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Infrared chemiluminescence study of CO produced by partial oxidation of butane on platinum

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The selective formation of CO and H_2 was observed by a molecular-beam catalytic reaction between n-C_4H_{10} and O_2 on a Pt surface from around 1000 to 1500 K. The infrared emission of the product CO desorbed from the surface showed that the CO molecules are vibrationally substantially excited but rotationally very cool (rotational temperature; $T_R = 360$ K). The present molecular-beam study showed that CO and H_2 were formed directly from the hydrocarbon and O_2 without involving formation of CO_2 and H_2O as primary products. The implications of these results are discussed for the partial oxidation of methane (and other alkanes) to synthesis gas using practical supported metal catalysts.

Keywords: Infrared chemiluminescence; molecular beam; partial oxidation; synthesis gas; infrared emission; vibrational excitation; rotational cooling

1. Introduction

The partial oxidation of methane (and the other alkanes such as propane) to synthesis gas ($CO+H_2$) over supported metal (Pt, Ru, Ir, Ni, and Rh) catalysts has recently attracted much attention in several catalytic research groups [1–7]. It has been suggested that the partial oxidation process over these metal catalysts involves a series of steps including the complete oxidation of the hydrocarbon to CO_2 and H_2O followed by the steam and carbon dioxide reforming reactions as well as the reverse water–gas shift reaction (the indirect mechanism) [3–5].

We have recently applied the molecular beam/infrared emission technique [8] to study the partial oxidation of the hydrocarbons, and observed the direct production of CO and H_2 (without the formation of CO_2 and H_2O) on a Pt surface. Moreover, the infrared emission spectra of the product CO desorbed from the Pt surface have been studied to elucidate the mechanism of the partial oxidation reaction [9]. The infrared chemiluminescence of the nascent product molecules can give us the information on the dynamics of surface-catalyzed reactions [8,10]. The

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CO oxidation on Pt and Pd surfaces is one of the most-studied surface-catalyzed reactions, and the information on the vibrational and rotational states of the product CO_2 have been obtained by this technique [8,10,11]. However, few experiments for the other catalytic systems have been reported so far.

In this letter, some aspects of the partial oxidation reaction of *n*-butane using molecular beams, in particular, the temperature dependence of the reaction rate, the effect of the O_2/n-butane ratio on the selectivity, and the rotational state distributions of the product CO molecules, will be reported. The implications of these results for the partial oxidation process using supported metal catalysts will be discussed.

2. Experimental

A molecular beam apparatus with a combination of an FT-IR spectrometer similar to the previous system [8] is used to measure infrared emission spectra of product molecules just desorbed from a Pt foil [12]. The foil was heated resistively up to 1500 K as measured by a thermocouple spotwelded to the back and was checked with an optical pyrometer. The flow rates of *n*-butane (C_4H_{10}) and O_2 were controlled and monitored by mass flow controllers. Typically the flux of the molecular beam of C_4H_{10} or O_2 was about 6×10^{18} molecules/cm^2 s when the flow rate was 30 STP cm^3/min. The Pt surface was pretreated at 1500 K by the O_2 beam (30 STP cm^3/min), and the infrared emission spectra of CO were measured during the $C_4H_{10} + O_2$ reaction on Pt by an FT-IR spectrometer (1 or 4 cm^{-1} resolution) equipped with an MCT detector. The amounts of both reactants and products were analyzed by a mass spectrometer [12].

3. Results and discussion

Fig. 1 shows the butane conversion to CO as a function of surface temperature when the $O_2 : C_4H_{10}$ ratio was 2 : 1. The production of CO and H_2 was observed at higher temperatures (above 1000 K). At this condition, no CO_2 was produced over the temperature range studied. A very small amount of H_2O was also observed, but no quantitative analysis of H_2O or H_2 was performed because of a large background of these molecules in the vacuum chamber. As shown in table 1, CO_2 was produced at the higher O_2/C_4H_{10} ratio, although the main product is CO at all the experimental conditions. These results showed that the partial selective oxidation of butane to synthesis gas ($CO+H_2$) occurred on the Pt surface.

