

Kinetic Energy of Methane Molecules Formed from Methyl Radicals Adsorbed on Copper

M. U. Kislyuk, V. V. Savkin, and I. I. Tretyakov[†]

Semenov Institute of Chemical Physics, Russian Academy of Sciences, Moscow, 117977 Russia

Received January 12, 2000

Abstract—The method of temperature-programmed reaction (TPR) with the spatial resolution of desorbed product molecules and the measurements of their average rates ($\langle v \rangle$) are used to study the transformation of methyl radicals adsorbed on polycrystalline copper. In the products of TPR, only methane is found. The spatial distribution of its desorption flow (SDDF) is described by the equation CH_3^{\cdot} . The results of SDDF and $I/I_0 = \cos^{16}\phi$ measurements agree with each other. Under these conditions, translationally excited methane molecules are desorbed from the copper surface. The energy of these molecules is 10–15 times higher than the thermal energy.

INTRODUCTION

The reactions of methyl radicals on metal surfaces are of considerable interest. They were studied on Pt(111) [1], Ni(100) [2, 3], Ni(111) [2, 3], Mo(100) [4], and polycrystalline Mo [5] surfaces.

The dissociative adsorption of methane has a high activation energy [6–8], and the reverse process (recombination) can lead to the desorption of translationally excited molecules characterized by the high-directivity spatial distribution of desorption flow (SDDF).

In this work, we studied the formation of methane in the layer of methyl radicals adsorbed on the surface of polycrystalline copper using the methods of temperature-programmed reaction with the spatial resolution of desorbed products. To determine the kinetic energy of desorbed methane molecules, we propose a new modification of the method for the measurements of the average rates of molecules.

EXPERIMENTAL

The method of SDDF measurements was described earlier in [9, 10]. A copper sample ($12 \times 4 \times 0.05$ mm) was cut off from a copper foil (99.99% purity) and mounted in a manipulator. A chromel-alumel thermocouple was welded to the rear of the sample.

Methyl radicals were generated by azomethane ($CH_3N=NCH_3$) pyrolysis in a quartz capillary heated to 1100 K. The same capillary was used to form the effusion radical beam directed at the right side of the sample at room temperature. In each run, methyl radicals were adsorbed until saturation. After adsorption, the sample (in different positions) was heated in a programmed mode at a rate of 30 K/s. TPR spectra were

recorded using an omegatron mass spectrometer or a Bayard–Alpert gauge.

Before experiments, the sample was thoroughly degassed and purified from carbon impurities by prolonged heating in a flow of oxygen ($P = 10^{-7}$ torr) at $T = 1000$ K until the complete cessation of CO and CO_2 desorption from the sample surface. Oxygen was removed from the surface by heating in hydrogen ($P = 10^{-6}$ torr) at $T = 1100$ K. The purification procedure was repeated after each series of measurements consisting of 10–15 “flashes” in which reproducible results were obtained.

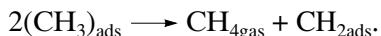
In this work, the method proposed earlier [11] for measuring the average rates of desorbed molecules was modified.

RESULTS AND DISCUSSION

1. TPR Spectra and the Spatial Distribution of Desorbed Methane Molecules

Only methane molecules were observed in the TPR spectra obtained by the above method. These molecules were characterized by the temperature of maximum $T_{\max} = 480$ K.

The absence of hydrogen traces from the TPR spectra can be evidence for the formation of methane by the disproportionation reaction



Another possible explanation for the absence of hydrogen is that hydrogen atoms formed by the decomposition of methyl radicals react with adsorbed radicals at a higher rate than with each other.

The results for the copper surface are completely different from those obtained in the case of molybdenum [5], for which we observed the formation of meth-

[†] Deceased.

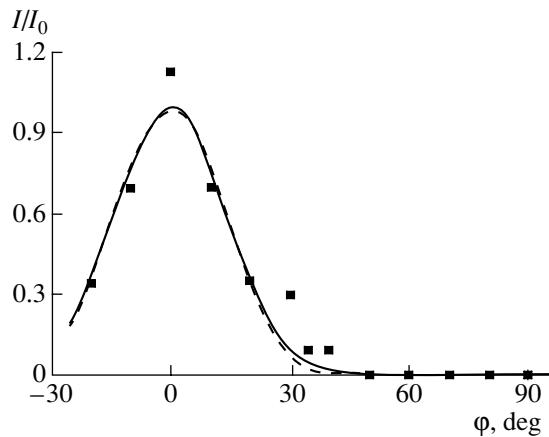


Fig. 1. SDDF of methane (points) and its approximation by Eqs. (1) with $n = 16$ (solid line) and (2) with $\varepsilon = 7.9$ (dashed line).

ane and hydrogen in comparable amounts. In the case of molybdenum, the rate constants of hydrogen atom recombination were the same as those for the recombination of hydrogen atoms and methyl radicals.

