Applied reaction dynamics: Efficient synthesis gas production via single collision partial oxidation of methane to CO on Rh(111)

K. D. Gibson, M. Viste, and S. J. Sibener[a)]

The James Franck Institute, Gordon Center for Integrative Science, The University of Chicago, Chicago, Illinois 60637 and Department of Chemistry, The University of Chicago, Chicago, Illinois 60637

Supersonic molecular beams have been used to determine the yield of CO from the partial oxidation of CH_4 on a Rh(111) catalytic substrate, $CH_4 + (1/2)O_2 \rightarrow CO + 2H_2$, as a function of beam kinetic energy. These experiments were done under ultrahigh vacuum conditions with concurrent molecular beams of O_2 and CH_4, ensuring that there was only a single collision for the CH_4 to react with the surface. The fraction of CH_4 converted is strongly dependent on the normal component of the incident beam's translational energy, and approaches unity for energies greater than ~ 1.3 eV. Comparison with a simplified model of the methane-Rh(111) reactive potential gives insight into the barrier for methane dissociation. These results demonstrate the efficient conversion of methane to synthesis gas, $CO + 2H_2$, are of interest in hydrogen generation, and have the optimal stoichiometry for subsequent utilization in synthetic fuel production (Fischer-Tropsch or methanol synthesis). Moreover, under the reaction conditions explored, no CO_2 was detected, i.e., the reaction proceeded with the production of very little, if any, unwanted greenhouse gas by-products. These findings demonstrate the efficacy of overcoming the limitations of purely thermal reaction mechanisms by coupling nonthermal mechanistic steps, leading to efficient C–H bond activation with subsequent thermal heterogeneous reactions. © *2006 American Institute of Physics*. [DOI: 10.1063/1.2336221]

INTRODUCTION

Methane is an abundant natural resource for making larger hydrocarbons through the Fischer-Tropsch process. To do this, it is necessary to partially oxidize the CH_4 to synthesis gas (syngas), CO and H_2, ideally in a 1:2 ratio. This is also a desirable feedstock for methanol synthesis. One method is the direct partial oxidation of methane,

$$CH_4 + (1/2)O_2 \rightarrow CO + 2H_2. \tag{1}$$
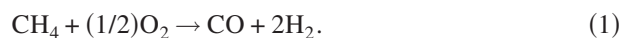
This process has been extensively studied using high surface area supported Rh catalysts in flow reactors at several Torrs.[1,2] Many catalysts have been investigated, and Rh was the best, being stable at high temperatures and giving a high CH_4 conversion efficiency and high selectivity for CO and H_2 rather than the complete oxidation products CO_2 and H_2O.[2] Reaction (1) offers, in principle, several benefits as compared to the multistep route to methane utilization, namely, steam reforming coupled with the water gas shift reaction.[1]

The dissociative adsorption of CH_4 is a first step in the partial oxidation reaction. Therefore, elucidating the mechanism involved is important to quantitatively understand the production of syngas. This has been studied on single crystal transition metal surfaces at low ambient pressures,[3–6] and with molecular beam techniques under ultrahigh vacuum (UHV) conditions.[4,5,7–11] Though the precise details are still not known, the principal mechanism is the direct dissociative chemisorption of the methane; the molecule loses at least one

H upon impact with the surface. This process is highly activated, being dependent on both the vibrational state and translational energy of the incident methane.[11,12] For the low index surfaces, there is a normal translational energy dependence; it scales as $E_i \cos^2 \Theta_i$, where Θ_i is the incident polar angle.

The flow reactor experiments on supported catalysts allow for the study of syngas production under continuous conditions by measuring the concentrations of reaction products as they are exposed to O_2 and CH_4. However, the reacting gas has a broad thermal distribution of energies, the catalyst surface is not well defined, and the impinging CH_4 has several collisions in which to react. The single crystal experiments allow for the study of one of the first steps in syngas production, the dissociative adsorption of methane. These experiments involve exposing the surface to a known flux of methane for a precise period of time, and then measuring the surface coverage of carbon. In these experiments, the energy of the methane and the condition of the surface can be precisely controlled. In this paper, we present the results of CH_4 dissociative adsorption measurements of this type on Rh(111).

