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# Interaction of Alcohols with Evaporated Metal Films

## Part 1.—Adsorption and Decomposition of Methanol on Metal Films of Nickel, Palladium and Aluminium

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The interaction of methanol with clean and oxidized films of Ni, Pd and Al has been investigated in the temperature range 223-450 K. Dissociative adsorption of methanol on the clean films occurred even at 223 K. A substantial fraction of the adsorption on oxidized Al film at 223 K was reversible. Further extensive adsorption of the alcohol took place on all surfaces, excluding oxidized Al, in the temperature range 290-450 K. Oxidation of Ni and Al films occurred through the reaction of the resulting surface methoxide and hydrogen adatoms in which gaseous methane was produced. The surface methoxide on Pd underwent a series of reactions by which $CH_2O$, CO and $H_2$ were formed. Carbon dioxide and water vapour were also detected in the gas phase subsequent to the methanol adsorption on oxidized Ni and Pd films at temperatures $< 290$ K. The rate of methanol adsorption on any film directly depended on the methanol pressure. The activation energy ($E_a$) of methanol adsorption as well as the pre-exponential factor ($A$) in the rate equation remained independent of the variation in the extent of adsorption. A linear relationship was found between the values of log $A$ and those of $E_a$ for the various surfaces, with the exception of Al, suggesting the operation of a compensation effect in the methanol adsorption and decomposition on such surfaces. Adsorption of monodeuterated methanol on the films over a similar temperature range was also carried out with the aim of examining the reactivity of the oxygen–hydrogen bond and to obtain information regarding the mode of alcohol adsorption and its subsequent decomposition on the surface.

Although a substantial amount of research has been carried out on the adsorption and the catalytic decomposition of methanol, much of this research has attempted to find effective catalysts for the synthesis of this alcohol or to obtain information on the production of other organic products. Moreover, most of the adsorption investigations with methanol have been carried out on surfaces other than metal films and generally at relatively high pressures or at high temperatures.[1-4] Thus, there is a lack of fundamental information on the adsorption of methanol on evaporated metal films under carefully controlled conditions. There is so far a considerable interest in the mechanisms of the formation and the decomposition of methanol on metal and metal oxide surfaces.

We have selected nickel, palladium and aluminium films on which, as well as on their oxidized surfaces, the adsorption and the decomposition of methanol have been studied. In order to examine the catalytic reactivity of the oxygen–hydrogen bond in methanol and to understand the mode of adsorption of the alcohol on the surface, the adsorption and the decomposition of the monodeuterated methanol have been performed on the same surfaces under similar experimental conditions.

## EXPERIMENTAL

The apparatus and the general technique employed in this work have been described[5,6] as have the preparation and the sintering of the evaporated films.[5,7] Nickel and palladium films were prepared from Johnson Matthey spectroscopically standardized wires (0.5 mm diameter) which were first reduced at 1300 K in a small pressure (*ca.* 6 N $m^{-2}$) of pure hydrogen, then degassed at a slightly higher temperature for not less than 6 h. Aluminium films were prepared from Specpure wire (0.5 mm diameter), which was supported on an electrically heated tungsten coil. During the deposition of each film the reaction vessel was pumped and the pressure was always $< 10^{-6}$ N $m^{-2}$. Each film was prepared at 78 K and sintered at 360 K (or 400 K) for 30 min before area measurements using krypton adsorption were made.

Methanol was a spectroscopic sample obtained from Hopkin and Williams. It was thoroughly degassed by repeated freezing and pumping operations. Oxygen was prepared by heating AnalaR $KMnO_4$ after prolonged degassing. Krypton was obtained from the British Oxygen Co. in sealed glass bulbs. Both oxygen and krypton were further purified before use.

The gas phase was analysed using a Quadruvac Q200 mass-spectrometer partial-pressure gauge, obtained from Lybold–Heraus, which operated on the quadrupole principle and covered the mass range 1-200 a.m.u. This instrument was combined with a pressure converter which could reduce the gas pressure under analysis to $< 10^{-1}$ N $m^{-2}$ without influencing its composition. The gauge head of the mass spectrometer for ion detection was supplemented by a Faraday cup for partial analysis down to $10^{-6}$ N $m^{-2}$. The reaction system was connected directly to the mass spectrometer to enable an analysis of the gas phase with time throughout the interaction of methanol with the metal films.

## RESULTS

### EXTENT OF ADSORPTION

The area of each film was determined from the krypton adsorption isotherm at 78 K before the admission of methanol doses. The extent of methanol adsorption on clean ($\theta$) and oxidized ($Y$) metal films were expressed as:

$$\theta = V_m / V_{Kr} \tag{I}$$

and

$$Y = V_m / \bar{V}_{Kr} \tag{II}$$

where $V_m$ represented the volume of methanol adsorbed, $V_{Kr}$ and $\bar{V}_{Kr}$ were the volumes of the krypton monolayer on clean and oxidized films, respectively; all the volumes were measured in units of $mm^3$ at s.t.p.

