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The Influence of Gaseous Oxygen Atoms on the Catalytic Oxidation of Ammonia on Pt–Rh

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The catalytic oxidation of ammonia on a Pt–Rh gauze has been studied in the presence and in the absence of oxygen atoms in the gas phase in order to ascertain whether the presence of gaseous atomic species can affect the kinetics of a heterogeneous catalytic process.

The catalytic oxidation has been studied in the temperature region between 350° and 750°K at pressures of the order of 1 Torr. The kinetics of the process is diffusional; NO and H_2O were practically the only oxidation products.

The presence of oxygen atoms in the gas phase significantly lowers the activation energy of the catalytic process. Small activation energies are compensated by correspondingly small pre-exponential factors.

The presence of unstable species in the gas phase (atoms, excited molecules, or ions) could in principle affect the kinetics of a heterogeneous catalytic process in different ways:

(a) There can be a contribution from reactions between chemisorbed species and gaseous unstable species.

(b) The adsorption equilibria of reactants and products can significantly be altered by the presence of unstable species in the gas phase, e.g., the fractional coverage of a catalytic surface with oxygen atoms can be different in the presence of molecular oxygen or in the presence of molecular plus atomic oxygen (*1*).

(c) Deactivation or recombination of unstable species can take place on the catalyst, thereby contributing an additional energy input to the catalytic surface. If this additional energy cannot be accommodated by the solid at a sufficient rate, the energy distribution within the chemisorbed layer could be significantly altered. As a consequence the kinetic parameters of the catalytic reaction are likely to be modified. A number of recent observations bear on this point and will be examined in the discussion.

An attempt has therefore been made to study the kinetics of the catalytic oxidation of ammonia on a Pt–10% Rh gauze both in the presence and in the absence of gaseous oxygen atoms, which were generated by means of a microwave discharge in a flow system.

In order to produce appreciable concentrations of oxygen atoms by electric discharges comparatively low pressures and high gas flow rates are necessary. It is furthermore required that practically the same catalytic surface should be active for both atom recombination and NH_3 oxidation. Under such conditions contact times with the catalyst are bound to be very short.

The catalytic oxidation of ammonia on Pt–Rh gauzes was therefore selected, as being one of the fastest catalytic reactions and because efficient recombination of oxygen atoms takes place on Pt–Rh surfaces.

Experimental Methods

A scheme of the apparatus is given in Fig. 1.