We also studied CO production under UHV conditions on a single crystal Rh(111) surface. The reaction was carried out with simultaneous molecular beams of O_2 and CH_4 having narrow kinetic energy distributions, under conditions where the quantities of adsorbed C and O, Θ_C and Θ_O, were small, and was monitored by measuring the CO product. These experiments demonstrate the efficient single collision production of syngas using high kinetic energy CH_4.

[a)]Author to whom correspondence should be addressed. Electronic mail: s-sibener@uchicago.edu
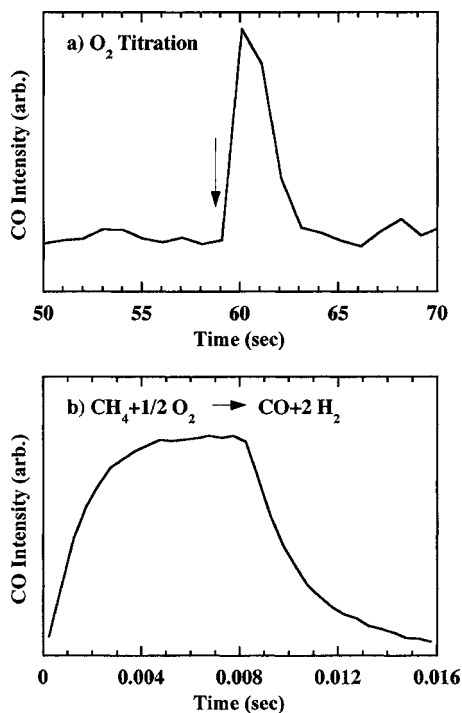
FIG. 1. (a) shows an example spectrum for the O_2 titration experiments; the arrow indicates the time at which the exposure to the O_2 beam was commenced. (b) shows an example spectrum from the modulated-beam reaction experiments. The conditions were the same: $\Theta_i = 10°$, $E_1 = 0.947$ eV, and $T_s = 800$ K.

EXPERIMENT

The details of the UHV machine and the cleaning procedure of the Rh(111) crystal have been discussed elsewhere,[13] so only the details particular to the present results will be discussed. The methane beam was produced by expanding a CH_4/H_2 mixture at 160 psi (gauge) through a 25 μm nozzle heated to 960 K. Only CH_4 and H_2 were detected in the beam under these conditions. Since the sticking is dependent on both vibrational and translational energies, the nozzle temperature was maintained at $T_N = 960$ K to keep the vibrational distribution constant, and the translational energy was adjusted by varying the CH_4/H_2 ratio. This gave energy distributions with average values between 0.95 and 1.34 eV, and a $\Delta E/E \approx 30\%$ at full width at half maximum (FWHM). The normal energy, $\frac{1}{2}m(v_i \cos(\theta_i))^2$, could be further controlled by varying the incident angle θ_i.

Two types of experiments were performed, samples of the data are shown in Fig. 1, taken with $\theta_i = 10°$, $E_i = 0.947$ eV, and $T_s = 800$ K. For the O_2 titration experiment, the surface was first exposed to the CH_4 beam for some period of time, the beam was stopped, and then the surface was exposed to an O_2 beam while the CO signal was monitored. Figure 1(a) shows an example spectrum, with the arrow indicating the time at which the O_2 exposure was commenced. To determine the total amount of C on the surface, the integrated signal could be compared to that of a ($\sqrt{3} \times \sqrt{3}$) CO overlayer ($\Theta_C = 1/3$ monolayers). From the CH_4 flux and the exposure time, the quantity dissociatively chemisorbed could be determined. As long as the total C coverage was less than about 1/6 of a monolayer, the results
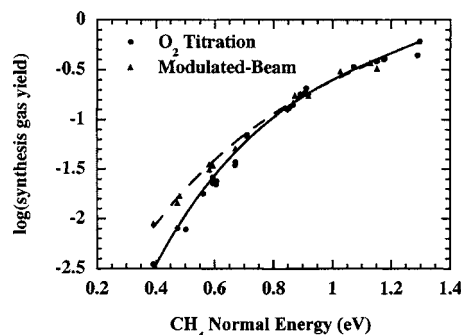
were linearly dependent on the exposure time and the initial sticking coefficient, S_0, could be calculated. We did not detect any CO_2 under the conditions of these experiments, and so all of the carbon desorbs as CO.

