A study on the reforming of natural gas with steam, oxygen and carbon dioxide to produce syngas for methanol feedstock

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Abstract

Reforming of natural gas with steam, oxygen and carbon dioxide to produce feedstock gases for methanol synthesis with lower energy consumption has been investigated over La_2O_3 or CeO_3 promoted Ni/Al_2O_3 catalysts by using a fixed-bed flow apparatus as well as by XRD and SEM technique. The Ni/Al_2O_3 catalysts promoted with additives were prepared either by the co-impregnation method or by the consecutive impregnation method. The results demonstrated that the bimetallic $Ni–Pt/Al_2O_3$ catalyst shows higher activity than that of individual Ni/Al_2O_3 or Pt/Al_2O_3 catalyst, and the activity of the Ni/Al_2O_3 catalyst promoted with CeO_3 or La_2O_3 is higher than that of the unpromoted Ni/Al_2O_3 catalyst. The Ni/Al_2O_3 catalyst promoted with La_2O_3 is more active and stable than the catalyst promoted with CeO_2. The catalyst promoted with 2% La_2O_3 remained stable over 240 h with high natural gas conversions and the value of R was approximately 2. The XRD and SEM results show that the addition of La_2O_3 to the Ni/Al_2O_3 catalyst can enhance surface Ni dispersion. The improvement in activity and stability of the catalyst was partly attributed to the promotion in higher Ni dispersion. © 1999 Elsevier Science B.V. All rights reserved.

Keywords: Natural gas reforming; Catalysts; Additives; Methanol feedstock; Activity; Stability

1. Introduction

An important commercial usage of natural gas is to reform it with steam to produce synthesis gas. The synthesis gas is a feedstock for many processes of great interest, such as the production of methanol [1,2] and ammonia, and the Fischer–Tropsch synthesis. Three routes were suggested to achieve such a conversion: (I) steam reforming of natural gas; (II) catalytic partial oxidation of natural gas; (III) CO_2 reforming of natural gas. Since the reforming of natural gas with steam or carbon dioxide is a strong endothermic reaction, and is a process of high energy consumption, the cost of synthesis gas production constitutes approximately 60% of the total cost of methanol or ammonia production.

In particular, process (I) has poor selectivity for CO and produces syngas with a high H2/CO ratio, while process (III) of CO_2 reforming of natural gas gives a high CO selectivity [3–6], and both of which are unsuitable for the me-

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thanol synthesis due to excess H_2 or CO. Although process (II) of catalytic partial oxidation of CH_4 has high activity and selectivity [7,8] and can produce syngas suitable for methanol synthesis, this process cannot be easily controlled because of the generation of hot spots in the catalytic bed [9–11].

In this paper, a new process has been developed by combining natural gas reforming with steam, oxygen and carbon dioxide for the production of methanol feedstock, which does not need any separation, and can be directly used in methanol synthesis with lower energy consumption. This process can save energy of about 70% in theory, comparing with the conventional steam reforming process. Our studies were aimed at investigating the effects of additives and preparation methods on the activities and stabilities of Ni-based catalysts. Excellent catalysts having high catalytic activities without suffering deactivation were obtained.

2. Experimental

2.1. Catalyst preparation

Pt-based and Ni-based catalysts were prepared by impregnating the α-Al_2O_3 (18–30 mesh) support with a solution containing a given concentration of H_2PtCl_6 and $Ni(NO_3)_2$. The impregnated samples were dried at 120°C and calcined at 400°C for 2 h in air. A series of Ni/Al_2O_3 catalysts promoted with additives of La_2O_3 or CeO_2 were also prepared either by the co-impregnation method or by the consecutive impregnation method, and the compositions of the prepared catalysts were listed in Table 1.

2.2. Catalytic activity

The reforming reaction was conducted in a fixed-bed quartz micro-reactor under conditions of 750°C, atmospheric pressure, and a gas mixture of natural gas/steam/CO_2/O_2 = 1/0.9/ 0.1/0.3 (mole ratio). Before reaction, the catalysts were activated in flowing H_2 at 700°C for 30 min, then the temperature was raised to 750°C in H_2 stream. The reactant gases were passed through the catalyst bed at a certain space velocity. The reaction products were analyzed on-line after water condensation, using propak-QS as the gas chromatograph column, with Ar as the carrier gas. The catalytic activity was represented by the mole fraction of the synthesis gas in gaseous products.

