yue-ping Zhang,^{†,††} Xin-li Zhu,^{†,††} Jijun Zou,^{†,††} Kai-lu Yu,^{†,††} and Baldur Eliasson^{†††}[†]State Key Laboratory of C₁ Chemistry and Technology and School of Chemical Engineering, Tianjin University, Tianjin 300072, P. R. China^{††}Tianjin University-ABB Plasma Greenhouse Gas Chemistry Laboratory, Tianjin University, Tianjin 300072, P. R. China^{†††}Energy and Global Change, ABB Corporate Research Ltd., CH5405, Switzerland

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Ni-Fe/La₂O₃ catalyst prepared by a glow discharge plasma treatment following calcinations thermally exhibits higher activity and selectivity compared to the Ni-Fe/La₂O₃ prepared conventionally. At the same reaction temperature, the CH₄ conversion, CO selectivity and H₂ selectivity obtained from the plasma prepared Ni-Fe/La₂O₃ are 5–9%, 4–7% and 9–15% higher than those from the conventional Ni-Fe/La₂O₃ catalyst, respectively. At the same methane conversion, the reaction temperature with the plasma prepared Ni-Fe/La₂O₃ is at least 100 °C lower than that with the conventional Ni-Fe/La₂O₃.

An intense investigation has been conducted worldwide on the utilization of methane for the production of more valuable chemicals since 1980s. The commercial methane utilization, however, still requires a multi-step process via syngas. The industrialized syngas production technology is the steam reforming of methane.^{1,2} But there exist some drawbacks with the steam reforming of methane. The steam reforming is an energy intensive reaction. The H₂/CO ratio of syngas produced is not suitable for further synthesis directly. As an alternative approach, the partial oxidation of methane into syngas has drawn more and more attentions recently.^{3–6}

Ni based catalysts have been extensively investigated for the partial oxidation of methane into syngas.^{7–10} The catalysts tested, however, require a high temperature activation. In addition, the catalysts easily lose their activity due to the serious carbon deposit. Choudhary et al.¹¹ reported a reduced reaction temperature with enhanced catalytic activity and improved CO selectivity by adding noble metal to Ni/Al₂O₃ catalyst. Nakagawa et al.¹² presented a La₂O₃ supported Ni catalysts that show some activity at lower temperatures. But a significant amount of carbon deposition was detected in the La₂O₃-supported Ni (10 wt%) catalyst.¹² In this work, we attempt to use plasma treatment following thermal calcinations to achieve a better low temperature activity of La₂O₃ supported Ni catalysts with Fe as a promoter.

The conventional wetness impregnation has been applied for the catalyst preparation (Ni : Fe : La₂O₃ = 7 : 3 : 90). The La₂O₃ support was first impregnated in an aqueous solution of Ni (NO₃)₂ and Fe (NO₃)₃. After impregnation, the resulted sample was then divided into two parts: one for calcinations at 600 °C for 6 h after drying at 90 °C for 16 h, and the other for plasma treatment for only 1 h before further calcinations at 600 °C for 6 h. In this work, we have successfully utilized a dc glow discharge for plasma treatment of catalyst. The catalyst was located in the “positive column” of glow discharge¹³ that was generated at ca. 12 Pa and at room temperature using argon as the glow discharge plasma-forming gas.

The catalyst (40–60 mesh; 40 mg), reduced by a flowing H₂ for 1 h at 650 °C, was then placed in a 6 mm i.d. quartz-tube flow reactor. The feed was the mixture of CH₄ : O₂ = 2 : 1. The feed and the product gases were analyzed by an on-line gas chromatograph (HP4890) using a thermal conductivity detector (TCD) with a TDX-01 column.

