Pulse study of methane partial oxidation to syngas over SiO₂-supported nickel catalysts

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The reaction behaviors of CH₄/O₂ (2/1) with unreduced and reduced SiO₂-supported nickel (10 wt% metal) catalysts were investigated in a pulse micro-reactor at temperatures ranging from 600 to 800°C. In the interaction of CH₄/O₂ with unreduced NiO/SiO₂, the products are exclusively CO₂ and H₂O at or below 700°C. At 800°C, besides CO₂ and H₂O, CO and H₂ are formed. The reactivity at 800°C can be ascribed to the net generation of metallic nickel site at this temperature. In the reaction of CH₄/O₂ over reduced Ni/SiO₂, the main products are CO and H₂ with CO₂ and H₂O being the minor ones. The results indicate metallic nickel is the active site for methane partial oxidation to syngas. Normal deuterium isotope effects of similar magnitude were observed on the overall, as well as on the CO and CO₂ formation reactions with insignificant change in the product selectivities when CD₄ was used instead of CH₄, indicating that methane dissociation is a key step and that CO and CO₂ are formed via some common intermediates which are subject to kinetic deuterium isotope effect. The results of deuterium isotope effects can be reasonably explained based on the methane pyrolysis mechanism.

Keywords: methane oxidation; syngas; SiO₂-supported nickel (Ni/SiO₂); deuterium isotope effect

1. Introduction

The partial oxidation of methane to syngas has received much attention in the past years. The reaction is mildly exothermic and usually, a H₂/CO ratio of about 2, suitable for methanol and Fischer–Tropsch syntheses, is obtained. This catalytic process is considered to be more feasible than the methane oxidative coupling one for the utilization of methane and has advantages over the conventional steam reforming of methane to make syngas. Supported nickel is one of the typical catalysts for this process [1–7].

In 1946, Prettre et al. first reported that synthesis gas could be produced from methane and oxygen using a supported nickel catalyst in the 735 to 900°C temperature range and concluded that the overall oxidation reaction involved an initial strongly exothermic complete oxidation reaction of methane to CO₂ and H₂O, followed by the endothermic reforming reaction of the remaining methane by H₂O and/or CO₂. This viewpoint was accepted by many recent researchers [2,3,8–11]. However, Schmidt and coworkers [7,12–14] have shown that syngas can be produced with high H₂ and CO selectivities (> 90%) and high CH₄ conversion (> 80%) over Pt- or Rh-coated alumina monoliths in an autothermal flow reactor at ca. 1000°C and at residence times between 10⁻² and 10⁻⁴ s, which was noticeably shorter than the time of ca. 1 s [15] usually adopted in a steam reforming reactor. With such short superficial contact time, they considered that the direct oxidation reaction should be independent of the reforming reactions and concluded that the primary surface reaction is methane pyrolysis followed by surface carbon oxidation and H₂ desorption. Choudhary and co-workers [4,5,16] reported that high selectivity to CO and H₂ could be achieved at temperature lower than 700°C on a variety of Ni- and Co-containing catalysts with high reactant gas space velocities (10⁵–10⁶ h⁻¹) and concluded that syngas was formed directly from methane oxidation. Matsumura et al. [10], however, pointed out that the amount of reactants fed in Schmidt’s as well as Choudhary’s cases was so large that the heat generated during the exothermic reaction would facilitate methane reforming via CO₂ and H₂O. Lunsford and co-workers [6] proved the existence of a large thermal gradient (as much as 300°C) within the catalyst bed during the methane oxidation reaction at high space velocities using an optical pyrometer and pointed out similar hot spots might be present on the catalysts studied by Choudhary et al. [4,5,16].

Concerning the active sites for methane partial oxidation to syngas, Lunsford and coworkers [3] proposed that the initial complete oxidation of methane to CO₂ and H₂O occurs on the unreduced NiO/Al₂O₃ catalyst and the reforming reactions of methane with the CO₂ and H₂O formed happen on the reduced Ni/Al₂O₃ catalyst. Buyevskaya et al. [17] suggested reduced and oxidized surface rhodium sites are the active sites for methane decomposition to surface carbon and methane complete oxidation to CO₂ respectively and CO is formed via a fast reaction of surface carbon species with CO₂ over Rh/Al₂O₃ catalyst.

