CH_4/CD_4 isotope effects in the carbon dioxide reforming of methane to syngas over SiO_2-supported nickel catalysts

Hai-You Wang and Chak-Tong Au [1]

Department of Chemistry, Hong Kong Baptist University, 224 Waterloo Road, Kowloon, Hong Kong

Received 8 August 1995; accepted 12 December 1995

By performing the $CH_4 + CO_2$ and $CD_4 + CO_2$ reactions alternately over SiO_2-supported nickel catalysts in a pulse micro-reactor, normal deuterium isotope effects on both the methane conversion reaction and on the CO formation reaction have been observed in the process of CO_2 reforming of methane. Based on the observed CH_4/CD_4 isotope effects, the pathways for the formation of CO are discussed.

Keywords: CH_4/CD_4 isotope effects; CO_2 reforming; methane; syngas; Ni/SiO_2 catalyst

Great attention has been paid to the conversion of methane and carbon dioxide to more valuable compounds, for they are cheap carbon-containing materials and are alleged to be greenhouse gases. The reforming of methane with carbon dioxide is a promising route for the utilization of methane and carbon dioxide. The syngas produced has low H_2/CO ratio and is particularly suitable for Fischer–Tropsch synthesis to liquid hydrocarbons. Supported nickel is one of the most typical catalysts for the process of CO_2 reforming of methane [1–6].

To develop a high performance catalyst, it is essential to elucidate the reaction mechanism. However, only limited attention has been given to this area and controversy concerning the reaction mechanism exists. In view of the equal rate constant observed between CO and H_2 production, Osaki et al. [4] proposed that $CH_{x,\mathrm{ads}} + O_{\mathrm{ads}} \rightarrow CO_{\mathrm{ads}} + xH_{\mathrm{ads}}$ is the rate-determining step. Kim et al. [5] proposed that in the process of methane reforming by CO_2, CO_2 hydrogenation proceeds through adsorbed species produced by dehydrogenation of methane and the dissociation of a C–H bond in methane would be the rate-determining step. Methane dissociation is also assumed to be the rate-determining step in the kinetic studies by Verykios et al. [6]. In the process of carbon dioxide reforming of methane, a C–H bond in methane should be cleaved. In order to clarify whether the dehydrogenation step of methane is the rate-determining step, CH_4/CD_4 isotope effects were investigated by performing the $CH_4 + CO_2$ and $CD_4 + CO_2$ reactions alternately over SiO_2-supported nickel catalysts in a pulse micro-reactor at the temperature of 700°C. So far, no such work has been reported in the literature.

The SiO_2-supported nickel catalysts were prepared by impregnating SiO_2 granules (Aldrich, 60–80 mesh, 406 m^2/g) with nickel nitrate methanol solution, followed by drying at 110°C for 12 h and annealing at 500°C for 2 h for decomposition. The catalysts were reduced with H_2 at 500°C for 1 h before use. The pulse reaction apparatus has been described previously [7], only the reactor used this time was made of quartz with 4 mm i.d. During the pulse experiments, there was a constant flow of helium through the reactor and the reactant gas mixture was flushed in by the carrier gas helium. Thus, the reactant gas had been diluted before passing the reactor. For each study, 50 mg of catalyst was used and the pulse volume of methane/carbon dioxide (1/1) was 1.03 ml. With the thermocouple inserted into the catalyst bed, no change in reaction temperature was observed when the methane/CO_2 pulse was brought in.