Figure 1 shows the effect of the temperature on methane conversion. In the following discussions, the conventional catalyst is referred to as Ni-Fe/La₂O₃(C), and the plasma treated catalyst is referred to as Ni-Fe/La₂O₃(P). The reaction initiation temperature with Ni-Fe/La₂O₃(P) was ca. 25 °C lower, compared to that with Ni-Fe/La₂O₃(C). The methane conversion obtained from Ni-Fe/La₂O₃(P) was 5–9% higher than that from Ni-Fe/La₂O₃(C) at the same temperature. At the same methane conversion, the reaction temperature with Ni-Fe/La₂O₃(P) is at least 100 °C lower than that with Ni-Fe/La₂O₃(C). The oxygen conversion was 100% for both cases. Especially, the initiation temperature for Ni-Fe/La₂O₃(P) was 600 °C, while the reaction started at about 750 °C for Ni/Al₂O₃ catalyst.¹¹ The Ni-Fe/La₂O₃(P) catalyst shows better low temperature activity. The effect of the temperature on CO and H₂ selectivity were presented in Figure 2 and Figure 3. The CO and H₂ selectivity for Ni-Fe/La₂O₃(P) were 4–7% and 9–15% higher, respectively, than those for Ni-Fe/La₂O₃(C). The H₂/CO ratio in syngas produced was 1.8–2.0 for Ni-Fe/La₂O₃(P), which is excellent for further synthesis. The CO selectivity was more than 85% for Ni-Fe/La₂O₃(P).

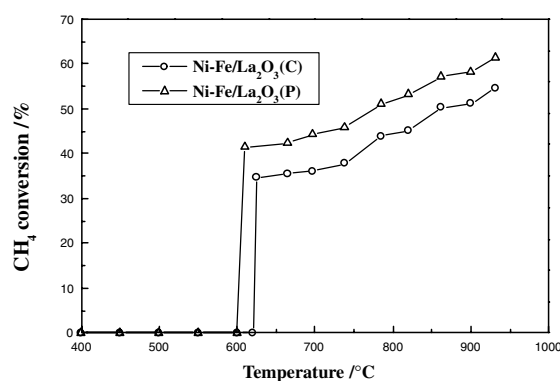


Figure 1. Effect of reaction temperature on CH₄ conversion. Reaction conditions: $P = 1$ atm, GHSV = 10000 cm³/g·h, CH₄/O₂ = 2.

It has been considered that the catalytically active species can be highly dispersed on the support during the plasma treatment and the particle size was also uniform after the calcinations of the plasma treated catalyst. Thereby the activity and selectivity of Ni-

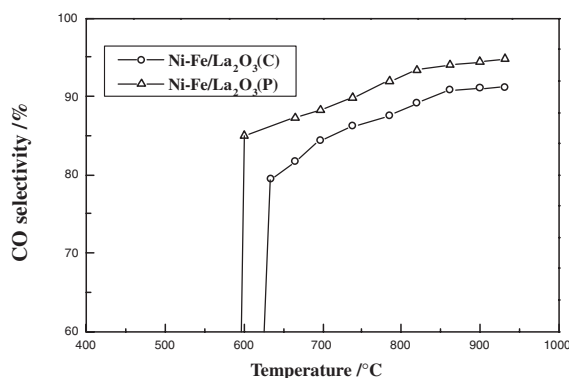


Figure 2. Effect of reaction temperature on CO selectivity. Reaction conditions: $P = 1$ atm, GHSV = 10000 cm³/g·h, CH₄/O₂ = 2.

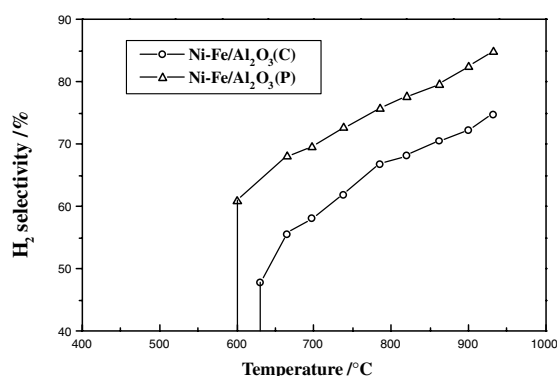


Figure 3. Effect of reaction temperature on H₂ selectivity. Reaction conditions: $P = 1$ atm, GHSV = 10000 cm³/g·h, CH₄/O₂ = 2.

Fe/La₂O₃(P) can be improved. In another investigation using Ni/CeO₂ catalyst,¹⁴ it has been found that the highly dispersed nickel oxide on the ceria support showed better activity and higher

selectivity. It would support that the highly dispersion of active species on the support induced from plasma treatment lead to enhanced activity and better selectivity. Further catalyst characterization is being conducted for better understanding of plasma-enhanced activity.

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