Meteoritics & Planetary Science 41, Nr 5, 715–729 (2006)
Abstract available online at http://meteoritics.org

An experimental study on Fischer-Tropsch catalysis: Implications for impact phenomena and nebular chemistry

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(Received 05 April 2005; revision accepted 31 December 2005)

Abstract–Fischer-Tropsch catalysis, by which CO and H_2 are converted to CH_4 on the surface of transition metals, has been considered to be one of the most important chemical reactions in many planetary processes, such as the formation of the solar and circumplanetary nebulae, the expansion of vapor clouds induced by cometary impacts, and the atmospheric re-entry of vapor condensate due to asteroidal impacts. However, few quantitative experimental studies have been conducted for the catalytic reaction under conditions relevant to these planetary processes. In this study, we conduct Fischer-Tropsch catalytic experiments at low pressures (1.3×10^{-4} bar $\leq P \leq 5.3 \times 10^{-1}$ bar) over a wide range of H_2/CO ratios (0.25–1000) using pure iron, pure nickel, and iron-nickel alloys. We analyze what gas species are produced and measure the CH_4 formation rate. Our results indicate that the CH_4 formation rate for iron catalysts strongly depends on both pressure and the H_2/CO ratio, and that nickel is a more efficient catalyst at lower pressures and lower H_2/CO ratios. This difference in catalytic properties between iron and nickel may come from the reaction steps concerning disproportionation of CO, hydrogenation of surface carbon, and the poisoning of the catalyst. These results suggest that nickel is important in the atmospheric re-entry of impact condensate, while iron is efficient in circumplanetary subnebulae. Our results also indicate that previous numerical models of iron catalysis based on experimental data at 1 bar considerably overestimate CH_4 formation efficiency at lower pressures, such as the solar nebula and the atmospheric re-entry of impact condensate.

INTRODUCTION

Fischer-Tropsch catalysis, by which CO and H_2 are converted to hydrocarbons, such as alkanes, alkenes, and alcohols, on the surface of transition metals, such as iron and nickel, has been suggested as playing a key role in abiotic organic synthesis under a variety of conditions in the solar system (e.g., Anders et al. 1973; Prinn and Fegley 1989; Kress and Tielens 2001; Hill and Nuth 2003; Sekine et al. 2003, 2005; Kress and McKay 2004). These conditions include the solar and circumplanetary nebulae, vapor clouds induced by impacts, and the atmospheric re-entry of vapor condensate due to asteroidal impacts. However, there are a number of problems in assessing the role of Fischer-Tropsch catalysis under these planetary conditions.

In the solar nebula chemistry, it has been suggested that the organic compounds in the carbonaceous chondrites might be produced by Fischer-Tropsch catalytic reaction (e.g., Studier et al. 1968; Anders et al. 1973; Hayatsu and Anders 1981; Bradley et al. 1984). However, it is still controversial whether the organics in meteorites are formed through Fischer-Tropsch catalysis in the solar nebula, because the experimental studies have shown that the isotopic fractionation patterns found in meteorites do not agree with those produced by Fischer-Tropsch catalysis (e.g., Cronin and Pizzarello 1990). Nevertheless, the important point is that Fischer-Tropsch catalysis would have been the only available thermally driven pathway to convert CO, which is energetically inhibited by the high activation barrier, into CH_4 in the solar nebula (Kress and Tielens 2001). Kress and

Tielens (2001) model Fischer-Tropsch reaction kinetics and apply it to the solar nebula conditions. Their results indicate that the present position of the asteroid belt may be the region where the Fischer-Tropsch catalysis occurs efficiently. More recently, several experiments were done under the conditions simulated for the nebula (e.g., Llorca and Casanova 1998, 2000; Fegley 1998; Llorca 1999; Ferrante et al. 2000; Hill and Nuth 2003). However, these measurements are not very quantitative. For example, the methane formation rate has not been measured. Recently, Sekine et al. (2005) conducted experiments under the condition of a circumplanetary subnebula and obtained the methane formation rate for metallic iron. Their result indicates that poisoning of the catalyst occurs even at very high H_2/CO ratios (e.g., 1000), and they apply the results to subnebula chemistry and the origin of methane on Titan. However, they use only iron as a catalyst. Under nebular conditions, nickel also exists as iron-nickel alloy. Although Llorca (1999) compares the difference between iron and kamacite in Fischer-Tropsch catalysis, the systematic study of the difference in catalytic efficiency among metallic iron, nickel, and iron-nickel alloy has not been conducted.

Fischer-Tropsch catalysis may also play an important role in asteroidal/cometary impacts on Earth and planets (Anders et al. 1973; Gerasimov et al. 2000; Sekine et al. 2003; Kress and McKay 2004). The impactor and a part of the target are vaporized upon impact of an asteroid/comet on a planet, and an impact vapor cloud is formed. Anders et al. (1973) suggest that catalytic reactions may occur on the surfaces of dust condensates in an expanding (and cooling) impact vapor cloud. In a cooling impact vapor cloud, gas-phase reactions are considered to quench around 2000 K (Fegley et al. 1986; Gerasimov et al. 1998). Around this temperature, the gas composition in the cloud is dominated by H_2, CO, and H_2O, which are generated by the dissociation of organics and water in meteorites and comets. At temperatures lower than 1000 K, CH_4 becomes thermochemically more stable than CO (McKay and Borucki 1997; Kress and McKay 2004). However, gas-phase reactions proceed extremely inefficiently at such low temperatures. When heterogeneous catalysts such as iron and nickel condensates exist in the cloud, CH_4 may be produced through heterogeneous catalytic reactions, such as Fischer-Tropsch catalysis (Kress and McKay 2004). Kress and McKay (2004) calculate the kinetics of the catalysis and assess the possibility of CH_4 production in cometary impact vapors.

Furthermore, after the expansion of impact clouds, a large amount of condensate is launched from the impact point, disperses globally, and re-enters the atmosphere, where it can then react with gas in the planetary atmosphere. Sekine et al. (2003) calculate global methane production via Fischer-Tropsch catalysis on the surface of re-entering condensates by iron meteorite impacts on early Earth. The methane produced in these impact phenomena may play an important role not only in the atmospheric evolution as a greenhouse effect gas (Sagan and Chyba 1997; Kress and McKay 2004), but also in the origin of life (Chyba and Sagan 1992).

In order to understand planetary processes such as nebular chemistry, impact vapor clouds, and the atmospheric re-entry of vapor condensates due to asteroidal impacts on early Earth, quantitative experimental data at lower pressures and over wide range of H_2/CO ratios need to be obtained, as described below in the next section of this paper. However, today's available quantitative data of Fischer-Tropsch catalysis have been obtained mainly in industrial chemistry (e.g., Vannice 1975; Krebs et al. 1979; Goodman et al. 1980). Since the productivities of the hydrocarbons are not very good at lower pressures, the laboratory data under conditions relevant to planetary processes have not been reported in industrial chemistry. Because of the absence of the experimental data under such reaction conditions, significant uncertainty remains in methane production via Fischer-Tropsch catalysis under planetary conditions (e.g., Kress and Tielens 2001; Sekine et al. 2003; Kress and McKay 2004). Thus, in this study, we conduct experiments on Fischer-Tropsch catalysis at lower pressures (<1 bar) and various H_2/CO ratios (0.25– 1000) using three types of catalysts: metallic iron, nickel, and iron-nickel alloys. We compare iron and nickel catalysts under these reaction conditions and investigate the relation among pure iron, pure nickel, and iron-nickel alloys as catalysts.

In the next section, we first describe the experimental system of this study. Second, we show the results for the gas species produced via catalytic reactions and the methane formation rates for the catalysts. Next, we discuss the difference between iron and nickel and the mechanism of the reaction at lower pressures. Finally, we describe the implications for nebular chemistry and impact phenomena.

EXPERIMENTAL

Conditions

The pressure, temperature, and H_2/CO ratio are the main variables in this experiment. However, the relevant reaction temperature ranges only from 400 to 700 K (e.g., Krebs et al. 1979; Sekine et al. 2005), but pressure and the H_2/CO ratio vary widely in nebulae and impact vapor. Thus, pressure and the H_2/CO ratio become especially important in this study. In this section, we describe the pressure and the H_2/CO ratio under nebular conditions, cometary impact vapor, and the atmospheric re-entry of vapor condensate due to asteroidal impacts on early Earth.

