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Catalytic Oxidation of Benzene by Doped Vanadium Pentoxide

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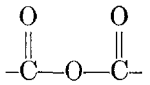
Rate data for the oxidation of benzene over a series of supported V_2O_5 catalysts have been obtained at various temperatures in the range 300–440°C. Additions of GeO_2 and MoO_3 to V_2O_5 did not affect the ratio of benzoquinone: maleic anhydride: carbon dioxide (from complete oxidation), obtained as reaction products. It is shown that addition of GeO_2 to V_2O_5 increased the apparent activation energy of the catalytic reaction, whereas, addition of MoO_3 had comparatively little effect. X-ray and semiconductivity data of these oxide systems indicate that within the limits used, up to a nominal 16 mole % GeO_2 and MoO_3, the additive was completely miscible with V_2O_5 and resulted in a decrease and an increase, respectively, of the number of quasi-free electrons associated with the host oxide. It is concluded that the slow stage in the catalytic oxidation of benzene, in the temperature range investigated, depends upon the electron concentration and the oxide composition at the catalyst surface.

I. Introduction

The effect of addition of altervalent ions to a NiO catalyst on the catalytic activity has been extensively studied (*1, 2, 3*). The principles governing this work stem originally from the observations of Verwey (*4*) and Dowden (*5*) on the changes in electrical conductivity induced by controlled addition of suitable ions to a catalyst having semiconducting properties. Correlation between catalytic activity and catalyst modification induced by doping in CO oxidation, H_2 oxidation, and N_2O decomposition occurs when a single chemisorption or desorption step dominates the catalytic reaction (*6*).

The work described in this paper attempts to extend these principles to the vanadium oxide system. It has been suggested, for instance, that the rate-controlling step in the oxidation of *o*-xylene to phthalic anhydride depends upon the availability of oxygen at the catalyst surface (*7*). This dependence upon oxygen has been demonstrated in the kinetic equations formulated by Mars and van Krevelen for benzene and naphthalene oxidation, where ring rupture occurs to produce the



$$-\overset{O}{\overset{\|}{C}}-O-\overset{O}{\overset{\|}{C}}-$$

grouping (*8*). If this is, in fact the case, and the rate-determining step depends upon oxygen adsorption it should be possible to modify the kinetics of the reaction by doping a V_2O_5 catalyst, particularly as oxygen adsorption is known to involve electron transfer from oxide to oxygen (*9*). Because of the potential similarity of these partial oxidation reactions to the reactions catalyzed by the oxide semiconductors mentioned, it was thought that an investigation of benzene oxidation over doped V_2O_5 would be worthwhile.

With this object in view a search was made for suitable oxide systems. The *n*-type semiconducting characteristics of V_2O_5 require the addition of stable hexavalent ions from group VI or tetravalent ions from group IV to increase or decrease, respectively, the quasi-free electron concentration associated with the V_2O_5 lattice. The oxides, GeO_2 and MoO_3, chosen for inclusion into V_2O_5 in this investigation were selected on the basis of the following facts: (*i*) valency of the metal ion; (*ii*) crystal radius of metal ions compared favorably with that of vanadium, e.g. V^{5+} 0.59; Mo^{6+} 0.62; Ge^{4+} 0.53; (*iii*) MoO_3 is known to form solid solutions with V_2O_5 up to addition of 25 mole % MoO_3 (*10*); (*iv*) GeO_2 is sufficiently soluble in water (0.4 g per 100 ml) to facilitate introduction into V_2O_5 prepared from a solution of ammonium metavanadate (MoO_3 can be introduced using ammonium molybdate); and (*v*) low volatility at the sintering temperature will reduce loss of additive before formation of solid solution.