Fig. 2 shows infrared emission spectra taken with 4 cm^{-1} resolution during the reaction at 1500 K. The emission spectra of the product CO centered at 2143 cm^{-1} were seen at all the conditions. The CO_2 emission spectrum at around 2300–2350 cm^{-1} was also observed when the O_2/C_4H_{10} ratio was higher (fig. 2a). Fig. 3 shows

Table 1
Effect of the O_2/C_4H_{10} ratio on the partial oxidation of *n*-butane on Pt at 1500 K. The O_2 flow rate was 80 STP cm^3/min

$O_2 : C_4H_{10}$	C_4H_{10} conversion (%)	Formation rate (STP cm^3/min)	
		CO	CO_2
8 : 1	19.6	5.8	2.0
4 : 1	15.6	12.3	0.2
8 : 3	14.7	17.6	0
2 : 1	12.1	19.4	0

an emission spectrum, taken at 1 cm^{-1} resolution, of the product CO generated by the partial oxidation of C_4H_{10} on Pt at 1500 K. The rotational lines (P and R branches) for the $v = 1$ to $v = 0$ transitions are clearly resolved. The other lines for the $v = 2$ to $v = 1$ etc. may also be identified, but the higher resolution measurements will be needed to analyze the vibrational states of CO in detail. By assuming a Boltzmann distribution of the vibrational levels, a vibrational temperature (T_v) of $\approx$ 2600 K was estimated from the integrated intensity of the CO emission spectrum [13]. This result suggests that the CO molecules produced by the partial oxidation reaction are substantially vibrationally excited beyond thermal equilibrium with the surface (surface temperature $T_s = 1500$ K).

Fig. 4 shows a semilog plot of the rotational line intensities against the energy contents of the rotational levels. The straight line result indicates a Boltzmann dis-

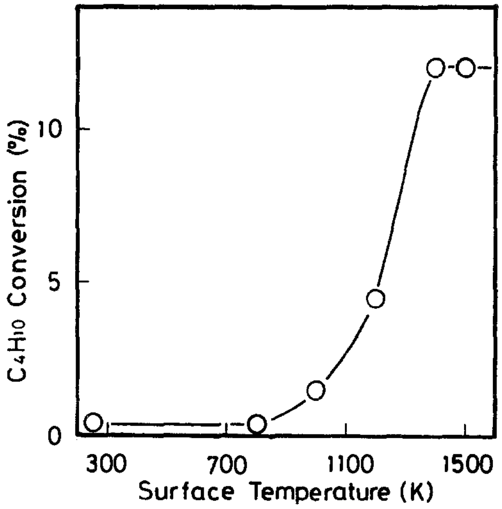

Fig. 1. Effect of surface temperature on the C_4H_{10} conversion to CO for the partial oxidation reaction on Pt. The C_4H_{10} flow rate was 40 STP cm^3/min, and the O_2/C_4H_{10} ratio was 2.

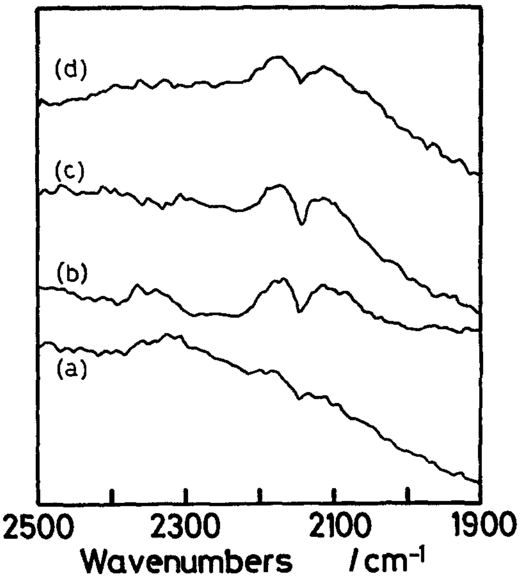

Fig. 2. Infrared emission spectra of CO and CO_2 produced by the butane oxidation on Pt at 1500 K. The O_2 : C_4H_{10} ratio; (a) 8 : 1, (b) 4 : 1, (c) 8 : 3, (d) 2 : 1. The O_2 flow rate was 80 STP cm^3/min, and the spectral resolution was 4 cm^{-1}.

