Experimental Study on Fischer-Tropsch Catalysis in the Circum-Saturnian Subnebula.
Y. Sekine[1], S. Sugita[1], T. Shido[2], T. Kadono[3], T. Matsui[4], T. Yamamoto[2], and Y. Iwasawa[2], [1] Dept. of Earth and Planetary Sci., Univ. of Tokyo, Bunkyo, Tokyo 113-0033, Japan, [2] Dept. of Chemistry, Univ. of Tokyo, Bunkyo, Tokyo 113-0033, Japan, [3] Institute for Frontier Research on Earth Evolution, Yokosuka, Kanagawa 237-0061, Japan, [4] Dept. of Complexity Sci. and Engineering, Univ. of Tokyo, Bunkyo, Tokyo 113-0033, Japan

1. Introduction: Fischer-Tropsch catalysis, which converts CO and H_2 into CH_4 on the surface of iron catalyst, has been suggested to play an important role in origin of CH_4 in the Titan atmosphere [1]. In the previous study [1], the methane formation rate due to this catalysis has been estimated by extrapolating an empirical power-law rate based on industrial laboratory data [2]. However the experimental conditions of laboratory data are limited to narrow temperature range ($T = 513 – 553$ K), fixed pressure ($P = 1$ bar), and low and narrow H_2/CO ratio ($H_2/CO = 0.6 – 15.1$), substantially different from the nebula condition. In this study, we conduct Fischer-Tropsch catalytic experiments under the conditions of the circum-planetary subnebula ($P = 0.09 – 0.53$ bar, $T = 500 – 650$ K, $H_2/CO = 1000$). Then, using this experimental result, we discuss the origin of CH_4 on Titan.

2. Experimental Results: We used iron powder as catalyst because it is much more abundant in the solar composition than other catalysts [3]. Our experimental setup is the closed-loop system. Prior to the measurement of catalytic reaction rate, the catalyst surface is cleaned with H_2 gas at $T = 700$ K and $P \sim 0.3$ bar for 1.5 hours. This pretreatment ensures that oxide iron is reduced to metallic iron before the main experiment. Next, we introduced reactant gas mixture to the reaction cell. After an arbitrary length of time, a part of the gas in the cell is taken out and analyzed by a gas chromatograph.

Figure 1 shows the methane formation rate as a function of temperature. At temperatures lower than 550 K ($1000/T > 1.82$), the methane formation rates increase exponentially as temperature rises. These temperatures are near the temperature of industrial laboratory data [2] ($T = 513 – 553$ K). We also show the extrapolated results of the empirical power law used in the previous work [1] in Fig. 1 (dotted lines).

Comparing our experimental data (solid lines) with the extrapolated results of empirical law (dotted lines), the absolute quantities of our experimental results are $10 – 30$ times larger than the extrapolated results of empirical power law at this temperature range. This may be caused by the difference in H_2/CO ratio of the reactant gas. These results suggest that the methane formation rates

estimated by the empirical power law may significantly underestimate the production in these conditions in the circum-planetary subnebula.

At temperatures higher than 550 K ($1000/T < 1.82$), methane formation rates decrease as temperature rises. This may be caused by "poisoning" of the catalyst. The poisoning is the gradual loss of catalyst activity by conversion of the surface carbide to unreactive graphite [4]. When poisoning occurs on the surface of catalyst, the slope of the methane production decreases gradually with time. To demonstrate this possibility, we show the methane production as a function of reaction time at $T = 600$ and 650 K in Fig. 2. Comparison between the results at the temperature of 600 K and 650 K indicate that the effect of poisoning may be larger at the higher temperature. After gradual decrease, methane formation rate approaches a steady-state in $1 \times 10^4 – 2 \times 10^4$ sec. Because the methane formation rate in Fig. 1 is the steady-state rate, the methane formation rate decreases as temperature rises above ~ 550 K.

These experimental results suggest that the methane production due to Fischer-Tropsch catalysis in the circum-planetary subnebula does not simply increase as temperature rises predicted by the previous work [1]. Our experimental results show that it proceeds most efficiently in a narrow region of the temperatures around 550 K.

Using this experimental result, we estimate the time scale of the conversion of CO into CH_4 in the circum-planetary subnebula. We assume that about 10 % of a cosmic component of Fe was present as metal in the accretion disk [5], and the particles were spherical and $r = 0.1 - 1$ μm. The number of density of CO is given by the solar composition [3]. Then, the CO in the region of the subnebula where $T \sim 550$ K will be converted into CH_4 in $\sim 10^5 – 10^6$ seconds.

3. Implications for Titan: We now focus on the implications for the current composition of Titan. In the previous study on the circum-planetary subnebulae [1], CH_4-rich subnebulae were thought to have formed based on the assumption that the subnebular gases were transferred outward by the strong turbulence. However, a recent observation by Galileo spacecraft suggests that Callisto may contain the preexisting CO_2-rich material in the

subsurface [6]. This result suggests that the circum-planetary subnebulae may not have been well mixed and CH_4-rich. In this study, we assume that the radial mixing of the gases was not efficiently in the circum-Saturnian subnebula. Then, the subnebular gas composition varies depending on the radial distance from the gas planet.

For investigating the volatile compositions incorporated in the satellitesimals formed in the circum-Saturnian subnebula, we calculate clathrate hydrate formation using the theory given by [7].