Under solar and circumplanetary nebular conditions, the H_2/CO ratio is estimated to be very high (~1000–1500) because their compositions are expected to be similar to the hydrogen-rich solar abundance (Anders and Grevesse 1989). In the solar nebula, the gas pressure at catalytically optimal

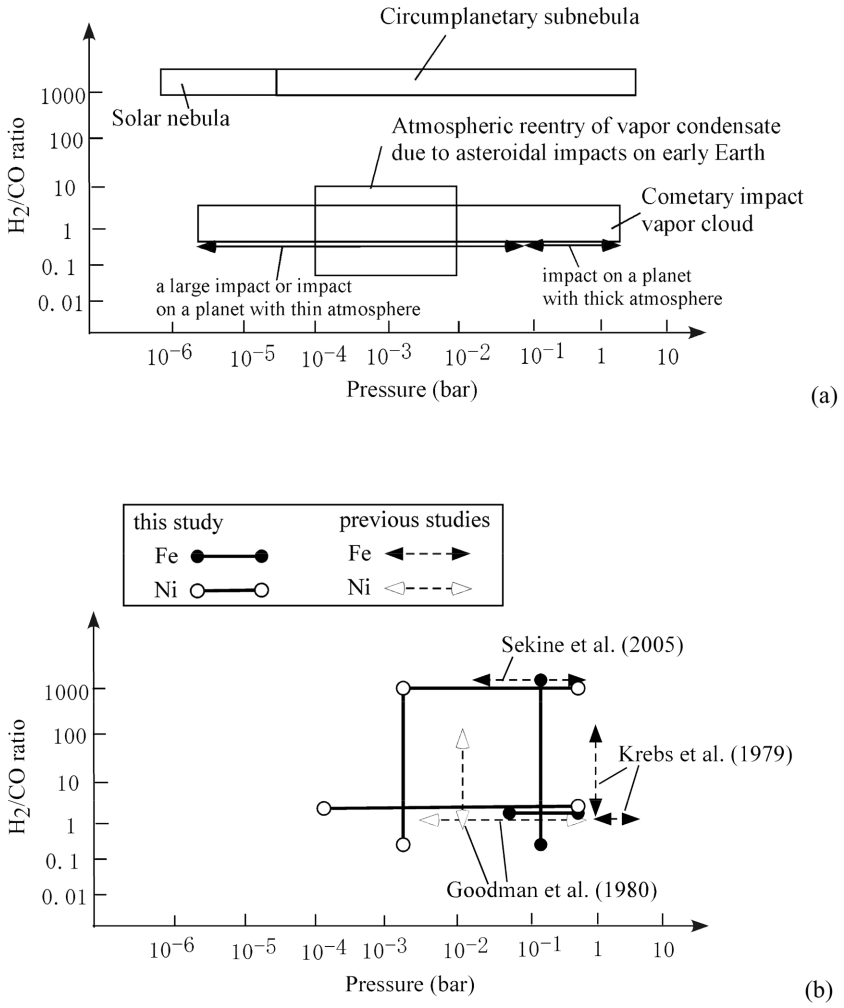

Fig. 1. a) Reaction conditions for Fischer-Tropsch catalysis in the solar nebula, a circumplanetary subnebula, cometary impact vapor clouds, and the atmospheric re-entry of vapor condensate due to asteroidal impacts on early Earth. b) The range of pressure and H_2/CO ratio of the previous experimental studies (broken lines) (Krebs et al. 1979; Goodman et al. 1980; Sekine et al. 2005) and that of this study for iron and nickel catalysts (solid lines).

temperatures (~400–700 K) (Sekine et al. 2005) is estimated to be about 10^{-6} to 10^{-4} bar (e.g., Lewis and Prinn 1980; Bell et al. 1997, 2000). In a circumplanetary subnebula, gas pressure is estimated to be 10^{-5} to 10 bar (e.g., Prinn and Fegley 1981; Coradini et al. 1989; Mousis et al. 2002; Mosqueira and Estrada 2003).

In cometary impact vapor, the abundance of CO at 2000 K (a typical quenching temperature of gas-phase reactions) is on the same order as that of H_2 (McKay and Borucki 1997; Kress and McKay 2004). When a planet has a thick atmosphere, the expansion of the vapor cloud stops at the ambient atmospheric pressure, and the catalysis may proceed at relatively high pressures (~1 bar) (Kress and McKay 2004). However, when a planet has a thin atmosphere or an impactor is large enough to surpass a planetary atmosphere, the resulting vapor plume expands into space. Catalysis then takes place at very low pressures (<< 1 bar).

In the atmospheric re-entry of impact condensate, the reaction pressure ranges from ~10^{-4} to 10^{-2} bar because the condensate reaches its slow terminal velocities at high altitudes of a planetary atmosphere (Sekine et al. 2003). A typical H_2/CO ratio is estimated to be 0.03–10 for early Earth's atmosphere (Sekine et al. 2003). Figure 1a shows the H_2/CO ratios and pressures estimated for nebular conditions, cometary impact vapor, and the atmospheric re-entry of impact condensate.

Figure 1b shows the range of pressure and H_2/CO ratio, for which the methane formation rate has been experimentally obtained for iron and nickel catalysts in the previous studies. In industrial chemistry, methane formation rates have been investigated experimentally at pressures higher than 1 bar and at H_2/CO = 4–100 for iron catalyst (Krebs et al. 1979) and at pressures higher than 1.3×10^{-3} bar and at H_2/CO = 4 for nickel catalyst (Goodman et al. 1980). More recently, Sekine

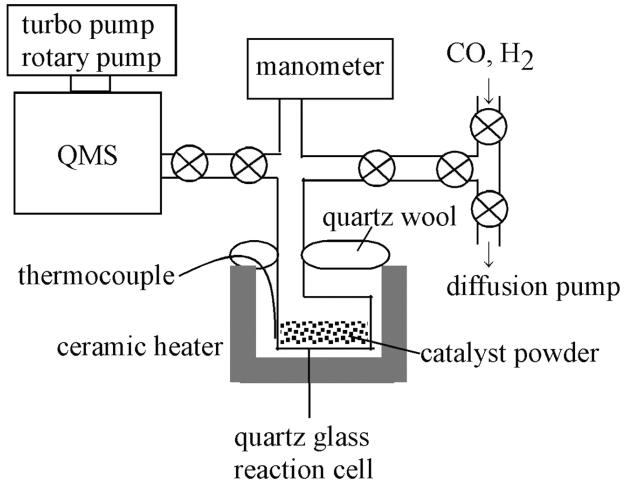

Fig. 2. A schematic diagram of the experimental system of Fischer-Tropsch catalysis, in which the gas mixtures are analyzed by a quadrupole mass spectrometer (QMS).

et al. (2005) obtained the methane formation rate for iron catalyst at $H_2/CO = 1000$ and $P = 2.0 \times 10^{-2} - 5.3 \times 10^{-1}$ bars. Thus, the range covered by the previous studies is much narrower than that needed for planetary applications.

In this study, we measure the methane formation rate and observe what gas species are formed as functions of pressure (1.3×10^{-4} to 5.3×10^{-1} bars) and the H_2/CO ratio (0.25–1000) for both metallic iron and nickel catalysts. Figure 1b also shows the range of experimental conditions in this study. Our experimental conditions do not cover the entire reaction range, where the catalysis may occur in the solar nebula, impact vapor, and the atmospheric re-entry of impact condensate. However, our study extends the range of both the pressure and the H_2/CO ratio significantly.

Catalysts

Under the conditions of the solar and circumplanetary nebulae, the impact vapor cloud, and the atmospheric re-entry of vapor condensate due to asteroidal impacts, iron and nickel may be the main catalysts in terms of Fischer-Tropsch reactions, because these elements are much more abundant metals in the solar nebula than other industrial Fischer-Tropsch catalysts, such as Ru and Co (Anders and Grevesse 1989). According to the estimates based on the C1-chondrite composition (Anders and Grevesse 1989), the Fe/H_2 ratio is 6.45×10^{-5}, and the Ni/H_2 ratio is about 1/20 times that of iron.