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In order to eliminate the hot spots, pulse technique was used to study the mechanistic aspects of the conversion of \( \text{CH}_4/\text{O}_2 \) to syngas [18,19]. Previously, the reaction behaviors of \( \text{CH}_4 \) and \( \text{CH}_3/\text{O}_2 \) with \( \text{SiO}_2 \)-supported copper and nickel catalysts at 600, 650 and 700°C were compared [19]. The results showed only in the reaction of \( \text{CH}_4/\text{O}_2 \) over reduced Ni/\( \text{SiO}_2 \), on which methane adsorbs dissociatively, would CO and H₂ be formed as main products, indicating that methane dissociation over metallic nickel sites is a key step for syngas formation and the reduced nickel sites are the active sites. However, it is not sure if the above conclusion is still correct at higher reaction temperature. In the present studies, pulse reaction of \( \text{CH}_4/\text{O}_2 \) with un-reduced and reduced \( \text{SiO}_2 \)-supported nickel catalysts was performed at a wide temperature range (from 600 to 800°C). In addition, in view of the fact that the C–H bonds in methane should be cleaved before CO formation in the process of methane partial oxidation to syngas, deuterium isotope effects were investigated by performing the \( \text{CH}_4 + \text{O}_2 \) and \( \text{CD}_4 + \text{O}_2 \) reactions alternately at 750°C to probe the mechanistic aspects of methane oxidation.

2. Experimental

2.1. Catalyst preparation

The \( \text{SiO}_2 \)-supported nickel catalysts (with 10 wt% metal) were prepared by impregnating \( \text{SiO}_2 \) granule (Aldrich, 60–80 mesh) with the nickel nitrate (BDH, A.R. grade) solution followed by drying at 100°C for 12 h and annealing at 500°C for 2 h for decomposition. The catalysts so prepared are the un-reduced ones and are signified as NiO/\( \text{SiO}_2 \). The catalysts treated in \( \text{H}_2 \) for 1 h at 500°C are the reduced ones and are expressed as Ni/\( \text{SiO}_2 \). (By means of \( \text{H}_2 \)-adsorption, nickel dispersion was determined to be 3.6%.)

2.2. Pulse reaction

The reaction was carried out in a pulse micro-reactor [18]. The reactor was made of quartz tube with 4 mm i.d. A chromel–alumel thermocouple was introduced from the top of the reactor and inserted into the catalyst bed to measure the reaction temperature. During the pulse experiments, there was a constant flow (17 ml/min) of helium through the reactor and the reactant gas mixture was diluted and flushed in by the carrier gas. For each study, 50 mg of catalyst was used. The pulse volume of methane/oxygen (2/1) was 1.03 ml. The reactants and products were analyzed on-line by a Shimadzu GC-8A gas chromatograph equipped with TCD (MS5A and Porapak Q as columns, 50°C; helium as carrier gas). Selectivities (mol%) were calculated on the basis of carbon contents in the products. In the \( \text{CH}_4/\text{O}_2 \) experiments, the results of carbon balance are estimated to be within 5% accuracy. In the absence of the catalysts, the blank runs showed almost no activity below 700°C, and ca. 6.5% of methane conversion at 800°C.

2.3. 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 pre-reduced 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 \( \text{CD}_4/\text{O}_2 \) the \( \text{CH}_4 + \text{O}_2 \) 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 CO and CO₂ 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 relative ratios (average value) of methane conversion, CO yield and CO₂ yield in the \( \text{CH}_4 + \text{O}_2 \) reaction to the corresponding ones in the \( \text{CD}_4 + \text{O}_2 \) reaction were used to express the magnitude of deuterium isotope effects.

Methane (99.9%), methane-\( d_4 \) (D, 99%), oxygen (99.7%), hydrogen (99.995%) and helium (99.995%) were used directly without further purification.

3. Results and discussion

3.1. \( \text{CH}_4/\text{O}_2 \) interactions with NiO/\( \text{SiO}_2 \)

The products of \( \text{CH}_4/\text{O}_2 \) (2/1) interaction with NiO/\( \text{SiO}_2 \) at 600 and 700°C were exclusively CO₂ and H₂O. As shown in fig. 1a, methane conversion at these two temperatures remained roughly at 28% during the eight reaction points of \( \text{CH}_4/\text{O}_2 \) pulses. Since there were no CO and H₂ formed, it can be concluded that gas-phase steam and CO₂ reforming reactions had not taken place at 600 and 700°C.

However, besides CO₂ and H₂O, CO and H₂ were formed at 800°C. As shown in figs. 1a and 1b, during the first three reaction points, methane conversion was ca. 44% and the corresponding selectivity of CO increased slightly from 7.0 to 12.5%. From the third reaction point onward, methane conversion increased in a zig-zag manner, while CO selectivity increased greatly in a continuous way and reached a level of ca. 94% from the sixth point onward. At the eighth reaction point, both methane conversion and CO selectivity over NiO/\( \text{SiO}_2 \) were comparable with those over the reduced Ni/\( \text{SiO}_2 \) catalyst (fig. 2). At 800°C, during the first two reaction points, CO selectivity was less than 8%, indicating the contribution of gas-phase steam and CO₂ reforming reactions to the generation of syngas at 800°C were minor.

As reported previously [19], methane complete oxida-