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Highly Active Supported Nickel Catalysts for Pre-reforming of Liquefied Petroleum Gas

Kui Shen, Xueguang Wang,* Xinxing Wang, Xiujing Zou, Xionggang Lu, and Weizhong Ding
Shanghai Key Laboratory of Modern Metallurgy and Material Processing, Shanghai University,
Yanchang Road No. 149, Shanghai 200072, P. R. China

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Mg–Al mixed oxide supported Ni catalysts were significantly more active than other catalysts so far reported for the pre-reforming of liquefied petroleum gas, in which LPG was completely pre-reformed to methane, carbon oxides, and hydrogen under high space velocity with low steam/carbon ratio of 2.0.

Hydrogen production via hydrocarbon fuel processing has attracted considerable interest for stationary and mobile applications of fuel cells because of the significant environmental benefits and the high intrinsic energy efficiency.[1,2] Compared to steam reforming of methane or natural gas, liquefied petroleum gas (LPG) is considered as a very promising candidate for on-board and on-site hydrogen production for fuel cell applications in China due to its higher energy density, easy storage, and well-established nationwide distribution infrastructures.[3,4] However, the higher hydrocarbons like LPG generally require first low-temperature steam reforming, also referred to as pre-reforming, to methane, hydrogen, and carbon oxides, followed by the reforming of the reformate into hydrogen and carbon oxides at temperatures above 700 °C with minimal risk of carbon formation.[5,6] The pre-reforming of LPG is usually carried out at 400–500 °C, relatively low gas hourly space velocity (SV) ($<3000\,h^{-1}$) with high steam/carbon ratios (>3).[5,7] In order to achieve high energy efficiency and reduce the size and weight of fuel processors, further research and development are necessary for economic catalysts with high activity and stability for pre-performing of LPG under sufficiently high space velocity with lower steam/carbon molar ratios.

Ni/γ-Al_2O_3 catalysts have been preferred for the steam reforming of hydrocarbons because of their high activity and low cost, but they are prone to deactivation resulting from carbon deposition.[8,9] To minimize coking, basic metal oxides such as MgO-promoted Ni/γ-Al_2O_3 catalysts have been investigated and show good resistance to carbon deposition for the reforming of hydrocarbons. Nevertheless, these catalysts show poor catalytic activity in the steam reforming of hydrocarbons at lower temperatures.[10–13] Recently, Ni–Mg–Al mixed oxides derived from hydrotalcite-like precursors have been used as catalysts for various reactions, such as methane steam reforming, methane partial oxidation reforming, and steam reforming of ethanol, with high activities and low coke formation.[14–16] The investigations showed that the structure and surface properties of these mixed oxides depended strongly on chemical composition and synthesis procedure, resulting in significant change in the catalytic performance. In this communication, Ni catalysts supported on Mg–Al mixed oxides by impregnation was first reported to completely pre-reform LPG to methane, hydrogen, and carbon oxides at very high SV with a low steam/carbon ratio of 2.0.

Mg–Al mixed oxides with different Mg/Al atomic ratios were obtained by calcining Mg–Al hydrotalcite-like precursors at 800 °C, which were prepared by coprecipitation from an aqueous solution of $Mg(NO_3)_2$ and $Al(NO_3)_3$ (Sinopharm Chemical Reagent Co., Ltd.) at pH 9.5 with minor modification.[17] Ni/Mg_xAl catalysts were prepared through impregnating Mg–Al mixed oxide supports with an aqueous solution of $Ni(NO_3)_2$ (Sinopharm Chemical Reagent Co., Ltd.). For comparison, 15%Ni/$Mg_{1.25}$Al-c catalyst was synthesized by coprecipitation from an aqueous solution of $Mg(NO_3)_2$, $Al(NO_3)_3$, and $Ni(NO_3)_2$ at pH 9.5, and 15%Ni/20%MgO/Al_2O_3 catalyst was prepared by impregnating γ-Al_2O_3 (Condea) with an aqueous solution of $Mg(NO_3)_2$ and $Al(NO_3)_3$. All the samples were calcined at 800 °C for 20 h. Powder X-ray diffraction (XRD) results in combination with temperature-programmed reduction (H_2-TPR) confirmed that the obtained catalysts mainly consisted of $Mg(Ni)Al_2O_4$, Al_2O_3, and Mg(Ni)O phases varying with elemental composition (ESI, Figures S1 and S2).[18] Table 1 showed that the Mg/Al atomic ratios in all Ni/Mg_xAl samples were close to the nominal values. Overall, the BET surface areas of the Ni/Mg_xAl catalysts increased from ca. 82 to $164\,m^2\,g^{-1}$ with Mg/Al ratio varying from 0 to 2.0, pore volumes were ca. $0.25\,cm^3\,g^{-1}$, and high Ni loading led to the decreases in BET surface area and pore volume.