We use metallic iron, nickel, and iron-nickel alloy powders as catalysts because these catalysts may exist in a variety of planetary environments as small particles. The typical size of dust particles in the solar nebula and the condensate particles in impact vapors are estimated to be between sub-micron size to some hundreds of micrometer (e.g., Prinn and Fegley 1989; Melosh 1982, 1989). The grain sizes of catalysts used in this study are ~250 μm for iron (Nilaco Corporation, 99.998% purity), ~63 μm for nickel (Nilaco Corporation, 99.9% purity), and ~40 μm for iron-nickel alloy (Koujundo-Kagaku Corporation, 99.9% purity) in diameter, respectively. The particle sizes of these catalysts are not exactly the same. However, according to Goodman et al. (1980), the size and shape of the catalyst do not affect the methane formation rate in Fischer-Tropsch catalysis significantly. We also use two types of iron-nickel alloy catalysts; Fe:Ni = 40:60 (mol%) and Fe:Ni = 90:10 (mol%).

In the following, we use a specific unit for a reaction rate: product molecules/site (= surface atoms)/s, in which the methane production rate (molecules/s) is normalized by the number of sites (i.e., surface atoms) of the catalysts. Thus, we need to measure the number of atoms (i.e., sites) on the surface of a catalyst. We measure the specific surface area (m^2/g) for the catalysts with the Brunauer-Emmett-Teller (BET) method using Kr gas as the adsorbate for iron. As for the nickel and iron-nickel alloy catalysts, we estimate the specific surface area by measuring the pressure decrease caused by the adsorption of CO on the surface of the catalysts. The number of surface sites is estimated to be 1.5 (± 0.1) × 10^{18} site/g for the iron catalyst, 1.6 (± 0.2) × 10^{18} site/g for the nickel catalyst, and 1.5 (± 0.2) × 10^{17} site/g for the two iron-nickel alloys. The numbers of surface sites per unit weight for iron and nickel powders are close despite the difference in particle size. This is because the surfaces of the powder are not smooth but very irregular. The number of surface sites of the iron-nickel alloys is about 1/10 times that of the metallic iron and nickel. This is because the alloy powders have very smooth surfaces and an almost spherical shape.

Experimental Systems

We constructed two experimental systems to measure Fischer-Tropsch catalytic reaction rates. Both systems are designed to be closed systems because low efficiency in the methane formation rate is expected at lower pressures. We use a gas chromatograph (GC) for one system, which is the same system used by Sekine et al. (2005). A schematic diagram is given in Fig. 1 by Sekine et al. (2005). We use a quadrupole mass spectrometer (QMS, MKS Instruments) for the other system. Figure 2 shows a schematic diagram of the experimental system using a QMS. A quartz reaction cell is located in a ceramic heater; the volume of the reaction cell is 155 ml. The powder of the catalysts is put in the reaction cell. A thermocouple, touching the reaction cell, is used to control the temperature. We used this system at reaction pressures lower than 2.0×10^{-2} bar because the GC is not suitable for experiments at such low pressures. The ratio of the number of surface sites of the catalysts to H_2 molecule gas (H_2 molecule/surface metal) in the systems varies about 10^3 to 10^5, depending on reaction conditions.

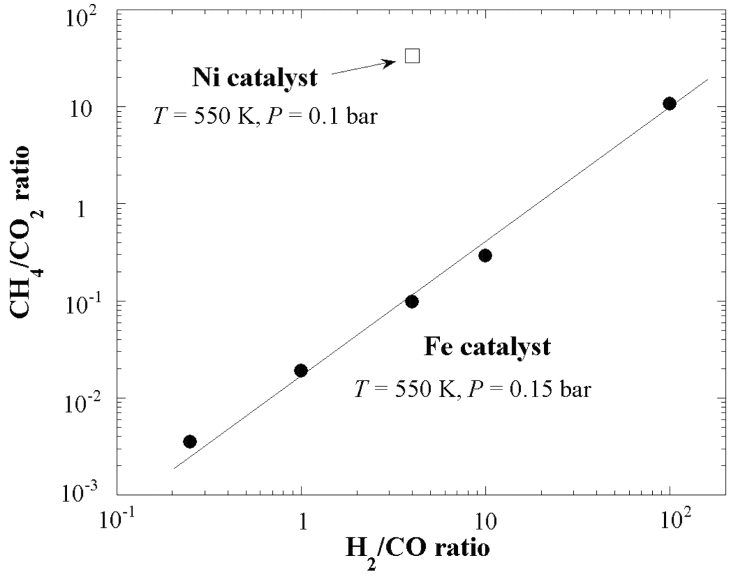

Fig. 3. The relationship between the production ratio of CH_4/CO_2 as a function of the initial H_2/CO ratio for iron (solid circles) and nickel catalysts (open square) ($H_2/CO = 4$, $T = 550$ K, and $P = 0.15$ bar for iron and $P = 0.1$ bar for nickel catalysts).

Because we followed the same experimental procedure used by Sekine et al. (2005), we describe it only briefly here. Prior to each measurement of reaction rate, the catalyst surface is cleaned with H_2 gas at T = 700 K and $P \sim 0.3$ bar for 1.5 hr. This pre-treatment ensures that oxides of iron, nickel, and the alloys are reduced to metal before the main experiment. After the pre-treatment of the catalysts, we introduce reactant gas mixtures to the reaction cell. After a prescribed length of time, a part of the gas in the reaction cell is extracted and analyzed with the GC and the QMS. We analyze the gas mixtures after 5–9 different reaction times for each experimental condition. The methane production increases linearly with time under a given reaction condition (see Fig. 2 of Sekine et al. 2005). The gradient of the fit line gives the methane formation rates (molecules/site/s) under the reaction conditions. In our experiments, we measure the methane formation rates before 10% of the initial amounts of CO are consumed by surface reactions. When we conduct a reaction experiment at high temperatures (>600 K), poisoning occurs. The poisoning is the gradual loss of catalytic activity by conversion of the surface carbide (C*) to unreactive graphitic carbon (G*) (e.g., Krebs et al. 1979). When the poisoning occurs on the surface of catalyst, the methane production decreases as reaction time. After equilibrium between C* and G* is achieved, the production rate approaches a steady state (e.g., Kress and Tielens 2001). In this study, we observed the poisoning at $T = 625$ K and $P < 8.7 \times 10^{-4}$ bar for the nickel catalyst and at $T = 625$ K and the entire range of pressure for the iron catalyst. When we observed the poisoning, we obtained the methane formation rate from the gradient of fitting line of methane production after the production proceeds in steady-state rate. This is because almost all the Fischer-Tropsch reaction in the solar nebula and impact phenomena proceeds at this steady-state rate.

RESULTS

In this section, we first compare the produced gas species between iron and nickel catalysts. Second, we compare the methane formation rates between the iron and the nickel catalysts as functions of H_2/CO ratio and pressure. The comparison reveals that there is a significant difference in catalytic properties between the iron and the nickel catalysts under planetary conditions. Third, we show the experimental results of the methane formation rate for the iron-nickel alloys and the relation among pure iron, pure nickel, and iron-nickel alloys at high and low H_2/CO ratios.