In this paper we report, first, on the catalysts used and confirm that the additive affected the electron concentration in the desired manner. This has been established by determining the semiconductivity of the mixed oxides. Also, since the $V_2O_5 + GeO_2$ system has apparently not been studied, V_2O_5 containing the maximum amount of GeO_2, i.e. $V_2O_5 + 15.9$ mole % GeO_2, used in this work has been analyzed by X-ray diffraction. Second, the initial kinetics of formation of benzoquinone, maleic anhydride, and carbon oxides from benzene using these modified catalysts have been determined. Finally, it is shown that the kinetics measured pertain to the chemical reaction at the surface and that diffusion rates are sufficiently fast compared with the rate of chemical reaction that they can be neglected.

II. EXPERIMENTAL

Apparatus. For the kinetic study a flow-type reaction system was used where the contact time defined as the ratio of catalyst volume (ml) to the flow rate (ml/sec) could be varied between 0 and 1.4 sec. This was done by changing the amount of catalyst in the converter and keeping the gas flow rate constant at 800 ml/min. In this way mass transfer effects to the external catalyst surface have been kept as constant as possible.

Oxygen and nitrogen supplied from B.O.C. cylinders of compressed gas were metered through capillary-type flow meters. The nitrogen stream was directed into a carburetor containing benzene (Hopkin & Williams—sulfur free). The carburetor was immersed in a mechanically stirred oil bath contained in a Dewar flask the temperature of which was maintained to ±0.1° of the desired temperature, by an electrical heater controlled by a contact thermometer, and an electronically operated relay. The nitrogen-benzene mixture was fed to the converter through wire-wound Pyrex-glass tubing held at 83–87°C. Oxygen was fed separately to the head of the converter where the gases were mixed before passing down through the catalyst bed. The feed gas composition was held constant at $p_{C6H6} = 9$ mm; $p_{N2} = 94$ mm; $p_{O2} = 657$ mm.

The converter was a Pyrex-glass tube of 1 inch id fitted with a number 1 porosity sintered disc to support the catalyst. This tube fitted into an electrically heated furnace the temperature of which was controlled by an Ether Transitrol. The gas stream leaving the converter could be directed either to vent or to a trapping system so that the reaction products could be collected for analysis. The trapping system was comprised of four double-walled vessels arranged in series. The inner wall of each trap, towards which the gas stream was directed, was cooled with solid CO_2. At the end of a run (usually a run was of one hour duration) the contents of the traps were washed out with acetone and made up to 200 ml in a standard flask.

Catalysts. These were prepared by impregnating Sil-O-Cel C22 (Johns Manville & Co.) sieved between 0.10–0.24 cm with solutions of AR grade ammonium metavanadate–ammonium molybdate or ammonium metavanadate–germanium dioxide, followed by heating at 350° and then at a higher temperature, 620°C, to ensure diffusion of the foreign ion into V_2O_5.

Analysis. Maleic anhydride was determined by titration with standard alkali.

Benzoquinone was determined by titration with standard $Na_2S_2O_3$ solution immediately after addition of KI/HCl.

Benzene was determined, after removal of benzoquinone and maleic anhydride, by measuring the absorption of a cyclohexane solution at 255 mμ with a Unicam S. P. 500.

Except in a few cases oxides of carbon, calculated as CO_2, have been estimated by difference in carbon balance across the converter from the compounds analyzed as above.

BET surface areas were measured by N_2 adsorption at −196°; an area of 16.2 Å was assumed for the nitrogen molecule.

Total porosity and particle density determinations of the catalysts were carried out by the method of Innes (*11*).

An X-ray powder photograph of V_2O_5 containing 15.9 mole % GeO_2 was taken using chromium K_α radiation with a vanadium filter to remove the β radiation. The exposure time was 8 hr.

Semiconductivity. Mixtures of V_2O_5 containing GeO_2 and MoO_3 were prepared by direct weighing of the oxides. These oxides were melted together, allowed to cool, and the solidified melt ground to a powder and compressed into pellets 127 mm in diameter and 2 mm thick. The pellets were sintered at 620°C overnight. The ac resistance of these pellets was measured with a Wayne-Kerr bridge, which was tuned to a suitable variable frequency signal source and detector.

