Conversion of CO_2 to CO with CH_4 over Ni/SiO_2 Catalyst: Photoacoustic Measurements of Reaction Rate

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The catalyzed reaction of carbon dioxide with methane to produce hydrogen and carbon monoxide, CO_2 + CH_4 → $2CO$ + $2H_2$ (ΔH^o=59.1 kcal/mol), has received increasing attention from both an environmental and an industrial perspective. The reaction is attractive because the greenhouse gases (CO_2 and CH_4) can be converted into a synthesis gas with a low H_2/CO ratio, which is suitable for the syntheses of valuable oxygenated chemicals such as aldehydes, methyl alcohol, acetic acid, and dimethyl ether. Ni, Pt, and Ru based catalysts are known to be effective for the CO_2-CH_4 reaction. One of the major problems is the deactivation of catalysts due to the formation of coke on the catalysts during the reaction. The noble metal based catalysts are less sensitive to coking compared to nickel based catalysts. Nevertheless, it is still worthwhile to develop the nickel-based catalysts resistant to the formation of coke because the noble metals are expensive and of limited availability. The reforming of methane with carbon dioxide over nickel based catalysts has been studied by many investigators. However, there are few reports about fundamental kinetic parameters at present and there are some disagreements on the reaction mechanism including the reaction orders and the activation energy.

The catalytic research involves the measurement of reaction rate and the investigation of factors influencing the reaction rate. An accurate description of the reaction rate can be obtained from a rate law which is essential in a reactor design. Although it is difficult to determine the accurate mechanism from an empirical kinetic expression, such empirical kinetic expression may be helpful to understand the catalytic reaction mechanism. The most important consideration in the kinetic experiments is to measure the concentration of reactants or products of interest as a function of time. To measure the concentration, absorption spectroscopy techniques have been generally used. However, their sensitivities may be diminished due to the difficulty in precise measurements of the difference between the incident and the transmitted intensities of radiation. The photoacoustic spectroscopy (PAS) being based on a direct measurement of acoustic waves generated owing to the absorption of optical energy provides highly selective

detection and extremely low molecular gas level detection, which enable us to obtain a signal with enough intensity for even time-resolved experiments. Further advantages of this technique can be found in the capability of the elimination of any sophisticated sampling techniques which are inevitable in the conventional techniques. The photoacoustic spectroscopy is thus believed to be a suitable technique for the *in situ* experiment of a catalytic reaction because it can directly measure the absorption characteristics of the samples of interest. In the previous works, we have shown that the photoacoustic spectroscopy is applicable to the kinetic studies of CO oxidation and water-gas shift reaction over catalysts.[1-3] In this work, the temporal change in the concentration of CO_2 in the catalytic CO_2-CH_4 reaction was measured *in situ* as a function of time by using a CO_2 laser-based photoacoustic spectroscopy with a suitable difference photoacoustic cell. The measurements were governed at a relatively low reactor pressure so that the technique provided precise kinetic data for the initial reaction stage characterized by high reaction rates. The kinetic data obtained were compared with those of other investigators.

Experimental Section

Ni/SiO_2 catalyst was prepared from nickel(II) nitrate hexahydrate (Aldrich Chemical Co. 99.999%) and powdered silica (80-100 mesh size, Aldrich Chemical Co. 99.6%). SiO_2 and $Ni(NO_3)_2 \cdot 6H_2O$ were weighed to give 17 wt.% Ni in its reduced form. The SiO_2 powder was impregnated with an aqueous solution of the $Ni(NO_3)_2 \cdot 6H_2O$, followed by drying at 100 °C for 24 h and subsequent calcination at 800 °C for 2 h in air. The details of the experimental arrangement was shown in the previous reports (Refs. 2 and 3). The CO_2-CH_4 reaction was performed in a closed-circulation fixed-bed type microreactor which was made of quartz with a volume of approximately 21 cm^3. The microreactor was placed in the electric furnace maintained at a constant temperature within 0.5 K by an electronic controller with a K-type thermocouple. The microreactor was directly connected to a photoacoustic cell by approximately 15 cm in distance with an adjoining tube.

The differential photoacoustic cell consisted of two compartments, *i.e.* a reference cell and a sample cell, separated from each other by a ZnSe window. Each photoacoustic cell

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was a Helmholtz resonator of 1.9 cm in diameter and 3.3 cm in length with an adjoining tube of 1.0 cm in diameter and 10 cm in length. The output beam of a cw CO_2 laser (Synrad Series 48-1-28) operating in multiline of 10.6 μm was modulated at 25 Hz. The nonresonant condition was used in order to prevent the change of the signal due to the variation in the resonance frequency followed by the temperature change in the Helmholtz resonator. The photoacoustic signals from the microphones attached at the reference cell (signal A) and the sample cell (signal B) connected to the microreactor were detected by a lock-in amplifier (Stanford Research Systems Model SR850), and the signal ratio (A/B) was recorded by a personal computer as a function of time.