2.3. Catalyst characterization

XRD powder analyses were carried out to identify the main phases of Ni/Al_2O_3 promoted with additives by A D/max-rB X-ray

Table 1
Compositions and preparation method of catalysts

Catalyst	Method	Metal (or oxide) loadings (mass%)
Fe/Al_2O_3	Impregnation	9.17% Fe
Co/Al_2O_3	Impregnation	9.17% Co
Ni/Al_2O_3	Impregnation	9.17% Ni
Pt/Al_2O_3	Impregnation	1% Pt
$Ni–Pt/Al_2O_3$	Impregnation of Pt prior to NiO	9.17% Ni, 1% Pt
$Ni + CeO_2/Al_2O_3$	Co-impregnation	9.17% Ni, 2% CeO_2
$Ni–CeO_2/Al_2O_3$	Impregnation of CeO_2 prior to NiO	9.17% Ni, 2% CeO_2
$CeO_2–Ni/Al_2O_3$	Impregnation of NiO prior to CeO_2	9.17% Ni, 2% CeO_2
$Ni + La_2O_3/Al_2O_3$	Co-impregnation	9.17% Ni, 2% La_2O_3
$Ni–La_2O_3/Al_2O_3$	Impregnation of La2O3 prior to NiO	9.17% Ni, 2% La_2O_3
$La2O_3–Ni/Al_2O_3$	Impregnation of NiO prior to La2O3	9.17% Ni, 2% La_2O_3

diffractometer using a Cu K$_\alpha$ radiation and a scanning speed of $10°/min$. The SEM micrographs were carried out on a Hitachi S-520 microscopy.

3. Results and discussions

3.1. Thermodynamic studies and the choice of active components of the catalysts

It is well known that thermodynamic data are useful for establishing optimum operation conditions. Thus, equilibrium product distributions were calculated. Table 2 shows equilibrium product distributions at different temperatures. Several trends are also evident at a given feed ratio as the temperature increases, namely, methane, carbon dioxide and steam conversions will increase, and the yields of H$_2$ and CO will also increase. The results show that if the reforming reaction is performed above 750°C, the constitution of products will be suitable for methanol synthesis.

The experimental results on the behaviors of Fe, Co, Ni and Pt as active components are given in Figs. 1 and 2. The presented results show that the order of activity in the reforming reaction is Ni–Pt/Al$_2$O$_3$ > Ni/Al$_2$O$_3$ > Pt/Al$_2$O$_3$ > Co/Al$_2$O$_3$ ≫ Fe2O$_3$/Al$_2$O$_3$. The results in Fig. 2 indicate that the catalytic performance depends on space velocity. The data in Fig. 2 also indicate that the bimetallic Ni–Pt/Al$_2$O$_3$ catalyst shows higher activity than
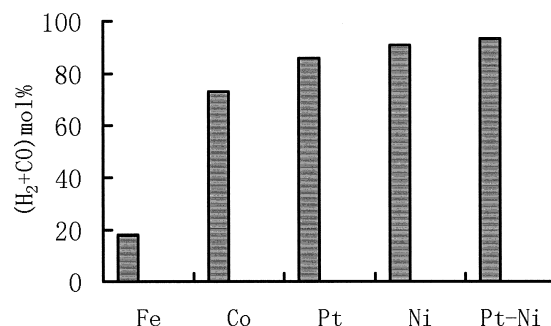

Fig. 1. Comparison of activities of catalysts. Temperature 750°C, pressure 0.1 MPa, GHSV = 17 200 h^{-1}, natural gas/O$_2$/CO$_2$/steam = 1/0.3/0.1/0.9.

that of the individual Ni/Al$_2$O$_3$ or Pt/Al$_2$O$_3$ catalyst. Otherwise, on the Pt/Al$_2$O$_3$ catalyst, the very fast loss of activity is accompanied with high space velocity.