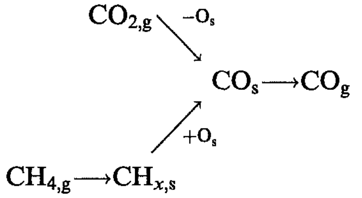
The experiment was carried out in such a manner that at first CH_4/CO_2 was pulsed over the pre-reduced catalyst to perform the $CH_4 + CO_2$ reaction; after the eighth CH_4/CO_2 pulse, $CD_4 + CO_2$ reaction was carried out by pulsing in CD_4/CO_2 instead. After the eighth pulse of CD_4/CO_2, the $CH_4 + CO_2$ reaction was carried out again. By performing the $CH_4 + CO_2$ and $CD_4 + CO_2$ reactions alternately in this way, CH_4/CD_4 isotope effects could be investigated. The ratio (in percentage) of CO formed in the reaction to the total feed before reaction on the basis of carbon contents was defined as the formation rate of CO. Average values of methane conversion, CO_2 conversion and CO formation rate in the $CH_4 + CO_2$ and $CD_4 + CO_2$ reactions were calculated with the exclusion of the first two points in each set of the eight reaction points. The relative ratios (average value) of methane conversion, CO_2 conversion and CO formation rate in the $CH_4 + CO_2$ reaction to the corresponding ones in the $CD_4 + CO_2$ reaction were used to express the magnitude of CH_4/CD_4 isotope effects.

---

[1] To whom correspondence should be addressed.

Fig. 1 shows the variations of methane conversion, CO_2 conversion and CO formation rate over the 10% Ni/SiO_2 catalyst at 700°C as related to the ordinal number of methane/carbon dioxide pulses. As shown in fig. 1, when the $CH_4 + CO_2$ reaction was alternated to the $CD_4 + CO_2$ reaction, methane conversion decreased noticeably; conversely, when $CD_4 + CO_2$ was changed to $CH_4 + CO_2$, methane conversion increased noticeably. The results indicated that the methane conversion reaction showed a normal deuterium isotope effect in the CO_2 reforming of methane, implying that the rate-determining step involved in the methane conversion reaction is a dehydrogenation step of methane. Previously, Cant et al. [8] observed a normal deuterium kinetic isotope effect in the $CH_4 + 2NO + O_2 \rightarrow CO_2 + N_2 + 2H_2O$ reaction over a Co-ZSM5 catalyst and concluded that the rate-determining step is the breaking of a carbon–hydrogen bond. The trend of CO formation rate was similar to that of methane conversion other than a smaller extent of fluctuation when $CH_4 + CO_2$ and $CD_4 + CO_2$ reactions were carried out alternately, indicating the normal isotope effect of deuterium in methane on the rate of CO formation reaction still existed. Methane conversion and CO formation rate in the $CH_4 + CO_2$ reaction were respectively 1.27 and 1.11 times that in the $CD_4 + CO_2$ reaction. CO_2 conversion follows a different trend compared with that of methane conversion and CO formation rate. With the exclusion of the first four points in the first set of eight reaction points of CH_4/CO_2 pulses, where a stable state has not yet been reached, CO_2 conversion in $CD_4 + CO_2$ was slightly higher than that in $CH_4 + CO_2$ reaction, indicating no such normal isotope effect of deuterium in methane on the rate of CO_2 conversion reaction existed.

