Isotopic study of the reaction of methane with the lattice oxygen of a NiO/MgO solid solution

Yun Hang Hu and Eli Ruckenstein *

Department of Chemical Engineering, State University of New York at Buffalo, Amherst, NY14260, USA

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The reaction between methane and the lattice oxygen of a NiO/MgO (1/1.85) solid solution was investigated by an isotopic pulse-GCMS method. During a single-pulse reaction of CH_4/CD_4 (1/1) with the lattice oxygen, besides CH_4, CD_4, carbon monoxide and water, very small amounts of CHD_3, CH_2D_2 and CH_3D were detected in the exit gas. Because the isotopic kinetic effect (K_H/K_D) was 1.01, the dissociation of CH_4 cannot constitute the rate-determining step. The rate-determining step is the reaction with the lattice oxygen, because of the high stability of the lattice oxygen in the NiO/MgO solid solutions.

Keywords: CD_4, CH_4, GC-MS, lattice oxygen, NiO, MgO, solid solution

1. Introduction

The NiO/MgO system forms solid solutions over the entire molar fraction range because of their similar lattice structures [1]. Their usefulness for catalysis was first noticed when the effect of the electronic interactions between cations on the catalytic activity and selectivity was recognized [2,3]. The characteristics of the NiO/MgO system were widely investigated [4–9]. Attempts were made to employ this solid solution as a catalyst for N_2O decomposition and CO or CO_2 hydrogenation, but with little success [10–12]. Nevertheless, recently, the solid solution attracted attention [13–16] because of its high activity and selectivity as well as high stability in the CO_2 reforming of methane at high space velocities of the feed gas [13,14].

In a previous paper, we reported that the lattice oxygen of NiO/MgO solid solution catalyst participates in the reaction of the CO_2 reforming of methane [17]. Because both the removing of the lattice oxygen of the NiO/MgO solid solution and the C–H cleavage of methane are involved in the reaction, it is important to identify which of them constitutes the rate-determining step during the reaction between methane and the lattice oxygen. In order to answer this question, we employ an isotope pulse-GCMS method to investigate the reaction between methane and the lattice oxygen of a NiO/MgO solid solution.

2. Experimental

2.1. Catalyst

The preparation of the NiO/MgO (molar ratio = 1/1.85) catalyst was carried out by impregnating MgO with an aqueous solution of nickel nitrate. The paste 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 of the catalyst, 20 m^2/g, was determined via nitrogen adsorption by using a Micromeritics ASAP 2000 instrument.

The phase analysis of the catalyst was carried out by X-ray powder diffraction (XRD) on a Nicolet X-ray diffraction equipment. Although the XRD patterns of MgO are very similar to those of NiO, there are some differences in their peak positions. For MgO, the peak positions for the (220), (311) and (222) faces are at $2\theta \approx 62.64$, 75.00 and 79.00°, respectively. For NiO, the peak positions for the same faces are by 0.60, 0.80 and 0.81°, respectively, higher. A mechanical mixture of NiO and MgO has three double peaks around the above 2θ values. In contrast, the catalyst prepared by impregnation has single peaks near the above 2θ values; this indicates that a solid solution was formed.

2.2. Gas chromatography–mass spectrum (GC-MS) analysis of a pulse reaction

The experiments were performed at 700 °C under a pressure of 20 psi. The catalyst powder (weight: 0.005 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. Helium (28 ml/min) was used as the carrier gas. The feed gas contained CH_4 and CD_4, and the ratio $CH_4/CD_4 = 1/1$ was employed in the experiments.

The experiment was carried out as follows: A gas pulse containing 0.30 ml methane ($CH_4/CD_4 = 1/1$) was injected through a 6-port valve into a carrier gas (He) which was allowed to flow through the reactor. The analysis of the exit gas was carried out with a GC-MS instrument (HP 5890 series II gas chromatograph and HP 5971 series quadru-

* To whom correspondence should be addressed.

pole mass-selective detector) equipped with a Porapak Q column.

2.3. The gas chromatography analysis of a pulse reaction

The experiments were performed at a pressure of 10 psi and 700 °C. The catalyst powder (0.005 g) was held on quartz wool in a vertical quartz tube reactor of 2 mm inside diameter. Helium (28 ml/min) was used as the carrier gas. The feed gas was either CH_4 or CD_4.

The experimental method can be described as follows: A gas pulse containing 0.30 ml methane (CH_4 or CD_4) was injected through a 6-port valve into a carrier gas (He) which was allowed to flow through the reactor. The analysis of the exit gas was carried out with a GC instrument (Varian model 3700 gas chromatograph) equipped with a Porapak Q column.

