JOURNAL OF CATALYSIS 37, 179–181 (1975)

Catalytic Decomposition of Methanol at Low Pressures by Nickel

The catalytic decomposition reactions of organic molecules at very low pressures on clean metal surfaces have been comparatively little investigated. We have chosen to study the reaction of methanol, at pressures between 1×10^{-6} and 1×10^{-7} Torr (1 Torr = 133.3 N m^{-2}), on a nickel filament. The reaction has previously been studied at intermediate pressures (10^{-2}–10^{-3} Torr) both on gold and on nickel wires (*1*) and it was reported that at low temperatures ($<$ 273 K) the carbon–oxygen bond was broken on the nickel surface; at a higher temperature (295 K) the main reaction was the formation of H_2(gas) and H_2O(gas) while further increase of temperature ($>$ 500 K) led to the formation, principally, of CO(gas) and H_2(gas).

The apparatus has been described previously (*2*) and was unchanged. Briefly, it consists of a glass ultrahigh vacuum section ($P_{\min} < 5 \times 10^{-10}$ Torr) to which gas can be admitted from either of two storage volumes through all-metal valves. The chamber is connected to the pumps by a similar valve. Adjustment of the aperture of this latter valve allows a suitable rate of flow of methanol vapor over the filament to be selected. The nickel filament had been cleaned previously by the oxidation and reduction procedure which is thought to remove carbonaceous impurities (*3*) and was a highly effective H_2/D_2 equilibration catalyst (*4*). However, it is not possible to make a quantitative assessment of the cleanliness of the filament (*4*) and it has been suggested that to produce the Ni(111) plane in a contamination-free state, supplementary argon-ion bombardment is necessary (*5*).

The decomposition reaction was observed mass spectrometrically by streaming methanol vapor (at room temperature) over the filament maintained between 160 and 1050 K. When steady-state conditions had been reached, the mass spectrum was recorded with an omegatron radiofrequency mass spectrometer. This instrument formed an integral part of the UHV system and was attached to the filament chamber by wide bore tubing. The only reaction that could be detected was the formation of carbon monoxide and hydrogen, which process started at filament temperatures above 370 K. The filament temperatures were visited in random order and no measurable decline in reactivity took place within any particular series of experiments. However, some slight degradation of methanol to surface carbon was also taking place as shown by the reduction in the reactivity of the filament over a prolonged period of experimentation. The initial reactivity could be restored by a sequence of oxidation and reduction.

In view of the observed decomposition reaction it was clearly necessary to characterize the behavior of the filament towards carbon monoxide and hydrogen separately. Previous measurements of the uptake of hydrogen (*2*) had shown that the surface coverage decreased continuously with increased filament temperature between 160 K (3.9×10^{14} mol cm^{-2}) and 430 K (immeasurably small). In similar experiments with carbon monoxide the uptake varied smoothly with changes in either gas pressure or filament temperature, and on flashing the CO-covered filament practically all of the gas had desorbed by the time the filament reached 490 K.

The observations on methanol at the higher filament temperatures agree entirely with the work of Roberts and Stewart (*1*); the differences at lower temperatures may well be due to the obscuring of the reaction by the wall effects which were prominent throughout our, low pressure, experiments.

The reactivity of the filament can conveniently be expressed by its efficiency *E*. This quantity is defined by the equation

$$E = \frac{\text{rate of CO production}}{\text{rate of } CH_3OH \text{ collision}}.$$

Under the steady-state conditions of the experiments the rate of production of CO must equal the rate at which it is pumped away. This latter rate is directly proportional to $p_{CO}k_{CO}$, where p_{CO} is the partial pressure of CO and k_{CO} is the first order pumping constant of the aperture of the exit valve. The partial pressure of CO due to decomposition is obtained from the measured peak height of mass 28, after this has been corrected for the background contribution to mass 28. The proportionality constant is calculated from the volume of the apparatus and the kinetic theory of gases. The rate of collision of methanol is calculated from its partial pressure (measured by the omegatron) and the area of the filament. The results of these experiments are shown in Fig. 1.

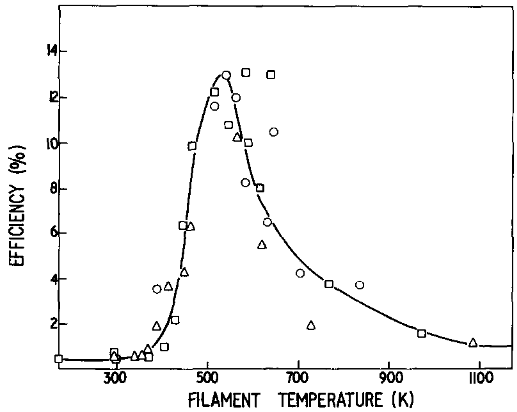

FIG. 1. Methanol decomposition on a nickel filament. (○) p_{MeOH}: 1×10^{-7} Torr, k_{CO}: 0.58 sec^{-1}; (△) p_{MeOH}: 2.4×10^{-7} Torr, k_{CO}: 0.33 sec^{-1}; (□) p_{MeOH}: 6×10^{-7} Torr, k_{CO}: 0.23 sec^{-1}.