The reference cell was filled with a gaseous mixture of CO_2 (0.2 Torr) and N_2 (39.8 Torr). The sample cell was connected to the microreactor loaded with the catalyst, in which the total pressure of gaseous mixture of CO_2 and CH_4 was kept at 40 Torr with N_2 buffer gas. The purity of CH_4, CO_2, and N_2 was greater than 99.99%. Gas pressure was monitored with a capillary silicon oil manometer (1/13 Torr precision) and a pirani gauge. Before each measurement, the catalyst (500 mg) loaded was reduced in H_2 flow at 650 °C for 8 h. After the pretreatment, the reactor was cooled down to room temperature and helium gas was passed to remove hydrogen gas remaining in the reactor. The reaction mixture containing methane and carbon dioxide was then admitted into the microreactor at given temperature of the reaction. It has been known for the CO_2-CH_4 reaction over Ni/SiO_2 catalyst that Ni particle sintering occurs at temperatures above 700 °C and various forms of coke accumulate outside the Ni particles during time-on-stream. In this work, we performed the catalytic reaction at temperatures less than 700 °C in order to minimize an effect of Ni particle sintering.

Results and Discussion

The XRD result for the Ni/SiO_2 catalyst treated in a flow of H_2 at 650 °C for 8 h clearly indicates the presence of nickel phase. TEM image of the Ni/SiO_2 catalyst after the H_2-reduction is shown in Figure 1. Nickel particle sizes on the Ni/SiO_2 catalyst distributed in a wide range less than 100 nm. EDX analysis was also performed for the H_2-reduced Ni/SiO_2 catalyst to investigate its composition and the EDX data showed that the ratio of Ni/Si was 12.3/87.7 by the weight percent. In general, the photoacoustic signal is directly proportional to the concentration of analyte in a given condition. However, it is desirable to keep the gas pressure as low as possible because the sensitivity of the photoacoustic signal increases with decreasing the total pressure of gas medium. Therefore, the total pressure of gaseous reactants in the reactor was kept at 40 Torr filled with N_2 as a buffer gas in this experiment. The CO_2 photoacoustic signal was found to be linearly varied with P_{CO_2} below 15 Torr. Thus all the experiments were carried out in the linear response range of the signal with respect to the partial pressure of CO_2 such as below 15 torr.

It is shown in the inset of Figure 2 that the variations of the
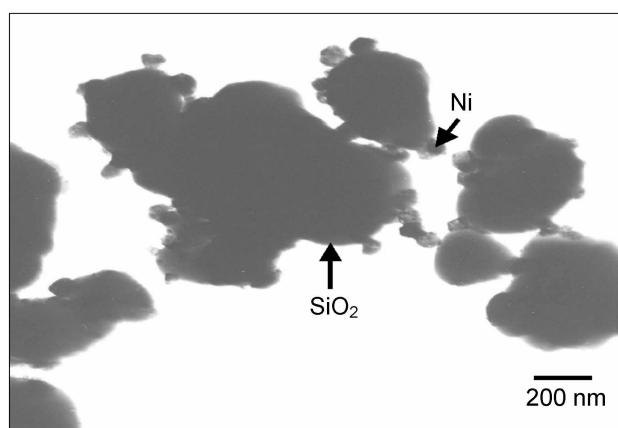
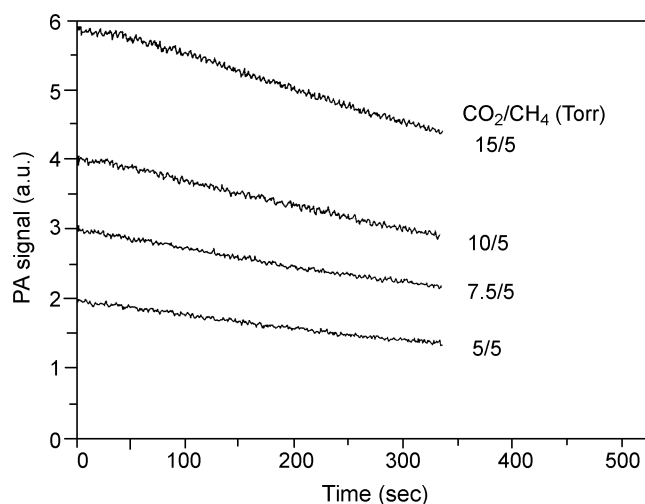Figure 1. TEM image of H_2-reduced Ni/SiO_2 catalyst.
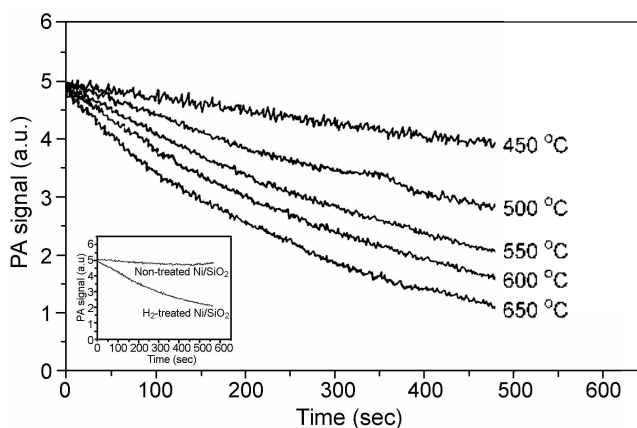
Figure 2. CO_2 photoacoustic signals for the CO_2-CH_4 reaction as a function of time at various temperatures on H_2-reduced Ni/SiO_2 catalyst; $CO_2(g)/CH_4(g)/N_2(g)$ (10/10/20 in Torr) reaction mixture. The inset shows the CO_2 photoacoustic signal on H_2-treated Ni/SiO_2 and non-treated Ni/SiO_2 catalysts at 600 °C for this reaction.

