JOURNAL OF CATALYSIS 34, 98–105 (1974)

Some Catalytic Exchange Reactions with Deuterium Oxide on Evaporated Metal Films

W. G. McNAUGHT, C. KEMBALL AND H. F. LEACH

Department of Chemistry, University of Edinburgh, West Mains Road,
Edinburgh, Scotland, EH9 3JJ

Received September 24, 1973

Exchange reactions of hydrogen with deuterium oxide have been studied over metal films. The observed pattern of activity, which is Pt > Rh > Pd >> Ni, is inversely related to the strength of adsorption of oxygen on the metals.

Exchange reactions of propene with deuterium oxide have been studied on films of the same metals and on alumina-supported nickel. Severe poisoning occurred with platinum films but the other catalysts gave constant activity for the exchange which was predominantly stepwise. All hydrogen atoms in the olefin were replaced at similar rates, and the mechanism was thought to involve the reversible formation of adsorbed alkyl radicals. Similar results were found with ethylene and deuterium oxide on nickel films; both olefins showed some self-hydrogenation in addition to exchange on these films.

Methane and propane did not exchange with deuterium oxide on nickel films but underwent reforming reactions at temperatures above 573 K.

INTRODUCTION

Evaporated metal films have been used extensively as catalysts for the exchange of saturated hydrocarbons and other molecules with deuterium, [see Bond (*1*) and Anderson and Baker (*2*)], but not for the corresponding reactions with deuterium oxide as the source of the tracer. The first object of the present work was to obtain results in this neglected area for comparison with the data available on exchange with deuterium. It was planned to examine reactions of deuterium oxide with hydrogen, propene or saturated hydrocarbons on films of nickel, palladium, platinum and rhodium. A further reason for studying the exchange of simple olefins and alkanes with deuterium oxide is to provide results relevant to a better understanding of the complex mechanism of steam reforming of hydrocarbons at higher temperatures. For this purpose it seemed desirable to compare results for the exchange of propene and deuterium oxide on nickel films and on a supported nickel catalyst.

The reaction between hydrogen and deuterium oxide (or between deuterium and light water) was one of the earliest exchange reactions to be studied extensively and platinum was used frequently as a catalyst either as wire, foil or platinum black. Reviews of this work have been given by Eley (*3*) and by Bond (*1*). The reaction also has some importance for the preparation of isotopically enriched material [see Hawes (*4*)].

Hirota (*5*) has reviewed recently the various investigations made by his group on the exchange of propene with deuterium oxide on metals and on supported metal catalysts. The emphasis of this work has been on the use of microwave spectroscopy to analyze the initial products and hence determine the relative rates of exchange of the different types of hydrogen atoms in the molecule; less attention was directed to the absolute rates of exchange with different catalysts although it was established that the exchange reaction is at least a factor of 100 slower than the corresponding hydrogenation and exchange of propene with deuterium (*6*). Considerable variation in the character of the exchange reaction was observed. Nickel or silica-supported nickel gave preferential exchange of the methynic hydrogen atom but palladium or alumina-supported nickel activated all hydrogen atoms to a comparable extent and with platinum *trans*-1-d_1-propene was formed more readily than *cis*-1-d_1.

Other olefins have been exchanged with deuterium oxide. Aman, Farkas and Farkas (*7*) showed that on palladium and nickel catalysts exchange occurred between ethylene or butene and water, and between ethylene and butene, but not between water and butane or between butane and ethylene. Thomson and Walton (*8*) investigated the platinum-catalyzed exchange between cyclohexene and tritiated or deuterated water, the reaction being accompanied by migration of the double bond. Extensive investigations have been made of the exchange of aromatic molecules with deuterium oxide on platinum catalysts (*9*) and on other metals as well (*10*) but these lie outside the scope of the present work.

EXPERIMENTAL METHODS

The exchange reactions were studied in a static system using a Pyrex glass reaction vessel (1.93×10^{-4} m^3) connected to an A.E.I. MS 10 mass spectrometer by a fine capillary leak.

Hydrogen (99.9%) was obtained from the Matheson Co. and purified by diffusion through a palladium thimble; deuterium oxide (99.7%) was supplied by I.C.I. Ltd. The source of the metals and the method of preparation of the films have been described (*11*). A supported metal catalyst containing 6.3% nickel on α-alumina was reduced in dry hydrogen for 24 hr at 733 K and supplied in sealed glass bulbs by the Agricultural Division of I.C.I. Ltd. To make this catalyst, pellets of α-alumina were impregnated with nickel nitrate solution, dried at 473 K and the nitrate decomposed at 773 K. The catalyst was then powdered and reduced in hydrogen. The nickel area, measured by adsorption of carbon monoxide, was 1.1 m^2 g^{-1}. The catalyst was used without further reduction.