The most interesting features of these results are:

1. the essentially zero activity for filament temperatures below 370 K;
2. the rapid rise in *E* above 370 K to a sharp maximum near 520 K;
3. the considerable fall in *E* above 550 K to a value at 1000 K which is only about 1/10th of the maximum.

When seeking an interpretation of these results it is natural to look first at the general features of the interactions of CO and H_2 with the filament. However, there does not seem to be anything in these to account for the rapid rise in *E* between 370 and 500 K since both gases appear to have a continuous range of binding sites on the surface. For neither gas, therefore, is there a filament temperature which can be called the "desorption temperature" above which the continuous decomposition of methanol might become measurable as the result of the rate-determining desorption of reaction products. We are thus led to support the earlier suggestion, made in relation to a reaction at much higher methanol pressures (*6*), that decomposition is controlled by the surface reactions of methanol itself. Such a conclusion is in accordance with the interpretation by Roberts and Stewart of their high temperature observations, though they attributed the smooth decomposition of the molecule, without cleavage of the C–O bond, to "extensively incorporated carbon during early stages of the interaction" (*1*).

If it is accepted that surface processes are rate-determining it becomes of interest to explore whether geometric factors are likely to be of particular importance in the decomposition process, that is to say, whether the reaction can be described as "demanding" (*7*). The surface of a well-annealed nickel filament, it is suggested, consists predominantly of two closely packed, low-index planes, namely, the (100) and the (111) planes (*2*). On one of these, the (111), the dimensions of the methanol mol-

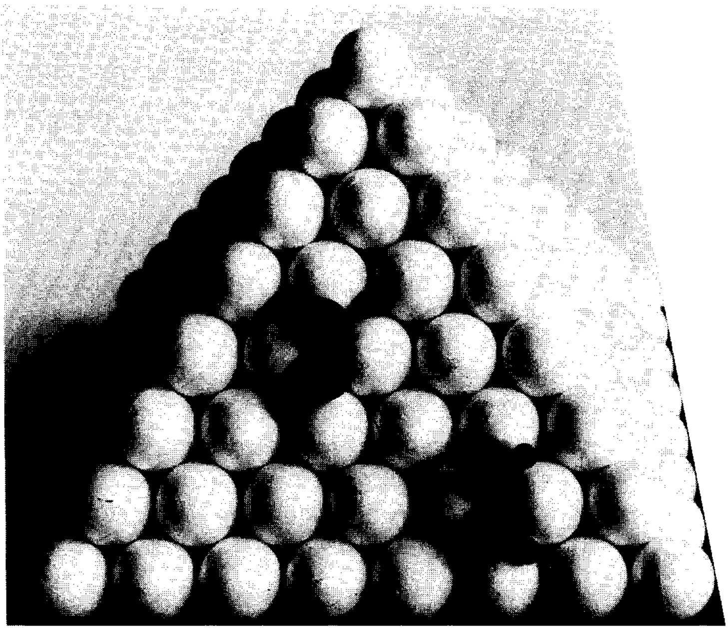

FIG. 2. Possible dissociation mechanism of methanol on Ni(111). At bottom right of diagram the molecule is in its initial adsorbed state. Decomposition proceeds by the breaking of the C–H bonds, as in top left of diagram, followed by recombination of hydrogen atoms and desorption of H_2 and CO.

ecule do indeed match the interatomic spacings and a possible mechanism for the decomposition process is shown in Fig. 2.

The temperature dependence of the reaction, which is much more marked than is usual with the reactions of simpler gases (*8–10*), may then be the balance between the tendency for the (activated) surface reaction to go more rapidly at higher temperatures and the decreasing probability that methanol molecules will meet the geometric demands of the initial adsorption process as their thermal agitation increases.

ACKNOWLEDGMENTS

We thank the Science Research Council, the Salters' Company and the Hildebrand Harmsworth Trust for their support.

REFERENCES

1. Roberts, M. W., and Stewart, T. I., *in* "Chemisorption and Catalysis" (P. Hepple, Ed.), *Proc. Conf. Inst. Petrol.* (London) *1970* p. 16.

2. Gasser, R. P. H., Roberts, K., and Stevens, A. J., *Trans. Faraday Soc.* **65**, 3105 (1969).

3. Eley, D. D., and Norton, P. R., *Discuss. Faraday Soc.* **41**, 135 (1966).

4. Gasser, R. P. H., Roberts, K., and Stevens, A. J., *Surface Sci.* **20**, 123 (1970).

5. Edmonds, T., and Pitkethly, R. C., *Surface Sci.* **15**, 137 (1969).

6. Yazumori, I., Nakamura, T., and Miyazaki, E., *Bull. Chem. Soc. Jap.* **40**, 1372 (1967).

7. Boudart, M., Aldag, A. W., Ptak, L. D., and Benson, J. E., *J. Catal.* **11**, 35 (1968).

8. Smith, J. N., and Fite, W. L., *J. Chem. Phys.* **37**, 898 (1962).

9. Madix, R. J., and Susu, A. A., *Surface Sci.* **20**, 377 (1970).

10. Madey, T. E., and Yates, J. T., Jr., *J. Chem. Phys.* **44**, 1675 (1966).

R. P. H. GASSER
K. ROBERTS
A. J. STEVENS

Physical Chemistry Laboratory
University of Oxford
Oxford, England

Received May 24, 1974