Deuterium isotope effects in methane partial oxidation to syngas

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Keywords: deuterium isotope effects, methane partial oxidation, rhodium catalyst.

In the past few years, there has been renewed interest in the partial oxidation of methane to syngas¹⁻⁷. The reaction is mildly exothermic and provides a H₂/CO ratio of about 2, which
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is more suitable for methanol and Fischer-Tropsch synthesis. The catalysts used are mainly supported group VII transition metals such as Ni, Ru, Rh, Pd, and Pt. Concerning the reaction pathway for methane partial oxidation to syngas, a unified viewpoint has not been reached so far. Many researchers\(^\text{1, 2}\) believe that two stages are involved in the process: (i) complete oxidation of methane to \(\text{CO}_2\) and \(\text{H}_2\text{O}\), (ii) reforming of the remaining methane by \(\text{H}_2\text{O}\) and/or \(\text{CO}_2\) formed in the first stage. Different from the above-mentioned viewpoint, Schmidt \textit{et al.}\(^\text{3, 4}\) proposed a mechanism of catalytic methane pyrolysis followed by the oxidation of surface carbon and hydrogen desorption. Buyevskaya \textit{et al.}\(^\text{5}\), however, suggested that \(\text{CO}\) is formed via a fast reaction of surface carbon species with \(\text{CO}_2\); both are primary products of methane interaction respectively with metallic and oxidized surface active sites.

As reported by Dissanayake \textit{et al.}\(^\text{6}\), hot spots or a large thermal gradient (as much as 300°C) in the catalyst bed could be created during the oxidation of methane at high space velocities. However, an appropriate measure to eliminate or minimize such a problem was not conducted in previous studies. Thus, it is hard to identify reliably the reaction mechanism from the data obtained in the conditions where hot spots might be a problem. In this communication, pulse technique was used to eliminate the problem of hot spots. Deuterium isotope effects in methane partial oxidation reaction were first investigated over \(\text{SiO}_2\)-supported rhodium catalysts at 700°C by performing the \(\text{CH}_4 + \text{O}_2\) and \(\text{CD}_4 + \text{O}_2\) reactions alternately.

1 Experimental

1.1 Catalyst preparation

The \(\text{SiO}_2\)-supported rhodium catalysts were prepared by impregnating \(\text{SiO}_2\) granule (60—80 mesh, 406 \(\text{m}^2/\text{g}\)) with \(\text{RhCl}_3 \cdot 3\text{H}_2\text{O}\) 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 \(\text{H}_2\) at 500°C for 1 h before use.

1.2 Pulse reaction

Pulse reaction apparatus has been described previously\(^\text{7}\), except that the reactor used in the present study 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. The reactants and products were analyzed on-line by a Shimadzu GC-8A gas chromatograph equipped with TCD (MSSA and Porapak Q as columns). For each study, 50 mg of catalyst was used and the pulse volume of methane/oxygen (2/1) was 1.03 ml. Selectivities (molar percentage) were calculated on the basis of carbon content in the products. The blank runs showed that gas-phase reactions of \(\text{CH}_4/\text{O}_2(2/1), \text{CH}_4/\text{CO}_2(1/1)\) and \(\text{CH}_4/\text{H}_2\text{O}(1/1)\) at atmosphere and 700°C were all negligible.

1.3 Investigation of deuterium isotope effects

The experiment was carried out in such a manner that \(\text{CH}_4/\text{O}_2\) was first pulsed over the prerduced catalyst to perform the \(\text{CH}_4 + \text{O}_2\) reaction; after the eighth \(\text{CH}_4/\text{O}_2\) pulse, \(\text{CD}_4 + \text{O}_2\) reaction was carried out by pulsing in \(\text{CD}_4/\text{O}_2\) instead. After the eighth pulse of \(\text{CD}_4/\text{O}_2\), \(\text{CH}_4 + \text{O}_2\) reaction was carried out again. By performing the \(\text{CH}_4 + \text{O}_2\) and \(\text{CD}_4 + \text{O}_2\) reactions alternately in this way, deuterium isotope effects could be investigated. Average values of methane conversion and yields of \(\text{CO}\) and \(\text{CO}_2\) in the \(\text{CH}_4 + \text{O}_2\) and \(\text{CD}_4 + \text{O}_2\) reactions were calculated with the exclusion of the first two points in each set of eight reaction points. The