Direct oxidation of CH$_4$ to syngas under non-equilibrium conditions*

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The conversion of methane to valuable chemical feed stock has been a challenge to researchers in the past 15 years. Many efforts have been devoted to the generation of C$_2$ hydrocarbons by the oxidative coupling of methane$^{1,2}$, but because of the shortcomings such as high reaction temperature and low C$_2$ yield, the process is far from being industrialized. Recently, researchers have turned their attention to the methane-to-syngas process$^{3-6}$. The reaction is characterized by its high activity, good selectivity, short contact time and relatively low reaction temperature. By yielding syngas with H$_2$/CO (molar ratio, 2), the catalytic process might replace the steam reforming as a feasible path for methanol and Fischer-Tropsch synthesis. Choudhary and coworkers$^{5,6}$ have reported their findings on this process over various nickel and cobalt catalysts. They observed that at high space velocity and at reaction temperature above 700 ℃, methane conversion as well as CO and H$_2$ selectivities were close to the expected equilibrium values. However, below 700 ℃, such values exceed the thermodynamic equilibrium prediction. Lunsford and coworkers$^{7}$, however, pointed out that the observations made by Choudhary's group was in fact a mistake due to the error in temperature measurement. Their results, in fact, did not deviate from the prediction of thermodynamic equilibrium and was still thermodynamically controlled. Hence all the studies reported so far were performed under Equilibrium conditions. In this communication, with careful temperature measurement method, we report the first time that by using very high space velocity, the methane-to-syngas reaction could be driven away from the reaction equilibrium and the CO and H$_2$ selectivities are less than their predicted thermodynamic equilibrium values.

1 Experimental

1.1 Catalyst preparation

The NiO/Al$_2$O$_3$ catalyst (with nickel of 10% in weight) was synthesized by impregnating

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Al₂O₃ powder with nickel nitrate (BDH, A. R. grade) solution. The paste generated was dried at 110°C and annealed at 400°C for decomposition. After being pressed and crushed, the material was sieved to a grain size of 20—40 mesh before being calcined at 800°C in air for 4 h.

1.2 Reaction

The catalytic reaction was carried out at the atmospheric pressure in a continuous flow microreactor (i.d. 4 mm) made up of quartz tube. Catalyst (15 mg) with a bed length of about 2.5 mm was placed inside the microreactor. A self-designed unsheathed chromel-alumel thermocouple was positioned with its tip located inside the catalyst bed to ensure accurate measurement of reaction temperature. The products were analyzed by on-line gas chromatography (Shimadzu). The feed composition was CH₄/O₂=2/1 and flow velocity was 167 mL/min.

2 Results and discussion

In order to drive the reaction towards thermodynamic non-equilibrium, very high space velocity (668 000 mL/g·h) was used. The catalyst was heated from room temperature under the flow of reactant gases until reaction took place. The results showed that the reaction did not start until the temperature of the catalyst reached 620°C. As soon as the reaction started, the catalyst temperature jumped to 880°C and the catalytic reaction was self-sustained without any further external heating due to its large exothermicity. The products were monitored for over 55 h. As shown in fig. 1, the reaction temperature and methane conversion dropped fairly rapidly in the first 3 h and then decreased gradually. After 30 h, the catalytic reaction stabilized with the reaction temperature and methane conversion staying at about 600°C and 30%, respectively. The abrupt jump of the catalyst temperature to 880°C at the beginning of the reaction is consistent with the observation of Lunsford and coworkers, indicating that our method for

Fig. 1. The relationship between catalyst temperature or CH₄ conversion and reaction time. Reaction condition: CH₄/O₂=2/1, GHSV=668 000 mL/g·h. ▲, CH₄ conversion; ■, catalyst temperature.
temperature measurement is acceptable. The final stabilized temperature of 600°C (our lowest) instead of 300°C (lowest of Choudary’s group) is another indication that our temperature measurements are correct.

Figure 2 shows that methane conversion decreased as temperature decreased and the amount of converted methane was less than the values expected at thermodynamic equilibrium at all the temperatures recorded, implying that the reaction was not at thermodynamic equilibrium. In other words, the reaction was governed by reaction kinetics. Fig. 3 shows that CO selectivity was also less than the expected values at thermodynamic equilibrium. Moreover, similar to the results at equilibrium, the decline of the reaction temperature would cause the decrease in CO selectivities. Hence, no matter whether the reaction is kinetically or thermodynamically controlled, the decline of reaction temperature was unfavorable for CO generation. Likewise, decrease in reaction temperature would cause H₂ selectivity to decrease.

During the reaction, although the conversion of methane decreased as the reaction
temperature declined, oxygen conversion was constantly 100% and was independent of the reaction temperature. This observation is consistent with the saying that there is reduced nickel sites on the surface of the catalyst[3].

3 Conclusion

Based on the above discussion, one can see that at very high space velocity, the methane-to-syngas reaction could be driven towards non-equilibrium and be governed by reaction kinetics. Once started, the catalytic reaction is self-sustained without any external heating and stabilizes at 600°C after 30 h. The CO and H₂ selectivities have been observed to be less than their thermodynamic equilibrium values. The decline of reaction temperature would result in the decrease in both CO and H₂ selectivities.

References