Figure 1 illustrates the results of SDDF measurements of methane. It is seen that the desorption flow of methane is concentrated along the normal to the sample surface and described by the equation

$$I/I_0 = \cos^n \phi \quad (1)$$

or by the Van Willigen equation [12]

$$I/I_0 = [(\varepsilon + \cos^2 \phi) \exp(-\varepsilon \tan^2 \phi)] / [(\varepsilon + 1) \cos \phi]. \quad (2)$$

In these equations, I_0 and I are the intensities of the desorption flow in the direction of the normal to the surface and at the angle ϕ to it, respectively; n is the exponent; and $\varepsilon = E_a/RT$, where E_a is the activation energy of adsorption. The values of n and ε are 16 ± 2 and 8 ± 1 , respectively.

Carbon, which is formed by the transformation of methyl radicals into methane, is probably dissolved in the sample bulk at high temperatures. This is evident from the fact that despite the formation of carbon in an amount of 0.25 monolayer, the TPR spectra are reproducible in 10–15 runs. In the case of a high surface coverage by carbon atoms or the formation of surface carbide, TPR spectra should have changed.

The activation energy of methane adsorption estimated using the values of ε and T_{\max} is 32 ± 5 kJ/mol. As we mentioned earlier [13, 14], this estimate can be strongly underestimated because of the roughness of polycrystalline copper surface.

2. Measurements of the Average Rates of Desorbing Methane Molecules

Figure 2 shows the fragment of the measurement cell employed in this work to determine the average

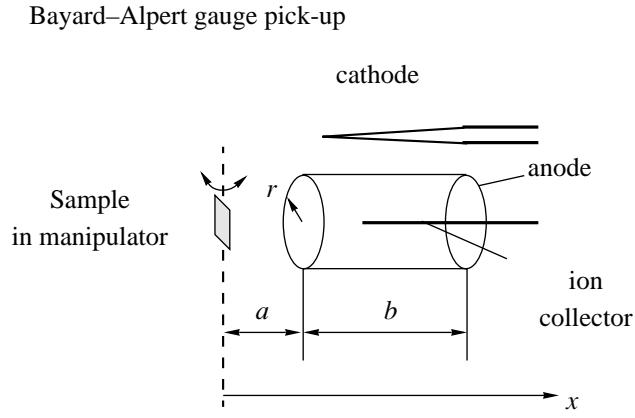


Fig. 2. Positions of the sample and the pick-up of the Bayard-Alpert gauge.

rates $\langle v \rangle$ and geometric parameters used in further developments below.

To derive necessary formulas, let us consider a vacuum system with a source of gas inleakage whose SDDF is described by Eq. (1).

These distributions are observed for effusion molecular beams [11] and desorption from flat surfaces [15]. In the second case, the axis of the flow coincides with the surface normal.

The value of total inleakage (L , molecule/s) from such a source is determined by the integral in spherical polar coordinates

$$L = I_0 \int_0^{2\pi} d\psi \int_0^{\pi} \cos^n \phi \sin \phi d\phi = 2\pi I_0 / (n + 1), \quad (3)$$

where ψ is the azimuthal angle.

The concentration of gas C in the system with inleakage and pumping-out is described by the equation [16]

$$V(dC/dt) = L - SC, \quad (4)$$

where V is the volume of the vacuum chamber, t is time, and S is the pumping rate.

Under stationary conditions and in the maximum of the TPR peak, the left-hand side of Eq. (4) can be neglected. Therefore, using Eq. (3), we arrive at the simple expression for the concentration C_1 of the randomized gas in the chamber:

$$C_1 = L/S = 2\pi(I_0/[S(n + 1)]). \quad (5)$$

The equation for the flow intensity (i , molecule $\text{cm}^{-2} \text{ s}^{-1}$)

$$i = C_n \langle v \rangle, \quad (6)$$

forms the basis for the method developed by us [11]. Here, C_n is the concentration of molecules in the flow and $\langle v \rangle$ is the average rate of their directed motion. The

independent determination of values i and C_n allows us to determine the average rate of molecules.

