Partial Oxidation of Butane to Syngas over Nickel Supported Catalysts Modified by Alkali Metal Oxide and Rare-Earth Metal Oxide

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Abstract: The partial oxidation of butane (POB) to syngas over nickel supported catalysts was first investigated with a flow-reactor, TG and UVRRS. The NiO/γ-Al$_2$O$_3$ is the most suitable for the POB among NiO/γ-Al$_2$O$_3$, NiO/MgO and NiO/SiO$_2$. And the reaction performance of the NiO/γ-Al$_2$O$_3$ shows little difference from those of the nickel supported catalysts modified by alkali metal oxide and rare-earth metal oxide. However, modification with Li$_2$O and La$_2$O$_3$ can suppress carbon-deposition of the NiO/γ-Al$_2$O$_3$, which contains graphite-like species during the POB reaction.

Keywords: Partial oxidation of butane, syngas, carbon-deposition, nickel supported catalysts.

There are abundant supplies of mixture gases containing CH$_4$, C$_2$H$_6$, C$_3$H$_8$ and C$_4$H$_{10}$, *etc.* from FCC (Fluidized Catalytic Cracking) tail gas, refinery gas, *etc.* Commonly, the mixture gases are primarily combusted to carbon dioxide because the complete separation of CH$_4$, C$_2$H$_6$, C$_3$H$_8$ and C$_4$H$_{10}$, respectively, from the mixture gases may not be economical. Provided that syngas (CO+H$_2$) could be produced from the mixture gases over nickel supported catalysts with high selectivity and conversion, it can be directly obtained from the mixture gases from FCC tail gas, refinery gas, *etc.* This may lead to better utilization of the light fractions from FCC tail gas and refineries, *etc.* Previously, we reported partial oxidation of methane, ethane and propane to syngas (POM, POE, POP) over the nickel-based catalysts modified by alkali metal oxide and rare earth metal oxide, and pointed out that ABNiO/γ-Al$_2$O$_3$ (A = Li, Na, K; B = La, Sm, Ce, Y) were good reaction catalysts[1-4]. In this letter, the partial oxidation of butane to syngas over the nickel supported catalysts was first reported.

Preparation of the nickel supported catalysts and characterization of catalyst have been described previously[1]. Catalysts were tested by flow-reaction in atmospheric pressure fixed-bed microreactor. Products of the reaction were analyzed by Gas Chromatography using a TCD detector. Conversion and selectivity were calculated on the basis of carbon numbers of the feed reacted.

The POM and POE reactions over the nickel supported catalysts were investigated under the high temperatures ranging from 973 to 1123 K[1,2,4], so we try to carry out the POP and POB reactions at the same high temperatures. The results indicate that, as the

temperature ranges from 923 to 1123K, above the catalyst and on the reactor, the gas phase takes place obviously, and there exists a large amount of coke from the thermal splitting decompositions of propane and butane.   The coke will block the reactor and cause the reaction not to be in progress after suitable time running. While the reaction temperature is below 873K, the gas phase occurs little.   Thus, the reaction performance of POB is studied below 873K.

The effect of temperature on the performance of the LiLaNiO/γ-Al$_2$O$_3$ is examined. The results indicate that butane and oxygen are almost converted completely.   When the reaction temperature is subsequently increased from 773 to 873K, the CO and H$_2$ selectivities increase, while the CH$_4$ and CO$_2$ selectivities decrease.   Under the constant space velocity by keeping the flow rate of C$_4$H$_{10}$ (11.0ml/min) and the total flow rate (95ml/min) of O$_2$ and Ar constant, the respective flow rates of O$_2$ and Ar are changed to obtain different O$_2$/C$_4$H$_{10}$ ratios. As the O$_2$/C$_4$H$_{10}$ ratio changes from 2.20 to 3.29, the CO and H$_2$ selectivities reduce, and the CH$_4$ and CO$_2$ selectivities rise.   The influence of space velocity on the performance of the LiLaNiO/γ-Al$_2$O$_3$ was also studied.   The results indicate that the influence of space velocity is not appreciable, *e.g.*, the LiLaNiO/γ-Al$_2$O$_3$ keeps good reaction performance with a wide range of space velocity, under 873K and O$_2$/C$_4$H$_{10}$/Ar ratio of 2.2/1/5.3.