CO_2 photoacoustic signal with time-on-stream for the reaction of CO_2 (10 Torr) and CH_4 (10 Torr) over both non-treated Ni/SiO_2 at various temperatures and H_2-treated Ni/SiO_2 catalysts at 600 °C. The H_2-treated catalyst showed catalytic activity in the reaction, on the other hand the non-treated catalyst showed almost no catalytic activity even at high temperature, indicating that a reduction treatment of catalyst was important on its catalytic activity for the CO_2-CH_4 reaction. The effect of temperature on the disappearance rates of CO_2 over Ni/SiO_2 catalyst was investigated in the temperature range of 450 to 650 °C. As shown in Figure 2 variations of the CO_2 photoacoustic signals with time-on-stream at various temperatures were recorded when the CO_2/ CH_4/N_2 (10 Torr/10 Torr/20 Torr) mixture was introduced over the H_2-reduced Ni/SiO_2 catalyst. The disappearance rates of CO_2 were estimated from the PAS data in the initial period of 0-30 sec time-on-stream. The initial reaction rates obtained were plotted as a function of reciprocal temperature according to the Arrhenius equation. The apparent activation energy from the Arrehenius plot was determined to be 11.1 kcal/mol. According to the data reported for the catalytic CO_2-CH_4 reaction, the apparent activation energies for CH_4

consumption varied with the types of catalyst and the values were found in a wide range from 7 to 86 kcal/mol.[4-8]

Bradford and Vannice[4] found from an analysis of the reported values for the CO_2 reforming of methane that 14 $\pm$ 1 kcal/mol was the most frequently observed in the distribution of apparent activation energies and the value was coincided with the activation energies of 13.3 = 1.5 and 12.6 $\pm$ 1.2 kcal/mol for CH_4 dissociation on Ni(110) and Ni(111), respectively.[9] Osaki *et al.*[10] and Sakai *et al.*[11] reported the activation energy of 13 kcal/mol for the CH_4 consumption in the CO_2 reforming of methane over Ni/SiO_2 catalyst, which was very close to the value of 11.1 kcal/mol obtained in this work. Generally the activation energy for the CO_2 consumption in the CO_2-CH_4 reaction is somewhat lower than that for the CH_4 consumption. For instance, Seshan *et al.*[12] demonstrated that the activation energies for the consumption of CH_4 and CO_2 over Ni/Al_2O_3 catalyst were 10 and 8 kcal/mol, respectively. Similarly the activation energies of 25.5 and 23.6 kcal/mol were reported for the consumption of CH_4 and CO_2, respectively, over $Ni/CaO-Al_2O_3$ catalyst by Lemonidou *et al.*[8] Although it is not possible to compare directly the present result with the reported data for Ni/SiO_2 catalyst because literature values were obtained from the rates of CH_4 consumption, the present value (11.1 kcal/mol) is believed to be in reasonable agreement with those of other investigators.[9-11]
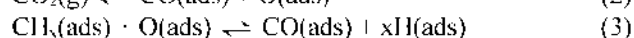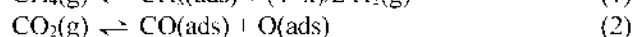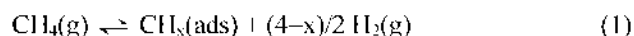
The dependence of CO_2 consumption rate is also investigated according to the partial pressure of CH_4 and CO_2 to determine the reaction orders being described by the equation, rate $= k\ P_{CO_2}{}^{\alpha}P_{CH_4}{}^{\beta}$. Figure 3 shows the variations of the CO_2 photoacoustic signal with time-on-stream at various P_{CO_2}'s at 600 °C. The reaction order with respect to CO_2 was determined from the intial rates obtained in the reaction period of 0 to 30 sec time-on-stream and the value was found to be 0.65. Figure 4 shows the CO_2 photoacoustic signals measured at various P_{CH_4}'s at 600 °C. The reaction order with respect to CH_4 was determined to be 0.32 from