Figure 1(b) shows the CO signal for the $CH_4 + (1/2)O_2 \rightarrow CO + 2H_2$ reaction. The O_2 beam was continuous, and the CH_4/H_2 beam was square-wave modulated by the source chopper. Results were signal-averaged over many cycles. No CO_2 was detected. Only the spectra where the CO signal returned to the baseline during each cycle were used; this ensured that there was no build up of C. We saw no oxygen in postreaction temperature-programed desorption (TPD) experiments, and spectra taken consecutively gave identical results. At $T_s = 800$ K, oxygen is only slowly adsorbed, and not absorbed at all, and any excess reacts with the H_2. From time-of-flight spectra, the CO velocity distribution was determined to be close to thermal at the surface temperature.

RESULTS AND DISCUSSION

Figure 2 shows the yield of CO as a fraction of the quantity of impinging CH_4 using different energy beams and incident angles. Under the UHV conditions of these experiments, the high energy CH_4 molecules have only a single collision with the Rh(111) in which to react. As on other metals, the result is strongly dependent on the normal energy. At high energies the reaction probability approaches unity; a single collision is sufficient for the complete reaction of the CH_4.

The solid lines are from least-squares fits to the data, using a previously suggested model,[9,10,14]

$$Y_\nu(E_N) = \frac{A_\nu}{2}\left[1 + \mathrm{erf}\left(\frac{E_N - V_\nu}{W_\nu}\right)\right], \qquad (2)$$

where $Y_\nu(E_N)$ is the yield as a function of the normal energy (E_N) with vibrational level ν, and A_ν, V_ν, and W_ν are fitting constants. The vibrations are all R-H stretches with $\hbar\omega_0 = 0.36$ eV. The vibrational temperature used was that of the nozzle, $T_N = 960$ K. The population of a vibrational state is

$$f_\nu(T_N) = g_\nu \exp\left[-\frac{\nu\hbar\omega_0}{RT_N}\right]\left[1 - \frac{\hbar\omega_0}{RT_N}\right]^4, \qquad (3)$$

where g_ν is the degeneracy ($g_0 = 1$ and $g_1 = 4$). Because of the nozzle temperature and the range of yields reported, only the

FIG. 2. The calculated values of the yield of CO relative to the CH_4 flux vs the normal energy, $\frac{1}{2}m(v_i \cos(\theta_i))^2$, as measured by the two types of experiment. The solid lines are from fits to the data (see text).

TABLE I. Parameters derived from fitting the yield data (see text).

	O_2 titration (eV)	Reaction (eV)
V_0	1.24	1.29
W_0	0.39	0.48
V_1	0.68	0.69
W_1	0.21	0.29

first two vibrational levels were considered $[f_0(960)$ $=0.9511$ and $f_1(960)=0.0474]$. This model was used with a least-squares fitting routine to derive the parameter values from the measured yield (Y_{exp}),

$$Y_{exp} = \sum_{\nu=0}^{1} f_\nu(T_N) \int_0^\infty Y_\nu(E_N) f(E) dE, \qquad (4)$$

where $f(E)$ is the energy distribution of the CH_4 beam. As was done previously, values of A_0 and A_1 were fixed at 1,[9,10] the values for the other parameters are given in Table I, and the lines through the data points in Fig. 2 are the results. The values are similar to those measured on Ru(0001) (Ref. 9)[9] and Ni(100).[10] Due to possible systematic errors in the measurement of the absolute value of the CH_4 flux, we estimate that the measured yield is accurate to within a factor of ~ 2. This introduces an uncertainty of $\pm 20\% - 30\%$ in the parameter values. Though we did not make measurements at different nozzle temperatures, the fitted parameters suggest that vibrational energy enhances the reaction probability at low normal energies. At high normal energies, most of the reaction is done by CH_4 in the vibrational ground state; the large yield of CO is due primarily to the increased translational energy.