Comparison between Iron and Nickel Catalysts

Gas Species

In our experiments, CH_4, CO_2, C_2H_6, and C_2H_4 were observed as products of Fischer-Tropsch catalysis. In particular, CH_4 and CO_2 are the main products under the reaction conditions of this study. The production of CO_2 at lower H_2/CO ratio can be explained by disproportionation of CO gas on the surface of the iron catalyst ($2CO \rightarrow CO_2 + C^*$; Boudouard reaction) (e.g., Wentrcek et al. 1976). Figure 3 shows the relationship between the production of CH_4/CO_2 and H_2/CO ratio for iron catalyst at 1.5×10^{-1} bar and 550 K and also the result for nickel catalyst at 1.0×10^{-1} bar and 550 K. This result, shown in Fig. 3, suggests that CO_2 production becomes predominant at low H_2/CO ratios for iron

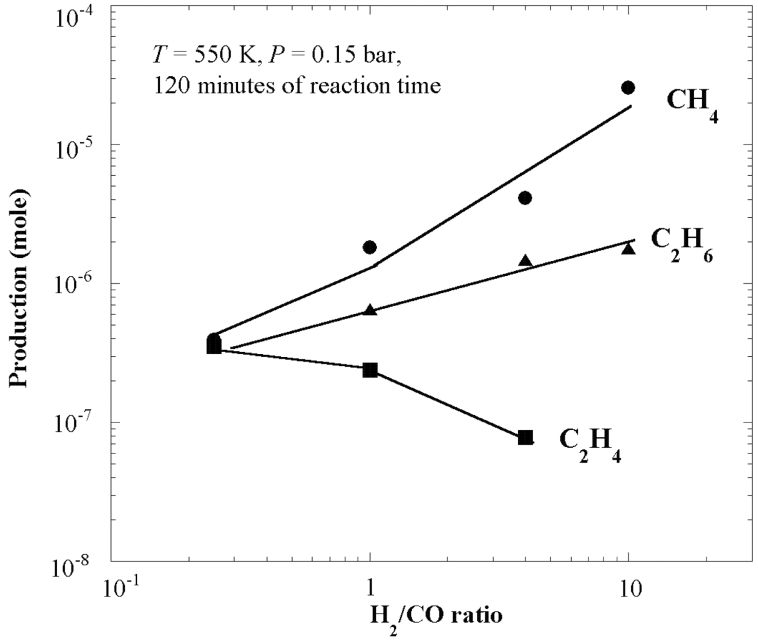

Fig. 4. The amount of hydrocarbons (CH_4 [circles], C_2H_4 [squares], and C_2H_6 [triangles]) produced using an iron catalyst as a function of H_2/CO ratio ($T = 550$ K, $P = 0.15$ bar, and 120 min of reaction time).

catalyst under these reaction conditions, while CH_4 production is predominant for nickel catalyst. The production ratio of CH_4/CO_2 for nickel catalyst is about 10^3 times that for iron catalyst at $H_2/CO = 4$. The reason for this difference in the product gas species is described below in the "Difference between Iron and Nickel Catalysts" section.

Both C_2H_4 and C_2H_6 as well as methane are observed for iron catalyst. However, the production of C_2H_4 and C_2H_6 are not observed for nickel catalyst; almost exclusively methane is formed. This is consistent with the results of previous study of nickel catalyst in industrial chemistry at higher pressures (Goodman et al. 1980). Figure 4 shows the abundance of hydrocarbons produced on the surface of an iron catalyst as a function of H_2/CO ratio. At lower H_2/CO ratios (<1), the production of C_2H_4 and C_2H_6 becomes comparable to that of methane. Figure 4 also indicates that lower H_2/CO ratios favor the formation of molecules with higher molecular weight for iron catalyst and also favor the formation of alkenes (such as C_2H_4) rather than that of alkanes (such as C_2H_6).

Methane Formation Rate

The effect of the H_2/CO ratio: Methane formation rates for iron and nickel catalysts as functions of H_2/CO ratio are shown in Fig. 5. We kept the pressure of reactant gas mixtures constant and changed the H_2/CO ratio of reactant gas mixtures. The experiments were done at 1.5×10^{-1} bar and 550 K for iron and at 2.0×10^{-3} bar and 550 K for nickel catalyst. For nickel catalyst, methane formation rate increases rapidly as the H_2/CO ratio increases from 0.25 to 4, but shows little change at higher H_2/CO ratios. Such a variation for nickel catalyst is reported for the methane formation rate on the (100) surface of nickel single crystal at 1.3×10^{-2} bar and 600 K (Goodman et al. 1980). Goodman et al. (1980) not only measured the methane formation rate but also observed the coverage of the surface carbon using Anger Electron Spectroscopy (AES). According to Goodman and coworkers (Goodman et al. 1980; Kelley and Goodman 1982), the methane formation rate is controlled by a delicate balance between carbon and hydrogen atoms adsorbed on the surface of the catalyst. At a given temperature, the concentration of surface hydrogen increases with hydrogen pressure until its saturation is achieved. Thus, the methane formation rate should increase with the concentration of hydrogen on the surface of the nickel catalyst. When the concentration of surface hydrogen reaches the saturation level, methane formation rate also reaches the maximum reaction rate. Further increase in the partial pressure of hydrogen in the reactant gas mixture leads to little change in methane formation rate. Thus, the data shown in Fig. 5 suggest that the surface hydrogen on the catalyst is saturated at H_2/CO ratios higher than 4 under this reaction condition.

However, the increase in methane formation rate for an iron catalyst as a function of H_2/CO ratio does not have a saturation point. Although there is no study observing the surface atom concentration similar to the case for nickel by Goodman et al. (1980), our results suggest that the hydrogen may not saturate on the surface of an iron catalyst even at a very high H_2/CO ratio (e.g., 1000).

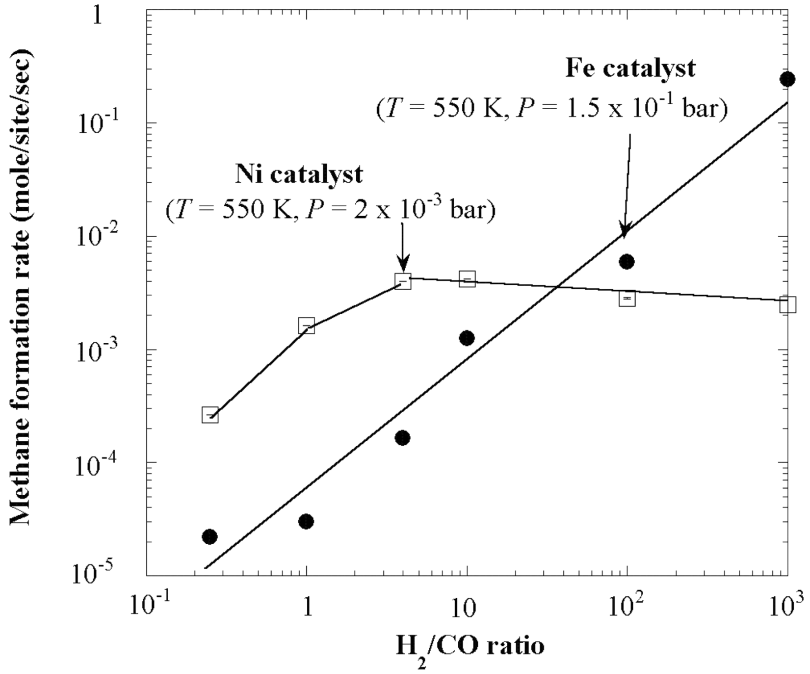

Fig. 5. Methane formation rates (molecules/site/s) for iron (solid circles) and nickel catalysts (open circles) as functions of H_2/CO ratio (T = 550 K and P = 0.15 bar for iron and $P = 2.0 \times 10^{-3}$ bar for nickel).

The effect of pressure: Figures 6 and 7 show methane formation rates for iron and nickel catalysts as functions of pressure. Figure 6 compares the data for two different H_2/CO ratios. The lower H_2/CO ratio (i.e., 4) simulates the reaction conditions in a cometary impact vapor cloud and the atmospheric re-entry of vapor condensate due to asteroidal impacts on early Earth, while the higher value (i.e., 1000) simulates nebular conditions. Figure 7 compares the pressure dependence of the formation rate for iron and nickel catalysts. Our data for nickel at T = 500 K and 625 K and H_2/CO = 4 show good agreement with those of Goodman et al. (1980).

Figure 6 shows that the methane formation rate for iron catalyst strongly depends on the H_2/CO ratio, while that for nickel depends little on the H_2/CO ratio. Thus, at the higher H_2/CO ratio (i.e., 1000), iron is a more efficient catalyst for methane formation than nickel, but the nickel catalyst is a more efficient catalyst than iron at lower H_2/CO ratios.