The pre-reforming reaction was carried out at atmospheric pressure in a flow fixed-bed reactor in the temperature range of 375–500 °C. The commercially available auto LPG consisting of 3.1 vol % C_2H_6, 84.0 vol % C_3H_8, and 12.9 vol % C_4H_{10} (Shanghai Auto Energy Co., Ltd.) was used without further purification. Before testing, the catalysts were reduced in a flow of 15 vol % H_2/N_2 at 800 °C for 5 h. The reaction results over Ni/Mg_xAl catalysts at 400 °C after 8 h on stream are listed in Table 1, together with those over 15%Ni/$Mg_{1.25}$AlO-c and 15%Ni/20%MgO/Al_2O_3. It is clear that Mg/Al ratios had significant influence on LPG conversion and the product selectivity. 10%Ni/Al_2O_3 and 10%Ni/MgO showed very low LPG conversions and CH_4 selectivities (Entries 1 and 10). For 10%Ni/Mg_xAl catalyst (Entries 2–9), LPG conversions rapidly increased from 7.5 to 97% with raising Mg/Al ratio to 1.25, meanwhile the selectivities of CO and CO_2 decreased from 1.7% and 90.4% to 1.0% and 29.3%, respectively, and the CH_4 selectivity increased from 7.9 to 69.8% with a decrease in H_2 selectivity from 94.8 to 28.8%. As the Mg/Al ratio was further raised, the LPG conversion started to decline, but the selectivities of CO, CO_2, CH_4, and H_2 had no obvious change. These results indicated that Mg–Al mixed oxide support favored both steam reforming of LPG and methanation of CO_x and H_2. The observed deviations from initial LPG conversions after 8 h on stream suggested that the catalysts in the Mg/Al range of 1.25–1.75 showed the optimum stability. The effect of Ni loading was also examined. Entries 11 and 12 in Table 1 display the results

Table 1. Physical properties of supported Ni catalysts and reaction results for pre-reforming of LPG after 8 h reaction[a]

Entry	Catalyst	Mg/A atomic ratio[b]	BET surface area /$m^2 g^{-1}$	Pore volume /$cm^3 g^{-1}$	LPG conversion[c] /%	Selectivity/%			
						CH_4	CO	CO_2	H_2[d]
1	10%Ni/Al_2O_3	—	82	0.24	2.4 (10.7)	8.8	2.7	88.5	97.3
2	10%Ni/$Mg_{0.25}Al$	0.22	94	0.37	7.5 (20.3)	7.9	1.7	90.4	94.8
3	10%Ni/$Mg_{0.5}Al$	0.51	69	0.24	40.2 (74.2)	66.2	0.9	33.9	36.4
4	10%Ni/$Mg_{0.75}Al$	0.74	83	0.27	85.6 (93.0)	71.8	0.8	27.3	25.6
5	10%Ni/Mg_1Al	1.00	107	0.24	93.0 (97.6)	71.4	0.8	27.8	26.2
6	10%Ni/$Mg_{1.25}Al$	1.31	126	0.25	97.0 (98.3)	69.8	1.0	29.3	28.8
7	10%Ni/$Mg_{1.5}Al$	1.57	129	0.25	93.4 (98.1)	69.8	0.9	29.3	28.1
8	10%Ni/$Mg_{1.75}Al$	1.74	157	0.26	88.8 (95.1)	70.4	1.0	28.6	28.0
9	10%Ni/Mg_2Al	2.05	164	0.31	66.8 (89.2)	70.6	0.7	28.7	28.3
10	10%Ni/MgO	—	39	0.14	19.2 (23.9)	32.1	1.9	66.1	77.9
11	15%Ni/$Mg_{1.25}Al$	1.31	114	0.23	100 (100)	70.6	1.0	28.4	29.1
12	20%Ni/$Mg_{1.25}Al$	1.31	39	0.13	98.1 (99.0)	72.6	0.7	26.8	23.8
13	15%Ni/$Mg_{1.25}Al$-c	1.27	145	0.56	91.6 (95.4)	73.5	0.8	25.8	24.2
14	15%Ni/20%MgO/Al_2O_3	—	77	0.29	6.5 (38.9)	9.2	2.3	88.6	95.8