Figure 3. P_{CO_2} dependence of CO_2 photoacoustic signal for the CO_2-CH_4 reaction on H_2-reduced Ni/SiO_2 catalyst at 600 °C.
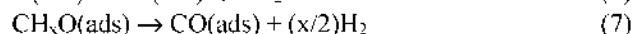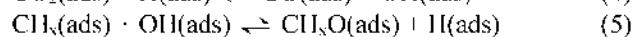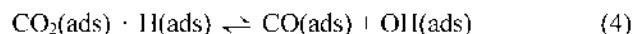
the initial rates obtained in the reaction period of 0 to 30 sec time-on-stream.

Although the CO_2-CH_4 reaction over Ni-based catalyst have been extensively studied by many investigators during the past 10 years, an accurate description of the reaction rate from kinetic data have not been suggested and a controversy is still remaining for the reaction mechanism. At present, there exist only a few reports of kinetic studies on the CO_2-CH_4 reaction over Ni/SiO_2 catalyst. In the early study of a reaction mechanism, it has been proposed that CH_4 and CO_2 are dissociatively adsorbed on the surface of the catalyst to yield H_2, involving the following steps in the reaction mechanism;[9-13]

$$CH_4(g) \rightleftharpoons CH_x(ads) + (4-x)/2\ H_2(g) \tag{1}$$
$$CO_2(g) \rightleftharpoons CO(ads) + O(ads) \tag{2}$$
$$CH_x(ads) \cdot O(ads) \rightleftharpoons CO(ads) + xH(ads) \tag{3}$$

where CO(ads) and H(ads) are evolved from the surface as gaseous molecules. Erdöhelyi *et al.*[14,15] and Rostrup-Nielson *et al.*[16] have suggested that CO_2 dissociation can be promoted by H(ads) and O(ads) reacts with adsorbed CH_x species to yield CO and H_2. Some investigators derived the rate expressions by the use of partial pressure data to describe the reaction kinetics quantitatively. However, no one has demonstrated the reaction mechanism from which the rate expression was derived.[6,7,17]

In recent, Bradford and Vannice[4,18] proposed the formation of CH_xO intermediate from the reaction of $CH_x(ads)$ and OH(ads) to model the reaction kinetics for the CO_2-CH_4 reaction quantitatively. According to their reaction model, CH_x species were formed by the dissociative chemisorption of CH_4 according to the equilibrium (1) and CO_2 adsorbed reacted with H(ads) to produce CO and H(ads), which were then proceeded as the followings;

$$CO_2(ads) \cdot H(ads) \rightleftharpoons CO(ads) + OH(ads) \tag{4}$$
$$CH_x(ads) \cdot OH(ads) \rightleftharpoons CH_xO(ads) + H(ads) \tag{5}$$
$$H(ads) + OH(ads) \rightleftharpoons H_2O \tag{6}$$
$$CH_xO(ads) \rightarrow CO(ads) + (x/2)H_2 \tag{7}$$

where CO and H_2 were produced from the decomposition of CH_xO intermediate. An overall reaction was then represented as

$$CH_4 + 2CO_2 \rightarrow H_2 + H_2O + 3CO \tag{8}$$
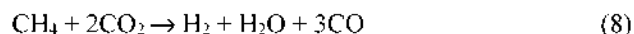
They derived a rate expression for the rate of CH_4 consumption by assuming that the most abundant intermediate was CH_xO;

