NOTES

Interactions of Methane with Tungsten, Molybdenum, and Platinum

The adsorption of saturated hydrocarbons, including methane, on transition-metal surfaces has been widely studied in the literature (*1, 2*), as has been the decomposition of methane on tungsten (*3–6*). The interaction of methane with molybdenum is less known. While chemisorption kinetics and heat effects have been studied, no data for methane decomposition at high temperatures or diffusion coefficients for carbon are available. Although the interaction of alkanes with platinum, which is a very well known catalyst for conversion of hydrocarbons, has been investigated many times, data for methane adsorption on platinum is not abundant and rates of methane decomposition have not been reported.

In the present contribution we report reaction rates for the decomposition of methane at 1 atm on tungsten, molybdenum, and platinum wires, and measure diffusion coefficients for carbon in tungsten and molybdenum. Reaction probabilities can be fitted with an Arrhenius expression

$$P_R = A \exp(-E_R/RT) \qquad (1)$$

while carbon diffusion coefficients are correlated with the equation

$$D = D_0 \exp(-E_D/RT) \qquad (2)$$

Here A and D_0 are preexponential coefficients, while E_R and E_D are the activation energies for reaction and diffusion, respectively, and T is the catalyst temperature.

The reaction was carried out in a Pyrex batch reactor. Total pressure was continuously monitored. Natural gas (97% CH_4) was purified by passage over hot Pt to burn traces of oxygen, bubbling in concentrated sulfuric acid, passage through an ascarite

filter and finally a cold trap. Catalysts were 0.0075-, 0.0127-, and 0.020-cm-diameter W, Mo, and Pt wires 99.98, 99.98, and 99.99% purity, respectively. A 12-cm-length of wire was welded to massive stainless-steel leads and kept straight and horizontal along a diameter of a 1000-cm^3 flask. Gas samples were drawn at intervals and injected in a gas chromatograph fitted with a Spherocarb-packed column and flame ionization detector. Conversions were kept below 10% so that initial rates were measured. Reaction rates were calculated from conversion versus time data.

Temperatures were measured, for the Pt catalyst, from the wire electrical resistance while a regulated power supply maintained specified temperatures constant to within a few degrees. When Mo and W were used as catalysts, continuous change in wire conductivity prevented temperature monitoring through electrical resistance measurements, while darkening of the flask walls by carbon impaired the use of an optical pyrometer. In these cases, power dissipated by the catalytic wire was measured and used to calculate wire temperature.

RATES OF CH₄ DECOMPOSITION

Figures 1–3 show the measured rates of methane decomposition, R, versus 1/T in pure methane at one atmosphere. The maximum temperature was limited by the melting point of platinum or the breaking of the brittle Mo and W carburized wires. Data shown on each figure were obtained on several wires cut from the same spool. All data were fitted by Eq. (1) with parameters shown in Table 1, except for the high-temperature reaction rates on W wires, where
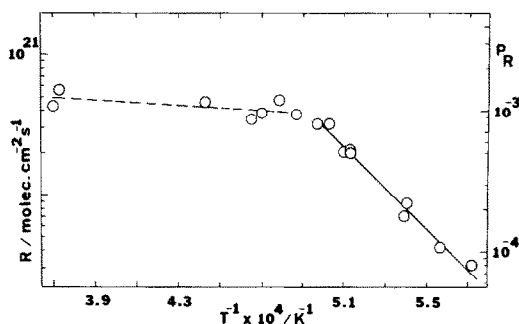
FIG. 1. Reaction rates and probabilities for methane decomposition on 0.0075-cm-diameter tungsten wire. Slope and intercept of full line give rate parameters shown in Table 1. Dashed line connects points in the mass transfer-controlled regime.

FIG. 3. Reaction rates and probabilities for methane decomposition on 0.020-cm-diameter platinum wire. Slope and intercept of this line give rate parameters shown in Table 1.

mass transfer resistances become important (8).

Reaction rates for methane decomposition on carburized tungsten wires have been presented by Boudart et al. (4) for pressures below 10^{-3} and catalyst temperatures above 2000 K, while Winters (5) reported measurements carried out on clean and partially carburized tungsten wires. Our results are in remarkable good agreement with the work reported by Boudart et al., in spite that their data have been obtained at much lower pressures. Agreement indicates that a single reaction rate expression,

R (molecules cm^{-2} sec^{-1}) = 5.4

$\times\ 10^{24}\ \exp(-65{,}800/RT)\ P$ (Torr)   (3)

describes this reaction between 10^{-4} and 770 Torr, a range over 10^6 in reactant pressure.

We know of no published rate data for methane decomposition on molybdenum or platinum wires. Our observations indicate that methane interacts with molybdenum as it does with tungsten, decomposing to hydrogen and leaving a carbon residue on the surface that subsequently diffuses into the metal bulk. The measured reaction rates on both metals are similar (within a factor of 5 or less). Platinum seems to be a much better catalyst for this reaction in the lower temperatures investigated. However, residual carbon soon forms a film on the metal sur-
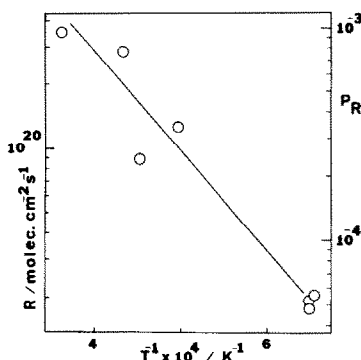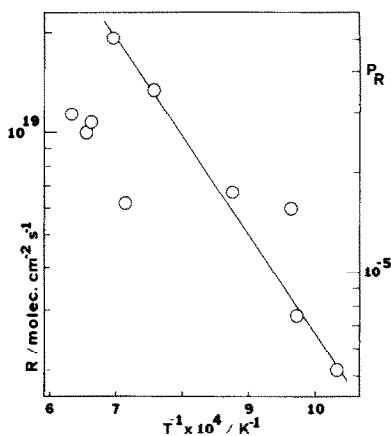

FIG. 2. Reaction rates and probabilities for methane decomposition on 0.0127-cm-diameter molybdenum wire. Slope and intercept of this line give rate parameters shown in Table 1.

