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Kinetic Study of Optimum Ni-Al-Zn Catalyst in the Steam Methane Reforming Reaction

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INTRODUCTION

Hydrogen plays an important role as fuel due to its high energy content, environmental friendliness, and numerous applications in petroleum and chemical processing industries [1-3]. One of the major hydrogen production methods is steam methane reforming. Steam reforming of methane has been used commercially on Ni/Al_2O_3 catalysts at 750-900 °C [1-3]. In this study, Ni-Al-Zn catalyst was synthesized and optimized in order to decrease the operational temperature of this process. Moreover, kinetic study of optimum catalyst was performed.

EXPERIMENTAL PROCEDURES

NI-AL-ZN CATALYST PREPARATION

Ni–Al-Zn was prepared by coprecipitation method according to the procedure described in literature [4]. XRD, BET, and ICP tests were used to characterize the prepared catalyst with different fraction of Ni (5-25% Ni). The CHN analysis was used to obtain the amount of carbon on the catalyst after the reactor experiments.

A schematic diagram of the methane steam reforming unit is shown in Figure 1. The feed section contains H_2, CH_4, CO_2 and N_2 with 99.9% purity. Following steps were applied to carry out the experiments.

1) First, the reactor bed and all the lines were washed by nitrogen at 400 °C during for 1 hr.

2) Hydrogen was passed through the catalyst bed at 600 °C in order to reduce the Ni/Al_2O_3 catalyst.

3) After the step 2, the nitrogen was used again, and the pressure of system was adjusted at the designed value by using needle valve V-02. Furthermore, the temperature of fixed bed catalytic reactor was set by an electric resistance heater.

4) When designed pressure and temperature were achieved, deionized water was delivered by a dosing pump to the heater where it vaporized into steam and was mixed with methane in a predetermined ratio.

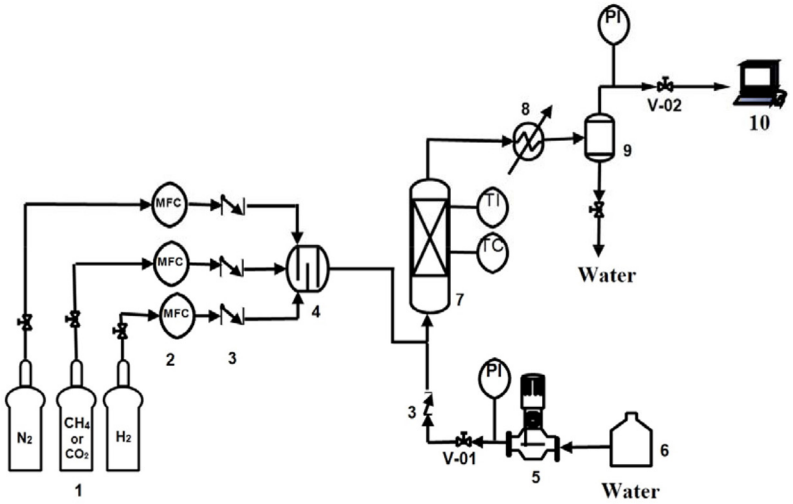

Figure 1: A schematic diagram of the steam reforming of methane experiments. 1: Feed cylinders, 2: Mass flow controller 3: Check valve, 4: Gas mixer, 5: Dosing pump 6: Water vessel, 7: Electric furnace and fix bed catalytic reactor, 8: condenser, 9: Gas-liquid separator, and 10: Gas chromatography.

The flow rate of methane was set by MFC (Alicat Scientific, M-1000SCCM-D). The time of experiment was measured by a chronometer.

5) The outlet gaseous products were sent to a condenser and a gas-liquid separator. Then, dry gas was sent to analysis section. The gases were analyzed by an online gas chromatography (TGF, 2552) equipped with Propack Q column, FID detector, and a methanizer.

RESULTS AND DISCUSSION

CATALYST CHARACTERIZATION AND PERFORMANCE

The XRD pattern of Ni-Al-Zn catalyst is shown in Figure 2. As expected, the $NiAl_2O_4$ and $ZnAl_2O_4$ crystals were appeared. The surface area for Ni-Al-Zn catalyst containing 5, 15, and 25 percent Ni was 184.45, 150.82, and 129.23, respectively.

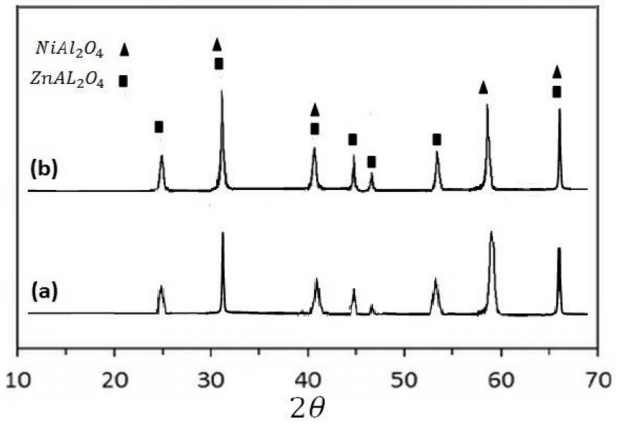

Figure 2: The XRD pattern of Ni-Al-Zn catalyst with a) 15 % Ni and b) 20 % Ni.