The reaction performances of partial oxidation of butane to syngas over NiO/γ-Al$_2$O$_3$, NiO/MgO and NiO/SiO$_2$ are compared.   The results are shown in **Table 1**. There are strikingly different performances when MgO or SiO$_2$ displaces the γ-Al$_2$O$_3$ support in the NiO/γ-Al$_2$O$_3$ catalyst.   C$_4$H$_{10}$, O$_2$ conversions and H$_2$ selectivity of the MgO or SiO$_2$ supported nickel catalyst are much lower than those of the NiO/γ-Al$_2$O$_3$ catalyst. The different behaviour of MgO or SiO$_2$ may be related with the interaction between nickel and support.   Previously, we carried out the POM, POE and POP reactions over the same catalysts [2,3,5].   The results show that the NiO/γ-Al$_2$O$_3$ is also the most suitable one for the three reactions from the three catalysts, however, the behaviour of the POB reaction is different among those of the POM, POE and POP reaction, and the activated behaviour of butane is not the same as those of methane, ethane, and propane. So it is necessary to study the reaction of partial oxidation of butane to syngas over the nickel-supported catalysts.

Table 1   Comparison of performance of different supported catalysts
(O$_2$/C$_4$H$_{10}$/Ar =2.2/1/5.3; SV= 5.7 x 10^4 h^{-1}; T=873K)

Catalyst	C$_4$H$_{10}$ Conv. (%)	O$_2$ Conv. (%)	CO Sel. (%)	CH$_4$ Sel. (%)	CO$_2$ Sel. (%)	H$_2$ Sel. (%)	H$_2$/CO (ratio)
NiO/γ-Al$_2$O$_3$	100	100	41.9	29.4	28.7	83.8	1.3
NiO/MgO	10.0	21.0	24.8	10.5	64.7	26.9	1.1
NiO/SiO$_2$	11.0	20.3	47.6	12.8	39.6	22.0	0.5

A series of ABCO/γ-Al$_2$O$_3$ (A= Li, Na, K; B= La, Sm, Ce, Y; C= Fe, Co, Ni) catalysts were prepared with the same preparation method and condition in order to investigate the action of different components.   The results are presented in **Table 2**. There are strikingly different performances when Fe or Co displaced the Ni component

in the LiLaNiO/γ-Al$_2$O$_3$ catalyst. C$_4$H$_{10}$, O$_2$ conversions and CH$_4$ selectivity of the Fe or Co-containing catalyst is much lower than that of the Ni-containing catalyst. The different behavior of Fe or Co may possibly be attributed to the differences in structure, ability to remove hydrogen, redox ability and the interaction between transition metal and Al$_2$O$_3$ support. The nickel is most suitable for the POP reaction according to the results listed in **Table 2**.

　　The reaction performance of the NiO/γ-Al$_2$O$_3$ shows little difference from those of the catalysts with different alkali metal oxides ALaNiO/γ-Al$_2$O$_3$ (A= Li, Na, K) and rare earth metal oxides LiBNiO/γ-Al$_2$O$_3$ (B=La, Sm, Y, Ce). Butane and oxygen are almost converted completely, the selectivities of CO and H$_2$, and H$_2$/CO ratio keep at ~45%, 80-85% and ~ 1.3, respectively. The results indicate that modification with alkali and rare-earth metal oxides does not significantly influence the reaction performance of the POB reaction over the NiO/γ-Al$_2$O$_3$ under these conditions. However, the modification can obviously affect the thermal stability of γ-Al$_2$O$_3$ and the sintering of nickel in the NiO/γ-Al$_2$O$_3$ catalyst[6].