In this work, the geometry of the registration system was modified compared to that described in [11], which enabled us to derive a more accurate expression for $\langle v \rangle$. To a first approximation, the sample was considered to be a single point.

The expression for the intensity of the flow through a pick-up at a distance x from the sample with the normal to the sample surface coinciding with the pick-up axis is as follows:

$$i(x) = (I_0/\pi r^2) \int_0^{2\pi} d\psi \int_0^{\arctan(r/x)} \cos^n \phi \sin \phi d\phi \\ = 2I_0 [1 - (x/\sqrt{x^2 + r^2})^{n+1}] / [r^2(n+1)], \quad (7)$$

where r is the radius of the pick-up anode (Fig. 2).

To describe the average concentration of molecular flow ($\langle C_n \rangle$) in the ionization space of gauge, let us use Eqs. (6) and (7) and integrate over the pick-up volume:

$$\langle C_n \rangle = \{2I_0/[(n+1)r^2b\langle v \rangle]\} \\ \times \int_a^{a+b} [1 - (x/\sqrt{x^2 + r^2})^{n+1}] dx, \quad (8)$$

where a and b are the parameters shown in Fig. 2.

The registration device was the open-type ionization Bayard-Alpert gauge positioned near the sample. In the experiments, we recorded its meterage corresponding to the sample positions.

The value C_1 was measured when the sample was positioned so that desorbing molecules fell into the gauge ionization space only after colliding with the walls of the vacuum chamber.

When the right face of the sample was turned to the pick-up and the surface normal coincided with the pick-up axis, the gauge registered the combined concentration of molecules C_2 escaped from the surface (primary species) and those collided with the walls of the vacuum chamber:

$$C_2 = C_1 + \langle C_n \rangle. \quad (9)$$

Using equations (5), (8), and (9), we arrive at the final expression for the average rate $\langle v \rangle$ of desorbing molecules:

Table

n	1	2	4	6	8	10	20	16*
$\int_a^{a+b} [1 - (x/\sqrt{x^2 + r^2})^{n+1}] dx, \text{ cm}$	0.620	0.874	1.297	1.645	1.932	2.175	3.011	2.735

* The value of n observed in the experiment.

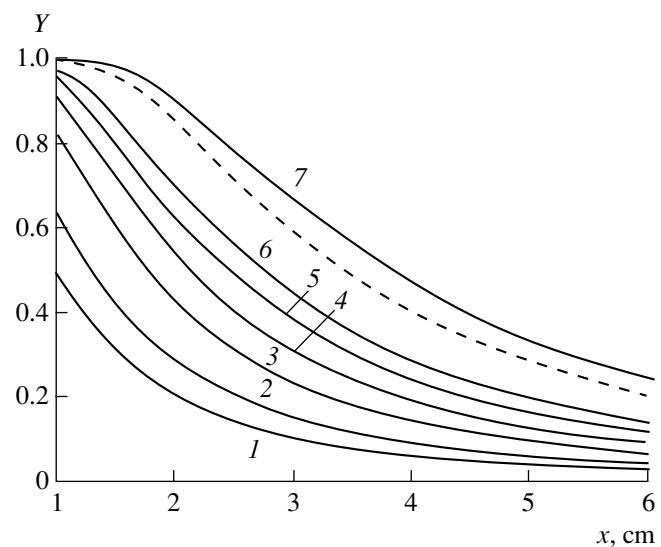


Fig. 3. Functions $Y = 1 - (x/\sqrt{x^2 + r^2})^{n+1}$, which are integrands in Eqs. (8) and (10) at $a = 1$, $b = 5$, and $r = 1$ cm and different values of the parameter n . Solid lines correspond to the calculation for n equal to (1) 1, (2) 2, (3) 4, (4) 6, (5) 8, (6) 10, and (7) 20. The dashed line corresponds to the experiment ($n = 16$).

$$\langle v \rangle = \{SC_2/[\pi r^2 b(C_2 - C_1)]\} \\ \times \int_a^{a+b} [1 - (x/\sqrt{x^2 + r^2})^{n+1}] dx. \quad (10)$$

Figure 3 shows the integrands of Eqs. (8) and (10) at $a = 1$, $b = 5$, and $r = 1$ cm and different values of the parameter n . The values of integrals obtained are given in the table.

