PARTIAL OXIDATION OF METHANE TO SYNGAS OVER $BATI_{1-X}NI_XO_3$ CATALYSTS

Cuili Guo, Jinli Zhang, Wei Li, Pingfan Zhang and Yiping Wang

School of Chemical Engineering, Tianjin University, Tianjin 300072, China

Introduction

Catalytic partial oxidation of methane to syngas is a slightly exothermic, highly selective, and energy efficient process. It gives syngas with H_2 to CO ratio of 2:1 that is suitable for F-T and methanol syntheses. Hence, much effort has been devoted to partial oxidation of methane to syngas in the presence of catalysts. Perovskite catalysts have attracted much attention for more than two decades due to their potential commercial applications as catalysts [1-3]. Lago et al[4] observed that a series of cobalt-containing perovskites $LnCoO_3$(Ln=La, Pr, Nd, Sm, and Gd) have high activity and selectivity for the partial oxidation of methane to syngas. Slagtern and Olsbye[5]and Provendier[6] concluded that the addition of a third metal into the perovskite structure is necessary to stabilize the catalytic system. Supported Ni catalysts on $CaTiO_3$,$SrTiO_3$ and $BaTiO_3$ oxides have been investigated[7]. Ni/$SrTiO_3$ and Ni/$BaTiO_3$ showed that high activity for POM.

In this study, partial oxidation of methane was investigated over $BaTi_{1-X}Ni_XO_3$ catalysts. We evaluated the catalysts prepared with different Ni loading amount and with different calcination temperatures. The reaction mechanism and activity are discussed.

Experimental

A series of $BaTi_{1-X}Ni_XO_3$ catalysts were prepared by the sel-gel method with x values ranged from 0 to 0.3. The calculated amounts of tetrabutyl titanate, citric acid and glycol were mixed and stirred to solution under reflux. The calculated amounts of $Ba(NO_3)_2$ and $Ni(NO_3)_2.6H_2O$ were added to the hot solution with stirring and to make nitrate decomposition. A gel was obtained by adding triethanelamine. The nanometer powders of $BaTi_{1-X}Ni_XO_3$ were made by calcining the dried gel for 2h at different temperature (600,700 and 800 °C).

X-ray diffraction（XRD）patterns were obtained with a Rigaku 2038 diffractometer using CuKα radiation at a rate of 4°/min. The XRD patterns of $BaTi_{1-X}Ni_XO_3$ shows that the pure perovskite structure is formed. The particle textures of the samples were investigated using a JEOL TEM-100X Ⅱ transmission electron microscope. The TEM images of $BaTi_{1-X}Ni_XO_3$ indicate that the mean sizes of the particles are 13 to 21 nm and particles distributions are uniform. Specific surface areas were derived from N_2 adsorption isotherms that were determined with a Chem BET-3000 instrument. The values of the BET specific surface area of $BaTi_{1-X}Ni_XO_3$ are in the 10-16 m^2/g.

The methane oxidation reaction was carried out in a fixed bed quartz reactor(8 mm in i.d.) filled with 300 mg catalyst at atmospheric pressure. The feed gas mixture were composed of CH_4,O_2 and N_2 with a space velocity of $3\times10^5\ h^{-1}g^{-1}$.The products were analyzed on-line by a SP3420 gas chromatograph equipped with TCD.

Results and Discussion

Table 1 lists the results of activity and selectivity of $BaTi_{1-X}Ni_XO_3$ with different x values(Ni content) in POM reaction at 950 ℃, which indicate that the activity of $BaTiO_3$ is very low and the activity of $BaTi_{1-X}Ni_XO_3$ increase significantly with the addition of Ni into the perovskite. The activity of $BaTi_{0.8}Ni_{0.2}O_3$ is the highest with CH_4 conversion of 95% and CO selectivity of 98%.

Table 1. Effect of x Value in $BaTi_{1-x}Ni_xO_3$ on the Activity at 950 ℃

X value	CH_4 conversion (%)	CO selectivity (%)
0($BaTiO_3$)	40	75
0.1($BaTi_{0.9}Ni_{0.1}O_3$)	89	97
0.2($BaTi_{0.8}Ni_{0.2}O_3$)	95	98
0.3($BaTi_{0.7}Ni_{0.3}O_3$)	86	96

Figure 1 shows the catalytic activity for partial oxidation of CH_4 at CH_4/O_2 mole ratio of 2:1 with a space velocity of $4.4\times10^5\ h^{-1}g^{-1}$ over $BaTi_{0.8}Ni_{0.2}O_3$ calcined at different temperatures. From Figure 1, we can see that with the increase of calcination temperature, the activation temperature of $BaTi_{0.8}Ni_{0.2}O_3$ decrease and the optimum reaction temperature scarcely change. It is suggested that the perovskite catalysts should be calcined at low temperatures, since the activity of $BaTi_{0.8}Ni_{0.2}O_3$ was significantly reduced with an increase of calcination temperature from 600 to 800 ℃.

