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Isotopic GCMS Study of the Mechanism of Methane Partial Oxidation To Synthesis Gas

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An isotopic pulse is combined with a gas chromatography−mass spectrum to investigate the mechanism of the partial oxidation of methane. For a pulse reaction of $CH_4/CD_4/O_2$ (1/1/1) at 600 °C over a reduced NiO/SiO_2 catalyst, besides CH_4 and CD_4, large amounts of CHD_3, CH_2D_2, and CH_3D were detected in the exit gas. This indicates that CH, CH_2, and CH_3 species are formed during the reaction, i.e., that CH_4 is activated via its dissociation before its oxidation. The amount of methane involved in the isotopic exchange reaction was larger than that converted to CO and CO_2. Consequently, the dissociation of methane is not rate determining. Over an unreduced NiO/SiO_2 catalyst, CH_4 and CD_4, without any CH_xD_y ($x + y = 4$), were detected in the exit gas, indicating that methane reacts directly with oxygen without its predissociation. For the reaction of CH_4/CD_4(1/1) with the lattice oxygen of the catalyst, CH_4 and CD_4, without any CH_xD_y ($x + y = 4$), were detected in the exit gas, indicating that methane reacts directly with the lattice oxygen without predissociation. Moreover, the $CH_4/^{16}O_2$ reaction over an unreduced NiO^{18} catalyst revealed that the lattice oxygen of the catalyst participates in the reaction of CH_4/O_2.

1. Introduction

Although methane is the most abundant of alkanes, it is also the least reactive. Therefore, its selective conversion to more useful chemical compounds is an important and challenging process. In the last 20 years, the attempts of direct conversion of CH_4 have focused on the oxidative coupling to ethylene and ethane[1,2] and on the oxygenation to methanol and formaldehyde.[3,4] Unfortunately, at the high temperatures (>700 °C) needed for high conversion, the formation of CO_2 is a highly favorable reaction ($\Delta G < -800$ kJ/mol). Therefore, renewed interest in methane transformation to synthesis gas,[5−15] which can be used to produce a variety of chemicals by the Fischer−Tropsch and methanol syntheses,[16,17] has arisen. Currently, the synthesis gas is commercially prepared by steam reforming. The process provides, however, low conversion or selectivity and too large a H_2/CO ratio for the above syntheses.

The catalytic partial oxidation offers the greatest potential for a fast, efficient, and economical conversion of methane to synthesis gas, due to the high conversion of methane, high selectivity, suitable H_2/CO ratio, and very short residence time. The investigations regarding the partial oxidation of methane, its mechanism, and the characterization of the catalyst have become one of the most active topics in catalysis.[11,18−32]

Two mechanisms have been suggested for the partial catalytic oxidation of methane to synthesis gas: (i) the combustion−reforming mechanism, in which CO_2 and H_2O are the primary products, and CO is a result of their reaction with CH_4; (ii) the pyrolysis mechanism, in which CO is produced via the pyrolysis products of CH_4 without the preformation of CO_2. Prettre et al.,[32] who were the first to study the CH_4 partial oxidation over a nickel catalyst, concluded that the overall oxidation involves two steps, an initial exothermic oxidation of CH_4 to CO_2 and H_2O, followed by the endothermic reactions $CH_4 + CO_2 \rightarrow 2CO + 2H_2$ and $CH_4 + H_2O \rightarrow CO + 3H_2$, i.e., the combustion−reforming mechanism. Some recent investigations brought support to this mechanism.[6,7,21−23] The other mechanism involves the pyrolysis $CH_4 \rightarrow CH_x + (4 - x)H$, followed by the oxidation of C species to CO.[11,23−29] Recently,[31] we demonstrated that the partial oxidation of methane follows different mechanisms over unreduced and reduced Ni-based catalysts. Over the unreduced NiO/SiO_2 catalyst, the reaction occurs via the Eley−Rideal mechanism; that is CH_4 in the gas phase reacts with O_2 in the adsorbed state and leads to CO_2. In contrast, over the reduced NiO/SiO_2 catalyst, the reaction takes place via a Langmuir−Hinshelwood mechanism; that is CH_4 and O_2 react in the adsorbed states via the pyrolysis mechanism and lead to CO and H_2. Nevertheless, no direct evidence appears to be available regarding whether methane is dissociated before its oxidation.