The calculation results show that there may be three different regions in the circum-Saturnian subnebula. (1) In the CH_4-rich subnebular gas region, where Fischer-Tropsch catalysis may proceed efficiently, our result indicates that CH_4-rich clathrate is formed. Figure 3 (a) shows the results of abundance of volatiles incorporated in clathrate relative to the amount of CH_4 incorporated. Such CH_4-rich satellitesimals may be suitable for Titan with a CH_4-rich atmosphere. (2) Outside this region of the circum-Saturnian subnebula, we assume that the gas composition is the same as that of the solar nebula. Recent observations of molecular clouds [8] and theoretical calculation of ionization reactions [9] suggest that CO_2 and CH_4 are present in the solar nebula in addition to CO. Figure 3 (b) shows that the abundance of volatiles incorporated in clathrate relative to the amount of CO_2 incorporated for a subnebular gas composition $CO:CO_2:CH_4 = 5:5:1$. Our calculation results suggest that CO_2-rich solids are formed in the outer region of the circum-Saturnian subnebula. (3) In the further inner region, clathrate may not be formed because of the high subnebular temperature.

4. Conclusions: The results of this study suggest that the CH_4 production may proceed efficiently in a narrow region around $T \sim 550$ K in the circum-Saturnian subnebula. The conversion of CO into CH_4 in this region may proceed in a short time ($\sim 10^5 - 10^6$ sec.). This result suggests that the chemical composition of volatiles in satellitesimals may be quite different depending on the radial distance from the gas planet. For the present state of Titan with CH_4-rich atmosphere, Titan may be formed at an opportune distance from the planet in the circum-Saturnian subnebula.

Refferences: [1] Prinn R. G., and B. Fegley Jr., in *Origin and Evolution of Planetary and Satellite Atmosphere*, Univ. of Arizona Press, 78 – 136, 1989, [2] Vannice, M. A., *Journal of Catalysis*, *37*, 449 – 461, 462 – 473, 1975, [3] Anders, E., and N. Grevesse, *Geochim. Cosmochim. Acta*, *53*, 197 – 214, 1989, [4] Krebs, H. J. et al. *Surf. Sci.*, *99*, 570 – 580, 1979, [5] Pollack, J. B. et al. *Astrophys. J.*, *421*, 615 – 639, 1994, [6] Hibbitts, C. A. et al. *J. Geophys. Res.* **107**, E10, 5084, 14-1 – 14-12 2002, [7] Lunine, J. I., and D. J. Stevenson, *Astrophys. J. Suppl.* **58**, 493 – 531 1985, [8] Gibb, E. L. et al. *Astrophys. J.* **536**, 347 – 356 2000, [9] Aikawa, Y. et al. *Astrophys. J.* **519**, 705 – 725 1999
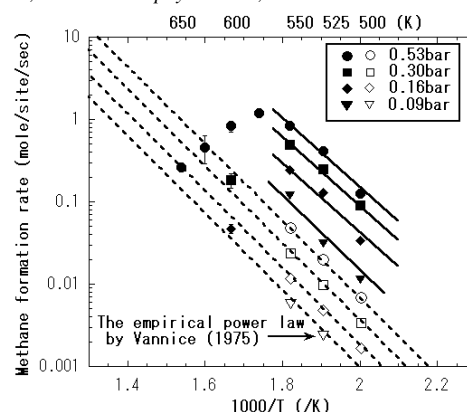

Figure 1. Methane formation rate as a function of temperature. The solid circles, squares, diamonds, and triangles indicate our experimental results at $P = 0.53$, 0.30, 0.16 and 0.09 bar, respectively. The open circles, squares, rhombuses, and triangles indicate the results derived from the empirical power law [2].
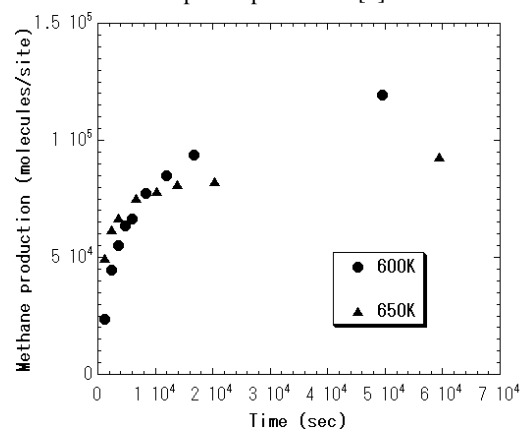

Figure 2. Methane production per surface site as a function of reaction time at different temperatures. ($T = 600$ (solid circles) and 650 K (solid triangles)).
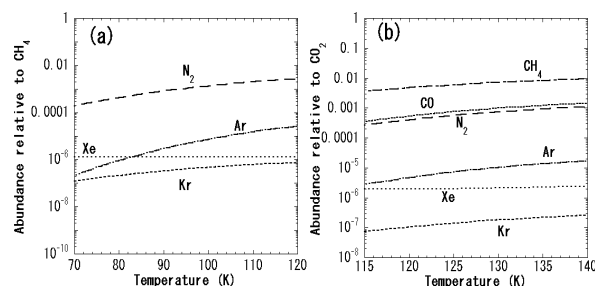

Figure 3. Abundance of volatiles incorporated in clathrate relative to (a) the amount of CO_2, and (b) the amount of CH_4 incorporated as a function of temperature. Note that CO_2 form in solid ice phase at temperatures lower than 115 – 120 K. This prevents CO_2 from being incorporated in a clathrate phase.