The exchange of hydrogen with deuterium oxide was followed by analyzing the relative amounts of H_2, HD and D_2 using 70 V electrons and calibrating the mass spectrometer to determine the sensitivities for the isotopic species. It was not possible to follow the amounts of the isotopic species of water; on admission of a sample of gas containing D_2O the peak at $m/e = 20$ increases slowly over a number of hours and the background peak corresponding to H_2O persisted for days. The exchange of the olefins with deuterium oxide was therefore followed by determining the amounts of the various isotopic olefins using 15 V electrons and allowing for naturally occurring isotopes and fragmentation on a statistical basis.

Results from the exchange reactions were plotted according to the usual first order reversible equations, see Lake and Kemball (*12*), and the initial rates k_0 (% min^{-1}) and k_ϕ (D atoms entering 100 molecules min^{-1}) were obtained. The ratio of these rates $M = k_\phi/k_0$ gave the mean number of deuterium atoms acquired by each olefin molecule in the initial stages of the reaction. Some metal films were used only at a single temperature. In other cases the exchange reaction was studied also at a second and higher temperature without changing the gas mixture or the film. Unless stated otherwise, agreement with the first order reversible equations was observed, which implied that catalytic activity was remaining constant.

RESULTS

Exchange of Hydrogen with Deuterium Oxide

The standard mixture consisted of 1 kN m^{-2} of each gas and an exchange rate of 1% min^{-1} corresponded to an absolute rate of 8.5×10^{15} molecules s^{-1}.

Rates of reaction on the metal films at 273 K are reported in Table 1. Platinum was the most active metal and the rate quoted is a minimum because of the possibility of some diffusion limitation. Experi-

TABLE 1

RATES OF EXCHANGE OF H_2 WITH D_2O AT 273 K AND COMPARABLE DATA FOR THE EXCHANGE OF HYDROXYL HYDROGEN ATOMS IN ALCOHOLS (*13*)

Reaction	Catalyst			
	Pt	Rh	Pd	Ni
H_2/D_2O (rate/% min^{-1} (10 mg)$^{-1}$)	>20	10.7	0.8	<0.05
H_2/D_2O ($r_0{}^a/10^{15}$ molecules s^{-1} m^{-2})	>3000	1030	450	<4
CH_3OH/D_2 ($r_0/10^{15}$ molecules s^{-1} m^{-2})	—	120	500	5
C_2H_5OH/D_2 ($r_0/10^{15}$ molecules s^{-1} m^{-2})	300	19	—	—

[a] Areas of Pt, Rh and Ni films assumed to be 0.057, 0.088 and 0.097 m^2 (10 mg)$^{-1}$ (*11*) and Pd films assumed to have a geometric area of 0.015 m^2.

ments were not attempted below 273 K because a reduction of the pressure of water vapor would have been necessary to avoid condensation. An approximate activation energy of 41 kJ mol^{-1} was derived for palladium films which gave rates of 2.5 and 2.6% min^{-1} at 292 K.

It was difficult to estimate the activity of nickel films for the exchange reaction because rates were slightly lower in the presence of nickel films than in blank reactions with the whole of the glass in the Pyrex reaction vessel available as a catalyst. There was an apparent negative activation associated with the blank reaction with rates decreasing from 0.18 to 0.044% min^{-1} when the temperature was increased from 292 to 415 K. This behavior presumably arises from a decrease in the amount of the appropriate adsorbed species with increase in temperature. The main reason for believing that some activity was attributable to the nickel films was an increase in the rate of the reaction with temperature. The result in Table 1 represents a maximum value for the nickel activity.

Exchange of Propene with Deuterium Oxide

The standard mixture consisted of 333 N m^{-2} of propene and 1 kN m^{-2} of deuterium oxide. A rate of 1% min^{-1} corresponded to an absolute rate of 2.6×10^{15} molecules s^{-1}. No exchange was observed in control experiments with Pyrex glass up to 673 K.