3. Analysis of MS data

The method of analyzing the mass spectrum data for mixtures containing CD_4, CD_3H, CD_2H_2, CDH_3 and CH_4 can be shortly described as follows: *The CD_4 and CD_3H molecular ion* intensities can be calculated directly from the peaks of mass 20 and 19 (it should be noted that the contribution of ^{13}C-methane 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 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 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 from the peak of mass 16.

4. Results and discussion

In order to obtain information about the intermediate species formed during the reaction of methane with the lattice oxygen, a CH_4/CD_4 (1/1) pulse GC-MS experiment was carried out. CH_4 and CD_4 were the main methane compounds in the exit gas, which contained also small amounts of CH_3D, CH_2D_2 and CHD_3.

Figure 2 shows that the CH_4 and CD_4 conversions in independent GC experiments are almost equal (22.2 and 21.9%, respectively) and that R_H/R_D is equal to 1.01. Consequently, there is no isotopic kinetic effect in the reaction between methane and the lattice oxygen of NiO/MgO. The isotopic kinetic effect can be evaluated in the following simple way: the rate of methane conversion to CO and CO_2 can be expressed as

$$R_H = A_1 \exp(-E_1/RT) f(CH_4, O_2), \quad (1)$$

$$R_D = A_2 \exp(-E_2/RT) f(CD_4, O_2), \quad (2)$$

where R_H and R_D are the rates of CH_4 and CD_4 conversions, A_1 and A_2 are preexponential factors, E_1 and E_2 are

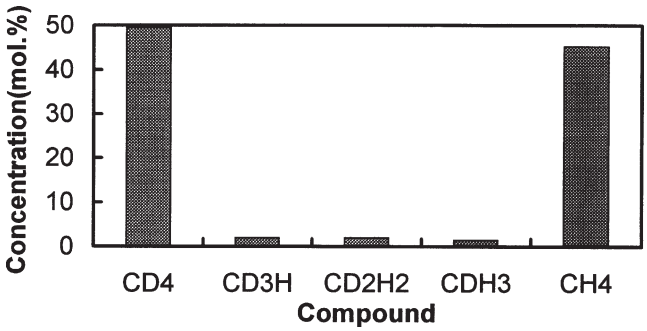

Figure 1. Methane isotopic species distribution in the methane converted to CO and CO_2 after a single CH_4/CD_4 (1/1) pulse reaction over the NiO/MgO solid solution catalyst at 700 °C.

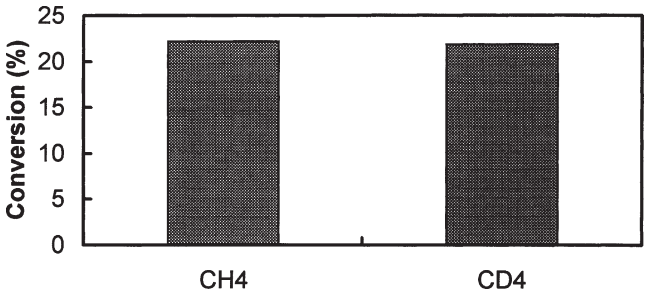

Figure 2. Comparison between CH_4 and CD_4 conversions in the reactions of single CH_4 and CD_4 pulses with the lattice oxygen over the NiO/MgO solid solution catalyst at 700 °C.

activation energies, R and T are the gas constant and temperature in K, and $f(CH_4, O_2)$ and $f(CD_4, O_2)$ are functions of the concentrations of CH_4 or CD_4, and O_2.

Dividing the above equations, one obtains

$$\frac{R_H}{R_D} = \frac{A_1}{A_2} \exp\left(-\frac{E_1 - E_2}{RT}\right) \frac{f(CH_4, O_2)}{f(CD_4, O_2)}. \quad (3)$$

Because the reactions of CH_4 and CD_4 have the same transition state, A_1 and A_2 should be equal. In addition, for the same CH_4 and CD_4 concentrations, $f(CH_4, O_2)$ and $f(CD_4, O_2)$ can be assumed equal. Therefore,

$$\frac{R_H}{R_D} = \exp\left(-\frac{E_1 - E_2}{RT}\right). \quad (4)$$

In the homogeneous dissociation of CH_4 (CD_4), the difference between the activation energies for the cleavage of C–H and C–D can be evaluated as the negative value of the difference of their zero-point energies (18 kJ/mol for C–H and 13 kJ/mol for C–D [18]), i.e., $E_1 - E_2 = -5$ kJ/mol. At 700 °C, the calculated value of the kinetic isotopic effect is 1.86, i.e., the rate of CH_4 dissociation is about two times faster than that of CD_4. Because in the initial state of the catalyst there are no Ni^0 sites which can activate the CH (or CD) bond, the kinetic isotopic effect should be 1.86 if the dissociation step is rate determining. The almost equal conversions of CH_4 and CD_4 in the reaction between methane and the lattice oxygen over NiO/MgO solid solution indicates that the C–H cleavage of CH_4 is not rate-determining. In other words, the rate-determining step is