For the highest normal energies, $\geqslant 0.8$ eV, the results for the two types of experiment are identical. For lower normal energies, where the yield is low, the values obtained from the two types of experiments diverge, with the reaction experiments having a larger value. Many of the points are from O_2 titration and reaction experiments run consecutively with all experimental conditions identical, so this is not a systematic error. We have considered several explanations. One is the difference in the amount of C on the surface, as much as $\sim 1/6$ of a monolayer for the titration experiments and only a few ten-thousandths for the reaction experiments. However, the results of titration experiments were coverage independent for $\Theta_C < 1/6$ of a monolayer, and for higher energies the yields were identical for both types of experiment. These observations are inconsistent with the reaction being strongly coverage dependent. A second possible factor is that during the kinetic experiments a small quantity of oxygen, and probably OH, was coadsorbed. However, at least on Pt(111) and Pd(110), the dissociation of CH_4 is inhibited by even small amounts of preadsorbed oxygen.[8] A third possibility is that the dissociation takes place preferentially at the small quantity of defects on the Rh(111) surface. If these defects have a much higher probability for dissociative chemisorption of CH_4, this would lead to the reaction experiments, where Θ_C was always low, measuring the sticking on these defects. That there is a higher dissociation probability at defects is possible; for Ni[6] and Ir[4], the rougher surfaces of the low-index planes are more active for CH_4 dissociation. During the titration experiments, where the final Θ_C is higher, the defects would be quickly blocked, and the measurement would be mainly due to the flat surface. However, if the CH_4 was preferentially dissociated at defects, the reaction experiments would give a higher S_0 until the value reached unity, which is not the case. It is important to restate that these considerations are only important at the lower normal energies, where there is a low probability of the dissociative adsorption of methane. At high normal energies, the two different experimental techniques agree, essentially quantitatively, and the probability of dissociation approaches unity.

CONCLUSIONS

We have measured the yield of CO from the partial oxidation of CH_4, $CH_4+(1/2)O_2 \rightarrow CO+2H_2$, on Rh(111) as a function of methane collision energy. This was accomplished by using concurrent molecular beams of O_2 and CH_4 converging on the sample in an UHV chamber. The translational energy of the CH_4 beam was controlled by a combination of elevated nozzle temperature and seeding with H_2. The reaction is highly activated, and is found to be dependent on the normal translational energy. As the normal energy gets much above ~ 1.3 eV, the conversion efficiency approaches unity. Comparison with a simplified model of the methane-Rh(111) reactive potential gives insight into the barrier for methane dissociation. These results were compared to measurements where the Rh(111) was first exposed to the CH_4 beam, and the amount of adsorbed C determined by the CO produced from an O_2 titration. For normal collision energies greater than ~ 0.8 eV, the yield of CO is the same. This is what is expected if the dissociation of the CH_4 is the first step in the partial oxidation reaction. For lower normal energies, near threshold for reaction, the results for the two types of experiments are found to differ slightly, with the modulated beam, i.e., lower coverage measurements, giving a modestly higher conversion of CH_4 to CO.

These results demonstrate the efficient conversion of methane to synthesis gas, $CO+2H_2$, are of interest in hydrogen generation, and have the optimal stoichiometry for subsequent utilization in synthetic fuel production (Fischer-Tropsch). Moreover, under the reaction conditions explored, no CO_2 was detected, i.e., the reaction proceeded with the production of very little if any unwanted greenhouse gas by-products. These findings demonstrate the efficacy of overcoming the limitations of using purely thermal reaction strategies by independently optimizing the nonthermal C–H bond activation step as well as the catalyst conditions which govern the subsequent thermal heterogeneous processes, leading to efficient and selective product formation. We believe that reaction strategies which combine such nonthermal chemical dynamics based methods with thermal processes will find applicability in a wide range of heterogeneous reactions.