According to methane conversion and hydrogen production, the optimum amount of Ni was 15%. Figure 3 shows the methane conversion of Ni-Al-Zn catalyst versus temperature. As can be seen, the methane conversion of Ni-Al-Zn catalyst is more than the methane conversion of industrial catalyst especially at low temperatures (600-700 °C). Moreover, the CHN analysis revealed that there was a negligible carbon in the synthesized catalyst after the reactor experiments at low temperatures. In sum, the Ni-Al-Zn catalyst was suitable for steam methane reforming at low temperatures.

KINETIC STUDY

The kinetic of optimum Ni-Al-Zn catalyst was studied. By considering the elementary steps in XU and Forment article [5], three rate equations were obtained for reactions of steam methane reforming according to the following Equations:

$$R_1=\frac{\frac{k_a}{P_{H_2}^{2.5}}\left[P_{CH4}P_{H_2O}-\frac{P_{H_2}^3 P_{CO}}{K_1}\right]}{DEN^2}$$

$$R_2=\frac{\frac{k_b}{P_{H_2}}\left[P_{CO}P_{H_2O}-\frac{P_{H_2}P_{CO_2}}{K_2}\right]}{DEN^2}$$

$$R_3=\frac{\frac{k_c}{P_{H_2}^{3.5}}\left[P_{CH_4}P_{H_2O}^2-\frac{P_{H_2}^4 P_{CO_2}}{K_3}\right]}{DEN^2}$$

$$DEN=1+K_{CH4}P_{CH4}+K_{CO}P_{CO}+K_{H_2}P_{H_2}+\frac{K_{H_2O}P_{H_2O}}{P_{H_2}}$$

The reaction rate and partial pressures obtained from experiments. Then, the unknown parameters (K_j and k_i) can be calculated by using Polymath software. The final values of the Arrhenius kinetic parameters and the apparent activation energies are presented in Table 1. The adsorption Parameters and adsorption enthalpies are shown in Table 2.

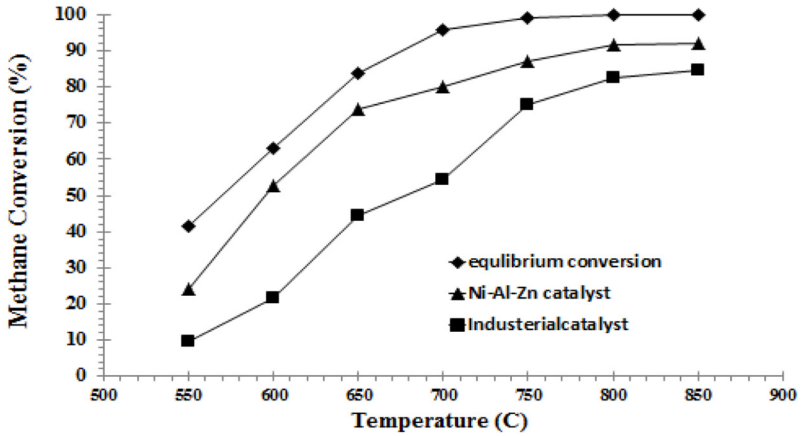

Figure 3: Methane conversion versus temperature for Ni-Al-Zn and industrial catalyst. The corresponding mixed oxides.

Table 1: Arrhenius kinetic parameter.

Reaction	E (kJ/mol)	$k_{0,i}$
1	219.4	8.33e+15
2	71.90	1.965e+6
3	221.04	1.38E+15

Table 2: Van't Hoff adsorption parameters.

Gas	ΔH_i(kJ/mol)	$k_{0,i}$
CO	-70.66	7.45e-5
H_2	-88.41	1.01e-8
CH_4	-34.99	1.57e-5
H_2O	91.49	3.6e5

CONCLUSION

In this article, kinetic of steam methane reforming with Ni-Al-Zn catalyst was studied. Catalyst Ni-Al-Zn was prepared. The results of XRD, ICP, and BET revealed that catalyst was appropriately synthesized. The optimum amount of Ni in the catalyst was 15% according to methane conversion and hydrogen production. The methane conversion of optimum catalyst was more than methane conversion of industrial catalyst especially at low temperature. The CHN analysis showed that there was a negligible carbon in the Ni-Al-Zn catalyst at low temperatures. Moreover, kinetic study of optimum catalyst was performed. The activation energy for reaction of methane to CO and H_2, water gas shift and methane to CO_2 and H_2 were 219.4 kJ/mol, 71.90 kJ/mole, and 221.04 kJ/mole, respectively.

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