Figure 7 shows that the iron catalyst depends more strongly on pressure than the nickel catalyst. For the nickel catalyst, poisoning is not observed in the entire pressure range from 10^{-3}–10^{-1} bar, and the methane formation rate at 625 K is higher than that at 500 K. However, for the iron catalyst, poisoning occurs at 625 K over the entire pressure range. We use the poisoned steady-state reaction rate of methane production as its formation rate for the iron catalyst at 625 K. Thus, the methane formation rate at 625 K is not significantly higher than that at 500 K. The trend shown in Fig. 7 indicates that iron is affected more by poisoning than nickel. For a nickel catalyst, the dependence on pressure becomes larger at higher temperatures (Goodman et al. 1980). In particular, the methane formation rate for nickel depends little on pressure at 500 K. These experimental results indicate that the nickel catalyst becomes more important at lower pressures than the iron catalyst. Such a catalytic property is important in both solar nebula chemistry and the atmospheric re-entry of vapor condensate due to asteroidal impacts, because the reaction pressures of Fischer-Tropsch catalysis for these situations are much lower than 1 bar. The reason for this strong pressure dependence for the iron catalyst is also discussed in the "Difference between Iron and Nickel Catalysts" section below.

Figure 8 shows the methane formation rate for a nickel catalyst as a function of pressure at H_2/CO = 4 and T = 625 K. The gradient of the slope appears to be slightly larger at pressures lower than 10^{-3} bar. The reason for this is discussed below in the "Poisoning" section.

Iron-Nickel Alloy

In both solar and circumplanetary nebulae and in impact vapor clouds, metallic dust particles may not exist as pure iron or nickel but will be most likely to exist as iron-nickel alloys. Thus, the methane formation rate on the surfaces of iron-nickel alloys is very important. In this section, we show the methane formation rate for iron-nickel alloys and discuss the relationship among pure iron, pure nickel, and iron-nickel alloys in terms of catalytic methane formation efficiency.

Figure 9 shows the methane formation rate as a function of the molar iron ratio, Fe / (Fe + Ni), in the catalyst at 500 K and 0.31 bars (Fig. 9a) and 0.16 bars (Fig. 9b). The data

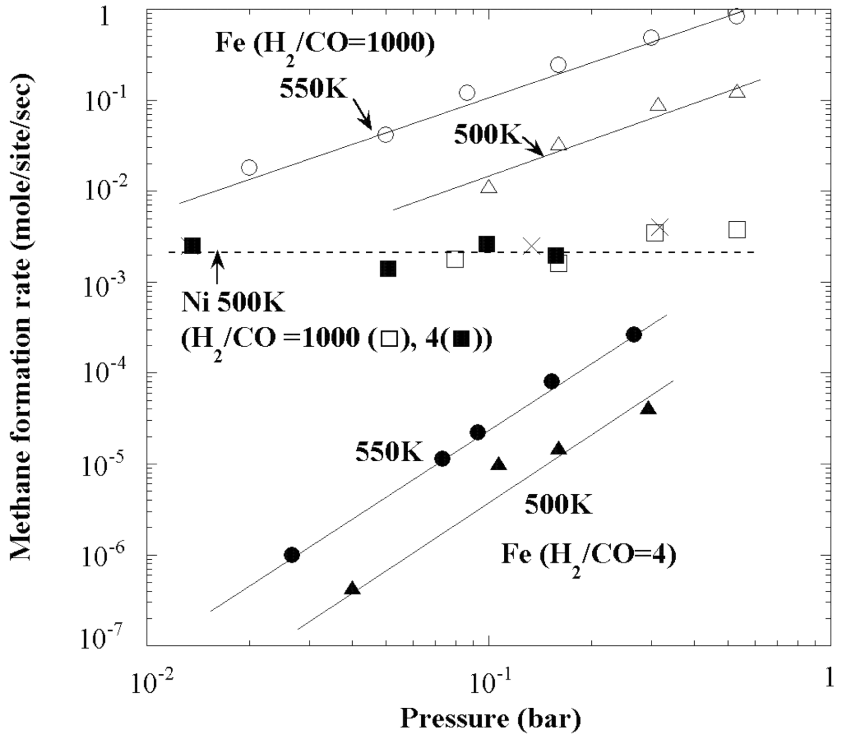

Fig. 6. Methane formation rate (molecules/site/s) as a function of pressure. Solid triangles and circles indicate results for an iron catalyst at $H_2/CO = 4$, and $T = 500$ K and 550 K, respectively. Open triangles and circles indicate the previous results for an iron catalyst at $H_2/CO = 1000$ and $T = 500$ K and 550 K, respectively (Sekine et al. 2005). Squares indicate results for a nickel catalyst at $T = 500$ K for $H_2/CO = 4$ (solid) and 1000 (open). Previous results for a nickel catalyst by Goodman et al. (1980) at $T = 503$ K and $H_2/CO = 4$ are also shown (crosses).

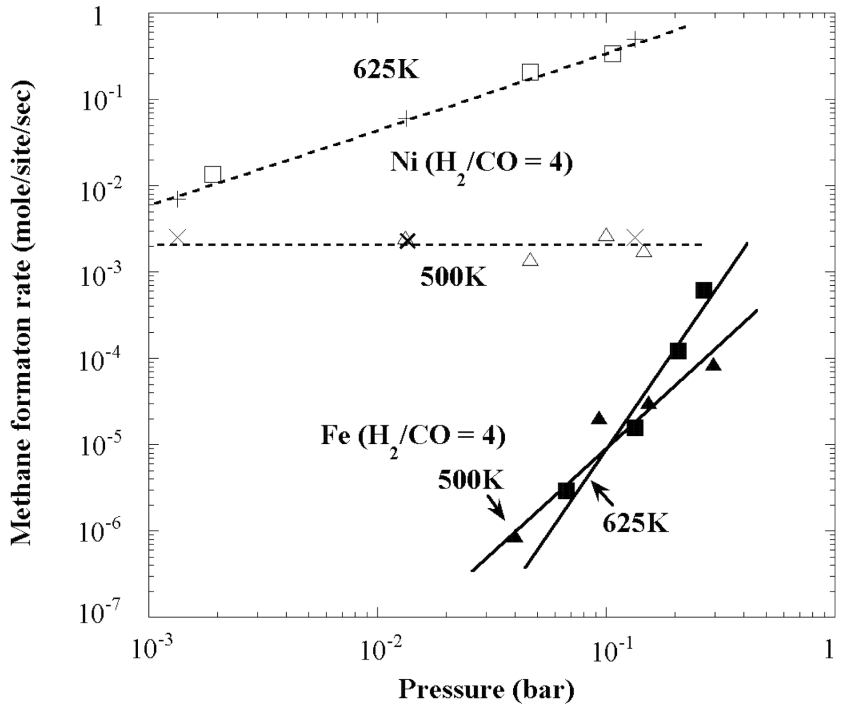

Fig. 7. A comparison of methane formation rate (molecules/site/s) as a function of pressure for an H_2/CO ratio of 4 between iron and nickel catalysts. Triangles are for iron (solid) and nickel (open) catalysts at $T = 500$ K. Squares are for iron (solid) and nickel (open) catalysts at $T = 625$ K. Previous results for a nickel catalyst at $T = 503$ K and 625 K by Goodman et al. (1980) are also shown (crosses).

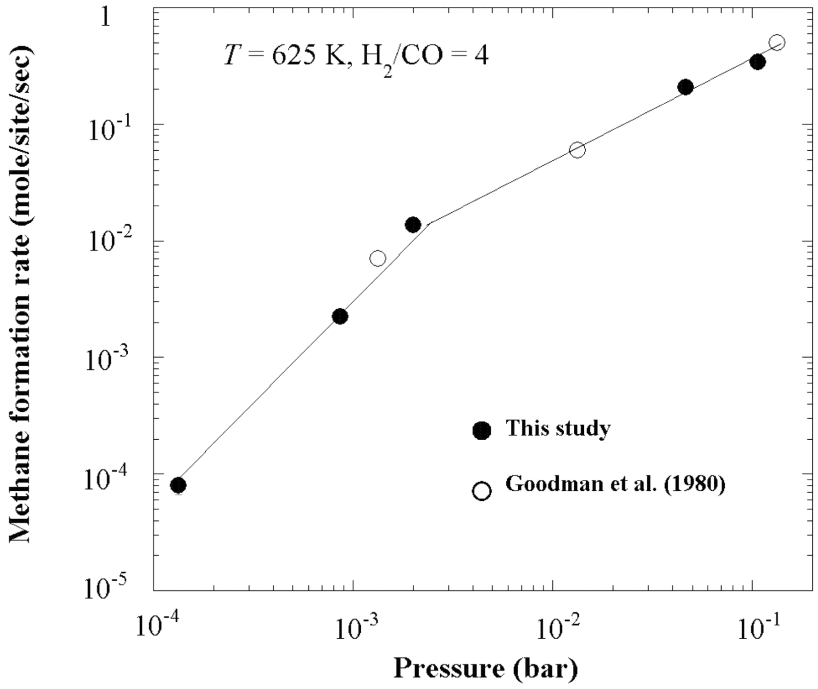

Fig. 8. Methane formation rate (molecules/site/s) for a nickel catalyst as a function of pressure ($H_2/CO = 4$ and $T = 625$ K). Solid and open circles are for data obtained in our study and those by Goodman et al. (1980), respectively.

shown in Fig. 9 indicate that the methane formation rate for iron-nickel alloys does not simply coincide with a linear interpolation of pure metals and that the real formation rate is lower than the linear interpolation line. However, it is important to note that methane formation rates for the alloys measured in this study are always between those for pure iron and pure nickel.