TABLE 1
DETAILS OF CATALYST COMPOSITION AND SURFACE AREA

Catalyst composition nominal	V_2O_5 on Sil-O-Cel (wt. %)	Dopent on Sil-O-Cel (wt. %)	Dopent in V_2O_5 (mole %)	Surface area (m^2/g)
V_2O_5 + 15 mole % MoO_3	10.1	1.52	16.0	4.0
V_2O_5 + 10 mole % MoO_3	8.7	0.65	8.6	4.3
V_2O_5	10.0	—	—	4.5
V_2O_5 + 5 mole % GeO_2	11.5	0.27	3.9	4.3
V_2O_5 + 10 mole % GeO_2	11.0	0.87	12.1	3.2
V_2O_5 + 15 mole % GeO	11.5	1.27	16.1	3.9

III. RESULTS

The composition of the catalysts employed in this investigation together with the corresponding surface areas are summarized in Table 1. An average value of the pore volume per gram (V_g) of the

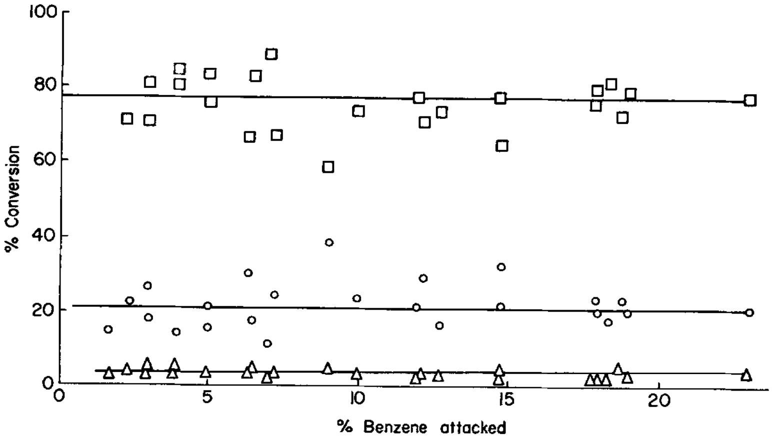


FIG. 1. Percentage conversion to products plotted against percentage of benzene decomposed in the temperature range 300–400°C for a typical catalyst; □, carbon dioxide; ○, maleic anhydride; △, benzoquinone.

catalysts was 0.97 cm^3/g and the particle density was 0.65 g/cm^3; the porosity given by the product of particle density and pore volume was, therefore, 0.63. Taking 4.0 m^2/g as the mean surface area per gram (S_g), the mean pore radius given by $2V_g/S_g$ is approximately 5000 Å (*12*).

Figure 1 shows the relationship between percentage conversion to products based upon benzene decomposed against benzene decomposed for a typical catalyst. Experimental points for all temperatures used are included in the same plot. These results have been interpreted assuming parallel first order reactions leading to benzoquinone, maleic anhydride, and CO_2 from complete oxidation, under initial reaction conditions, such that decomposition of maleic anhydride or benzoquinone to oxides of carbon may be neglected.

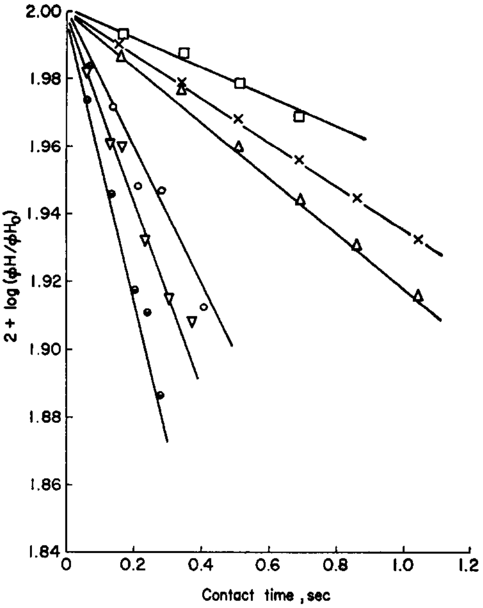
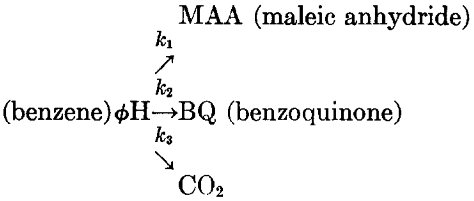