Methanol, in the pressure range 1-14 N $m^{-2}$, was admitted to the film at 223 K and the adsorption was followed until the rate of uptake fell below $10^{-5}$ $mm^3$ $s^{-1}$ $cm^{-2}$. The film was then warmed in successive stages up to 450 K and the reaction at each stage was followed in a similar manner; the gas phase at each temperature was analysed with time with the aid of the mass-spectrometer partial-pressure gauge.

### ADSORPTION OF METHANOL AT 223 K

Fast, irreversible adsorption of methanol occurred on Ni films at 223 K up to $\theta = 1.1$. Further adsorption took place at a rate which decreased with increasing values of $\theta$, the rate of methanol uptake became $10^{-5}$ $mm^3$ $s^{-1}$ $cm^{-2}$ when $\theta$ was 1.32. A small pressure of hydrogen (*ca.* $10^{-1}$ N $m^{-2}$) was observed at such surface coverage with methanol. The initial adsorption of methanol on Pd films at 223 K was similar to that on Ni; there was a rapid methanol uptake to a final pressure of $10^{-4}$ N $m^{-2}$ up to $\theta = 1.5$. Beyond such a coverage the adsorption continued at a slow rate which decreased considerably with time. At $\theta = 1.5$, some formaldehyde appeared in the gas phase and its amount increased slightly as $\theta$ increased. The maximum extent of methanol adsorption on Pd film at 223 K corresponded to $\theta = 2.1$.

At 223 K, there was an irreversible and instantaneous uptake of methanol on Al film until $\theta$ became 0.5 under a pressure of $10^{-3}$ N $m^{-2}$. Further methanol adsorption on Al film was accompanied by the evolution of methane and hydrogen. Methanol adsorption and the accompanying liberation of $H_2$ and $CH_4$ continued on the film until $\theta$ became 0.96 when the rate of methanol uptake became extremely slow; some CO gas was also detected when $\theta$ approached 0.96. Table 1 shows the surface area ($V_{Kr}$), the total methanol uptake ($V_m$) and the corresponding values of $\theta$ on the three metal films.

TABLE 1.—ADSORPTION OF METHANOL ON FILMS OF Ni, Pd AND Al AT 223 K

| film | $V_{Kr}$ | $V_m$ | $\theta$ |
|---|---|---|---|
| Ni | 28.0 | 37.0 | 1.32 |
| Pd | 50.2 | 105.4 | 2.10 |
| Al | 5.2 | 5.0 | 0.96 |

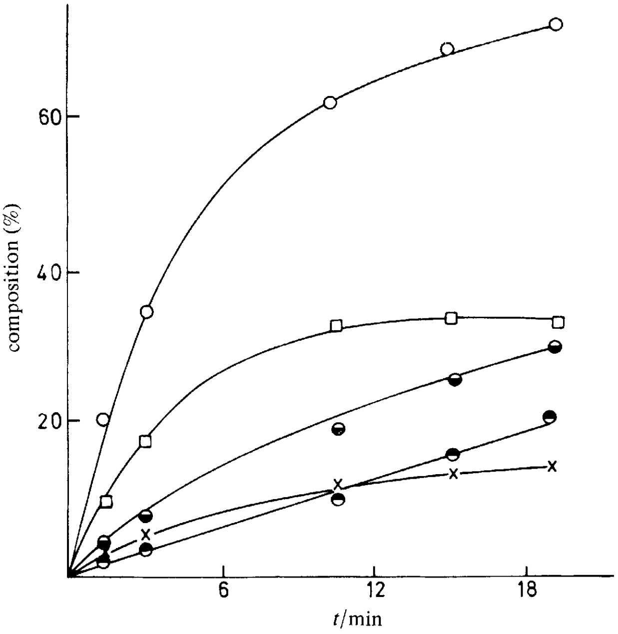


FIG. 1.—Analysis of the gas phase throughout the interaction of methanol with Ni film at 333 K. The points on each plot represent the changes in the percentage (%) of the gas with time. ○, $CH_4$; □, $CH_2O$; ◒, $H_2$; ◓, $C_2H_6$; ×, CO. The points corresponding to methanol were deleted.