3.2. The effect of impregnation order of additives on the activity of Ni-based catalysts

Since α-Al$_2$O$_3$ is a stable support, we select it as the catalyst support. Because it is difficult to disperse Ni on the α-Al$_2$O$_3$ surface due to its lower specific area, so additives were added to the catalysts to modify the catalytic properties. The influence of impregnation order of nickel on catalytic activity was also investigated. The results in Fig. 3 demonstrated that the effects of additives on syngas production are sensitive to the impregnation order of nickel and promoter onto the alumina. Syngas production decreased in the following order: Ni–M$_X$O/Al$_2$O$_3$ >

Table 2
Equilibrium product distributions at different temperatures

T (°C)	Product distribution (mol%)					(H$_2$ + CO)[a] (mol%)	R[a]
	CH$_4$	CO$_2$	H$_2$O	CO	H$_2$		
650	6.400	8.545	14.775	16.875	54.205	82. 059	1.855
700	2.725	6.349	12.194	19.925	58.808	89.666	1.997
750	0.932	5.036	11.175	22.045	60.812	93.301	2.059
800	0.292	4.294	11.085	23.075	61.254	94.842	2.080
850	0.094	3.799	11.323	23.695	61.125	95.610	2.088

Natural gas/steam/CO$_2$/O$_2$ = 1/0.9/0.1/0.3, pressure 0.1 MPa.
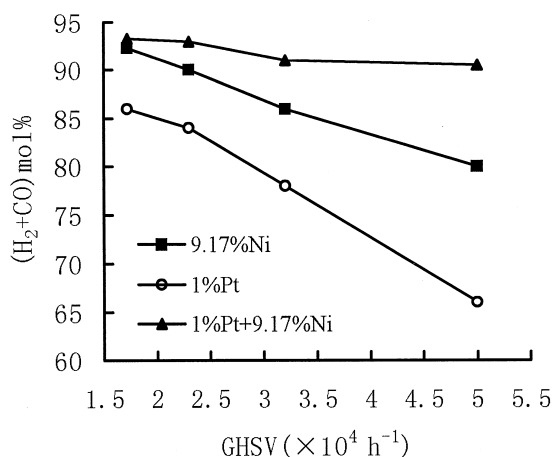[a]Net gas in which steam is deducted from the products, $R = (H_2 - CO_2)/(CO + CO_2)$.

Fig. 2. Comparison of activities of catalysts. Temperature 750°C, pressure 0.1 MPa, natural gas/O_2/CO_2/steam = 1/0.3/0.1/0.9.

$Ni + M_XO/Al_2O_3 > M_XO–Ni/Al_2O_3$ (M = La, Ce). That is to say, the impregnation of additives (La_2O_3, CeO_2) prior to nickel results in the best promotion effect on syngas production (Fig. 3a,b). Examination of literature data indicated that the rare earth ions might have incorporated into the crystallite lattice of nickel, and on the $Ni–La_2O_3/Al_2O_3$ catalyst, an interaction (SMSI) may mainly be embedded [12]. Therefore, in order to identify the effect of the impregnation order of nickel on the dispersion

of active components, XRD studies were carried out. According to the XRD results (Fig. 4), it is obvious that with impregnation of La_2O_3 prior to NiO on alumina, the diffraction peak of the nickel crystal phase becomes small. This is in agreement with the results in literature [13]. Because the active components were embedded or dispersed [14], the activity of catalysts prepared by the impregnation of La_2O_3 prior to NiO was higher than that of the $La_2O_3 + Ni/Al_2O_3$ and the $La_2O_3–Ni/Al_2O_3$ catalysts. But if the surface of the catalyst was previously covered by NiO, then La_2O_3 was impregnated on the NiO/Al_2O_3, the promotion effect on the dispersion of active components was smaller than that of the $Ni–La_2O_3/Al_2O_3$ catalyst due to the fact that surface Ni crystal grains were not finely dispersed by La_2O_3. For this reason, the catalytic activity of $La_2O_3–Ni/Al_2O_3$ or $La_2O_3 + Ni/Al_2O_3$ is lower comparing with the $Ni–La_2O_3/Al_2O_3$ catalyst (Fig. 3).