Rhodium and Palladium

Apart from a slight decrease in the rate of exchange in the first few minutes, the results on these two metals followed the usual first order reversible equations closely. The exchange involved a stepwise replacement of the hydrogen atoms by deuterium atoms and the agreement obtained between experimental distributions of products and the corresponding calculated distributions at all stages in the reactions confirmed that all six hydrogen atoms were replaceable at similar rates. The results for rhodium are given in Table 2 and the derived Arrhenius parameters in Table 3. The results for palladium are shown in Fig. 1 together with some preliminary values reported by Patterson (*14*) using a similar technique. The values of M for all the ex-

TABLE 2

RATES OF EXCHANGE OF C_3H_6 WITH D_2O

Catalyst	Wt (w/mg)	Temp (T/K)	Initial rate ($r_0/10^{15}$ molecules $s^{-1}m^{-2}$)	M
Rh	4.5	373	1.5	1.16
	3.7	411	4.8	1.26
	4.5	451	8.6	1.12
	11.3	457	22	1.05
	3.7	473	69	1.44
	5.8	497	47	1.13
	5.8	553	104	1.13
Ni	9.4	323	10	1.00
	5.6	351	11	1.03
	9.4	373	30	1.15
	5.6	433	104	1.13
	12.3	447	106	1.10
Ni/α-Al_2O_3	560	380	1.0	1.00
	700	405	2.1	0.83
	560	449	4.4	1.00

TABLE 3

ARRHENIUS PARAMETERS FOR OLEFIN EXCHANGE

Reaction	Catalyst	Activation energy (E/kJ mol^{-1})	Log$_{10}$ A (A/molecules s^{-1} m^{-2})	Rate at 400 K ($r_0/10^{15}$ molecules s^{-1} m^{-2})
C_3H_6/D_2O	Pd	22	20.9	1800
C_3H_6/D_2O	Rh	42	21.1	4.0
C_3H_6/D_2O	Ni	28	20.3	48
C_3H_6/D_2O	Ni/α-Al_2O_3	27	18.8	1.7
C_2H_4/D_2O[a]	Ni	35	20.9	18

[a] The reaction includes some production of ethane.

periments with palladium lay between 1.00 and 1.18. Patterson also showed that oxygen poisons the exchange of propene with deuterium oxide on palladium. Using a mixture of 216, 360 and 760 N m^{-2}, respectively, of oxygen, propene and deuterium oxide, he observed very little exchange at 333 K but at higher temperatures various side reactions occurred in which propan-1-ol and propan-2-ol and traces of propane were produced.

Nickel

The character of the exchange reaction of propene with deuterium oxide on nickel films was generally similar to the behavior with palladium or rhodium films except that more of a species of mass 44 (either $C_3H_4D_2$ or C_3H_8) than expected was produced in the first few minutes of the reaction. Experiments were carried out with propene and light water both using the mass spectrometer and in another apparatus with a gas chromatograph, and it was confirmed that a few percent of propane was produced in the initial period. Some 2% was formed at 273 K and about 6% at temperatures between 300 and 473 K but no further propane production was noted after 15 min. It is clear that the propane formed in the presence of D_2O must also be C_3H_8 and not C_3H_7D or $C_3H_6D_2$ which would have given rise to peaks corresponding to *m/e* of 45 or 46, respectively. This self-hydrogenation of propene did not occur to any appreciable extent below 373 K when propene was admitted to a nickel film in the absence of water.

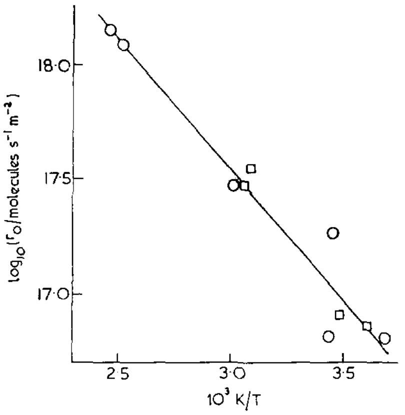

FIG. 1. Arrhenius plots for the initial rates of exchange of propene with deuterium oxide on palladium films: (○), present work; (□) results from Patterson (*14*). Values of *M* ranged from 1.00 to 1.18 but showed no correlation with temperature.

As the formation of propane ceased after about 15 min it was possible to correct the mass spectral data to allow for the presence of some 6% of C_3H_8. The corrected values could then be used to determine the rate of exchange of propene. The rates and *M* values are given in Table 2 and the derived Arrhenius parameters in Table 3. These tables also include results for the exchange using the Ni/α-Al_2O_3 catalyst upon which no significant propane formation occurred.

