Selective Methanation of Carbon Monoxide in Hydrogen-rich Reformate Using Microstructured Reactor

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Selective methanation of CO in a H_2-rich stream performed over different supported-nickel catalysts showed that Ni–CeO_2 and Ni–Cr_2O_3 were the most effective catalysts for complete removal of CO through selective methanation to decrease a concentration of CO from 1.6 vol % to ppm level (<50 ppm) in a microchannel reactor, and among them a nickel catalyst promoted by Cr_2O_3 proved to be robust for over 180 h without any degradation in performance of selective CO methanation.

The catalytic hydrogenation of carbon monoxide and carbon dioxide has been developed and widely used as a gas-purification process in hydrogen and ammonia plants.[1] Hydrogen-powered fuel cells are expected to become important energy carriers for sustained energy consumption with reduced impact on the environment. One of the major problems for the introduction of low-temperature polymer electrolyte fuel cells (PEFC) as the power source for electrically operated vehicles is the delivery of "nearly CO-free" feed gas, which becomes problematic whenever H_2 is generated from fuels such as methanol or methane, as the fuel cell anodes can be poisoned even by trace impurities of CO. As a consequence, it is essential to reduce CO content to a level below 100 ppm for state-of-art PtRu anode electrocatalysts and preferably below 10 ppm for Pt anode electrocatalysts.[2] The preferential oxidation of CO (PrOx) has been proposed and most often studied by many investigators.[3,4] However, this approach requires the addition of oxygen in the hydrogen-rich gas stream, creating various potential problems related to reduced hydrogen yield, dilution, and safety issues during the operation. Recently, selective methanation of carbon monoxide has emerged as a promising alternative route to remove CO in the reformate stream down to extremely low level for the use of PEFC.[5–8] It is essential to develop highly active, selective, and stable methanation catalysts, able to efficiently and selectively remove CO from hydrogen-rich reformate gas to levels lower than those dictated by the poisoning limits of fuel cells.

In the present communication, bimetallic Ni-based catalysts with different promoters and different metal loadings supported on Al_2O_3 were explored in the selective methanation reaction so as to decrease CO content from percent level to ppm level within a microchannel reactor.

CO and CO_2 methanation was carried out on a supported catalyst in a flow-type apparatus with a microchannel reactor (channel dimensions $500 \times 500\,\mu m^2$) at atmospheric pressure and a temperature range from 150 to 350 °C, which has been described in detail elsewhere.[9] The wash-coated Ni-based catalysts (ca. 40-μm thickness) were reduced in 20% H_2/N_2 at 430 °C for 2 h prior to the catalytic test. The compositions of reactor effluents were analyzed by on-line gas chromatography.

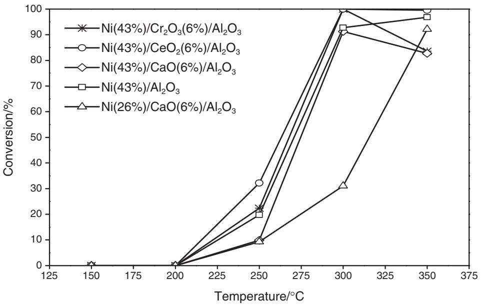


Figure 1. CO conversion as a function of reaction temperatures in methanation over Ni-based catalysts. Feed composition (vol %):H_2 (37.5), CO (1.6), CO_2 (12.5), H_2O (25), N_2 (balance gas); Total flow rate 60 mL min^{-1}, $W/F = 0.417$ gcat·min L^{-1}.

The results for the selective CO methanation of Ni-based catalysts were studied and are presented in Figure 1, in which the conversion of CO is shown as a function of reaction temperature. Over all the catalysts, only methane was observed as a hydrogenated product. For all catalysts studied, an increase of the reaction temperature leads to a considerable increase of the CO conversion. However, significant differences between them in terms of activity and selectivity were found. In descending order, the following sequence could generally be established for the activity: Ni(43 wt %)/Cr_2O_3/Al_2O_3 ≈ Ni(43%)/CeO_2/Al_2O_3 > Ni(43%)/Al_2O_3 > Ni(43%)/CaO/Al_2O_3 > Ni(26%)/CaO/Al_2O_3. It was observed that, under the experimental conditions employed, Ni–Cr/Al_2O_3 and Ni–Ce/Al_2O_3 catalysts are significantly more active and that the full CO conversion was achieved at a temperature of 300 °C for these catalysts.