Furthermore, the SEM results indicated that the addition of rare earth oxides (La_2O_3 or CeO_2) would cause the catalyst particles to become smaller than the unpromoted Ni/Al_2O_3 catalyst. This is similar to the results of litereture [15]. Literature results [12,13] also indicated that when the La_2O_3 content is lower than 7 mass%, La_2O_3 covers the α-Al_2O_3 surface in
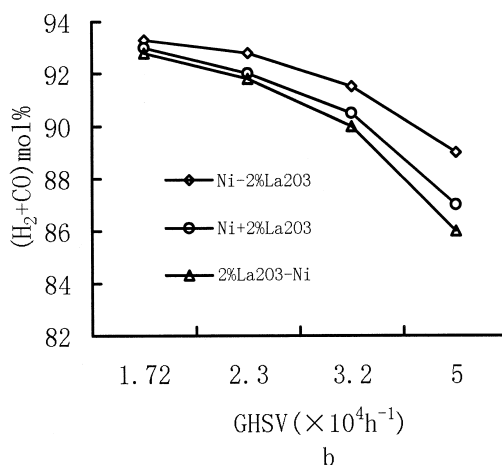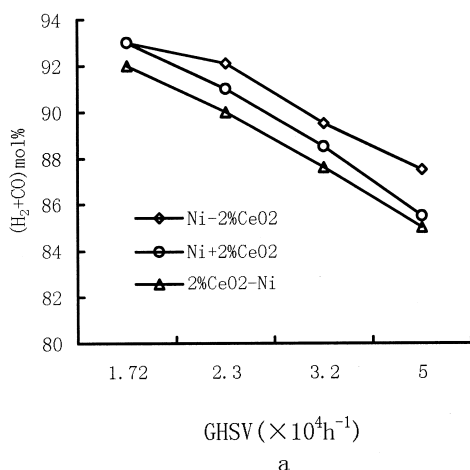

Fig. 3. Influence of impregnation order on catalyst activity. Temperature 750°C, pressure 0.1 MPa, natural gas/O_2/CO_2/steam = 1/0.3/0.1/0.9.
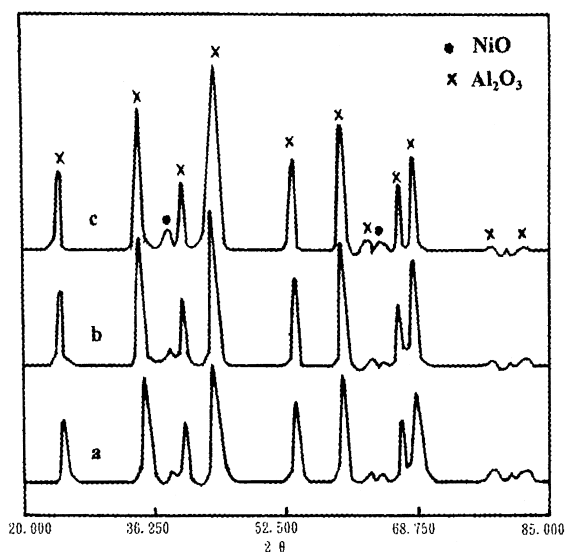
Fig. 4. XRD spectra of catalysts. (a) Impregnation of La_2O_3 prior to NiO, (b) co-impregnation, (c) impregnation of NiO prior to La_2O_3.

Fig. 5. Influence of CeO_2 content on catalytic activity. Temperature 750°C, pressure 0.1 MPa, natural gas/O_2/CO_2/steam = 1/0.3/0.1/0.9.

mono-layer dispersion and Ni dispersion is the biggest (the surface area of α-Al_2O_3 is 27 m^2/g). As the surface properties of the supports are modified by the mono-layer dispersed La_2O_3, the loaded metal particles become smaller and more thermal stable [15]. The surface area of α-Al_2O_3 used here is about 10 m^2/g, therefore, it is suggested that the addition of 2% La_2O_3 on the Ni–La_2O_3/Al_2O_3 catalyst might lead to a mono-layer dispersion of La_2O_3, which can significantly improve Ni dispersion and increase its activity and thermal stability.

3.3. The activity of Ni-based catalyst promoted with additives

Activities of a series of samples with the addition of different metal oxides to Ni-based catalysts are compared. The experimental results show that addition of La_2O_3 or CeO_2 to the Ni/Al_2O_3 catalyst increases the catalytic activity (Figs. 5 and 6). It has been found that the catalyst with 2% La_2O_3 or CeO_2 has the highest activity among the catalysts with different amount of La_2O_3 or CeO_2.
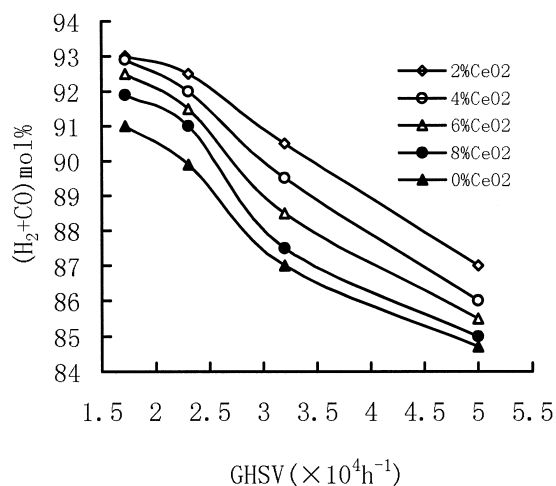
By comparing the activities of two catalysts promoted with La_2O_3 (Fig. 6) and CeO_2 (Fig. 5), it can be seen that the Ni–2%La_2O_3/Al_2O_3 catalyst is more active and stable than that of the Ni–2%CeO_2/Al_2O_3 catalyst.