In this paper, we combined an isotope pulse with a gas chromatography−mass spectrum (GC−MS) to gather (i) evidence regarding whether methane is dissociated before its oxidation and (ii) information about the rate-determining step during the reaction between CH_4 and O_2 over unreduced and reduced NiO/SiO_2 catalysts.

2. Experimental Section

2.1. Catalyst Preparation. The NiO/SiO_2 (containing 13.6 wt % Ni) catalyst was prepared by impregnating SiO_2 (Aldrich) with an aqueous solution of nickel nitrate (Alfa). The paste thus obtained was dried at room temperature in air and then decomposed and calcined at 800 °C in air for 1.5 h. The BET surface area and average diameter of the pores, which were determined via nitrogen adsorption by using a Micromeritics ASAP 2000 instrument, were 362 m^2/g and 52 Å, respectively.

The $Ni^{18}O/SiO_2$ catalyst was prepared by reducing the $Ni^{16}O/SiO_2$ at 600 °C for 45 min with H_2 and reoxidizing with pulses of $^{18}O_2$ until no O_2 was consumed.

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2.2. GC−MS Analysis of a Pulse Reaction. The experiments were performed mostly at 600 °C under a pressure of 20 psi. The catalyst powder (weight, 0.02 g) was held on quartz wool in a vertical quartz tube reactor of 2 mm inside diameter, in an electronically controlled furnace of large heat capacity in order to keep the temperature constant. The reduced catalyst was prepared by the in situ temperature-programmed reduction (H_2 flow rate = 20 mL/min) of the NiO/SiO_2 from room temperature to 600 °C; further, the catalyst was kept for 30 min in flowing H_2 at 600 °C. Helium (28 mL/min) was used as the carrier gas. The gas pulse contained CH_4, CD_4, and O_2, and the ratio $CH_4/CD_4/O_2 = 1/1/1$ was employed in the experiments.

The experimental method can be simply described as follows. A gas pulse containing 0.3 mL methane ($CH_4/CD_4 = 1/1$) and 0.15 mL O_2 was injected through a 10-port valve into a carrier gas (He), which was allowed to flow through the reactor. The reactants and products have been detected with a GC−MS instrument (HP 5890 Series II gas chromatograph and HP 5971 Series quadrupole mass selective detector) equipped with a Porapak Q column.

3. Analysis of MS Data

In the mass spectra of mixtures containing CD_4, CD_3H, CD_2H_2, CDH_3, and CH_4, some molecular ion peaks overlap with fragment ion peaks. Therefore, to obtain the intensity of each molecular ion of the mixture sample, one must subtract all possible fragment ion contributions from each molecular ion peak.

CD_4 and CD_3H molecular ion intensities can be calculated directly from the peaks of mass 20 and 19, because there are no fragment ions of D-isotopic methanes that contribute to the two peaks. (It should be noted that the contribution of the ^{13}C-methane impurity to the MS peaks must be subtracted.) The CD_2H_2 molecular ion intensity can be obtained by subtracting the contribution of the CD_3 fragment ion (resulting from the cleavage of CD_4^+ or CD_3H^+) from the peak of mass 18. The CDH_3 molecular ion intensity can be obtained by subtracting the contribution of the CD_2H fragment ion (resulting from the cleavage of $CD_2H_2^+$ or CD_3H^+) from the peak of mass 17. The CH_4 molecular ion intensity can be obtained by subtracting the contribution of the CD_2 and CH_2D fragment ions (resulting from the cleavage of $CD_2H_2^+$ or CD_3H^+) from the peak of mass 16. To perform the calculations, one must carry out experiments with standard samples for calibration.

4. Results

4.1. Reaction of CH_4/CD_4 (1/1) with O_2 over NiO/SiO_2 Catalysts. The reaction between methane and O_2 was carried out using pulses of $CH_4/CD_4/O_2$ (1/1/1) at 600 °C. Figure 1 shows that 12% methane and 40% oxygen were converted over unreduced and 28% methane and 100% oxygen were converted over reduced catalysts, that CO_2 without CO was formed over the unreduced NiO/SiO_2 catalyst, and that 41% CO_2 and 59% CO were produced over the reduced NiO/SiO_2 catalyst.