Oxygen atoms were produced in a stream of molecular oxygen containing approxi-

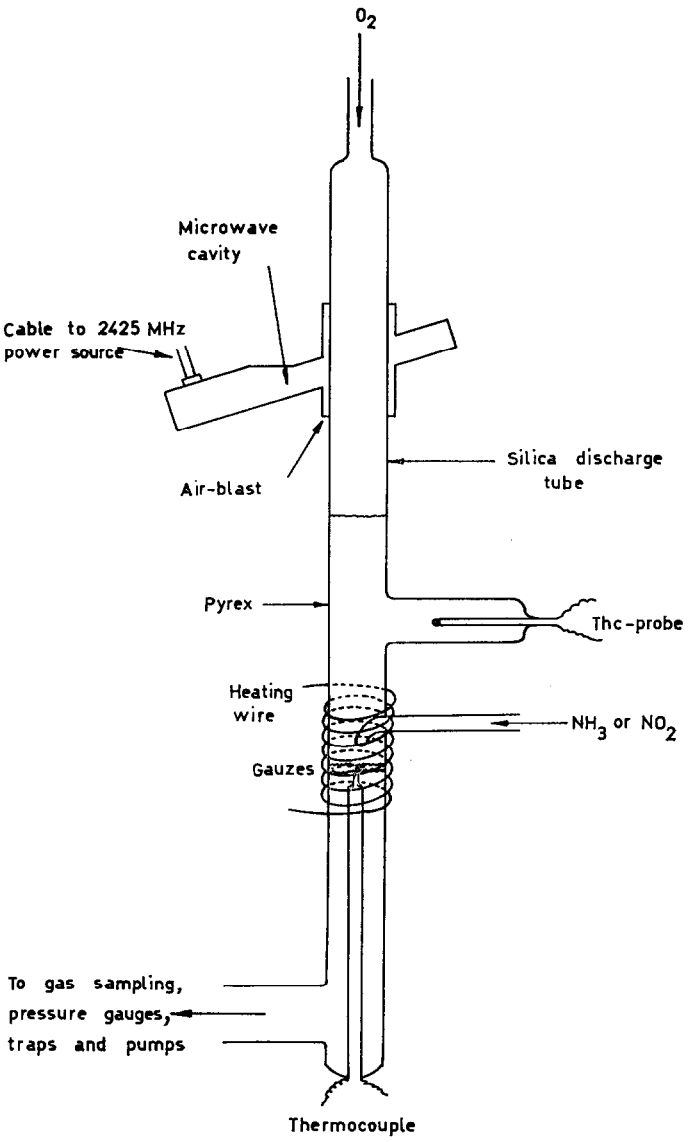

FIG. 1. A scheme of the apparatus.

mately 1% water, by means of a microwave discharge. The discharge was excited by a commercial microwave power source (2425 MH_z, max. output 200 W) coupled to the discharge region by a coaxial cable and a specially designed cavity. The oxygen atom concentration was measured by chemical titration with NO_2 (*2*). Injection of NO_2 into the $O_2 + O$ stream produces an intense glow according to:

$$O + NO_2 \xrightarrow{\text{very rapid}} NO + O_2$$
$$O + NO \rightarrow NO_2 + h\nu.$$

Extinction of the glow occurs when [O] = [NO_2]. Measurement of the NO concentration in the gas stream at the extinction point by mass spectrometric analysis gives the concentration of oxygen atoms at the injection point. This method avoids the rather inconvenient metering of the NO_2 flow.

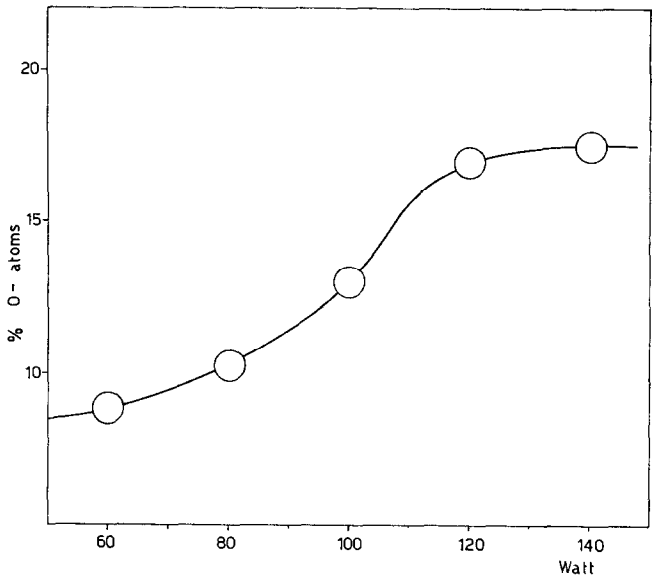

FIG. 2. Per cent concentration of oxygen atoms in the gas phase as a function of the power output of the microwave power source.

Figure 2 shows the dependence of the O-atom concentration in the gas phase on the power output of the microwave source, at an oxygen flow rate of 215 cc (STP)/min and at a pressure of 1.1 Torr.

The above flow rate and pressure conditions were found to give the highest concentration of O atoms. The catalytic oxidation of ammonia both in the presence and in the absence of oxygen atoms was therefore studied under these conditions. The concentration of O atoms was monitored by a Fe-consantan thermocouple probe with silver tip, inserted in a sidearm of the discharge tube. Cylinder ammonia (Matheson, 99.99%) and oxygen (99.9%) of high purity were used in the experiments. The flow rates of the two gases were regulated by means of needle valves and metered by means of calibrated capillary flow meters.