FIG. 2. First order decomposition of benzene in the temperature range 300–400°C. □, 300°; ×, 320°; △, 340°; ○, 360°; ▽, 380°; ◒, 400°C.



$$\begin{array}{l} \qquad\quad \text{MAA (maleic anhydride)} \\ \quad \overset{k_1}{\nearrow} \\ (\text{benzene})\phi\text{H} \xrightarrow{k_2} \text{BQ (benzoquinone)} \\ \quad \underset{k_3}{\searrow} \\ \qquad\quad \text{CO}_2 \end{array}$$

The concentration of reaction products is then given by:

$$[\text{MAA}] = (k_1/k)[\phi\text{H}_0](1 - e^{-kt})$$

$$[\text{BQ}] = (k_2/k)[\phi\text{H}_0](1 - e^{-kt}), \text{ etc.}$$

where $k = k_1 + k_2 + k_3$; t = contact time; and $[\phi\text{H}_0]$ = initial benzene concentration.

Figure 2 shows the first order decomposition of benzene over the V_2O_5 catalyst without additive in the temperature range 300–400°C. Values of k may be obtained from the slope of these plots, and the apparent activation energy 18 ± 3 kcal/

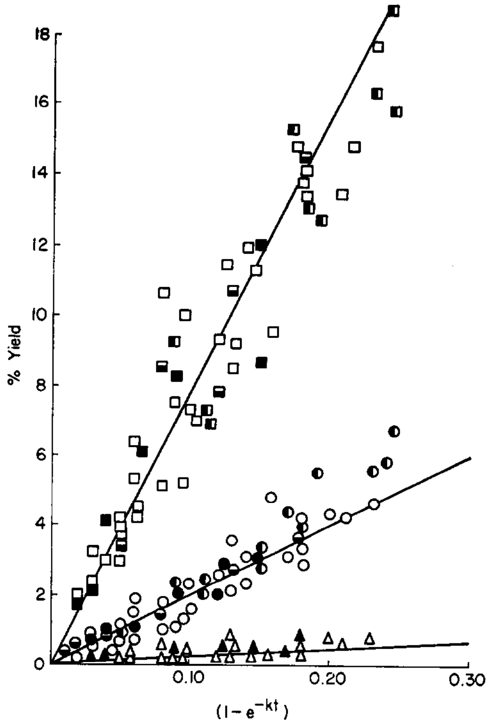


FIG. 3. Per cent of products plotted against $(1 - e^{-kt})$ compiled from results obtained with various catalysts in the temperature range 300–440°C.

Product			Catalyst
CO_2	MAA	BQ	
□	○	△	V_2O_5
■	●	▲	V_2O_5 + 12.1 mole % GeO_2
◧	◑	◭	V_2O_5 + 8.6 mole % MoO_3
⬓	◒	▲	V_2O_5 + 16.1 mole % GeO_2

MAA, maleic anhydride; BQ, benzoquinone.