Since the CH_4/CD_4 isotope effect was more noticeable on the methane conversion reaction than on the CO formation reaction, it can be concluded that the rate of CO formation reaction was not totally governed by the rate-determining step involved in the methane conversion reaction, implying that besides from the methane conversion reaction, CO was also formed from the CO_2 dissociation reaction. In addition, since CO_2 conversion was slightly higher in the $CD_4 + CO_2$ reaction than in the $CH_4 + CO_2$ reaction, it can be inferred that the CO_2 dissociation reaction took place prior to the methane conversion reaction and the O_s formed in the decomposition of CO_2 participated in the CO formation reaction ($CH_{x,s} + O_s \rightarrow CO_s$) in the process of CO_2 reforming of methane. In the methane/CO_2 reaction (whether CH_4 or CD_4 as reactant), the conversion of CO_2 was higher than that of methane, implying O_s formed from the dissociation of CO_2 also participated in some side reactions such as $O_s + \mathrm{H(or\ D)}_s \rightarrow \mathrm{OH(or\ D)}_s$ and $\mathrm{OH(or\ D)}_s + \mathrm{H(or\ D)}_s \rightarrow \mathrm{H(or\ D)}_2\mathrm{O}_g$. Though the reaction rate of O_s for $CH_{x,s} + O_s \rightarrow CO_s$ reaction decreased with the decrease in the dissociation rate of methane due to the normal CH_4/CD_4 isotope effect when $CH_4 + CO_2$ was changed to $CD_4 + CO_2$, the side reaction rate of O_s increased due to the inverse H/D isotope effect, which would promote the dissociation of CO_2. Thus, the normal isotope effect of using CD_4 on the dissociation of CO_2 was counteracted and consequently the conversion of CO_2 did not decrease as that of methane when the reactant gas mixture was changed from CH_4/CO_2 to CD_4/CO_2. Based on the above discussion, a scheme of the reaction pathways for the formation of CO in CO_2 reforming of methane can be presented as follows:



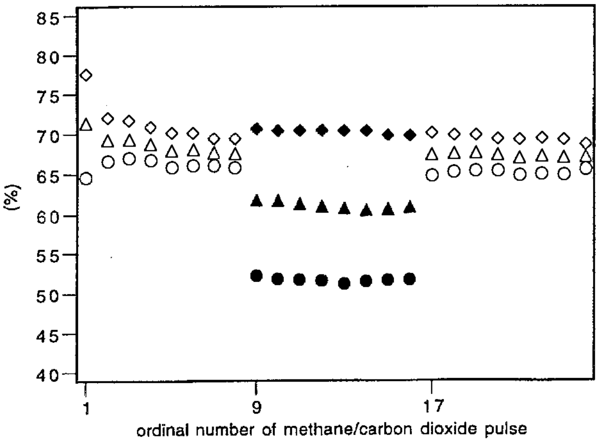


Fig. 1. The relationships of methane conversion (○), CO_2 conversion (◇) and CO formation rate (△) with the ordinal number of methane/carbon dioxide (open symbols for CH_4/CO_2, and solid symbols for CD_4/CO_2) pulsing over 10% Ni/SiO_2 catalyst at 700°C.

In summary, CH_4/CD_4 isotope effects in carbon dioxide reforming of methane over SiO_2-supported nickel catalysts were investigated for the first time by performing the $CH_4 + CO_2$ and $CD_4 + CO_2$ reactions alternately in a pulse micro-reactor. The normal deuterium isotope effect was more noticeable on the methane conversion reaction than on the CO formation reaction, while no such effect was observed on the CO_2 conversion reaction. It can be concluded that there are two different pathways for the formation of CO, i.e., the oxidation of $CH_{x,s}$ species and the dissociation of CO_2 and the latter takes place prior to the former in the process of carbon dioxide reforming of methane.

Acknowledgement

The project was supported by the Hong Kong Research Grants Council, UGC.

References

[1] T. Sodesawa, A. Dobashi and F. Nozaki, React. Kinet. Catal. Lett. 12 (1979) 107.
[2] A.M. Gadalla and B. Bower, Chem. Eng. Sci. 43 (1988) 3049.
[3] A.M. Gadalla and M.E. Sommer, Chem. Eng. Sci. 44 (1989) 2825.
[4] T. Osaki, H. Masuda and T. Mori, Catal. Lett. 29 (1994) 33.
[5] G.J. Kim, D.S. Cho, K.H. Kim and J.H. Kim, Catal. Lett. 28 (1994) 41.
[6] Z.L. Zhang and X.E. Verykios, Catal. Today 21 (1994) 589.
[7] C.T. Au, Y.H. Hu and H.L. Wan, Catal. Lett. 27 (1994) 199.
[8] A.D. Cowan, R. Dumpelmann and N.W. Cant, J. Catal. 151 (1995) 356.