[a] Reaction conditions: Reaction temperature, 400 °C; SV = 28900 mL $g_{cat}^{-1} h^{-1}$, S/C = 2. [b] Determined by energy-dispersive X-ray (EDX) analysis. [c] The values in parentheses are initial LPG conversions at 0.5 h. [d] The percentage of the molar number of H_2 in the effluent gas to the molar number of all products containing hydrogen, multiplied with the proper factor.

for the reforming of LPG over the Ni/$Mg_{1.25}Al$ catalysts with 15 wt% and 20 wt% Ni loadings. 15%Ni/$Mg_{1.25}Al$ catalyst showed the highest catalytic activity and could completely convert LPG to CH_4, CO, CO_2, and H_2. 15%Ni/$Mg_{1.25}Al$-c and 15%Ni/20%MgO/Al_2O_3 catalysts were also tested for the steam reforming of LPG under the same reaction conditions. The reaction results (Table 1, Entries 13 and 14) showed that, compared to 15%Ni/$Mg_{1.25}Al$ by impregnation, these two catalysts showed much lower activities and stability.

The thermodynamic equilibrium analyses showed that the steam reforming of all higher hydrocarbons ($n \geq 2$) (eq 1) could be considered irreversible under the present operating conditions; namely, the conversion of LPG was 100% when the reaction system reached chemical equilibrium. This implied that the steam reforming of LPG over 10%Ni/$Mg_{1.25}Al$ was governed by reaction kinetics. The selectivities of CH_4, CO, and CO_2 were close to the corresponding equilibrium values (S_{CH_4}, 72%; S_{CO}, 0.7%; S_{CH_2}, 27.2%), which were estimated on the basis of the total small gas molecules (CH_4, CO, CO_2, H_2, and H_2O) except LPG in the exit gas at Mg/Al ratio >0.5. This indicated that the methanation of CO_x (eqs 2 and 3) and water-gas-shift reaction (eq 4) reached chemical equilibrium. With Mg/Al ratio ≤0.5, the selectivities of CO and CO_2 were more than the corresponding equilibrium values, and the CH_4 selectivity was lower than the corresponding equilibrium values. These meant that the CO_2 formation was mainly responsible for the steam reforming of LPG rather than the water-gas-shift reaction (eq 4).

$$C_nH_m + H_2O \rightarrow CO_x + H_2 \quad \Delta H(25\,°C) > 0 \ (x = 1 \text{ or } 2) \tag{1}$$

$$CO + 3H_2 \rightleftharpoons CH_4 + H_2O \quad \Delta H(25\,°C) = -205.9\,kJ\,mol^{-1} \tag{2}$$

$$CO_2 + 4H_2 \rightleftharpoons CH_4 + 2H_2O \quad \Delta H(25\,°C) = -164.7\,kJ\,mol^{-1} \tag{3}$$

$$CO + H_2O \rightleftharpoons CO_2 + H_2 \quad \Delta H(25\,°C) = -41.1\,kJ\,mol^{-1} \tag{4}$$

Considering in the industrial pre-reforming process, the catalysts should be capable of completely reforming higher hydrocarbons to CH_4, CO_x, and H_2 to prevent the possible coke deposition in the subsequent methane reforming at high temperatures. Therefore, the possible SVs used in the pre-reforming of LPG were examined at different temperatures and S/C = 2. Figure 1 displays the maxima of the SVs with 100% conversion of LPG and the product selectivities over 15%Ni/$Mg_{1.25}Al$ catalyst in the temperature range of 375–500 °C after 8 h on stream. It can be seen that the SV for 100% LPG conversion was ca. 15900 mL $g_{cat}^{-1} h^{-1}$ at 375 °C. As the reaction temperature was elevated to 500 °C, the SV almost linearly increased to ca. 86800 mL $g_{cat}^{-1} h^{-1}$. Such high SVs for complete conversion of higher hydrocarbons at lower temperatures have never been reported in the previous literature. The selectivities of CO, CO_2, and H_2 gradually increased with the reaction temperature accompanied by a decrease in the CH_4 selectivity, which was consistent with the exothermic nature of methanation of CO_x and

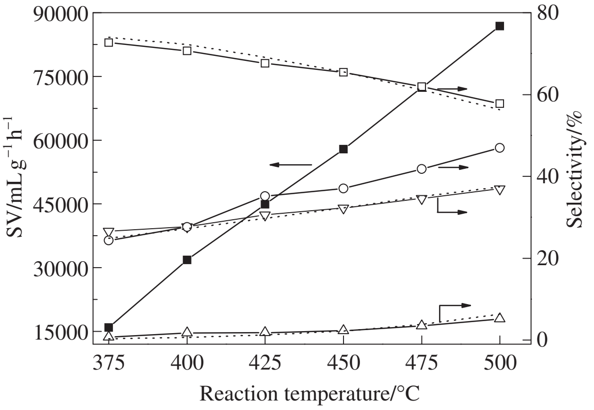

Figure 1. The space velocities (■) of completely converting LPG and the product selectivities over 15%Ni/$Mg_{1.25}Al$ catalyst at different temperatures and S/C = 2.0, and the corresponding equilibrium values of product selectivities (dot line). (□) CH_4, (△) CO, (▽) CO_2, and (○) H_2.