## EFFECT OF TEMPERATURE ON METHANOL ADSORPTION

The metal film, after saturation with methanol at 223 K, was warmed to 290 K or to a higher temperature in the presence of gaseous methanol, at a pressure of 6-12 N $m^{-2}$. The rate of methanol uptake was measured at the new temperature and the gas phase was analysed to make an estimation of the products. When Ni film was treated in this manner a further slow adsorption of methanol occurred together with the evolution of $H_2$ at 290 K. On raising the film temperature to 333 K, the rate of

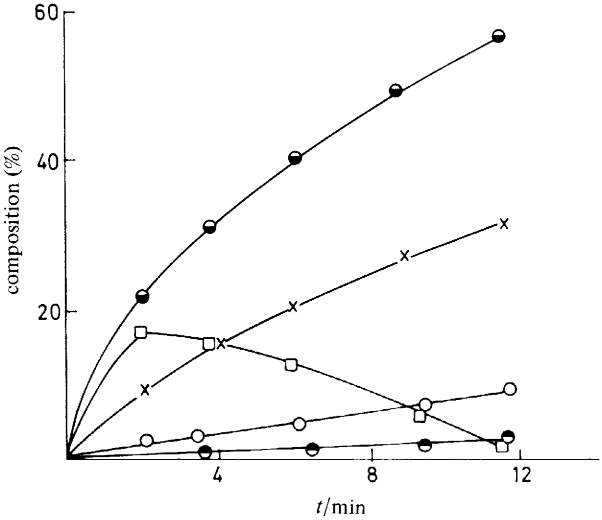


FIG. 2.—Analysis of the gas phase for the adsorption of methanol on a Pd film at 393 K. The symbols are as in fig. 1.

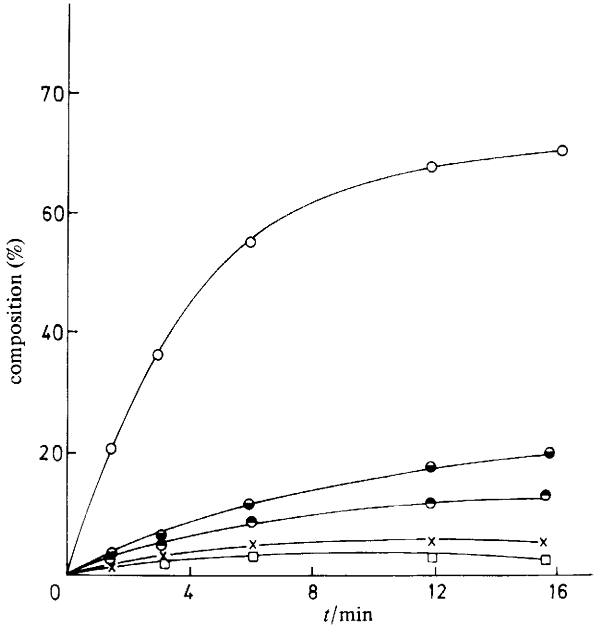


FIG. 3.—The gas-phase analysis throughout methanol interaction with Al film at 393 K.

methanol adsorption increased; meanwhile some $CH_4$, $H_2$, CO, $CH_2O$ and $C_2H_6$ appeared in the gas phase. The pressure of $CH_2O$ remained almost constant while those of $CH_4$, $H_2$, CO and $C_2H_6$ increased with time as indicated in fig. 1. The pressure of $CH_2O$ decreased at 363 K and the evolution of CO, $H_2$ and $C_2H_6$ gases was less pronounced than at 333 K. Methane remained the main gaseous product of methanol adsorption on Ni film at temperatures > 333 K.

The evolution of the gaseous products ceased on evacuating the reaction vessel for

15 min at 363 K. When methanol was subsequently admitted to the system at the same temperature further adsorption occurred with the evolution of mainly methane.

Warming the adlayer on Pd to 290 K resulted in further methanol adsorption and in the evolution of a substantial amount of $H_2$ and CO gases. On heating the film in the presence of methanol to 333 and 363 K, mainly $CH_2O$ and $H_2$, together with smaller amounts of CO, $CH_4$ and $C_2H_6$, appeared in the gas phase. The pressure of $CH_2O$ decreased and those of $H_2$ and CO gases increased as more methanol was taken up by the Pd film at 393 K (fig. 2). Methane and ethane evolution started at 290 K but their amounts increased only slightly in the temperature range 290-400 K.

When the adlayer on Al film at 223 K was warmed to 290 K further methanol adsorption took place which was accompanied by the evolution of $H_2$ and $CH_4$. At $\geqslant$ 333 K, adsorption of methanol continued at higher rates and methane was the main gaseous product while the minor products involved $H_2$, CO, $C_2H_6$ and $CH_2O$; the analysis of the gaseous products with time at 393 K is depicted in fig. 3.