DISCUSSION

Difference between Iron and Nickel Catalysts

As shown in Fig. 3, the CH_4/CO_2 ratio in the product of Fischer-Tropsch catalysis is different for iron and nickel catalysts. CH_4 is the dominant product for the nickel catalyst, whereas CO_2 is dominant for the iron catalyst at $H_2/CO = 4$. Figure 7 shows that the methane formation rate for an iron catalyst depends strongly on pressure, but such dependence is much smaller for a nickel catalyst.

These differences between iron and nickel catalysts may result from the difference in the rate of disproportionation of CO on iron and nickel catalysts. Hydrogenation of surface carbide ($C^* + 4H^* \rightarrow CH_4$) removes carbides from surface sites and forms methane as a gas product. The disproportionation of CO ($2CO \rightarrow CO_2 + C^*$) supplies surface carbides and forms CO_2 as a gas product. Figure 10a shows a schematic diagram in which the disproportionation rate of CO (supply of carbide) is higher than the hydrogenation rate of C* (removal of carbide) on the surface of the catalyst. If this is the case, the concentration of surface carbide would be high and CO_2 gas would be a dominant product. However, if the hydrogenation rate of C* (removal of carbide) is higher than the disproportionation rate of CO (supply of carbide) on the surface of the catalyst (Fig. 10b), the main product will be methane and the concentration of surface carbon will be low. Our experimental data of gas products (Fig. 3) suggest that the catalytic reaction illustrated in Fig. 10a occurs more frequently on iron surfaces and that the reaction in Fig. 10b occurs more frequently on nickel surfaces.

According to AES observations of nickel catalysts by Goodman et al. (1980) and Kelley and Goodman (1982), a low concentration of surface nickel carbide induces efficient methane formation (see the "Methane Formation Rate" section). Jung and Thomson (1992) conduct dynamic X-ray diffraction observations of iron catalysts, which indicate that higher concentration of surface iron carbide induces lower catalytic activity for methane production. This is because the conversion of ε'-iron carbide ($Fe_{2.2}C$) to χ-iron carbide ($Fe_{2.5}C$) produces excess carbon on the surface ($2.5Fe_{2.2}C \rightarrow 2.2Fe_{2.5}C + 0.3C$). These carbons prevent efficient methane formation and act as nucleation sites for further carbon deposition via Boudouard reaction ($2CO \rightarrow CO_2 + C$). These previous studies are consistent with our discussion of the surface properties of iron and nickel catalysts illustrated in Fig. 10.

When the total pressure decreases, both the hydrogenation rate of C* and the disproportionation rate of

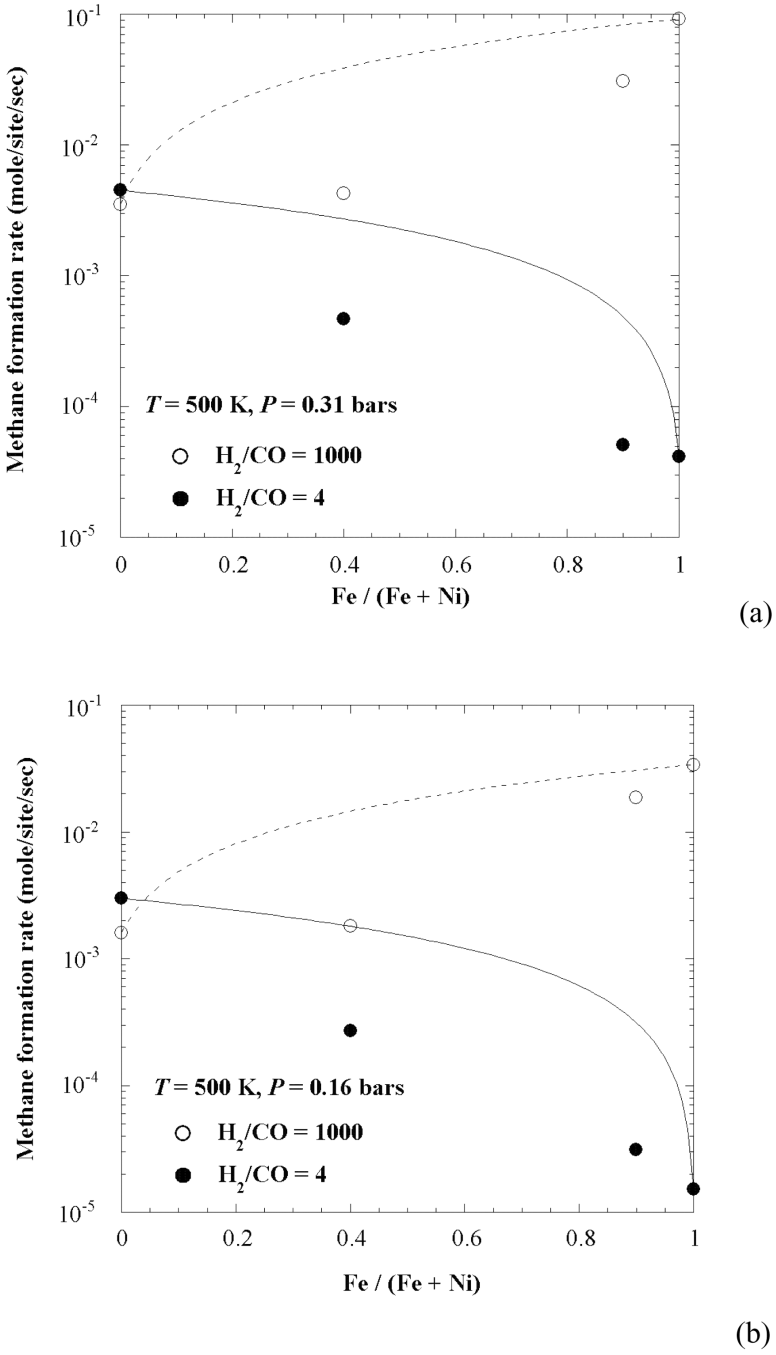

Fig. 9. Methane formation rate (molecules/site/s) as a function of the relative molar abundance of iron in an alloy catalyst (Fe/(Fe + Ni)) at 500 K. Two different pressures, 0.31 bars (a) and 0.16 bars (b), are used. The data at Fe/(Fe + Ni) = 0 and 1 are for pure nickel and iron, respectively. The solid and broken curves are the linear combinations of the data of pure iron and nickel at $H_2/CO = 4$ and 1000, respectively.