The concentration of NH_3 in oxygen was varied between 4.5% and 16%; most of the measurements were taken at a concentration of 10%. Two Pt–10% Rh gauzes (1024 mesh/cm^2 of 0.06 mm wire) were placed perpendicularly to the gas stream, 1 cm below the injection point of NH_3. The catalyst temperature was varied by means of an electrically heated nichrome wire wound around the catalyst region. The tip of a thin Pt/Pt–Rh thermocouple was inserted into a mesh of the gauze to measure the catalyst temperature.

The streaming gas was sampled and analyzed in a mass spectrometer. Condensable products were trapped into two large traps, in series with a metal vacuum valve and a 350 liter/min rotary oil vacuum pump.

EXPERIMENTAL RESULTS

Catalyst activation. The Pt–Rh gauze was practically inactive when first used for the oxidation reaction both in the presence and in the absence of O atoms. It did however show an appreciable activity for the recombination of the atoms. Treatment of the gauze in a stream of O_2 + O and NH_3 at 620°K progressively activated the catalyst until a limiting value of the activity was reached after 100–150 min. Measurements reported below were taken after the activation treatment.

Catalyst temperature. A stationary temperature higher than the initial temperature of the gauze was observed when the discharge was switched on, as a consequence of the liberation at the surface of the heat of

recombination of the oxygen atoms. Addition of ammonia to the $O_2 + O$ stream had two opposite effects on the stationary temperature, according to whether the temperature of the catalyst in the $O_2 + O$ stream was below or above 400°K. This is clearly shown in Fig. 3, where the stationary temperature

At temperatures above 400°K in the presence of O atoms, or at temperatures above 515°K in the presence of molecular oxygen, addition of NH_3 to the gas stream entrained an almost instantaneous increase of the gauze temperature which reached the stationary value in approximately 1 min.

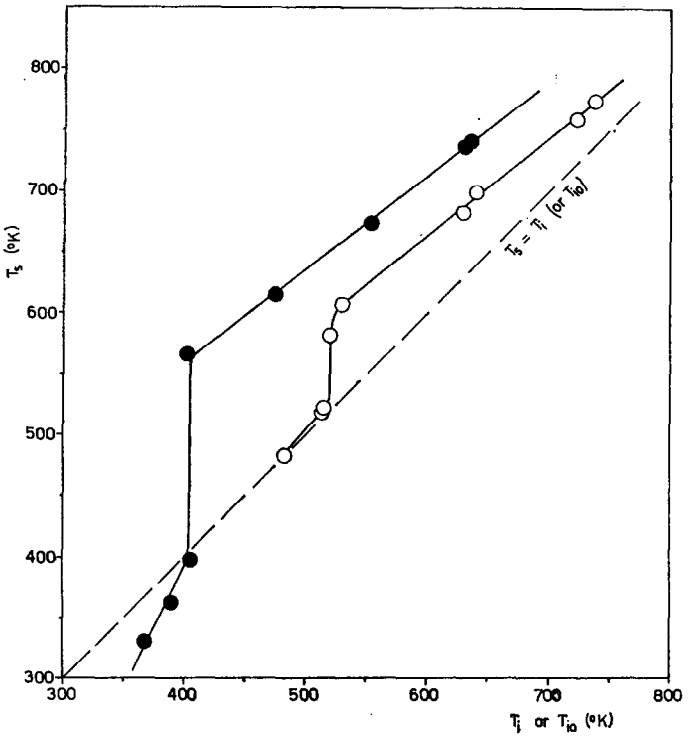

FIG. 3. ○—Oxidation in molecular oxygen—a plot of the stationary temperature of the gauze T_s as a function of the initial temperature of the gauze T_i. ●—Oxidation in the presence of oxygen atoms—a plot of T_s as a function of the initial temperature of the gauze in the presence of oxygen atoms in the gas phase T_{i0}.

of the gauze in the presence of ammonia (T_s) has been plotted against the initial temperature in the $O_2 + O$ stream (T_{i0}) for the oxidation in the presence of oxygen atoms, and against the initial temperature in molecular oxygen (T_i), for the oxidation with molecular oxygen.