## ADSORPTION ON OXIDIZED FILMS

In a series of experiments, the metal films were saturated with oxygen ($V_{O_2}$) at 300 K under oxygen pressure of 1.3 N m$^{-2}$. The film was then cooled to 223 K, the gaseous oxygen was pumped out for 10 min until the pressure in the reaction system became *ca.* $10^{-4}$ N m$^{-2}$ and thereafter methanol was admitted to the film in doses and the adsorption was followed in a similar manner to that described for the clean films. Table 2 summarizes the extents of oxygen adsorption ($V_{O_2}$) on the films at 300 K and the subsequent methanol uptake ($V_m$) at 223 K together with the krypton monolayers on the clean ($V_{Kr}$) and the oxidized ($\bar{V}_{Kr}$).

TABLE 2.—ADSORPTION OF METHANOL ON OXIDIZED FILMS OF Ni, Pd AND Al AT 223 K

| film | $V_{Kr}$ | $V_{O_2}$ | $\bar{V}_{Kr}$ | $V_m$ | $Y$ |
|---|---|---|---|---|---|
| Ni | 17.0 | 61.2 | 14.0 | 37.8 | 2.70 |
| Pd | 41.5 | 118.3 | 38.0 | 117.8 | 3.10 |
| Al | 3.95 | 6.7 | 5.86 | 9.91 | 1.69 |

Methanol adsorption on oxidized Al film occurred rapidly to the extent $Y = 1.2$. The adsorption was thereafter slower and its rate became $10^{-3}$ mm$^3$ s$^{-1}$ cm$^{-2}$ at $Y = 1.69$. No gaseous products were observed at any stage at this temperature. When the film was pumped at this stage down to $10^{-3}$ N m$^{-2}$ further fast methanol adsorption was possible at the same temperature (223 K); this was estimated to amount to 20% of the total methanol uptake on the oxidized film. When the adsorbed layer was heated gradually up to 400 K, methanol desorption occurred; it was possible to remove some 80% of the adsorbed methanol by such a heat treatment.

Oxidized Ni and Pd films adsorbed methanol at 223 K instantaneously to $Y$ values of 2.7 and 3.1, respectively, and the adsorption was not accompanied by the liberation of gases. On warming the film to 290 K, some methanol desorption occurred by which the value of $Y$ decreased to 2.45 on Ni and to 2.68 on Pd; such amounts of desorbed methanol were found to be removable even by pumping the film at 223 K for a few minutes. Further slow adsorption began at 290 K and the rate increased with temperature. The major gaseous products of the methanol interaction with both films at temperatures $\geqslant$ 290 K involved $H_2$, CO, $H_2O$, $CO_2$, $CH_2O$ and $CH_4$. Table 3 shows the composition of the gas phase at three temperatures on oxidized Ni and Pd films.

TABLE 3.—GAS-PHASE ANALYSIS FOR THE ADSORPTION AND DECOMPOSITION OF METHANOL ON OXIDIZED Ni AND Pd FILMS

The amount of each constituent is expressed by its percentage in the gas mixture. The analysis at 363 and 400 K was made after 5 and 10 min, respectively, of attaining these temperatures.

| film | temp./ K | $CH_3OH$ | $CH_2O$ | CO | $H_2O$ | $CO_2$ | $CH_4$ | $H_2$ |
|---|---|---|---|---|---|---|---|---|
| Ni | 333 | 53.4 | 10 | 15 | 10 | 3.9 | 3.0 | 5.0 |
| | 363 | 45.3 | 4.5 | 18 | 9.2 | 4.2 | 3.5 | 15.2 |
| | 400 | 2.2 | 1.2 | 27.2 | 20 | 10 | 6.0 | 29.5 |
| Pd | 333 | 51.7 | 13.5 | 10 | 7.5 | 2.5 | 6.2 | 5.6 |
| | 363 | 28.0 | 5.3 | 25 | 10.0 | 7.0 | 7.0 | 14.0 |
| | 400 | 2.3 | 4.1 | 38 | 15.0 | 10.0 | 7.5 | 19.0 |

TABLE 4.—ANALYSIS OF THE GAS PHASE, AS A PERCENTAGE OF EACH CONSTITUENT, AT A GIVEN TIME THROUGHOUT THE INTERACTION OF $CH_3OD$ WITH OXIDIZED Ni AND Pd FILMS AT 363 K

| composition | oxidized Ni (%) | oxidized Pd (%) |
|---|---|---|
| $CH_3OD$ | 22.3 | 26.6 |
| $H_2$ | 24.6 | 13.3 |
| CO | 17.5 | 20.0 |
| HDO | 5.0 | 6.0 |
| $H_2O$ | 1.0 | 1.0 |
| $D_2O$ | 4.0 | 5.0 |
| $CH_3D$ | 3.0 | 5.0 |
| $CH_4$ | 1.3 | 2.0 |
| $CO_2$ | 5.3 | 7.0 |
| $CH_2O$ | 1.0 | 2.1 |
| $D_2$ | 8.0 | 6.5 |
| HD | 5.0 | 4.5 |

## ADSORPTION OF MONODEUTERATED METHANOL

The adsorption and the decomposition of $CH_3OD$ on clean and oxidized metal films of Ni, Pd and Al have also been investigated in a similar manner to that of $CH_3OH$. The adsorption pattern and the general behaviour in the temperature range 223-450 K were very similar to that of $CH_3OH$.