TABLE 2

SUMMARY OF KINETIC CONSTANTS WITH CATALYST COMPOSITION

Catalyst composition	Temp. range (°C)	E_a[a] (kcal/mole)	k at 653°K ($\text{sec}^{-1}\text{m}^{-2}\text{cm}^3$)	log k_0
V_2O_5 + 16.0 mole % MoO_3	300–380°	14	0.10	3.7
V_2O_5 + 8.6 mole % MoO_3	300–380°	16	0.67	5.1
V_2O_5	300–400°	18	0.34	5.5
V_2O_5 + 3.9 mole % GeO_2	360–420°	32	0.03	9.1
V_2O_5 + 12.1 mole % GeO_2	320–400°	37	0.16	11.5
V_2O_5 + 16.1 mole % GeO_2	380–450°	39	0.12	12.1

[a] The E_a values quoted are subject to an error of ± 3 kcal/mole.

mole for benzene decomposition over this catalyst can be found from the slope of the plot of log k against $1/T$.

Figure 3 shows a plot of percentage yield of product against $(1 - e^{-kt})$ compiled from results obtained from all the catalysts at various temperatures in the range 300–440°C. The slopes of these plots give the approximate values of k_1/k, k_2/k, and k_3/k as 0.2, 0.02, and 0.79, respectively, in agreement with the results given in Fig. 1.

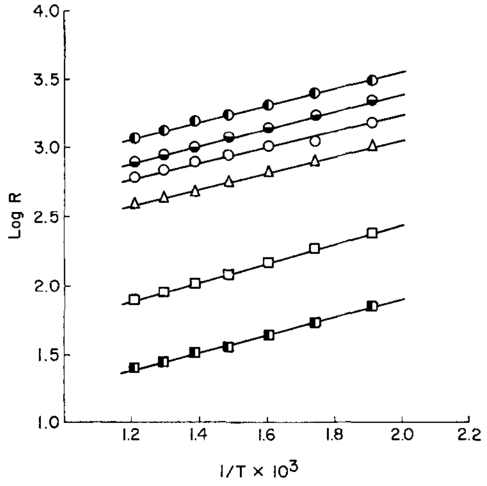


FIG. 4. Comparison of the resistances of pelleted samples of V_2O_5 containing GeO_2 and MoO_3 as a function of temperature, measured at a frequency of 0.1 Mc/s. △, V_2O_5; □, V_2O_5 + 6.2 mole % of MoO_3; ◧ V_2O_5 + 16.5 mole % MoO_3; ○, V_2O_5 + 2.6 mole % GeO_2; ⊖, V_2O_5 + 7.4 mole % GeO_2; ◐, V_2O_5 + 15.9 mole % GeO_2.

Table 2 summarizes the results of the kinetic measurements obtained for all the catalysts used in this work. The variation of the pre-exponential factor k_0 in Arrhenius' equation $k = k_0 \exp - E_a/RT$, where E_a is the apparent activation energy, has been obtained from experimental k values at 653°K which have been corrected for catalyst surface area per unit catalyst-reactor volume. A plot of log k_0 against E_a from the data in Table 2 gives a reasonable straight line showing that the "theta rule" is being obeyed. It is evident from the data that this is because the value of k_0 is largely determined by the exponential term in the equation owing to the low values of k.

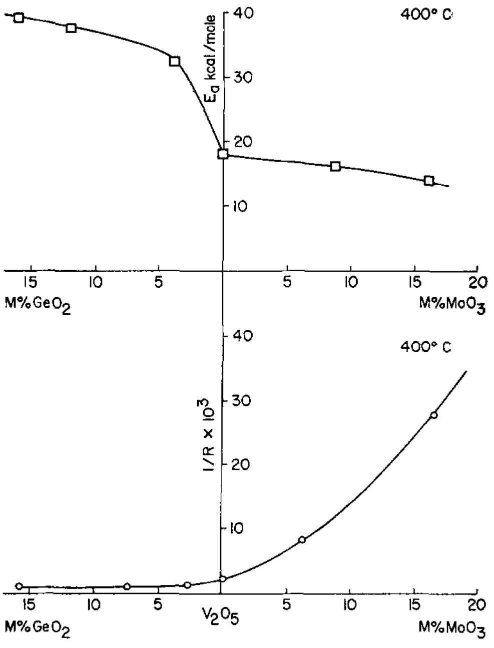


FIG. 5. Comparison of apparent activation energy of catalytic oxidation reaction with electrical conductivity at 400°C.