Table 2　Comparison of performance of different catalysts
(O$_2$/ C$_4$H$_{10}$/Ar =2.2/1/5.3; SV= 5.7 x 10^4 h^{-1}; T=873K)

Catalyst	C$_4$H$_{10}$ Conv.(%)	O$_2$ Conv.(%)	CO Sel.(%)	CH$_4$ Sel.(%)	CO$_2$ Sel.(%)	H$_2$ Sel.(%)	H$_2$/CO (ratio)
NiO/γ-Al$_2$O$_3$	100	100	41.9	29.4	28.7	83.8	1.3
LiNiLaO/γ-Al$_2$O$_3$	100	100	48.4	24.4	27.3	84.4	1.3
LiCoLaO/γ-Al$_2$O$_3$	16.8	33.3	44.4	1.0	54.6	77.3	1.3
LiFeLaO/γ-Al$_2$O$_3$	32.3	85.0	16.9	1.8	81.3	9.0	0.7
NaNiLaO/γ-Al$_2$O$_3$	100	100	45.4	27.1	27. 5	83.5	1.3
KNiLaO/γ-Al$_2$O$_3$	100	100	45.6	27.0	27.4	85.7	1.3
LiNiCeO/γ-Al$_2$O$_3$	100	100	48.4	26.5	25.1	82.1	1.2
LiNiYO/γ-Al$_2$O$_3$	100	100	46.6	27.3	26.1	80.2	1.3
LiNiSmO/γ-Al$_2$O$_3$	100	100	49.4	27.4	23.2	80.7	1.2

　　The addition of Li and La not only can improve the thermal stability of the NiO/γ-Al$_2$O$_3$ and prevent the sintering of nickel[6], but more importantly, the addition of Li and La enhances the ability of carbon-deposition resistance. The deposition of surface carbon over the NiO/Al$_2$O$_3$ catalyst during the POM reaction was undesirable and resulted in the deactivation of the NiO/Al$_2$O$_3$[7]. A hydrocarbon with higher C/H ratio favors carbon deposition on the surface of a catalyst in comparison with lower C/H ratio. Therefore, it is reasonable that the amount of carbon-deposition for the POB reaction is more than for the POM reaction over the NiO/Al$_2$O$_3$, and carbon- deposition also results in the deactivation of the NiO/Al$_2$O$_3$ for the POE reaction. It is well known that the acidity of the catalyst surface favors carbon-deposition, while the basicity of the catalyst surface prevents carbon-deposition. Because the acidity intensity of LiLaNiO/γ-Al$_2$O$_3$ is much lower than that of NiO/γ-Al$_2$O$_3$ catalyst[4], the addition of Li and La should be beneficial to the prevention of carbon-deposition over catalyst surface. The TG results of the samples after the POB reaction for 5h indicate the amount of carbon-deposition over the LiLaNiO/γ-Al$_2$O$_3$ was only 1/2 of that over the NiO/γ-Al$_2$O$_3$ under 873K, C$_4$H$_{10}$/O$_2$/Ar ratio of 1 /1.8 /5.3, and space velocity of 5.0 x 10^4 h^{-1}. It is shown that the

introduction of Li and La can suppress carbon-deposition of the nickel-based catalyst.

In order to determine the carbon-deposition species formed on the catalysts, the samples performed under the same reaction conditions were characterized by UV Resonance Raman Spectra (UVRRS), which has been demonstrated to be a powerful tool for catalysis and surface science studies, with the advantage of avoiding the surface fluorescence which frequently occurs in visible Raman spectra of many catalysts[8]. The samples used for the UVRRS were manipulated in air prior to the analysis. The results show only one band at 1580 cm^{-1} is present clearly in the spectra, which is close to the characteristic band of graphite[9] at 1575 cm^{-1}. The results reveal that the carbon-deposition formed on the nickel-based catalysts contains graphite-like species (amorphous forms of carbon may not be detected by UVRRS).

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