The major gaseous products on clean Ni film in the temperature range 290-450 K were mainly $CH_3D$ and to a less extent $CH_4$, together with such gases as HD, $D_2$, $C_2H_6$, CO and $CH_2O$. On Pd film in the same temperature range $H_2$, HD, CO and $CH_2O$ were the major products. Other gases which were detected in comparatively smaller amounts were $CH_4$, $CH_3D$, $D_2$ and $C_2H_6$. With Al film under the same experimental condition, gases such as $CH_3D$, $D_2$, $CH_4$, HD, $H_2$, $C_2H_6$, CO and $CH_2O$ were observed.

The interaction of $CH_3OD$ was also studied with the oxidized films of Ni, Pd and Al in exactly the same way as described with $CH_3OH$ on such surfaces. Molecular adsorption of $CH_3OD$ took place on oxidized Al film at 223 K and the desorption of the adsorbed alcohol was the main process on warming the film in presence of the gas to 450 K. On oxidized Ni and Pd films chemisorption of $CH_3OD$ took place between 223 and 450 K. The evolution of products began above 290 K and involved $H_2$, CO, HDO, $H_2O$, $D_2O$, $CH_3D$, $CO_2$, $CH_4$, and HD. Table 4 shows the analysis of the gas phase at a given time throughout the interaction of $CH_3OD$ with oxidized Ni and Pd films.

### KINETICS OF ADSORPTION

The pressure dependence of the methanol reaction with each film was calculated from the variation of the adsorption rate at two different constant methanol pressures ($P_m$) within the same value of $\theta$ or $Y$; the values obtained were very close to unity.[5, 8] A check of such a value was to plot log $P_m$ as a function of time for different films, as indicated in fig. 4.

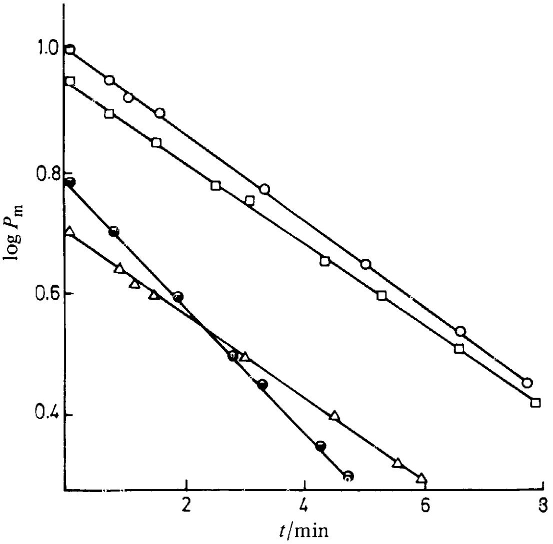


FIG. 4.—First-order plots for the adsorption of methanol on Ni (○) at 363 K, Pd (□) at 393 K, Al (△) at 423 K and oxidized Ni (◒) at 423 K. The methanol pressure ($P_m$) was expressed in N $m^{-2}$.

Activation energies ($E_a$) of the methanol adsorption and the pre-exponential factors ($A$) were derived from Arrhenius plots as shown in fig. 5. The values of $E_a$ and $A$ for each film remained constant independent of the extent of methanol uptake ($\theta$ or $Y$). Table 5 gives the values of $E_a$ and $A$ and the corresponding changes in $\theta$ or $Y$ for the adsorption on the different clean and oxidized films.

A plot of log $A$ values against $E_a$ for clean and oxidized films is shown in fig. 6.