Figure 4 shows the effect on the resistance of pelleted samples of V_2O_5 with controlled additions of GeO_2 and MoO_3. Relative displacements of the plots of log R against $1/T$ show that the inclusion of MoO_3 improved the conductivity, whereas, GeO_2 tended to lessen the conductivity. A composite diagram summarizing the relationship at 400°C between the semiconductivity and E_a for the catalytic oxidation over the oxide systems investigated is given in Fig. 5.

An X-ray powder photograph of a sample of V_2O_5 containing 15.9 mole % of GeO_2 previously used in the conductivity experiments showed no difference from that obtained with pure V_2O_5. It was concluded that addition of up to 15.9 mole % GeO_2 to V_2O_5 did not affect the crystal lattice of V_2O_5 or cause the separation of another solid phase.

IV. Discussion

The results of the conductivity experiments given in Fig. 4 show that the effect of the MoO_3 was greater than that of GeO_2. The composition of V_2O_5 as normally prepared will lie close to the stoichiometric formula, the slight oxygen deficiency will cause a low concentration of V^{+4} ions in the V_2O_5 matrix. Inclusion of GeO_2 will tend to promote these V^{4+} to V^{5+} but because of their low concentration no marked change in conductivity will be apparent. The presence of MoO_3, on the other hand, can increase the concentration of V^{4+} considerably, i.e., until the presence of MoO_3 can no longer be tolerated by the V_2O_5 lattice. We shall examine the consequences of this effect on the catalytic activity later in the discussion.

Preliminary experiments carried out at the commencement of the work emphasized the importance of the physical condition of the catalyst when comparatively mild oxidizing conditions to yield partial oxidation products were required. It was found that an unsupported granulated V_2O_5 catalyst, having a surface area of about 1.0 m^2/g was initially satisfactory but that the activity varied considerably with use. Various silica and alumina supporting materials were tested and a kieselguhr type of diatomaceous earth was found to be best for our purpose. It can easily be shown that this material when impregnated with V_2O_5 gave a catalyst in which the chemically active components were exposed to the gas phase reactants in such a way that virtually all the surface was available for oxidation (*12*). Taking the bulk diffusion coefficient D_B for benzene in oxygen at 380°C [calculated using Gilliland's formula (*13*)] as about 0.15 cm^2/sec and pores of 5000 Å radius, the Knudsen diffusion coefficient D_K at this temperature is about 1.42 cm^2/sec. Then, since $D = D_B\ [1 - \exp(-D_K/D_B)]$ where D is the diffusion coefficient within a catalyst pore, we see that $D \sim 0.15$ cm^2/sec. In other words, Knudsen diffusion is unimportant with these catalysts. If we take an average value for the size of a catalyst granule sieved between 7–16 BSS as 0.17 cm, a value of 0.47 g/cm^3 for the bulk density and 1.0 for the pore volume per gram, we find from the data of Table 2 and the results of Fig. 2 that the ratio of the experimental rate constant to the theoretical one is of the order 10^{-2}–10^{-3}. This result indicates that the internal surface is completely available for reaction and under these conditions it is possible to assume that the contribution of diffusional factors to the measured kinetics is negligible.

The conversion data and kinetic interpretation shown in Figs. 1 and 3, illustrate the course of the chemical oxidation process. The absence of any maximum on the benzoquinone curves shows that benzoquinone is not formed as an intermediate in the formation of maleic anhydride. Furthermore, the rising trend of the curves of Fig. 3 shows that the maximum conversion to benzoquinone and maleic anhydride has not yet been obtained and justifies the use of the simple kinetic scheme used in this work. It is worth mentioning in this connection, that at comparatively low contact times at all temperatures the products collected in the traps were tinged yellow due to the presence of benzoquinone. At longer contact times and higher temperatures the yellow coloration of the products persisted until the maximum was reached; beyond this point the products were colorless. It was not possible to detect phenol in the oxidation products and if formed as a primary oxidation product it must be inherently unstable under the experimental conditions we have used (*7*). We are currently studying the kinetics of the oxidation of phenol in an attempt to clear up this point.