To obtain information about the intermediate species, the isotopic composition after reaction was determined (Figure 2). As shown in Figure 2, only CH_4 and CD_4 without CH_xD_y ($x + y = 4$, x and $y > 0$) were present in the product obtained over the unreduced catalyst. In contrast, besides CH_4 and CD_4, CH_xD_y were detected in the product obtained over the reduced catalyst (3% CH_4, 31% CH_3D, 38% CH_2D_2, 20% CHD_3, and 8% CD_4). While 28% of the methane (CH_4 and CD_4) in the feed gas was converted to CO and CO_2, a larger amount (65%) of methane participated in the isotopic exchange reaction over the reduced catalyst. This indicates that the isotopic exchange reaction is faster than the partial oxidation over the reduced catalyst. In contrast, over the unreduced catalyst, no isotopic exchange reaction occurred (Figure 2).

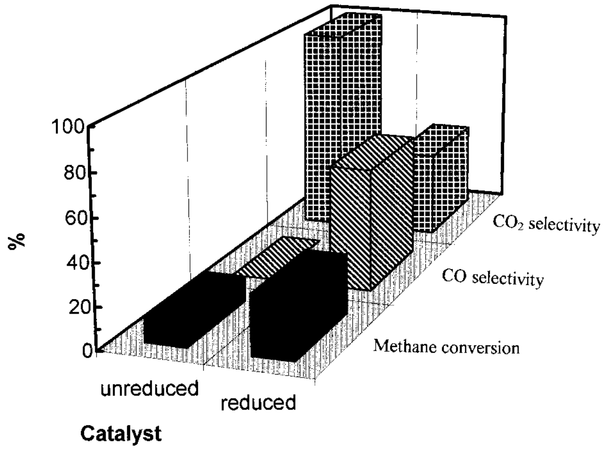

Figure 1. Methane conversion and CO and CO_2 selectivities for the reaction of a $CH_4/CD_4/O_2$ (1/1/1) pulse over unreduced and reduced NiO/SiO_2 catalysts at 600 °C. (Oxygen conversion was 40% over the unreduced catalyst and 100% over the reduced one.)

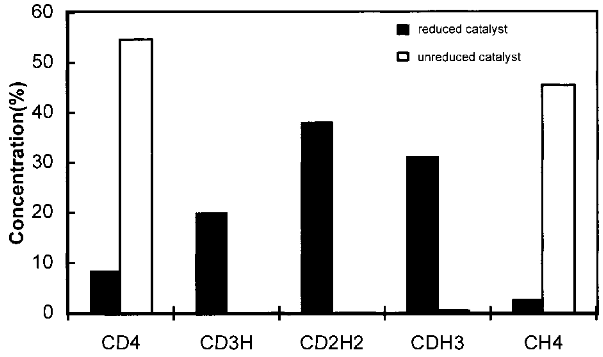

Figure 2. Isotopic species distribution in the methane converted to CO and CO_2 after the $CH_4/CD_4/O_2$ (1/1/1) pulse reaction over unreduced and reduced NiO/SiO_2 catalysts at 600 °C.

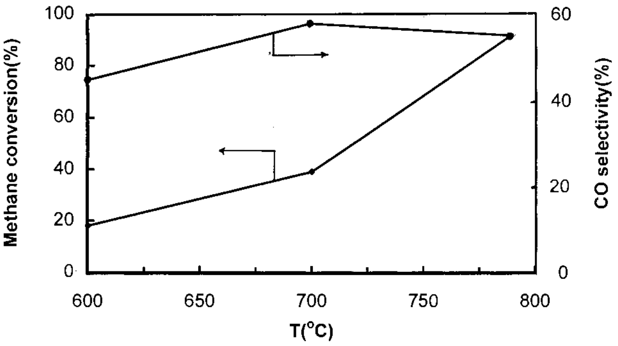

Figure 3. Methane conversion and CO selectivity for the reaction of the CH_4/CD_4 (1/1) pulse over the unreduced NiO/SiO_2 catalyst.

4.2. The Reaction between Methane and Lattice Oxygen over NiO/SiO_2 Catalyst. The reaction between the lattice oxygen of NiO/SiO_2 and methane free of oxygen was carried out by using pulses of CH_4/CD_4 (1/1). Figure 3 shows that the methane conversion was 18% at 600 °C, 39% at 700 °C, and 92% at 790 °C and that the selectivity for CO was 45% at 600 °C, 58% at 700 °C, and 55% at 790 °C. Figure 4 reveals that,