[1] D. A. Hickman, E. A. Haupfear, and L. D. Schmidt, Catal. Lett. **17**, 223 (1993); D. Wang, O. Dewaele, and G. F. Froment, J. Mol. Catal. A: Chem. **136**, 301 (1998); Z. Tian, O. Dewaele, and G. B. Marin, Catal. Lett. **57**, 9 (1999); K. Heitnes Hofstad, J. H. B. J. Hoebink, A. Holmen, and G. B. Marin, Catal. Today **40**, 157 (1998); K. A. Williams, C. A. Leclerc, and L. D. Schmidt, AIChE J. **51**, 247 (2005).

[2] D. A. Hickman and L. D. Schmidt, Science **259**, 343 (1993); P. M. Torniainen, X. Chu, and L. D. Schmidt, J. Catal. **146**, 1 (1994).

[3] A. C. Luntz and H. F. Winters, J. Chem. Phys. **101**, 10980 (1994); T. A. Jachimowski, C. J. Hagedorn, and W. H. Weinberg, Surf. Sci. **393**, 126 (1997).

[4] D. C. Seets, C. T. Reeves, B. A. Ferguson, M. C. Wheeler, and C. B. Mullins, J. Chem. Phys. **107**, 10229 (1997).

[5] D. C. Seets, M. C. Wheeler, and C. B. Mullins, J. Chem. Phys. **107**, 3986 (1997).

[6] T. P. Beebe, Jr., D. W. Goodman, B. D. Kay, and J. T. Yates, Jr., J. Chem. Phys. **87**, 2305 (1987).

[7] C. N. Stewart and G. Ehrlich, J. Chem. Phys. **62**, 4672 (1975); A. C. Luntz and D. S. Bethune, *ibid.* **90**, 1274 (1989); R. W. Verhoef, D. Kelly, C. B. Mullins, and W. H. Weinberg, Surf. Sci. **311**, 196 (1994); D. Kelly and W. H. Weinberg, J. Vac. Sci. Technol. A **15**, 1663 (1997); R. W. Verhoef, D. Kelly, C. B. Mullins, and W. H. Weinberg, Surf. Sci. **325**, 93 (1995); M. B. Lee, Q. Y. Yang, and S. T. Ceyer, J. Chem. Phys. **87**, 2724 (1987); C. T. Rettner, H. E. Pfnür, and D. J. Auerbach, Phys. Rev. Lett. **54**, 2716 (1985); J. Chem. Phys. **84**, 4163 (1986).

[8] M. Valden, J. Pere, M. Hirsimaki, S. Suhonen, and M. Pessa, Surf. Sci. **377–379**, 605 (1997).

[9] J. H. Larsen, P. M. Holmblad, and I. Chorkendorff, J. Chem. Phys. **110**, 2637 (1999).

[10] P. M. Holmblad, J. Wambach, and I. Chorkendorff, J. Chem. Phys. **102**, 8255 (1995).

[11] L. B. F. Juurlink, P. R. McCabe, R. R. Smith, C. L. DiCologero, and A. L. Utz, Phys. Rev. Lett. **83**, 868 (1999).

[12] M. P. Schmid, P. Maroni, R. D. Beck, and T. R. Rizzo, J. Chem. Phys. **117**, 8603 (2002); R. D. Beck, P. Maroni, D. C. Papageorgopoulos, T. T. Dang, M. P. Schmid, and T. R. Rizzo, Science **302**, 98 (2003); P. Maroni, D. C. Papageorgopoulos, M. Sacchi, T. T. Dang, R. D. Beck, and T. R. Rizzo, Phys. Rev. Lett. **94**, 246104 (2005); R. R. Smith, D. R. Killelea, D. F. DelSesto, and A. L. Utz, Science **304**, 992 (2004); L. B. F. Juurlink, R. R. Smith, D. R. Killelea, and A. L. Utz, Phys. Rev. Lett. **94**, 208303 (2005).

[13] D. F. Padowitz and S. J. Sibener, Surf. Sci. **254**, 125 (1991); J. I. Colonell, K. D. Gibson, and S. J. Sibener, J. Chem. Phys. **103**, 6677 (1995).

[14] H. A. Michelsen, C. T. Rettner, D. J. Auerbach, and R. N. Zare, J. Chem. Phys. **98**, 8294 (1993).