TABLE 1

Parameters for Reaction Probability (Eq. (1)) and Diffusion Coefficients (Eq. (2))

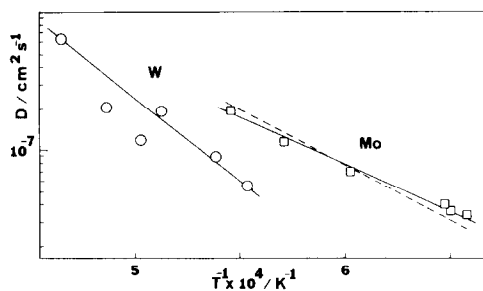| Metal	E (cal/g mol)	A (molec/cm^2 sec)	E_D (cal/g mol)	D_0 (cm^2/sec)
W	65,800	1.06×10^4	55,000	0.22
Mo	20,320	3.364×10^{-2}	30,600	7.48×10^{-4}
Pt	7,620	4.08×10^{-4}	—	—

FIG. 4. Diffusion coefficients for carbon diffusion in tungsten and molybdenum. Slope and intercept of straight full lines give diffusion parameters shown in Table 1. Dashed line shows diffusion coefficient for ^{14}C in Mo, as given in Ref. (10).

face, inhibiting the reaction. Portions of this film peel off, exposing the metal substrate. We believe this phenomenon to be the cause of the scattering in the datapoints shown in Fig. 3. This carbon poisoning of the Pt wire has recently been observed in our laboratory when studying the kinetics of hydrogen cyanide synthesis from ammonia and methane for methane molar fractions greater than 0.5.

DIFFUSION COEFFICIENTS

The variation with reaction time of the electrical conductivity of tungsten and molybdenum wires can be fitted with the solution of the diffusion equation for cylindrical geometry given by Crank (9) for values of the diffusion coefficient plotted in Fig. 4. From the slope and intercept of the straight lines, values for the activation energies and preexponential factors shown in Table 1 were obtained.

Figure 5 shows a plot of diffusion coefficients for carbon in tungsten as a function of temperature calculated using Eq. (1) with parameter values from Table 1 and from literature references. The large dispersion (over six orders of magnitude) in the results from different authors clearly indicates that more detailed experiments are needed.

While we found no published data for carbon diffusion in molybdenum, the diffusion coefficients for this system shown in Fig. 4 do not deviate much from those calculated introducing in Eq. (1) parameter values for molybdenum diffusion in ^{14}C cited in Ref. (10).
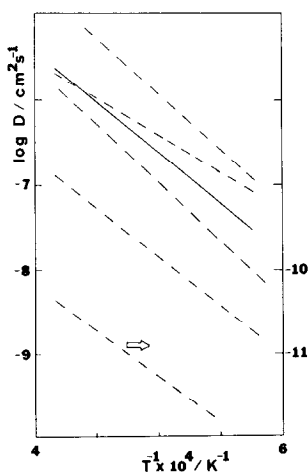
FIG. 5. Display of reported diffusion coefficients for carbon diffusion in tungsten calculated using Eq. (1) with parameters from Ref. (11) (dashed lines) and from Table 1 (full line).

REFERENCES

1. Bond, G. C., "Catalysis by Metals." Academic Press, New York, 1962.
2. Frennet, A., Catal. Rev. 10, 37 (1974).
3. Andrews, M., and Dushman, S., J. Phys. Chem. 29, 462 (1925).
4. Boudart, M., Ollis, D. F., and Harris, G. W., Trans. Faraday Soc. 65, 519 (1968).
5. Winters, H. F., J. Chem. Phys. 62, 2454 (1975); 64, 3495 (1976).
6. Suárez, M. P., and Löffler, D. G., React. Kinet. Catal. Lett. 23, 191 (1983).
7. Smutek, M., and Cerny, S., J. Catal. 47, 178 (1977).
8. Löffler, D. G., and Schmidt, L. D., IEC Fundam. 16, 362 (1977).
9. Crank, J., "The Mathematics of Diffusion." Oxford Univ. Press, London/New York, 1956.
10. "CRC Handbook of Chemistry and Physics," 58th Ed. CRC Press, Boca Raton, Fla., 1977–1978.

11. Rawlings, K. J., Foulias, S. D., and Hopkins, B. J., *Surf. Sci.* **109,** 513–521 (1981) and references cited therein.

M. PATRICIA SUÁREZ
JORGE O. CECHINI
DANIEL G. LÖFFLER

Institute of Materials Science and Technology (INTEMA) Universidad Nacional de Mar del Plata, CONICET Juan B. Justo 4302 7600 Mar del Plata, Argentina