3.4. The stability of La_2O_3 (2%) promoted Ni/Al_2O_3 catalyst

The stability of Ni/Al_2O_3 catalyst promoted with La_2O_3 (2%) has been examined under the
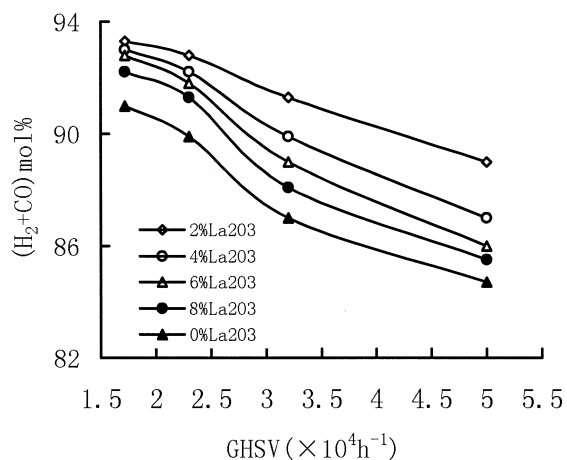

Fig. 6. Influence of La_2O_3 content on catalytic activity. Temperature 750°C, pressure 0.1 MPa, natural gas/O_2/CO_2/steam = 1/0.3/0.1/0.9.
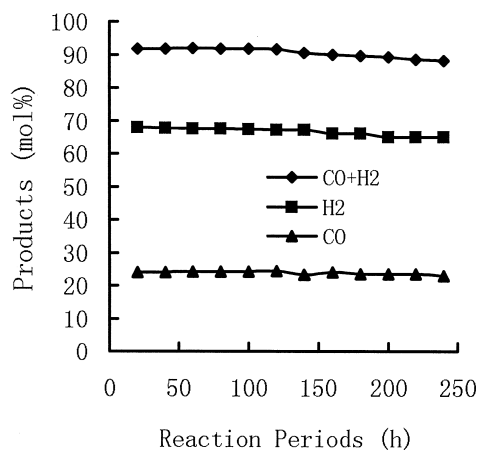
Fig. 7. The stability of the Ni–2%La$_2$O$_3$/Al$_2$O$_3$ catalyst. Temperature 750°C, pressure 0.1 MPa, natural gas/O$_2$/CO$_2$/steam = 1/0.3/0.1/0.9.

conditions of 750°C and 0.1 MPa. The results obtained show that the activity and selectivity are close to the thermodynamic equilibrium data and high activity and selectivity of the catalyst tested kept constant during the first 120 h. The value of R was approximately 2, which is suitable for methanol synthesis. The activity loss of the catalyst is only 2% during 120–240 h on stream. Moreover, coke formation on this catalyst was negligibly small and no shattering phenomenon happened after 240 h of reforming reaction. This indicates that the Ni–2% La$_2$O$_3$/Al$_2$O$_3$ catalyst not only has high activity and selectivity, but also has high strength and stability (Fig. 7).

4. Conclusions

The data reported above can be summarized as follows: (1) when the reforming reaction was performed at 750°C with feed ratios of natural gas/CO$_2$/O$_2$/steam = 1/0.1/0.3/0.9 (mole ratio), the constitution of the syngas produced is suitable for methanol synthesis. The order of catalytic activity in the reforming reaction is Pt–Ni/Al$_2$O$_3$ > Ni/Al$_2$O$_3$ > Pt/Al$_2$O$_3$ > Co/Al$_2$O$_3$ ≫ Fe/Al$_2$O$_3$; (2) impregnation of La$_2$O$_3$ or CeO$_2$ prior to nickel on the Ni-based catalyst results in the best promotion effect on syngas production. The Ni/Al$_2$O$_3$ catalyst promoted with 2% La$_2$O$_3$ has high activity, selectivity and stability for reforming natural gas with steam, oxygen and carbon dioxide.

Acknowledgements

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