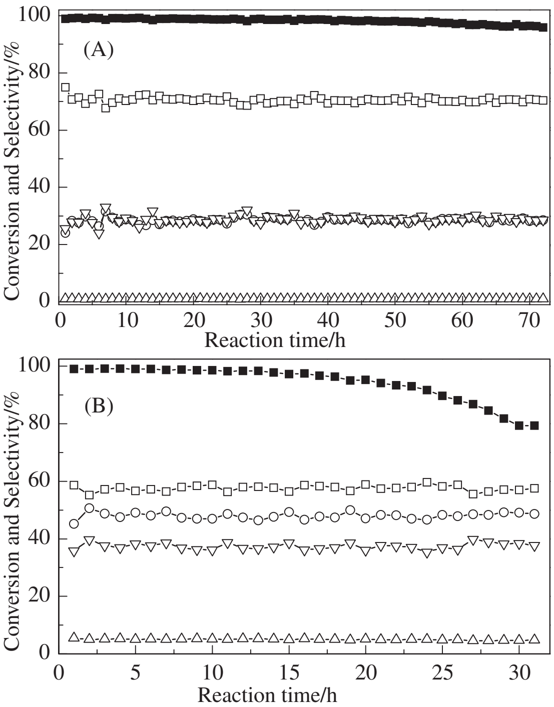

Figure 2. Stability of the 15%Ni/$Mg_{1.25}Al$ catalyst for the pre-reforming of LPG at S/C = 2.0. (A) SV = 36180 mL g_{cat}^{-1} h^{-1} for 400 °C and (B) SV = 93780 mL g_{cat}^{-1} h^{-1} for 500 °C. (■) LPG, (□) CH_4, (△) CO, (▽) CO_2, and (○) H_2.

H_2. The comparison between the selectivities of CH_4, CO, and CO_2 and their corresponding equilibrium curves (dot line) in Figure 1 showed that the reforming system with 100% LPG conversion could reach chemical equilibrium.

The stability test was carried out for the steam reforming of LPG under the reaction conditions with ca. 99% initial conversion of LPG, which was governed by chemical kinetics. Figures 2A and 2B exhibit the LPG conversions and product selectivities as a function of reaction time over the 15%Ni/$Mg_{1.25}Al$ catalyst at 400 and 500 °C, respectively. It seems that the catalyst exhibited excellent stability at 400 °C. During the tested period of ca. 72 h, the LPG conversion was kept above 95%. For the reforming at 500 °C, the catalyst was stable with LPG conversion above 95% during the initial 20 h. With prolonging the reaction time, the LPG conversion rapidly declined to 79% at 31 h. This is likely due to more coke deposition. The results estimated from the TG profiles of the used 15%Ni/$Mg_{1.25}Al$ catalysts showed that the rate of coke formation at 500 °C was 0.778 mg g_{cat}^{-1} h^{-1}, much higher than that of 0.326 mg g_{cat}^{-1} h^{-1} at 400 °C, while the XRD patterns (not shown) of the catalyst reduced at 800 °C for 5 h and the used catalysts had no obvious change, implying that the reaction atmosphere had little influence on the reduced Ni particles and the structure of the catalyst. Figure 2 showed the product selectivities almost did not change with the reaction time. This means that the steam reforming of LPG over 15%Ni/$Mg_{1.25}Al$ catalyst was more sensitive to coke deposition on the catalyst surface than the methanation of carbon oxides and water-gas-shift reactions.

In summary, Mg–Al mixed oxide supported Ni catalysts were first found to be very active for the low-temperature steam reforming of LPG in the temperature range of 375–500 °C and S/C = 2.0. Mg/Al atomic ratios were very important for the catalytic activity and product selectivity. The 15%Ni/$Mg_{1.25}Al$ catalysts showed excellent promise in pre-reforming of LPG at high space velocity with lower steam to carbon ratios. These results will also contribute to the development of highly active Ni-based catalysts for low-temperature steam reforming of other higher hydrocarbons.

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