## DISCUSSION

### ADSORPTION AT 223 K

The evidence indicates that dissociative adsorption of methanol on all films occurred even at 223 K. This was reflected in the liberation of such gases as $H_2$, CO, $CH_4$ and $CH_2O$ at this temperature, although the production of these gases was only detected at the high surface coverages ($\theta > 1.0$) of the films with methanol. More extensive adsorption of methanol occurred on the oxidized films of the metals at

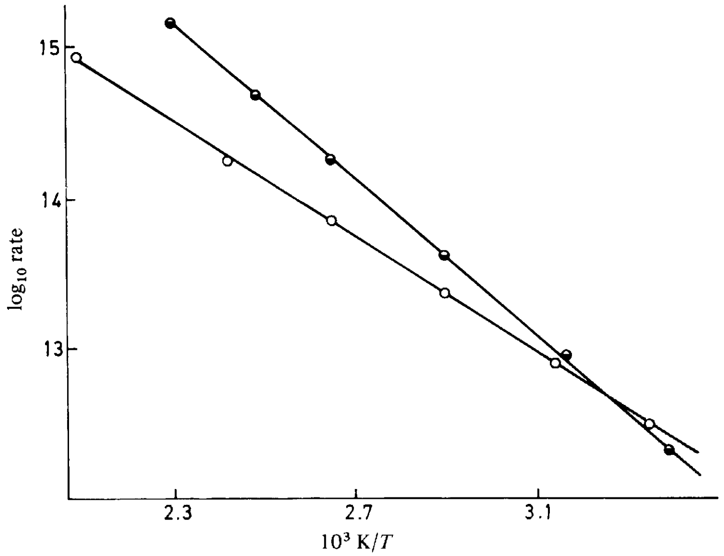


FIG. 5.—Arrhenius plots for the interaction of methanol with Ni (○) and oxidized Ni (●) films. The rate of methanol adsorption was expressed in molecule $cm^{-2}$ $s^{-1}$.

TABLE 5.—ACTIVATION ENERGIES ($E_a$) AND THE PRE-EXPONENTIAL FACTORS ($A$) FOR THE ADSORPTION OF METHANOL ON FILMS OF Ni, Pd AND Al

| film | temp. range/K | $E_a$/kJ $mol^{-1}$ | $A$/molecule $s^{-1}$ $cm^{-2}$ | $\theta$ or $Y$ |
|---|---|---|---|---|
| Ni | 290-450 | 36.9 | $1.38 \times 10^{19}$ | 1.32-9.5 |
| Pd | 290-400 | 57.0 | $3.98 \times 10^{19}$ | 2.7-11 |
| Al | 293-423 | 61.6 | $6.31 \times 10^{19}$ | 2.1-6.8 |
| oxid. Ni | 290-423 | 49.1 | $2.00 \times 10^{19}$ | 3.1-8.9 |
| oxid. Pd | 292-423 | 67.4 | $1.100 \times 10^{20}$ | 1.0-3.5 |

223 K, this was indicated in the greater final values of $Y$ on such surfaces at 223 K as compared with the corresponding final values of $\theta$ on the clean films (tables 1 and 2).

Part of the methanol adsorption on the oxidized Ni and Pd films was shown to be reversible; this could be removed from the surface by pumping the film at 223 K or on warming to 290 K. The adsorption of methanol on oxidized Al films at 223 K was mainly molecular; a substantial fraction (80 %) of the adsorbed methanol could be removed from the surface on heating the film to higher temperatures (*ca.* 400 K).

## ADSORPTION ABOVE 223 K

The adsorption and the subsequent decomposition of methanol on metal films of Ni, Pd and Al became extensive at temperatures $\geqslant$ 290 K, as indicated by the variety and greater extent of the decomposition products. Among the gaseous products on Ni and Al films, methane evolution was far more extensive. The main gaseous products on Pd films in the same range of temperatures were $CH_2O$, CO and $H_2$.

It is likely that methanol undergoes adsorption on all films with the formation of methoxide radicals as probably the most abundant species on the surface. The dissociative adsorption of the alcohol may be represented as:

$$CH_3OH(g) \rightarrow CH_3O(a) + H(a)$$

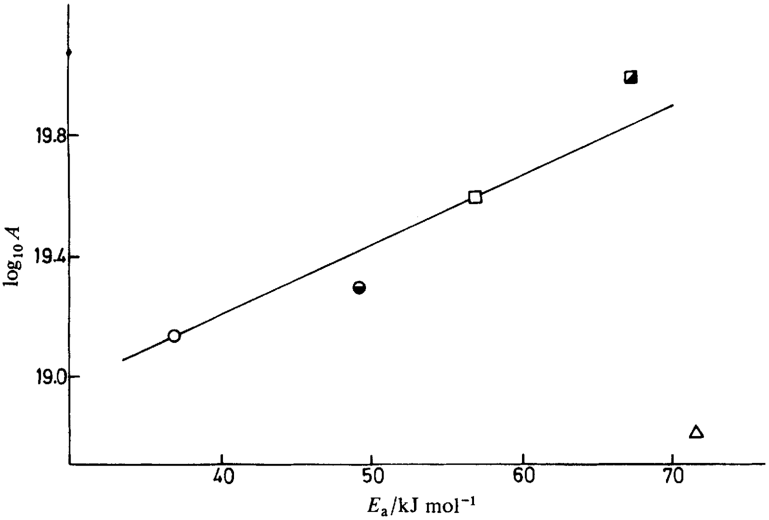


FIG. 6.—Variation of log $A$ with $E_a$ for the interaction of methanol with Ni (○), Pd (□), Al (△), oxidized Ni (◒) and oxidized Pd (◪) films. $A$ was expressed in molecule cm$^{-2}$ s$^{-1}$.