CO decrease. If the rate of decrease in the disproportionation rate of CO accompanying pressure decreases is lower than that of the hydrogenation rate of C*, the concentration of the surface carbide becomes higher at lower pressures. In this case, the methane formation rate will become lower at lower pressures, because the increase in surface carbon leads to a decrease in the methane formation rate. If this is the case, then the ratio of CH_4 to CO_2 will increase with pressure. Figure 11 shows the ratio of CH_4 production to that of CO_2 as a function of pressure. The results shown in Fig. 11 support the above hypothesis. The positive gradient observed in iron indicates that the ratio of CO_2 to CH_4 increases as pressure decreases. This result strongly suggests that the disproportionation of CO (supply of C*) proceeds more rapidly than the

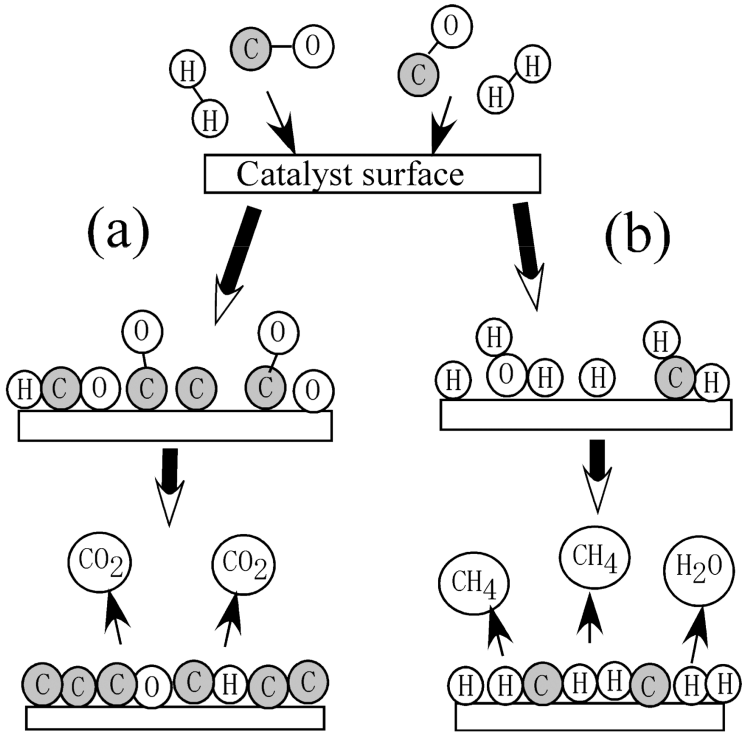

Fig. 10. A schematic diagram of the disproportionation of CO and the hydrogenation of C* on the surface of catalysts. a) When the hydrogenation rate of C* is lower than the disproportionation rate of CO, CO_2 becomes the dominant product and the surface is covered with carbon. b) When the hydrogenation rate of C* is higher than the disproportionation rate of CO, CH_4 becomes the dominant product. The concentration of surface H also becomes high.

hydrogenation of C* (removal of C*) as the pressure decreases on the surface of the iron catalyst. This process might increase the concentration of surface carbon and lead to the observed low methane formation rate at lower pressures for the iron catalyst. In contrast, the CH_4/CO_2 ratio for the nickel catalyst is higher at lower pressures. This suggests that the hydrogenation of C* on the surface of the nickel catalyst proceeds rapidly at lower pressures. This may account for the observed high methane formation rates at lower pressures for the nickel catalyst.

Poisoning

As shown in Fig. 8, we observed that the methane formation rate at 625 K for a nickel catalyst depends on pressure and that its dependence becomes slightly stronger at $P \leq 10^{-3}$ bar. This may be due to the effect of poisoning of the catalyst. At pressures higher than 1.3×10^{-3} bar, the production rate is constant throughout the experimental time; no poisoning are observed for this reaction period. However, at 1.3×10^{-4} bar and 8.7×10^{-4} bar, the production rate of CH_4 decreases as reaction time increases; poisoning occurs. As described above in the "Methane Formation Rate" section, nickel is affected less by poisoning than iron. However, this result indicates that the poisoning tends to occur at lower pressures ($P < 10^{-3}$ bar) and becomes an important reaction step in estimating methane production even for the nickel catalyst.

The reason why the poisoning tends to occur at lower pressures may be explained as follows: At 625 K, methane formation rate decreases as pressure increases, as shown in Fig. 8. According to Kelley and Goodman (1982), a decrease in the methane formation rate is caused by an increase in the concentration of surface carbide. When the concentration of carbide increases and methane formation becomes inefficient, the residence time of surface carbide becomes long. This long residence time may permit carbide converting into graphitic carbon on the surface of the catalyst (i.e., poisoning). Although this hypothesis is promising, more detailed experimental studies on the characterization of the surface of catalysts, such as total organic carbon (TOC) analysis, transmission electron microscopy (TEM), and X-ray diffraction (XRD) measurements, are needed before a decisive conclusion is made.

IMPLICATIONS FOR PLANETARY SCIENCE

Nebular Chemistry

The reaction conditions in the solar nebula at the temperature range from 400 to 700 K, where Fischer-Tropsch catalysis takes place efficiently, are estimated to have H_2/CO

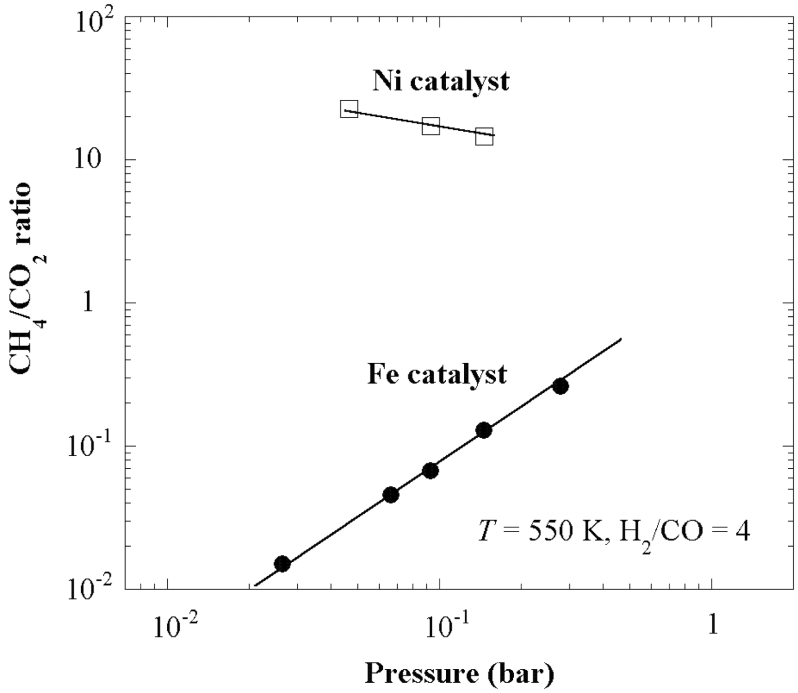

Fig. 11. The production ratios of CH_4/CO_2 for iron (solid circles) and nickel catalysts (open circles) as functions of pressure (H_2/CO = 4 and T = 550 K).

ratio ranging from 1000 to 1500 and pressure ranging from 10^{-6} to 10^{-4} bar (Anders and Grevesse 1989; Prinn 1993; Bell et al. 1997, 2000). Those for a circumplanetary subnebula are estimated to have similar H_2/CO ratios and pressures from 10^{-5} to 10 bars (Prinn and Fegley 1981, 1989; Coradini et al. 1989; Mousis et al. 2002; Mosqueira and Estrada 2003). We did not conduct experiments under all of these conditions in this study because some conditions are out of the range covered by our experimental systems. However, some implications of Fischer-Tropsch catalysis for nebular chemistry may be predicted based on the results of our experiments.

As shown in Fig. 6, we observed that iron might be a more effective catalyst for methane formation via Fisher-Tropsch catalysis under the conditions of a circumplanetary subnebula (i.e., a high H_2/CO such as 1000) than nickel. Subnebula chemistry, including methane production by iron catalysts, is already discussed in our previous study (Sekine et al. 2005).

Under the conditions of the solar nebula (i.e., lower pressures), the results of our experiments cannot directly determine which metal is the main catalyst in the Fischer-Tropsch reaction, because the methane formation rate for an iron catalyst has a stronger pressure dependence than for a nickel catalyst (Figs. 6 and 7). It is difficult to conduct experiments under true solar nebula conditions, such as at very low pressures (10^{-6}–10^{-5} bar) and long reaction times (10^{13} s, the life time of the solar nebula; see Prinn 1993).

