

Effect of Different Metal Promoters on Ni-Based Catalyst for CO₂ Reforming and Partial Oxidation of Methane to Syngas

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The combining CO₂ reforming and partial oxidation of methane to syngas over modified Ni catalysts has been researched. A series of alkali metal and alkaline earth metal-modified Ni catalysts have been prepared by co-impregnation. The catalytic activity of these catalysts was evaluated by conducting the combining CO₂ reforming and partial oxidation of methane in a fixed-bed reactor. Results of the investigation suggested that alkaline earth metal-modified Ni catalysts exhibited an excellent catalytic activity and stability in comparison with with alkali metal-modified Ni catalysts in the combined reaction processes. The order of catalytic activity among these catalysts was 12Ni-2Ca/Al₂O₃ > 12Ni-2Ba/Al₂O₃ > 12Ni-2Mg/Al₂O₃ > 12Ni-2Na/Al₂O₃ > 12Ni-2K/Al₂O₃.

Key Words: Methane, Reforming, Syngas, Ni catalyst.

INTRODUCTION

Methane and carbon dioxide are harmful greenhouse gases. Methane and carbon dioxide can be converted into valuable syngas by the CO₂ reforming of methane which is one of the most promising utilization approaches of natural gas and carbon dioxide and has attracted great attention during the past decades^{1,2}. However, CO₂ reforming of methane has high energy consumption and catalysts are easy to deactivate due to carbon deposition. The combining CO₂ reforming and partial oxidation of methane can overcome above shortcomings. Therefore, the combining CO₂ reforming and partial oxidation of methane to syngas has been investigated by many researchers^{3,4}.

Noble metals have high activity and stability for the methane reforming reaction⁵, but noble metals are expensive and rare. Ni-based catalysts have also high catalytic activity for the reforming of methane besides noble metals. However, Ni catalysts are easy to deactivate under the reforming conditions. Therefore, efforts should be directed to develop efficient Ni-based catalysts with high activity and stability^{6,7}.

In order to reduce the carbon deposition on the Ni-based catalyst and improve its catalytic activity and stability, we introduced other metals as promoter into the Ni-based catalysts. In this paper, we prepared alkali metal and alkaline earth

metal-modified Ni catalysts by co-impregnation, and investigated activity and stability of these catalysts by the combining CO₂ reforming and partial oxidation of methane to syngas.

EXPERIMENTAL

Catalyst preparation: The different metal oxide promoted Ni-based catalysts were prepared by incipient wetness co-impregnation of the calcined Al₂O₃ with the mixed aqueous solution of Ni(NO₃)₂·6H₂O and other metallic nitrates, followed by drying at 393 K overnight, then calcined in air at 1123 K for 4 h. The loadings of nickel and other metals referred to the weight percent of metals in the catalyst.

Activity test: The reaction of CO₂ reforming of methane combined with partial oxidation was carried out in a stainless steel-tube fixed bed microreactor at atmospheric pressure. A thermocouple was placed in the center of the catalyst bed to measure the reaction temperature. Before the reaction, the catalysts (0.5 g) were reduced for 1 h at 973 K in flowing 50 % H₂/N₂ at a flow rate of 50 mL/min. The volume ratio of the feed gases, CH₄ : CO₂ : O₂ : N₂, was 1 : 0.7 : 0.35 : 2, with a space velocity of 19560 mL h⁻¹ g⁻¹. The reaction temperature used were 1023 K. The feed gas was controlled by mass flow controllers. The effluent gas cooled in an ice trap from the reactor were online analyzed using a gas chromatography (SP-

2100A) equipped with a thermal conductivity detector and two columns (Molecular Sieve 5A, Porapak T).

The conversions (X) of reactants (CH₄, O₂ and CO₂) and yields (Y) of products (H₂ and CO) were calculated according to the following formulae:

$$X_{\text{CH}_4} \% = \frac{F_{\text{CH}_4,\text{in}} - F_{\text{CH}_4,\text{out}}}{F_{\text{CH}_4,\text{in}}} \times 100$$

$$X_{\text{CO}_2} \% = \frac{F_{\text{CO}_2,\text{in}} - F_{\text{CO}_2,\text{out}}}{F_{\text{CO}_2,\text{in}}} \times 100$$

$$X_{\text{O}_2} \% = \frac{F_{\text{O}_2,\text{in}} - F_{\text{O}_2,\text{out}}}{F_{\text{O}_2,\text{in}}} \times 100$$

$$Y_{\text{H}_2} \% = \frac{F_{\text{H}_2,\text{out}}}{2 \times F_{\text{CH}_4,\text{in}}} \times 100$$

$$Y_{\text{CO}} \% = \frac{F_{\text{CO},\text{out}}}{F_{\text{CH}_4,\text{in}} + F_{\text{CO}_2,\text{in}}} \times 100$$

$$F_{i,\text{in/out}} = F_{\text{total}} \times C_i$$

where, $F_{i,\text{in/out}}$ is the flow rate of each component in the feed or effluent, F_{total} represents the total flow rate of gaseous products and C_i is the molar fraction of component i in the gaseous effluent.