where the symbols (a) and (g) denote an adsorbed or gaseous species, respectively. The methoxide radicals give rise to various products through two main paths: (1) The radicals may react with the adsorbed hydrogen atoms to form methane, which enters the gas phase, and oxygen atoms which combine with the metal

$$CH_3O(a) + H(a) \rightarrow CH_4(g) + O(a). \tag{1}$$

This reaction is likely to predominate on adsorbents having a high tendency for oxidation, as in the case of Ni and Al films. The sulphidation of nickel film between 273 and 313 K through the adsorption of methyl mercaptan is reported[9] to occur through a similar mechanism. (2) The methoxide radicals may undergo further decomposition in gradual steps as:

$$CH_3O(a) \rightarrow CH_2O(a) + H(a) \tag{2a}$$

$$CH_2O(a) \rightarrow CO(g) + H_2(g) \tag{2b}$$

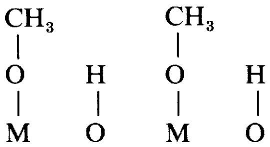
$$H(a) + H(a) \rightarrow H_2(g) \tag{2c}$$

$$CH_2O(a) \rightarrow CH_2O(g). \tag{2d}$$

This does not eliminate the possibility of the further decomposition of $CH_2O(a)$ to form CHO(a) and H(a) with the subsequent decomposition of the CHO(a) to form CO(g) and H(a). Reactions (2*a*)-(2*c*) were shown to predominate on Pd films, and the behaviour possibly arises through the high tendency of Pd to adsorb hydrogen. Reaction (2*d*) may account for the liberation of $CH_2O(g)$ as well as for its disappearance with the rise of the temperature. The reactions suggested [(2*a*)-(2*c*)] may account for the formation of the gases CO, $H_2$ and $CH_2O$ and agree with those suggested by McKee[10] and many others[1] for the catalytic decomposition of methanol over a number of metals.

The formation of ethane, which occurred only to a very small extent as compared with the amounts of the main products, may take place by the combination of methoxide radicals as well as by the direct union of some methyl radicals which may be attached to the metal surface.

The decomposition products on oxidized Ni and Pd films involved CO, $H_2$, $CH_2O$, $H_2O$, $CO_2$ and to a less extent $CH_4$. This suggests that reaction (2) has become less effective on the oxidized Ni films and the formation of CO, $CH_2O$ and $H_2$ is likely to proceed through the reactions (2*a*)-(2*d*). The factors controlling the changeover in mechanism on Ni may be the concentration of hydrogen atoms on the metallic sites which decreased due to the preoxidation of the film. The tendency of the Ni film for oxidation by methanol has also diminished as a consequence of its saturation with oxygen. The surface phase may involve:



$$\begin{array}{cccc} CH_3 & & CH_3 & \\ | & & | & \\ O & H & O & H \\ | & | & | & | \\ M & O & M & O \end{array}$$

where M is the Ni or Pd atom. The adsorbed $CH_3O$ may undergo further reactions such as reactions (2*a*)-(2*c*) to produce the gases CO, $CH_2O$ and $H_2$. Such a surface structure resembles those suggested for the adsorption of methanol on magnesium oxide,[11] zinc oxide[12] and other oxides.[13, 14]

Other gaseous products on oxidized Ni and Pd were $H_2O$ and $CO_2$, together with some $CH_4$. The formation of $H_2O$ may take place through such reactions[13, 15] as

$$CH_3OH(g)+O(a) \rightarrow CH_3O(a)+OH(a). \qquad (3a)$$

The reaction of methanol thereafter continues with OH(a) as

$$CH_3OH(g)+OH(a) \rightarrow CH_3O(a)+H_2O(a) \qquad (3b)$$

$$H_2O(a) \rightarrow H_2O(g). \qquad (3c)$$

There is also a possibility of the reaction of OH(a) with the hydrogen adatoms on some metallic sites as

$$OH(a)+H(a) \rightarrow H_2O(a). \qquad (3d)$$

The production of $CO_2$ gas as a consequence of methanol interaction with oxidized Ni and Pd at temperatures $\geqslant 290$ K may proceed through the reaction of the surface methoxide $CH_3O(a)$ with the surface oxygen O(a) as:

$$CH_3O(a)+O(a) \rightarrow H_2COO(a)+H(a) \qquad (4a)$$

$$H_2COO(a) \rightarrow HCOO(a)+H(a) \qquad (4b)$$

$$HCOO(a) \rightarrow CO_2(g)+H(a). \qquad (4c)$$

The hydrogen atoms released in the various steps either recombine to form $H_2$ or reduce the surface oxygen to $H_2O$. Such a mechanism was verified for the oxidation of methanol on Ag (110) using surface oxygen-18; the resulting gaseous $CO_2$ was shown to contain both oxygen-16 and oxygen-18.