For estimating methane production under the reaction conditions beyond the parameter range in our experiments, model calculations of the kinetics of Fischer-Tropsch catalysis are useful (e.g., Kress and Tielens 2001). According to the numerical results by Kress and Tielens (2001), the methane formation rate for an iron catalyst is calculated to be ~10^{-1} molecules/site/s at $P = 5 \times 10^{-4}$ bar, T = 500 K, and H_2/CO ~1430. However, Fig. 6 indicates that the methane formation rate is ~10^{-2} molecules/site/s at $P = 10^{-1}$ bar, T = 500 K, and H_2/CO = 1000. This result strongly suggests that the methane formation rate at 5×10^{-4} bar, at which Kress and Tielens (2001) calculate the methane formation rate, should be much lower than the theoretical prediction by Kress and Tielens (2001) because of the strong pressure dependence of the iron catalyst. This discrepancy between numerical results and laboratory data is caused by the difference in catalytic properties between iron and nickel at lower pressures. As described in the introduction, the laboratory data on the methane formation rate for iron catalysts had not been obtained at lower pressures (<1 bar), while those for nickel catalysts have been investigated (Goodman et al. 1980). Kress and Tielens (2001) model the methane formation rate for iron catalysts via Fischer-Tropsch catalysis based on industrial data at 1 bar (Krebs et al. 1979) and calculate the methane formation rate for an iron catalyst at lower pressures with the assumption that the pressure dependence of iron catalysts is the same as for nickel. Thus, the numerical results for an iron catalyst by Kress and Tielens (2001) depend weakly on pressure; they considerably overestimate the rate of methane formation by iron catalysts in the solar nebula.

For a more accurate estimate of methane production in the solar nebula, we need to understand the series of reaction steps that control the entire reaction on the surface of catalysts and what determines the differences between iron and nickel catalysts. Our laboratory data suggest that the reaction steps involved in the disproportionation of CO, the hydrogenation of C* and poisoning (see the "Discussion" section) determine the difference of catalytic properties between iron and nickel and are important for establishing the kinetic model of Fischer-Tropsch catalysis under planetary conditions. More laboratory data, such as in situ AES observations on the surface of individual iron catalysts, will be needed to develop such a kinetic model of Fischer-Tropsch catalysis.

Impact Phenomena

As discussed in the introduction, Fischer-Tropsch catalysis may play a key role in chemical reactions occurring in expanding impact vapor clouds and in the atmospheric re-entry of vapor condensate due to asteroidal impacts on early Earth (Anders et al. 1973; Gerasimov et al. 2000; Sekine et al. 2003; Kress and McKay 2004). Under conditions that might occur during the atmospheric re-entry of impact vapor condensate on the early Earth (H_2/CO = 0.03–10, $P = 10^{-4}$–10^{-2} bar) (Sekine et al. 2003), our experimental results suggest that metallic iron is not an effective catalyst because of its strong dependence on both pressure and H_2/CO ratio. These results reduce the methane production rate estimated by the theoretical calculation by Sekine et al. (2003), because their kinetic model is also based on the results of methane formation for an iron catalyst at 1 bar as Kress and Tielens (2001). However, when nickel exists in the impact phenomena as iron-nickel alloy and/or as pure nickel metal, then the methane formation rate does not decrease as drastically as for a pure iron catalyst. This is because the methane formation rate for nickel catalysts depends on pressure only very weakly at low H_2/CO ratio (Fig. 7). Figure 9 shows that the methane formation proceeds more efficiently on the surface of higher fraction of nickel in the iron-nickel alloy at H_2/CO = 4. This result strongly suggests that nickel may play an important role in the formation of methane in the atmospheric re-entry of impact vapor condensate.

Recently Hill and Nuth (2003) conducted Fischer-Tropsch catalytic experiments simulating the reaction in the solar nebula. They report that CN-bearing gas species, such as acetonitrile (CH_3CN), were formed from H_2, CO, and N_2 gas mixtures on the surfaces of iron silicate dust. Such production of CN-bearing gas species via Fischer-Tropsch catalysis also may have taken place during the atmospheric re-entry of impact condensate on the early Earth. Hashimoto and Abe (1995) calculate the atmospheric composition of Earth in the accretion stage, which indicates that a hydrogen-rich atmosphere has been formed. Recently, Tian et al. (2005) re-estimated the escape rate of hydrogen from Earth's early atmosphere. Their results indicate that the balance between the low hydrogen escape and volcanic outgassing could have maintained a hydrogen mixing ratio of more than 30%. These studies suggest that H_2 may have been one of the main gas species of Earth's early atmosphere, in addition to N_2, CO_2, and CO proposed by previous photochemical model (e.g., Kasting 1990). In order to assess more precisely the role of the condensate during the re-entry process as a source of prebiotic molecules important for the origin of life, however, we need to conduct experiments with initial gas mixtures containing N_2 and measure the formation rate of CN-bonded and other gas products on the surfaces of iron-nickel alloy particles at lower pressures.

In cometary impacts onto planets/satellites with thick atmospheres (Kress and McKay 2004), the catalysis will occur at relatively high pressures (~1 bar) compared to that for atmospheric re-entry of impact condensate. Under such conditions, both iron and nickel catalysts are efficient in promoting the Fischer-Tropsch reaction (Fig. 7). The H_2/CO ratio in cometary impact vapor is estimated to be low (i.e., ~1–10) (Kress and McKay 2004). Our experimental data in Fig. 4 show that the production of higher hydrocarbon, such as C_2H_4 and C_2H_6, becomes comparable to the methane production at lower H_2/CO ratio. Since such higher hydrocarbons may have played an important role in the abiotic Earth after an impact, the formation rate of such higher hydrocarbons need to be studied more extensively as well.

SUMMARY

We measured the methane formation rate and analyzed the gas products via Fischer-Tropsch catalysis for iron and nickel catalysts. We compared the properties of these catalysts and investigated the relationship among pure iron, pure nickel, and iron-nickel alloys. We conducted experiments over a wide range of H_2/CO ratio and pressures lower than 1 bar, where the data on Fischer-Tropsch catalysis is important in planetary science. We can summarize our experimental results as follows:

1. The production ratio of CH_4/CO_2 is significantly different between iron and nickel catalysts. The CH_4/CO_2 ratio in the products is much higher for nickel catalysts (CH_4 dominant) than that for iron catalysts (CO_2 dominant) at H_2/CO = 4.
2. The methane formation rate for iron catalysts increases monotonically with H_2/CO ratio, whereas that for nickel saturates at H_2/CO = 4.
3. The methane formation rate for iron catalysts depends more strongly on pressure than for nickel catalysts. The methane formation rate for iron catalysts drastically decreases as pressure decreases.
4. The reason for the strong pressure dependence of iron catalysts may be due to the change in concentration of

surface carbide produced by the disproportionation of CO. The disproportionation of CO on the surfaces of iron catalysts may proceed more rapidly than does the hydrogenation of surface carbide at lower pressures.

5. For nickel catalysts, no poisoning can be observed at higher pressures ($P > 10^{-3}$ bar), but a significant rate of poisoning is observed at lower pressures.
6. The methane formation rate for iron-nickel alloy departs considerably from the linear interpolation line of data for pure iron and pure nickel metals, but is always found between the formation rates for pure iron and nickel catalysts.

Our experimental results suggest that the catalytic property of nickel becomes important under the reaction conditions formed in the atmospheric re-entry of vapor condensates due to asteroidal impacts on the early Earth, while iron is efficient in a circumplanetary subnebula. Under conditions with low H_2/CO ratios (<10), such as in a cometary impact vapor cloud, our data also suggest that a large amount of C_2H_4 and C_2H_6 can be produced via Fischer-Tropsch catalysis. Thus, such larger hydrocarbons may be supplied to the prebiotic Earth due to impacts. Our data also suggest that the previous numerical studies (Kress and Tielens 2001; Sekine et al. 2003) overestimate the methane formation rate in the solar nebula and during the atmospheric re-entry of impact condensate. This is because the laboratory data concerning the methane formation rate for iron catalysts had not been obtained at lower pressures and they assumed that the pressure dependence for the methane formation rate for iron catalysts is same as that for nickel.

Our results suggest further that the three reaction steps concerning 1) the disproportionation rate of CO; 2) the hydrogenation rate of surface carbon; and 3) the poisoning rate of the catalyst determine the overall difference in the catalytic properties of iron and nickel. Furthermore, these three factors are important for establishing a kinetic model of Fischer-Tropsch catalysis under planetary conditions.

Acknowledgments–Y. Sekine thanks Takehiko Sasaki and Yoshimichi Namai for valuable discussions on the experiments. We greatly thank Joseph A. Nuth III and anonymous reviewer for their careful reviews and constructive comments. This research is partially supported by a Grant in Aid from Japan Society for the Promotion.

Editorial Handling—Dr. Scott Sanford

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