The results plotted in Fig. 3 have been selected from typical runs with all the catalysts in the temperature range in which they were used. It can be seen that the distribution of products formed from benzene oxidized remained constant and was independent of the type or extent of catalyst doping. We conclude that the catalytic specificity was not affected by doping, a result which may be explained by the fact that although doping modified the electron availability at the surface, the geometry of participating surface sites was not changed. Another consequence of the fixed product distribution ratio is that the apparent activation energies determined from the temperature coefficients of the reaction by plotting logarithm of k, k_1, k_2, k_3 against $1/T$ will all be the same, i.e., E_a for the formation of benzoquinone will be the same as that for formation of maleic anhydride, etc.

The constancy of the distribution ratio for formation of maleic anhydride compared with complete oxidation of benzene has been noted previously, although the ratio $k_1/k \sim 0.2$ is considerably lower than the value 0.7 reported by other workers (*7*). There are three features of our work that may account for this discrepancy. First, we are concerned primarily with the comparison of different catalysts that have been modified by doping. These catalysts have been selected because of their ease of preparation and reproducibility rather than their ability to give maximum conversion to maleic anhydride. Second, oxygen rather than air has been employed since this enables a large excess of oxygen over aromatic to pass through the converter while maintaining a flow rate of less than one liter per minute. Experimentally this was advantageous because trapping of the products on the exit side of the apparatus was simplified with low flow rates. Third, catalysts prepared by impregnating the support with V_2O_5 or $V_2O_5 + MoO_3$ showed a marked increase in activity above about 400–420°C. At least a five- or sixfold improvement in yield of maleic anhydride was obtained, but no benzene was recoverable.

The results given in Table 2 summarize the apparent activation energies E_a found for the six catalysts studied. According to these findings addition of MoO_3 tends to decrease and addition of GeO_2 increases the value of E_a. Generally, this is the result that would be expected if the electron availability at the surface was controlling the rate of chemical reaction by controlling the rate of oxygen adsorption and ionization at the catalyst surface:

$$\tfrac{1}{2}O_2 + e(\text{from catalyst}) \rightarrow O^-$$

Without detailed information on the heats of adsorption of reactants on these catalysts the precise relationship between the measured activation energy and the true activation energy is not known. Other things being equal, however, the fact that little change in E_a was observed up to inclusion of 16.0 mole % MoO_3 into V_2O_5 indicates that the upward movement of the Fermi level, caused by the increase in donor impurity concentration, was probably small and consequently little change in chemisorption heats on V_2O_5 and $V_2O_5 + MoO_3$ catalysts was obtained.

Figure 5 shows that the behavior of a V_2O_5 catalyst doped with GeO_2 was more marked than the effect of MoO_3. The addition of GeO_2 apparently not only reduces the electron concentration at the surface but also decreases the number of catalytically active sites. Evidence has been accumulating that an oxide of vanadium having a composition $V_2O_{4.34}$ or V_6O_{13} is the real catalytic agent in oxidation reactions (*14, 15*). This oxide formed at the surface will exist in equilibrium between V_2O_5 and V_2O_4. Additions of MoO_3 and GeO_2 will be equivalent (from the point of view of vanadium valency) to shifting the equilibrium towards V_2O_4 and V_2O_5, respectively. The composition V_6O_{13} lies closer to the reduced condition V_2O_4, and because of this MoO_3 will have less effect on the catalytic activity. The presence of GeO_2, on the other hand, will favor a shift in equilibrium towards V_2O_5; this will make the V_6O_{13} condition more difficult to be realized under reaction conditions. It is likely, in fact, only to be achieved by raising the temperature of the system, a feature in agreement with our findings.

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