$$\text{rate} = \frac{A P_{CH_4} P_{CO_2}}{B P_{CO_2} P_{H_2}^{(4-x)/2} + [1 - C P_{CH_4}] P_{CO_2}} \tag{9}$$

where A, B, and C are the constants to be determined from the equilibrium constants and the specific rate constants. They showed two examples clearly demonstrating this rate expression to experimental data for Ni/MgO and Pt/TiO_2 catalysts. The partial pressure data were optimized to Equation (9) by assuming a value of x = 2 and the values of
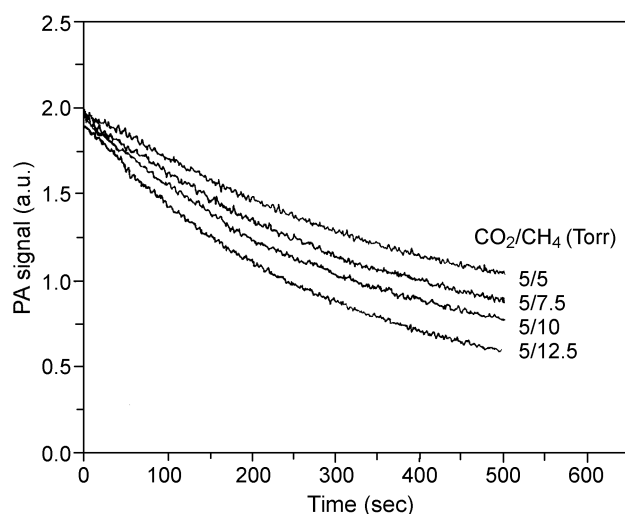
Figure 4. P_{CH_4} dependence of CO_2 photoacoustic signal for the CO_2-CH_4 reaction on H_2-reduced Ni/SiO_2 catalyst at 600 °C.

optimized model parameters were determined. The results showed that the reaction orders to P_{CH_4} and P_{CO_2} were variable with the region of partial pressures.

Several investigators reported the reaction orders with respect to CO_2 and CH_4 for the CO_2-CH_4 reaction over Ni/ SiO_2 catalyst, however the values were found to be different from one another. Osaki *et al.*[11] reported that the reaction orders with respect to CO_2 and CH_4 were 0.16 and -0.30, respectively for the reaction over 20 wt.% Ni/SiO_2 catalyst. Sakai *et al.*[10] measured the rates of CH_4 consumption over 13 wt.% Ni/SiO_2 catalyst and found that the reaction orders were 0.5-0.6 with respect to CO_2 and 0.02-0.05 to CH_4 in the temperature range from 550 to 700 °C, indicating that the reaction rate was practically independent on the P_{CH_4}. The reaction orders determined in this work were 0.65 with respect to CO_2 and 0.32 to CH_4. The 0.65-order to CO_2 was close to that of Sakai *et al.*,[10] while the 0.32-order to CH_4 was different from those of Sakai *et al.*[10] and Osaki *et al.*[11]

The disagreement in the reaction orders is likely due to different experimental techniques or reaction condition employed in the studies. Namely, we measured the rate of CO_2 consumption by using a closed-circulation reactor at low pressures below 0.053 atm. On the other hand, Sakai *et al.*[10] and Osaki *et al.*[11] measured the rate of CH_4 consumption by using a continuous flow reactor in the partial pressure ranges of 0.26-0.74 atm and 0.15-0.60 atm, respectively. These results may support a validity of the Bradford and Vannice's reaction model in which the kinetic orders are variable with the region of partial pressures. This means that CH_xO species seem to be most likely formed as intermediates in the CO_2-CH_4 reaction and subsequently decomposed to CO and H_2.

The kinetic data for the initial reaction stage measured in this work are somewhat different from those for the stage showing a constant catalytic activity after the initial reaction stage. Moreover, the analysis was carried out generally from the data obtained up to 30 sec time-on-stream to provide the kinetic information for the early reaction stage. Nevertheless, the PAS technique would provide more precise kinetic information for the CO_2-CH_4 reaction at a relatively clean surface of the catalyst because the present experiments were governed at the conditions of a relatively low reactor pressure. In the present experiment, only CO_2 concentration can be monitored due to the limitation of excitation source. In order to analyze various species in the reaction at the same time, it is required to operate the system at different wavelengths, which is not easily feasible with conventional IR lasers. However, applications of such photoacoustic measurements for the kinetic study with the detection of all IR-observable species can be extended when an IR lamp of strong power in the conjunction with an appropriate bandpass filter is adapted.

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