Platinum

An initially rapid exchange of propene with deuterium oxide occurred but the rate decreased with time and on raising the temperature a temporary increase of rate was followed by further self-poisoning. A number of different kinds of experiments involving various pretreatments of the films were carried out and some of the results

TABLE 4
RATES OF EXCHANGE OF C_3H_6 WITH D_2O ON Pt FILMS

Expt	Pretreatment conditions	Reaction temp (T/K)	Initial rate[a] k_ϕ	Interval (t/min)	Subsequent rate[a] k'_ϕ
1	None	295	9.5	130	1.6
2	Use in Expt 1	373	6.0	160	0.26
3	D_2O, 20 min, 293 K	293	3.2	80	0.81
4	C_3H_6/D_2O, 150 min, 293 K	495	6.3	150	6.3
5	C_3H_6, 20 min, 293 K	498	19	35	19
6	568 K	573	2.3	130	2.3

[a] The initial rate k_ϕ is expressed as D atoms entering 100 molecules of olefin min^{-1} (10 mg)$^{-1}$ and the subsequent rate k'_ϕ is the corresponding extrapolated value of the rate at zero conversion but based on the final section of the experiment.

are shown in Table 4. Catalysts pretreated with water behaved similarly to untreated films. Pretreatment with propene or with a reaction mixture led to substantial reduction in activity but constant rates were found at the higher temperatures required in these experiments. The poisoning was clearly associated with the interaction of propene with the films and was greater the higher the temperature of pretreatment.

The values of M for exchange of propene on all platinum films, untreated or pretreated, were about 2 and the initial products contained all species from C_3H_5D to C_3D_6 but with decreasing amounts of the more highly exchanged molecules.

Exchange of Other Compounds with Deuterium Oxide

Unsuccessful attempts were made to exchange propane or methane with deuterium oxide over nickel films. In both cases breakdown to other products occurred on raising the reaction temperature; propane formed mainly carbon dioxide and methane at 573 K and methane formed carbon monoxide, carbon dioxide and hydrogen above 673 K. Exchange of these saturated hydrocarbons was not examined on the other three metals.

The reaction of ethylene with deuterium oxide was studied over nickel films at temperatures from 373 to 573 K. The main reaction was a stepwise exchange of the olefin but some multiply-exchanged products were observed and as the reaction proceeded further the growth of peaks corresponding to m/e of 33 to 36 indicated the presence of a range of deuterated ethanes. Subsidiary experiments with a C_2H_4/H_2O mixture confirmed that ethane was formed in increasing amounts as the temperature was raised from 300 to 573 K. Detailed analysis of the C_2H_4/D_2O reaction was not attempted but Arrhenius parameters for the total rate of disappearance of C_2H_4, by exchange and by the minor reaction to form ethanes, were evaluated and are given in Table 3.

DISCUSSION

Chemisorption of Water

It is appropriate to consider the chemisorption of water on metals before discussing the results for the exchange reactions. There is an extensive literature (*15–17*) concerning the chemisorption of hydrogen and oxygen on metals but there is much less quantitative information about the chemisorption of water molecules. If dissociative adsorption occurs it may be partial

$$H_2O \rightarrow H_{ads} + OH_{ads} \qquad (1)$$

or complete

$$H_2O \rightarrow 2H_{ads} + O_{ads}. \qquad (2)$$

It is useful to note the standard enthalpy changes (*18*) for the following processes involving gaseous species:

	$\Delta H_{298}{}^0$(kJ mol^{-1})	
$H_2O \rightarrow H_2 + \frac{1}{2} O_2$,	246	(3)
$H_2O \rightarrow H + OH$,	498	(4)
$OH \rightarrow H + O$	446	(5)

Using the datum for reaction (3), it is obvious that reaction (2) will be exothermic if

$$q_{H_2} + \frac{1}{2} q_{O_2} > 246 \text{ kJ mol}^{-1},$$

where q_{H_2} and q_{O_2} are the heats of chemisorption of hydrogen and oxygen, respectively. The heats of chemisorption of hydrogen on the four metals nickel, palladium, platinum and rhodium are similar (*15*) and may be taken as 110 kJ mol^{-1}. It follows that reaction (2) will only be exothermic on any of these metals if $q_{O_2} > 272$ kJ mol^{-1}. The values of q_{O_2} reported by Brennan, Hayward and Trapnell (*19*) are 267, 280, 318 and 448 kJ mol^{-1}, respectively for platinum, palladium, rhodium and nickel. Hence strong adsorption by reaction (2) should occur on nickel and probably on rhodium, but is not very likely on the other two metals. When the adsorption of oxygen on a metal is exceptionally strong as with tungsten ($q_{O_2} = 812$ kJ mol^{-1}), additional adsorption of water with displacement of hydrogen from the surface has been observed (*20*).