RESULTS AND DISCUSSION

Effect of promoters on the catalytic activity of Al₂O₃-supported Ni catalyst: The initial catalytic activities of different catalysts for the combining CO₂ reforming and partial oxidation of methane were shown in Table-1. Under our reaction conditions, the oxygen in the feed gas was completely consumed in all cases. It can be seen that the H₂/CO ratio of synthesis gas was found to be 1.1 in all catalysts (Table-1, entries 1-5). However, the initial conversions of CH₄ and CO₂ and yields to CO and H₂ were different with addition of different metal. Among the Mg-, Ca-, Ba-, Na- and K- modified Ni catalysts, the order of conversions of CH₄ and CO₂ displayed was Ca > Ba > Mg > Na > K and the order of yields to H₂ was Ba > Ca > Na > Mg > K. In a word, alkaline earth metal-modified Ni catalysts have better catalytic activity than alkali-modified Ni catalysts under the same catalyst preparation and reaction condition.

TABLE-1
EFFECT OF PROMOTERS ON THE INITIAL ACTIVITIES
OF Al₂O₃-SUPPORTED Ni CATALYSTS

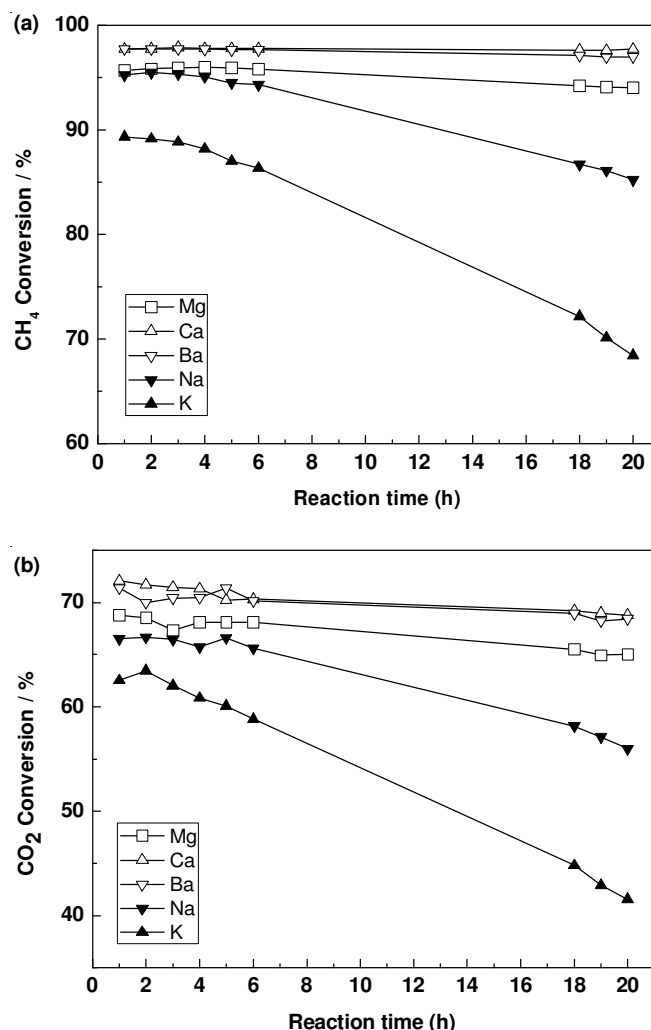
Entries	Catalysts	Conversion (%)		Yield (%)		H ₂ /CO
		CH ₄	CO ₂	H ₂	CO	
1	12Ni-2Mg/Al ₂ O ₃	95.7	68.8	74.1	81.9	1.1
2	12Ni-2Ca/Al ₂ O ₃	97.7	72.1	79.4	88.7	1.1
3	12Ni-2Ba/Al ₂ O ₃	97.7	71.4	80.2	84.2	1.1
4	12Ni-2Na/Al ₂ O ₃	95.2	66.5	75.8	82.3	1.1
5	12Ni-2K/Al ₂ O ₃	89.3	62.5	70.4	77.5	1.1