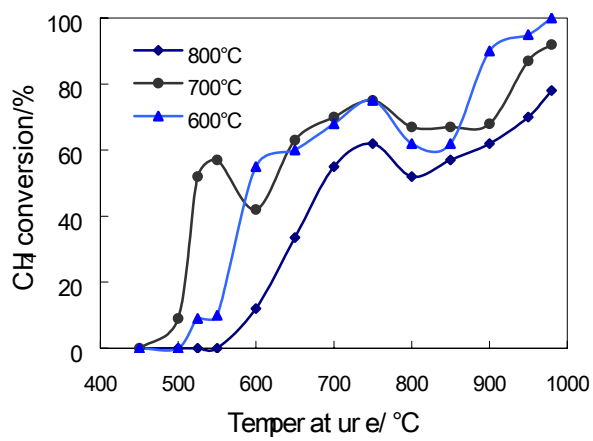

Figure 1. CH_4 conversion versus temperature

The results reveal that the calcination temperature of the $BaTi_{1-X}Ni_XO_3$ has a close relation with activity. The increase of calcination temperature can lead to a decrease in surface area and an increase in crystal size, which make concentration of active oxygen decrease. Thereby the catalytic activity of $BaTi_{1-X}Ni_XO_3$ decreases.

Figure 1 shows CH_4 conversion increase with the increase of reaction temperature. It is found from experiments that the temperature difference between reaction temperature and control temperature changed from 24℃ to -4℃ with the increase of reaction temperature, which indicate the heat of reaction gradually decrease. These results suggest that the combustion of a part of CH_4 to H_2O and CO_2 (exothermic reaction) first took place in the lower temperature and reforming reaction of CH_4 with H_2O and CO_2 (endothermic reaction) was followed in the higher temperature for POM over $BaTi_{1-X}Ni_XO_3$. This result is agreement with the results in literature [7].

Figure 2 shows the catalytic activity for partial oxidation of methane at CH_4/O_2 mole ratio of 2:1 with a space velocity of $4.4\times 10^5 h^{-1}g^{-1}$ over $BaTi_{0.8}Ni_{0.2}O_3$ at different reaction time. The results show that the catalytic activity of $BaTi_{0.8}Ni_{0.2}O_3$ increases with the increase of the reaction time. When the reaction time is over 3h, the catalytic activity of $BaTi_{0.8}Ni_{0.2}O_3$ remained unchanged after 40h of operation at 950 ℃. This indicates that the activation stage of the catalyst is needed at the initiation stage of reaction and that catalyst is stable under the POM reaction at 950℃ for 40h.

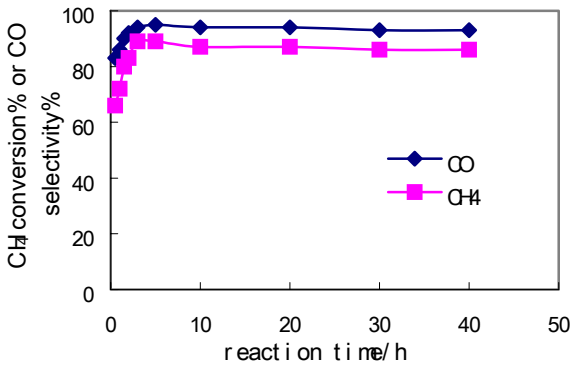

Figure 2. CH_4 conversion and CO selectivity versus reaction time

Conclusions

From the results above, we can conclude that perovskite $BaTi_{1-X}Ni_XO_3$ are highly efficient catalysts for POM. The calcination temperature of the $BaTi_{1-}Ni_XO_3$ can affect the activation temperature. The addition of Ni into the perovskite structure makes activity increase significantly. The most active system $BaTi_{0.8}Ni_{0.2}O_3$ presents a stable activity, with no deactivation at 950℃ during 40h test.

References

(1) Ferri, D.; Forni, L. *Appl. Catal. B.* **1998**, *16*, 119.

(2) Cimino, S.; Lisi, L.; Pirone, R.; Russo, G.; Turco, M. *Catal. Today* **2000**, *59*, 19.

(3) Shu, J.; Kaliaguine, S. *Appl. Catal. B.* **1998**, *16*, L303.

(4) Lago, R.; Bini, G.; Pena, M.A.; Fierro, J.L.G. *J. Catal*. **1997**, *167*, 198.

(5) Slagtern, A.; Olsbye, U. *Appl. Catal. A.* **1994**, *110*, 99.

(6) Provendier, H.; Petit,C.; Estournes, C.; Libs, S.; Kiennemann, A. *Appl. Catal. A.* **1999**, *180*, 163.

(7) Takehira, K.; Shishido, T.; Kondo, M. *J. Catal.*, **2002**, *207*, 307.