Figure 2 shows the composition of the off-gas of the methanation, with varying reaction temperature, obtained from Ni–Cr_2O_3/Al_2O_3 catalyst. In the reformate surrogate, CO concentration decreases when a temperature of 250 °C is achieved at which point methane is first detected in the off-gas while CO_2 concentration remains constant. This would suggest that the preferential methanation of CO is most favorable at the relatively low temperature window from 250 to 300 °C. The complete removal of CO was achieved at 300 °C with a relatively low CO_2 conversion of 7% and a methanation selectivity of 70%, probably due to the preferential adsorption of CO on the catalyst. Significant increase of methane formation was observed at 350 °C with the concomitant decrease of CO_2 concentration. At 350 °C, CO concentration increases again (ca. 2000 ppm), probably due to the reversed water-gas-shift reaction, which is

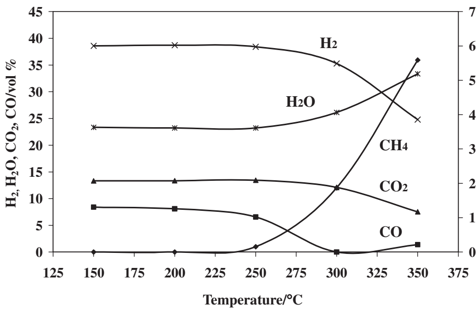


Figure 2. Concentration profile of reformate surrogate methanation over Ni(43%)/Cr_2O_3/Al_2O_3 catalyst.

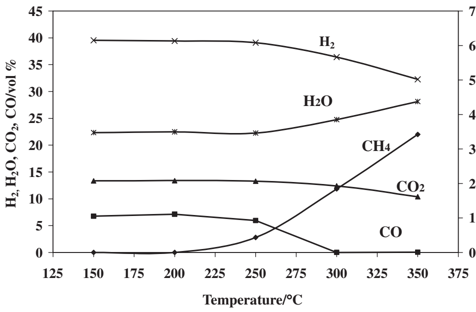


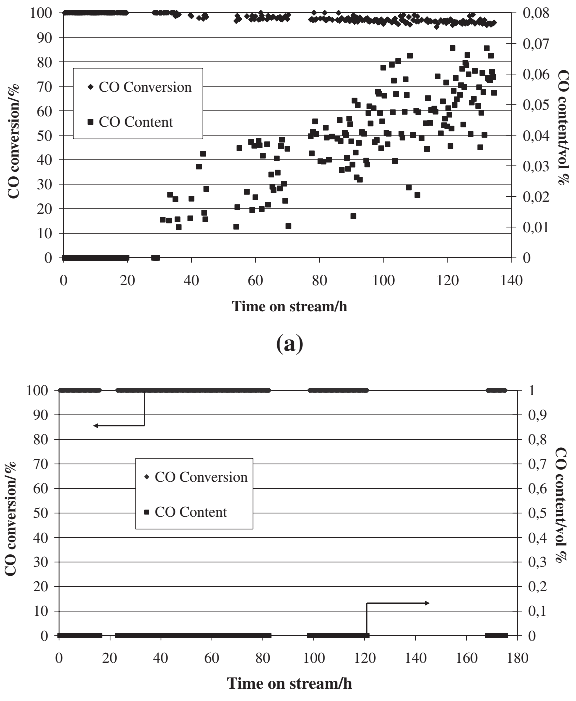
Figure 3. Concentration profile of reformate surrogate methanation over Ni(43%)/CeO_2/Al_2O_3 catalyst.

preferential at higher temperatures owing to thermodynamic equilibrium. A further increase of methane formation is mainly attributed to the methanation of CO_2.

Figure 3 shows a very similar concentration profile change by variation of the reaction temperature over Ni(43%)/CeO_2/Al_2O_3 catalyst. Nevertheless, at the highest reaction temperature, the CO level was found to be at a much lower level of 100 ppm, an order of magnitude lower than that from Ni–Cr catalyst, indicating that reverse water-gas-shift reaction does not occur appreciably over this catalyst.

Furthermore midterm durability tests for the two catalysts were performed. For the first 30 h of operation, full conversion was observed for both catalysts (Figure 4). Then Ni(43%)/CeO_2/Al_2O_3 catalyst slowly began to deactivate, as shown in Figure 4a, culminating in a conversion of 95% after 130 h and giving rise to a CO level of 700 ppm in the end. In contrast to this, Ni(43%)/Cr_2O_3/Al_2O_3 catalyst operated for 180 h without any detectable degradation in activity or selectivity. Full CO conversion is achieved and CO level was kept at below 50 ppm during the entire run of time on stream. The promotion role of Cr and Ce is likely to be related to metal–support interactions which modify the electronic state and the redox behavior of the active metal, thus affecting both CO and hydrogen adsorption properties in selective methanation. The nature of such a metal–support interaction and the origin of the catalyst deactivation will be examined by further investigation.

Summarizing, catalytic behavior of selective methanation has been investigated over various nickel-supported catalysts in a microchannel reactor. Among the tested catalysts, the Ni–Cr and Ni–Ce catalysts have remarkably high initial activity for the selective methanation and carbon monoxide is completely converted into methane at 300 °C (<50 ppm). Catalytic activity of the Ni–Ce catalyst gradually decreased with reaction time at 300 °C, despite its high initial activity. In contrast, no degradation of Ni–Cr catalyst is observed, and complete removal of carbon monoxide is sustained at 300 °C over 180 h in the realistic reformate atmosphere, suggesting that under realistic reaction conditions the Ni/Cr_2O_3/Al_2O_3 catalyst is very stable and, therefore, is a promising candidate for use in fuel processing applications.



(a)

(b)

Figure 4. Durability test of selective methanation over Ni(43%)/CeO_2/Al_2O_3 and Ni(43%)/Cr_2O_3/Al_2O_3 catalyst.

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