Effect of promoters on the stability of Ni/Al₂O₃ catalysts: The stability of modified Ni catalysts was also examined. The time-dependent conversions of CH₄ and CO₂ and yields

to CO and H₂ were shown in Fig. 1 (a)-(d). It can be seen that the catalytic activity of alkali-modified Ni catalysts decreased rapidly in the course of reaction. The 12Ni-2K/Al₂O₃ catalyst presented the lowest catalyst activity and stability. The X_{CH₄} and X_{CO₂} of 12Ni-2K/Al₂O₃ catalyst decreased from 89.3 % and 62.5 % to 68.4 % and 41.6 % after reaction 20 h. Furthermore, X_{CH₄} and X_{CO₂} of 12Ni-2Na/Al₂O₃ catalyst decreased from 95.2 % and 66.5 % to 85.2 % and 56.0 % after reaction 20 h. The deactivation of alkali-modified Ni-based catalysts during the reforming of methane was attributed to coke deposition or sintering of supported nickel particles. However, alkaline earth metal-modified Ni catalysts still maintained high methane and carbon dioxide conversion without significant loss of activity over a reaction period of 20 h. Their CH₄ and CO₂ conversions were similar, X_{CH₄} > 97 % and X_{CO₂} > 68 % for 12Ni-2Ca/Al₂O₃ and 12Ni-2Ba/Al₂O₃ catalysts. The catalytic activity of 12Ni-2Mg/Al₂O₃ was a little lower than that of 12Ni-2Ca/Al₂O₃ and 12Ni-2Ba/Al₂O₃, obtained 94 % CH₄ conversions and 65 % CO₂ conversions after reaction 20 h.

Conclusion

Simultaneous oxidative conversion and CO₂ reforming of CH₄ to syngas were conducted by using modified Ni/Al₂O₃ catalysts prepared by the co-impregnation method. The Al₂O₃-supported Ni catalysts, especially alkaline earth metal-modified Ni catalysts exhibited a high catalytic activity and



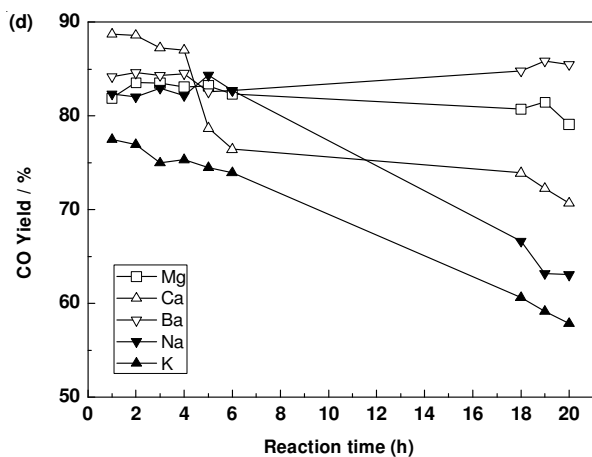
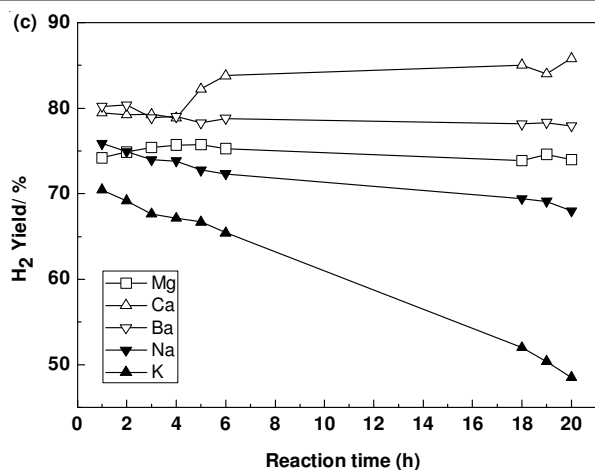


Fig. 1. Time-dependent conversions of CH₄ (a) and CO₂ (b) and yields to H₂ (c) and CO (d) over 12Ni-2Mg/Al₂O₃ (□), 12Ni-2Ca/Al₂O₃ (△), 12Ni-2Ba/Al₂O₃ (▽), 12Ni-2Na/Al₂O₃ (▼) and 12Ni-2K/Al₂O₃ (▲)

stability in the combining CO₂ reforming and partial oxidation of methane. Whereas, the catalytic activity of alkali-modified Ni catalysts decreased rapidly in the course of reaction. The order of catalytic activity among these catalysts was 12Ni-2Ca/Al₂O₃ > 12Ni-2Ba/Al₂O₃ > 12Ni-2Mg/Al₂O₃ > 12Ni-2Na/Al₂O₃ > 12Ni-2K/Al₂O₃.

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