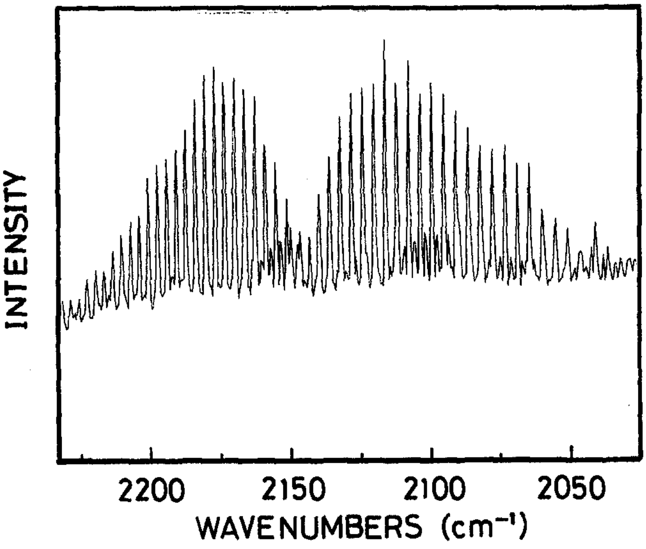

Fig. 3. Infrared emission spectrum of CO produced by the partial oxidation of *n*-butane on Pt at 1500 K. The spectral resolution was 1 cm^{-1}. The C_4H_{10} flow rate was 30 STP cm^3/min, and the O_2 : C_4H_{10} ratio was 1 : 1.

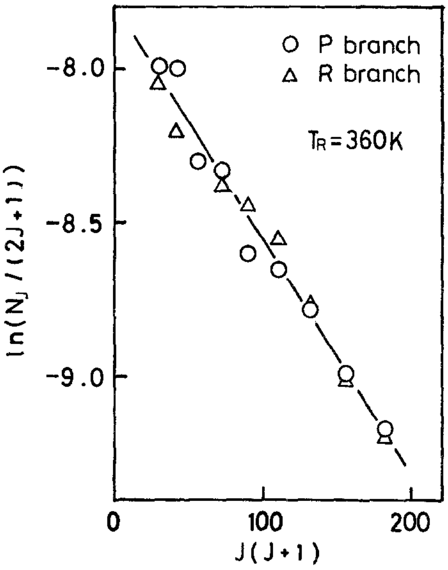

Fig. 4. Rotational state distributions of the P and R branches from the emission spectrum of CO in fig. 3: relative state populations $\ln[N_J/(2J+1)]$ plotted as a function of $J(J+1)$.

tribution, and a rotational temperature (T_R) of 360 K was estimated from the slope of the line. The T_R value is far below the surface temperature ($T_s = 1500$ K). The low T_R value was not due to the rotational relaxation by the gas phase collision [12,13], but the product CO molecules were desorbed without being thermally accommodated to the surface (rotational cooling). It should be noted that the rotational cooling phenomena have been found in NO scattering experiments [14,15], in which rotational temperature (T_R) of scattered NO molecules is significantly lower than surface temperature (T_s). This work shows the first result on the rotational cooling of CO formed by catalytic reactions.

The first crucial step in the partial oxidation process should be the dissociative adsorption of the hydrocarbon on the Pt surface. Our molecular-beam experiments [9] showed that almost no product was observed on Pt at the temperature range studied (300–1500 K) by the oxidation reaction of methane probably because the dissociative sticking probability of CH_4 is very small [16,17]. The dissociative sticking probability of C_4H_{10} may be significantly higher than that of CH_4. However, the higher T_s (above 1000 K) was needed to get a considerable C_4H_{10} conversion (fig. 1). The result may be in qualitative agreement with that of Sault and Goodman [18] who observed the increase in the dissociative sticking coefficient (s_0) of n-C_4H_{10} with increasing surface temperature of Ni(100). However, the decrease of s_0 with increasing surface temperature was also observed in a n-C_4H_{10}/Ir(110) system [19]. More detailed studies on the dissociative chemisorption of the alkanes will be required for the understanding of both the precursor-mediated dissociation and the direct collisional activation [20].

The final step in the partial oxidation process may be the reaction between C_{ad} and O_{ad} on the Pt surface since similar results on the vibrational and rotational states (high T_V and low T_R values) of the product CO have been obtained for the partial oxidation reactions of propane and isobutane [9]. The CO molecules formed by the direct reaction between C_{ad} and O_{ad} are desorbed from the surface into the gas phase without being thermally accommodated, and vibrationally substantially excited but rotationally very cool ($T_R = 360$ K). As the O_2/C_4H_{10} ratio was increased, the surface coverage of O_{ad} may be increased, which would result in the increase of the reaction probability between O_{ad} and CO_{ad} to form CO_2.