It is not possible to make detailed comments on the relative importance of reactions (1) and (2) except to note that entropy considerations and the relative values for the enthalpy changes of reactions (4) and (5) would suggest that complete dissociation is more likely than partial dissociation the lower the coverage.

The Exchange of Hydrogen with Deuterium Oxide

All four metals are very active catalysts for the exchange of hydrogen with deuterium and rates of reaction in excess of 10^{20} molecules s^{-1} m^{-2} have been reported for metal films at 293 K (*21*). The results in Table 1 show that the H_2/D_2O reaction is slower than the H_2/D_2 exchange by factors ranging from about 10^2 for platinum to 10^5 for nickel. The order of activity for the four metals is Pt > Rh > Pd ≫ Ni and there is an inverse correlation between this order and the heat of adsorption of oxygen on the metals. Since we have argued that the strength of adsorption of water on the metals should parallel the strength of adsorption of oxygen, it seems likely that the more strongly the water is adsorbed the more it reduces the rate of the reversible dissociation of hydrogen and as a consequence also the rate of the H_2/D_2O exchange reaction. Thus platinum, rhodium and palladium are good catalysts for the exchange because they do not adsorb water strongly. The relatively poor catalytic activity of nickel can be attributed to its greater affinity for oxygen and correspondingly stronger adsorption of water. The alternative explanation that the rate of the exchange is limited by the rate of the reversible dissociation of the water molecules seems less attractive.

The additional data in Table 1 show that the pattern of activity of the metals for the exchange with deuterium of the hydroxyl hydrogen atoms in methanol and ethanol (*13*) resembles that now established for the exchange of hydrogen with deuterium oxide. The rates for the H_2/D_2O and CH_3OH/D_2 reactions are also similar.

The Exchange of Propene and Other Molecules

The exchange reactions of propene with deuterium oxide on the metal films are very much slower than the reactions of exchange and deuteration which occur with ethylene and deuterium (*22*) and they are also slower than the exchange reactions of hydrogen with deuterium oxide. The three metals rhodium, palladium and nickel as films do not appear to show preferential exchange of any of the different types of hydrogen atom in the propene molecule; stepwise exchange predominates and all 6 atoms are replaced at similar rates. These facts about the character of the exchange reactions suggest that the mechanism may involve interconversion between adsorbed olefin molecules and adsorbed alkyl radicals (1-propyl and 2-propyl). Mechanisms involving other intermediates seem less probable as they would be likely to give exchange of the different hydrogen atoms at significantly different rates.

The order of activity of the metals for the C_3H_6/D_2O exchange is not the same as for the H_2/D_2O reaction. The situation is clearly more complicated in the presence of the olefin molecules since there are alternative processes which can occur to a greater or lesser extent such as the self-hydrogenation with nickel films or the poisoning reactions with platinum films. The limiting step is likely to be the rate of interconversion between adsorbed olefin and adsorbed propyl radicals; the reversible adsorption of the olefin molecules must be more rapid as the exchange is mainly stepwise. The frequency factors for the olefin exchange reactions on the films (Table 3) are similar and the differences in activity are mainly due to the variations in the activation energies. Conversely, the difference between nickel film and supported nickel catalysts is associated with a lower frequency factor for the supported catalyst indicating that only a fraction of the metal sites on this latter material may be effective. The similarity in the rates of reaction of ethylene and propene on nickel films is further support for a mechanism involving adsorbed alkyl species.

Self-hydrogenation of propene in the presence of water seems to occur only with nickel films and not with supported nickel or the other metals in the temperature ranges used for the exchange reaction. The process must involve the simultaneous formation of adsorbed species containing less hydrogen than the olefin molecules and might lead to some poisoning of the catalyst. In fact, substantial poisoning was observed only with platinum films which did not appear to cause self-hydrogenation of the olefin. Cormack, Thomson and Webb (*23*) have studied the retention of adsorbed ^{14}C-labeled ethylene on alumina-supported metals during subsequent hydrogenation and they found that the percentages retained varied according to the pattern $Pd > Ni = Rh > Pt$. Such data do not explain the severe poisoning we encountered with platinum but results with supported catalysts are not necessarily a good indication of behavior to be expected with films. Thomson and Wishlade (*24*) observed retentions varying from 53 to 89% with films of nickel compared with 20% for the alumina-supported nickel catalysts; results are not available on platinum films. The presence of the water vapor is clearly an important factor and probably provides some protection to nickel films thus reducing the extent of the reaction between the olefin molecules and the metal surface. It is not easy to understand why poisoning occurred mainly with platinum and not with palladium or rhodium films. Aman, Farkas and Farkas (*7*) observed some poisoning of the exchange of ethylene with deuterium oxide on charcoal-supported palladium when low pressures of water were used. It is interesting that palladium films are much more active for the C_3H_6/D_2O reaction than the other catalysts we examined but yet are significantly poisoned by small pressures of oxygen (*14*).