## ADSORPTION OF $CH_3OD$

The results of $CH_3OD$ adsorption and subsequent decomposition on Ni films indicated the evolution of $D_2$ gas at 223 K. The major gaseous products above 223 K was $CH_3D$ together with some $CH_4$. The results agree well with the suggested mechanisms for the adsorption and decomposition of methanol on Ni. The formation of $CH_4$ may result from the reaction of adsorbed $CH_3O(a)$ or of adsorbed $CH_3$ with hydrogen atoms resulting from further decomposition of the methoxide radicals according to reactions (2*a*)-(2*c*). The formation of $H_2$, HD and $D_2$ gases is expected to be due to the existence of adsorbed hydrogen and deuterium atoms on the film. A careful analysis of the gas phase did not indicate the formation of deuterated formaldehyde at any stage throughout the interaction of methanol with the films. This agrees with the lesser tendency of the carbon–hydrogen bonds to undergo exchange with deuterium and may also indicate that reactions (2*a*)-(2*c*) are mainly unidirectional. The adsorption and the decomposition of $CH_3OD$ on Al films were generally similar to those on Ni.

The results of $CH_3OD$ investigations on Pd films above 223 K indicated the formation of $H_2$, HD and $D_2$ together with CO, $CH_2O$ and some other gases. The results are again in agreement with the proposed reactions of adsorption and decomposition on the films.

The nature and the proportions of the gaseous products on $CH_3OD$ adsorption on oxidized Ni and Pd films could be considered as further support for the suggested mechanism [reactions (2) and (3)]. Among the expected products were $H_2O$, HDO and $D_2O$, which were formed by the recombination of the different adsorbed deuterium or hydrogen atoms with the adsorbed hydroxyl radicals (OH or OD) as well as by reactions such as (3*b*).

## KINETIC DATA

The kinetic data for the methanol interaction with clean and oxidized films of Ni, Pd and Al in the temperature range 290-450 K revealed the following: (1) The rate of methanol adsorption depended only and directly on the pressure ($P_m$) of the gaseous methanol, as indicated by the values of the pressure dependence of unity together with the linear relationship of log $P_m$ with time (fig. 4). The presence or the absence of the gaseous products at any stage did not influence the rate of methanol adsorption on any film. (2) The activation energy of adsorption ($E_a$) and also the pre-exponential factor ($A$) for each film were constant and did not alter with the extent of adsorption ($\theta$ or $Y$). (3) There was an approximately linear relationship between log $A$ and $E_a$ for the various surfaces (fig. 6) with the exception of Al which showed an anomalously low pre-exponential factor.

The constancy of $E_a$ values for each metal, or oxidized metal, together with the direct dependence of the methanol uptake on its pressure, may suggest that the rate-determining step in the reaction involves the adsorption of methanol followed by its dissociation at the metal surface. The cationic diffusion of the metal atoms through the tarnish layer (mainly the oxide) and electron transport could be ruled out as possible steps in the reaction in view of the pressure dependence of the reaction rate.

The relationship between $E_a$ and log $A$ suggests the operation of a compensation effect[16, 17] in the methanol adsorption and subsequent decomposition on the various surfaces over the experimental temperature range 223-450 K. The point corresponding to Al film is shown to deviate from the linear relationship of fig. 6, probably because the value of log $A$ is lower than expected. The tarnish oxide layer on Al surface probably raises the energy of activation for methanol adsorption, a process which has been found to occur with the adsorption of other gases on Al film.[7]

The fact that the values of $E_a$ and log $A$ for methanol adsorption on the oxidized films are higher than the corresponding values on the clean films suggest a higher energy requirement for the adsorption on the oxide surface sites as compared with the adsorption on the metal, in parallel with the proposed interpretation of the compensation effect.[16-18] With a thoroughly pre-oxidized Pd catalyst[15] methyl formate was produced through methanol adsorption with an activation energy of 63.4 kJ mol$^{-1}$, whereas with a reduced metallic catalyst complete oxidation to $CO_2$ and $H_2O$ took place with an activation energy of 44.3 kJ mol$^{-1}$.

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