In this study, we have used molecular beams of the hydrocarbon and O_2 reacting on the Pt surface, and suggested that the direct formation of CO and H_2 is possible if the experimental conditions are met properly (a high dissociative sticking probability of the hydrocarbon and a low surface oxygen coverage etc.). In practical catalysts using the supported metals [1–7], however, CO and H_2 were formed via H_2O and CO_2; i.e. the reaction pathway involves an initial conversion of some methane (or propane etc.) to CO_2 and steam, followed by a sequence of the steam reforming and reverse water–gas shift reactions etc. (the indirect mechanism). It should be noted here that the dissociative chemisorption of methane occurs substantially in practical catalyst systems because of higher partial pressures of CH_4 (the pressure gap) [17,21]. In the indirect mechanism, because the highly endothermic reactions (the steam reforming of methane etc.) are involved in the reaction pathway, higher reaction temperatures (e.g., above 1000 K) would be required to achieve almost 100% conversion [1–6]. However, the overall reaction for the partial oxidation process is mildly exothermic, and the equilibrium conversion is almost 100% over a wide range of reaction temperature. Therefore, the direct formation of CO and H_2 from the hydrocarbon and O_2 may be feasible even at the lower reaction temperatures, if a good catalyst system is developed [22], although the indirect mechanism including the complete oxidation to CO_2 and H_2O (the highly exothermic reaction) is very likely prevailing on the usual supported metal catalysts. In practice, more extensive studies on the catalyst research and development as well as the detailed process engineering will be required for a practical use of the partial selective oxidation process.

Note added in proof

After the submission of this paper, a study of low-temperature selective oxidation of methane to syngas over a NiO–CaO catalyst even below 973 K was published [22]. They claimed that syngas is formed on the catalyst with extremely high space-time-yield directly from methane without involving formation of CO_2 and H_2O as primary products quite unlike the indirect mechanism.

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References

[1] A.T. Ashcroft, A.K. Cheetham, J.S. Foord, M.L.H. Green, C.P. Grey, A.J. Murrell and P.D.F. Vernon, Nature 344 (1990) 319.
[2] P.D.F. Vernon, M.L.H. Green, A.K. Cheetham and A.T. Ashcroft, Catal. Lett. 6 (1990) 181.
[3] J. Barbier Jr. and D. Duprez, Appl. Catal. A85 (1992) 89.
[4] K. Kunimori, S. Umeda, J. Nakamura and T. Uchijima, Bull. Chem. Soc. Japan 65 (1992) 2562.
[5] J. Nakamura, S. Umeda, K. Kubushiro, K. Kunimori and T. Uchijima, J. Petroleum Soc. Japan, in press.
[6] D. Dissanayake, M.P. Rosynek, K.C.C. Kharas and J.H. Lunsford, J. Catal. 132 (1991) 117.
[7] R.H. Jones, A.T. Ashcroft, D. Waller, A.K. Cheetham and J.M. Thomas, Catal. Lett. 8 (1991) 169.
[8] D.A. Mantell, K. Kunimori, S.B. Ryali, G.L. Haller and J.B. Fenn, Surf. Sci. 172 (1986) 281.
[9] K. Kunimori, H. Uetsuka and T. Iwade, to be published.
[10] K. Kunimori and G.L. Haller, Bull. Chem. Soc. Japan 65 (1992) 2450.
[11] G.W. Coulston and G.L. Haller, J. Chem. Phys. 95 (1991) 6932.
[12] K. Kunimori, T. Watanabe and S. Ito, J. Surf. Sci. Soc. Japan 12 (1991) 635.
[13] K. Kunimori, H. Uetsuka, T. Iwade, T. Watanabe and S. Ito, Surf. Sci. 283 (1993) 58.
[14] M. Asscher, W.L. Guthrie, T.-H. Lin and G.A. Somorjai, J. Chem. Phys. 78 (1983) 6992.
[15] A. Mödl, H. Robota, J. Degner, W. Vielhaber, M.C. Lin and G. Ertl, J. Chem. Phys. 83 (1985) 4800.
[16] A.C. Luntz and D.S. Bethune, J. Chem. Phys. 90 (1989) 1274.
[17] S.T. Ceyer, Science 249 (1990) 133.
[18] A.G. Sault and D.W. Goodman, J. Chem. Phys. 88 (1988) 7232.
[19] A.V. Hamza, H.-P. Steinruck and R.J. Madix, J. Chem. Phys. 86 (1987) 6506.
[20] C.R. Arumainayagam and R.J. Madix, Progr. Surf. Sci. 38 (1991) 1.
[21] L. Hanley, Z. Xu and J.T. Yates, Surf. Sci. 248 (1991) L265.
[22] V.R. Choudhary, A.M. Rajout and B. Prabhakar, Catal. Lett. 15 (1992) 363.