In the series of measurements, we determined the values of C_1 and C_2 for methane desorption from the saturated layer of methyl radicals on the copper surface. The value of $C_2/(C_2 - C_1)$ in Eq. (10) is 3.1 ± 0.2 , according to these data. The rate of methane pumping-out from the vacuum system was $S = 460 \pm 50$ l/s. When these values, as well as the value of the integral (2.735 cm) and the geometric parameters ($b = 5$ cm and $r = 1$ cm), are substituted into Eq. (10), we obtain $\langle v \rangle = 2400 \pm 500$ m/s.

The activation energy of methane adsorption E_a was calculated by the formula [14]

$$E_a = \frac{\mu}{2} \left[\langle v \rangle - \left(\frac{2RT_{\text{surf}}}{\pi\mu} \right)^{1/2} \right]^2, \quad (11)$$

where μ is the molecular weight of methane, R is the universal gas constant, and T_{surf} is the surface temperature (480 K).

As a result, the activation energy $E_a = 34 \pm 16$ kJ/mol which coincides with the value obtained by SDDF analysis (32 ± 5 kJ/mol) within the indicated accuracy.

Thus, two methods showed that, under given conditions, translationally excited methane molecules are desorbed from the copper surface with energy that is 10–15 times higher than the thermal energy.

The values of the activation energy obtained in this work are most likely the lower estimates since the desorbing molecules can be excited along internal degrees of freedom [17, 18].

ACKNOWLEDGMENTS

This work was supported by the Russian Foundation for Basic Research (project no. 99-03-32114).

REFERENCES

1. Fairbrother, D.H., Peng, X.-D., Stair, P.C., *et al.*, *Symp. on Methane and Alkane Conversion Chemistry*, 207th ACS National Meeting, San Diego: American Chemical Society, 1994, p. 280.
2. Hall, R.B., Castro, M., Kim, C.-M., *et al.*, *Symp. on Methane and Alkane Conversion Chemistry*, 207th ACS National Meeting, San Diego: American Chemical Society, 1994, p. 282.
3. Yang, Q.Y. and Ceyer, S.T., *J. Vac. Sci. Technol. A*, 1988, vol. 6, no. 3, p. 851.
4. Smudde, G.H., Jr. and Min Yu Stair, P.C., *J. Am. Chem. Soc.*, 1993, vol. 115, no. 5, p. 1988.
5. Kislyuk, M.U., Tret'yakov, I.I., Savkin, V.V., and Sinev, M.Yu., *Kinet. Katal.*, 2000, vol. 41, no. 1, p. 71.
6. Verhoef, R.W., Kelly, D., Mullins, C.B., and Weinberg, W.H., *Surf. Sci.*, 1993, vol. 287/288, no. 1, p. 94.
7. McMaster, M.C. and Madix, R.J., *J. Chem. Phys.*, 1993, vol. 98, no. 1, p. 12.
8. Kislyuk, M.U., Savkin, V.V., and Tret'yakov, I.I., *Kinet. Katal.*, 2000, vol. 41, no. 1, p. 82.
9. Savkin, V.V., Kislyuk, M.U., and Sklyarov, A.V., *Kinet. Katal.*, 1987, vol. 28, no. 6, p. 1409.
10. Kislyuk, M.U., Migulin, V.V., Savkin, V.V., *et al.*, *Kinet. Katal.*, 1990, vol. 31, no. 6, p. 1392.
11. Kislyuk, M.U., Savkin, V.V., Vlasenko, A.G., and Bartan, A.O., *Izv. Akad. Nauk, Ser. Khim.*, 1995, no. 1, p. 30.
12. Van Willigen, V., *Phys. Lett. A*, 1968, vol. 28, no. 2, p. 80.
13. Kislyuk, M.U. and Bakuleva, T.N., *Izv. Akad. Nauk, Ser. Khim.*, 1990, no. 6, p. 2699.
14. Savkin, V.V. and Kislyuk, M.U., *Kinet. Katal.*, 1997, vol. 38, no. 5, p. 793.
15. Kislyuk, M.U. and Rozanov, V.V., *Kinet. Katal.*, 1995, vol. 36, no. 1, p. 89.
16. Trendelenburg, E.A., *Ultrahochvakuum*, Karlsruhe: G. Braun, 1963, p. 286.
17. Kori, M. and Halpern, B.L., *Chem. Phys. Lett.*, 1986, vol. 129, no. 4, p. 407.
18. Mantell, D.A., Kunimori, K., Ryali, S., *et al.*, *Surf. Sci.*, 1986, vol. 172, no. 2, p. 281.