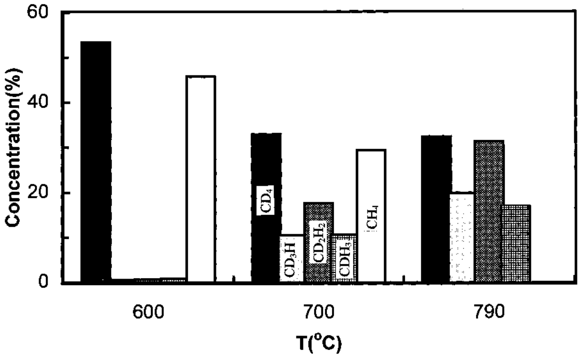

Figure 4. Isotopic species distribution in the methane converted to CO and CO_2 after the reaction of the CH_4/CD_4 (1/1) pulse over the unreduced NiO/SiO_2 catalyst.

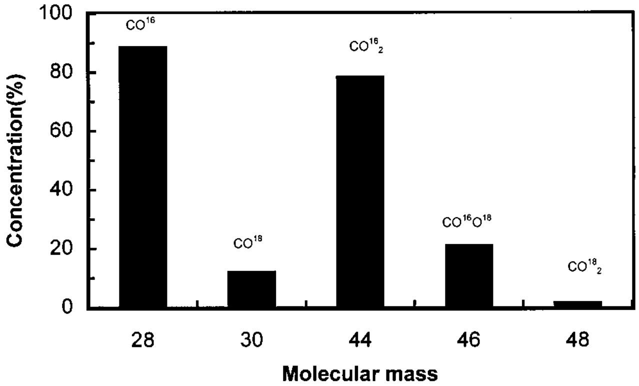

Figure 5. ^{18}O Isotopic species distribution of CO and CO_2 for the $CH_4/^{16}O_2$ (1/1/1) pulse reaction over unreduced $Ni^{18}O/SiO_2$ catalysts at 600 °C.

at 600 °C, only CH_4 and CD_4 free of any CH_xD_y were present in the exit gas. However, above 700 °C, CH_xD_y were also detected.

4.3. Reaction between Methane and $^{16}O_2$ over the Isotopic $Ni^{18}O/SiO_2$ Catalyst. The partial oxidation of methane was carried out by introducing pulses of $CH_4/^{16}O_2$ (2/1) over the unreduced $Ni^{18}O/SiO_2$ catalyst. As shown in Figure 5, besides $C^{16}O$ and $C^{16}O_2$, $C^{18}O$, $C^{16}O^{18}O$, and $C^{18}O_2$ were detected in the product, namely $C^{18}O_2/C^{16}O_2 = 0.018$, $C^{16}O^{18}O/C^{16}O_2 = 0.265$, and $C^{18}O/C^{16}O = 0.13$. This indicates that the lattice oxygen participates in the reaction over the unreduced catalyst, even when the reactant mixture contains oxygen.

5. Discussion

Even though many authors suggested that the dissociation of methane constitutes the first step in the methane oxidation, no direct evidence was yet brought in this direction. Our experiments revealed that, over the reduced catalyst, large amounts of CHD_3, CH_2D_2, and CH_3D were formed in the pulse reaction of methane with oxygen ($CH_4/CD_4/O_2 = 1/1/1$) (Figure 2). This indicates that CH, CH_2, and CH_3 species are formed on the catalyst and demonstrates that the reaction follows the pyrolysis mechanism. Moreover, over the reduced catalyst, the amount of methane involved in the exchange between CH_4 and CD_4 is larger than that involved in the conversion to CO and CO_2. Consequently, the exchange between CH_4 and CD_4 is faster than the conversion of methane to CO and CO_2, and the methane cleavage cannot be rate determining as suggested in ref 33. In other words, the rate-determining step is the reaction of the CH_x species with oxygen. Therefore, the reaction mechanism over the reduced catalyst can be expressed as follows:

$$CH_4 + Ni \rightarrow CH_{x(s)} + (4 - x)H_{(s)} \tag{1}$$

$$O_{2(g)} + Ni \rightarrow 2O_{(s)} \tag{2}$$

$$CH_{x(s)} + (1 + x)O_{(s)} \rightarrow CO_{(s)} + xHO_{(s)} \tag{3}$$

$$CO_{(s)} \rightarrow CO_{(g)} \tag{4}$$

$$CO_{(s)} + O_{(s)} \rightarrow CO_{2(s)} \rightarrow CO_{2(g)} \tag{5}$$

$$2H_{(s)} \rightarrow H_{2(s)} \rightarrow H_{2(g)} \tag{6}$$

$$HO_{(s)} + Ni \rightarrow O_{(s)} + H_{(s)} \tag{7}$$

$$OH_{(s)} + H_{(s)} \rightarrow H_2O_{(s)} \rightarrow H_2O_{(g)} \tag{8}$$

$$O_{(s)} + 2H_{(s)} \rightarrow H_2O_{(s)} \rightarrow H_2O_{(g)} \tag{9}$$

For the unreduced catalyst, only CD_4 and CH_4, free of any CD_xH_y, were detected. This means that no isotopic exchange reaction occurs over the unreduced catalyst. In other words, methane reacts directly with oxygen without its predissociation. The reaction mechanisms are different over the reduced and unreduced catalysts because only in the former case there are Ni^0 sites, which activate the methane. Methane is activated by Ni^0 present on the reduced Ni-based catalyst as a result of the $\sigma-\pi$ coordination between the σ bonds of C−H in CH_4 and the d orbitals of Ni. This decreases the C−H binding energy via the electron donation from the σ bond of C−H to a vacant d orbital of Ni and the electron back-donation from the filled d orbital of Ni to the vacant antibonding σ^* orbital of C−H. Over the unreduced NiO/SiO_2 catalyst, methane is not activated before reacting with oxygen.[31]

In the reaction at 600 °C between the lattice oxygen and CH_4/CD_4 (1/1) free of O_2, a negligible amount of CH_xD_y was detected. This indicates that no cleavage of methane takes place before its oxidation. At higher temperatures (>600 °C), the Ni^0 formed via the reduction of NiO by CH_4, activates the CH_4 molecules, resulting in the formation of CH_xD_y (Figure 4).

Over the unreduced $Ni^{18}O/SiO_2$, $C^{16}O^{18}O$ and $C^{18}O$ were detected during the reaction of methane with $^{16}O_2$ at 600 °C. This means that the lattice oxygen participates in the reaction even in the presence of gas-phase oxygen. This further confirms our previous results.[31]

Over the unreduced catalyst, the methane conversion for its reaction with the lattice oxygen (18%) is higher than for its reaction with gas oxygen (12%). This means that the reaction with the lattice oxygen is more facile than that with the gas oxygen. According to the above results, it is reasonable to suggest that CH_4 is oxidized substantially by the oxygen of the lattice, which is replenished by the oxygen of the gas atmosphere. This mechanism can be expressed as follows:

$$CH_4 + 2NiO \rightarrow CO_2 + 2H_2 + 2Ni \tag{10}$$

$$2Ni + O_{2(g)} \rightarrow 2NiO \tag{11}$$

Because the Ni^0 oxidation is fast, the reaction between the lattice oxygen and methane may constitute the rate-determining step.

The above mechanisms, suggested on the basis of isotopic pulses, describe the reactions over the initial states of the reduced and unreduced catalysts. Under steady-state conditions, some NiO will be reduced by the CH_4 of the feed gas and some Ni^0 will be reoxidized by the O_2 of the feed gas. Consequently, under steady-state conditions, there are both Ni^0 and NiO sites on the catalyst surface. Because the activity of Ni^0 is much higher than that of NiO, Ni^0 constitutes the main active site of the steady-state catalyst and the pulse reaction over the reduced catalyst can represent the steady-state reaction.

6. Conclusion

In the present paper, an isotopic pulse method is combined with GC−MS to obtain information about the mechanism of the partial oxidation of methane. The reaction of $CH_4/CD_4/O_2$ (1/1/1) over the reduced NiO/SiO_2 catalyst occurs via the pyrolysis mechanism, with the cleavage of methane faster than the oxidation of CH_x. This indicates that the dissociation of methane is not rate determining.

Over the unreduced NiO/SiO_2 catalyst, no isotopic exchange reaction of methane occurs. This indicates that there is no dissociation of methane before its oxidation.

For the reaction of CH_4/CD_4 (1/1) with the lattice oxygen of the NiO/SiO_2 catalyst at 600 °C, the mechanism is as for the reaction of methane with the gas-phase oxygen over the unreduced catalyst. Further, the reaction of CH_4 with $^{16}O_2$ over the $Ni^{18}O/SiO_2$ catalyst indicates that the lattice oxygen participates in the reaction even in the presence of the gas-phase oxygen. As a possible mechanism, we suggest that methane reacts substantially with the lattice oxygen, while O_2 of the gaseous phase reoxidizes the reduced NiO.

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