The absence of any exchange of either propane or methane with deuterium oxide on nickel films is noteworthy. The adsorptions of the saturated hydrocarbon appear to be essentially irreversible in the presence of the adsorbed water so that reforming reactions occur in preference to exchange. Ross and Steel (*25*) have very recently reported a similar absence of exchange of methane with D_2O (or with $D_2 + H_2O$) or on alumina-supported nickel catalyst.

ACKNOWLEDGMENTS

One of us (W.G.McN.) held a C.A.P.S. studentship from the S.R.C.; and we are grateful to the Agricultural Division of Imperial Chemical Industries Ltd. for supplying supported nickel catalysts.

REFERENCES

1. BOND, G. C., "Catalysis by Metals" Chap. 9 and 10. Academic Press, London, 1962.

2. ANDERSON, J. R., AND BAKER, B. G., *in* "Chemisorption and Reactions on Metallic Films" Academic Press, London and New York, 1971, Vol. 2, p. 63.

3. ELEY, D. D., *in* "Advances in Catalysis" (W. G. Frankenburg, V. I. Komarewsky and E. K. Rideal, Eds.), Vol. 1, p. 157. Academic Press, New York, 1948.

4. Hawes, M. G., *Platinum Metals Rev.* **3,** 118 (1959).
5. Hirota, K., *Proc. Int. Congr. Catalysis, 5th, 1973* **1,** 37.
6. Hirota, K., and Hironaka, Y., *J. Catal.* **4,** 602 (1965).
7. Aman, J., Farkas, L., and Farkas, A., *J. Amer. Chem. Soc.* **70,** 727 (1948).
8. Thomson, S. J., and Walton, A., *Trans. Faraday Soc.* **53,** 821 (1957).
9. Garnett, J. L., and Sollich-Baumgartner, W. A., *in* "Advances in Catalysis" (D. D. Eley, H. Pines and P. B. Weisz, Eds.), Vol. 16, p. 95. Academic Press, New York, 1966.
10. Hirota, K., and Ueda, T., *Bull. Chem. Soc. Jap.* **35,** 228 (1962).
11. Kemball, C., *Proc. Roy. Soc., Ser. A* **214,** 413 (1952).
12. Lake, I. J. S., and Kemball, C., *Trans Faraday Soc.* **63,** 2535 (1967).
13. Anderson, J. R., and Kemball, C., *Trans. Faraday Soc.* **51,** 966 (1955).
14. Patterson, W. R., PhD thesis, The Queen's Univ. of Belfast, 1963.
15. Hayward, D. O., and Trapnell, B. M. W., "Chemisorption" Butterworth, London, 1964.
16. Hayward, D. O., *in* "Chemisorption and Reactions on Metallic Films," Vol. 1, p. 225. Academic Press, London, 1971.
17. Geus, J. W., *in* "Chemisorption and Reactions on Metallic Films," Vol. 1, p. 327. Academic Press, London, 1971.
18. Franklin, J. L., Dillard, J. G., Rosenstock, H. M., Herron, J. T., Draxl, K., and Field, F. H., *Nat. Stand. Ref. Data. Ser. Nat. Bur. Stand.* **26,** (1969).
19. Brennan, D., Hayward, D. O., and Trapnell, B. M. W., *Proc. Roy. Soc., Ser. A* **256,** 81 (1960).
20. Imai, H., and Kemball, C., *Proc. Roy. Soc., Ser. A* **302,** 399 (1968).
21. Bond, G. C., "Catalysis by Metals" Chap. 8. Academic Press, London, 1962.
22. Kemball, C., *J. Chem. Soc.* p. 735 (1956).
23. Cormack, D., Thomson, S. J., and Webb, G., *J. Catal.* **5,** 224 (1966).
24. Thomson, S. J., and Wishlade, J. L., *Trans. Faraday Soc.* **58,** 1170 (1962).
25. Ross, J. R. H., and Steel, M. C. F., *J. Chem. Soc. Faraday Trans. I* **69,** 10 (1973).