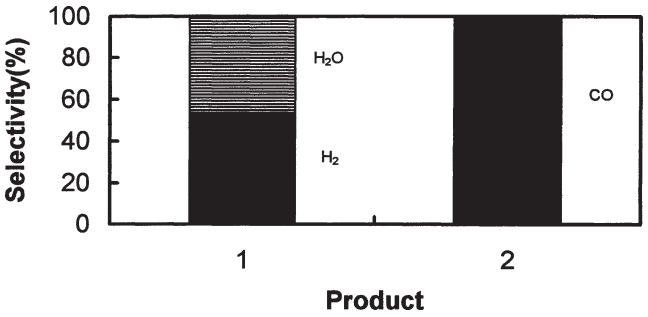

Figure 3. Methane conversion and product selectivities for the reaction of a single CH_4 pulse over the NiO/MgO catalyst at 700 °C.

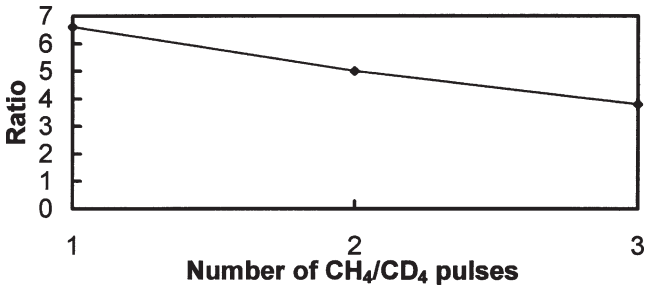

Figure 4. The ratio of methane converted to methane exchanged vs. the number of CH_4/CD_4 (1/1) pulses in the reaction of methane with the lattice oxygen over the NiO/MgO solid solution catalyst at 700 °C.

the removing of the lattice oxygen by CH_4. Otsuka et al. also reported that the reaction between methane and the lattice oxygen of CeO_2 has a small kinetic isotopic effect ($K_H/K_D = 1.1 \pm 0.1$) [19], indicating that the C–H cleavage is not the key step of the reaction rate. It was previously noted [20] that the oxidation of methane by the lattice oxygen occurs with higher difficulty over the NiO/MgO solid solution than over the pure NiO. The lattice oxygen has a higher stability in the solid solution than in the pure NiO due to the coordination of the O atoms to both Mg and Ni. XPS indicated that electron transfer from NiO to MgO occurs, which, increasing the strength of the binding between the two oxides, is responsible for the higher stability of the lattice oxygen [8].

The CH_4 pulse GC experiment showed that the CO selectivity was 100% (no CO_2 was detected), while the H_2 and H_2O selectivities were 54 and 46%, respectively (figure 3). The different results regarding H_2O and CO_2 might occur because MgO, which is a base, can strongly adsorb CO_2 which can be reduced by hydrogen to CO and H_2O. While the lattice oxygen of NiO/MgO solid solution has a low oxidation ability, since it leads only to CO, that of NiO/Al_2O_3 or NiO/La_2O_3 has a higher one, since it generates only CO_2 [21].

Because the amount of CH_x species is small and the rate-determining step is the oxidation process, the reaction mechanism is likely to involve mainly the direct oxidation of methane without the pre-cleavage of C–H at least during the first pulse. However, as the number of pulses of methane increases, the amount of Ni^0 generated, which can activate the methane, increases because of NiO reduction. As a result, the C–H cleavage becomes easier and the H–D exchange reaction of methane also increases. Indeed, the ratio between methane converted to CO and methane exchanged decreases with the pulse number being 6.6 for the first pulse, 5.0 for the second one and 3.8 for the third one (figure 4). By increasing the number of pulses, the conversion decreases; it is 22% for the first pulse, 20% for the second and 18% for the third one. While the amount of oxygen available decreases, and this decreases the conversion, the activation by the Ni^0 formed increases and this increases the conversion. This explains why the conversion decreases slowly with the number of pulses.

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