In the absence of O atoms addition of ammonia was practically without any influence on the catalyst temperature up to about 515°K. Above 515°K the stationary temperature of the gauze was always higher than the initial one. This behavior is also clearly shown by Fig. 3.

The catalytic oxidation in molecular oxygen. Mass spectrometric analysis of the reacted gas revealed that in most of the experiments NO and water were practically the only oxidation products. Only occasionally was N_2 detected in the reacted gas. The N_2 concentration never exceeded 5% of the NH_3 inlet concentration. At the temperatures and pressures investigated the homogeneous oxidation of NO by O_2 is too slow to be observed. However, when the reacted gas was passed through the traps cooled at liquid nitrogen temperature a green solid formed, which explosively decomposed

into a blue solid. Upon warming to room temperature a white solid residue was left in the traps and gas was evolved. Chemical, UV, and X-ray analysis of the white solid revealed the presence of NH_4NO_3, NH_4NO_2, and of a third component which was not identified. The gas evolved contained, beside unreacted ammonia, N_2O, NO, N_2, and H_2O. Obviously a partial oxidation of NO was occurring in the traps and a number of reactions then become possible both at low temperature and upon warming (*3*).

The oxidation experiments in molecular oxygen were generally preceded by oxidation experiments in the presence of O atoms.

The rates of ammonia oxidation have been plotted as a function of the stationary temperature of the gauze in Fig. 4. The maximum rate observed corresponds to 62% oxidation and to a contact time of about 2 μsec.

Curve 1 refers to a new gauze after "activation" in a stream of O_2, O atoms, and NH_3 at 620°K. After a period of constant activity the gauze was removed and again used about 1 month later. It turned out that the original activity of the gauze could only partially be restored by the activation treatment at 620°K. The results for this partially deactivated gauze are represented by Curve 3. A rather unexpected and unexplained feature of the gauze is that the experimental points for both the active and the partially deactivated catalyst scatter around two curves, corresponding to a higher and a lower activity of the gauze. The lower curve of the active catalyst and the upper curve of the partially deactivated catalyst are found to coincide within the experimental errors (Curve 2). The presence of an upper and a lower state of activity has also been ascertained in a similar study, presently in

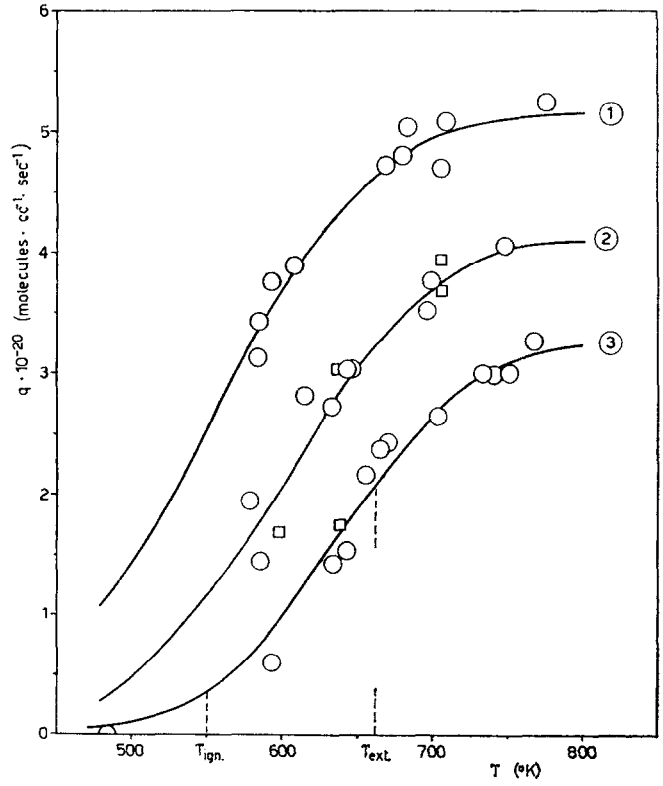

FIG. 4. A plot of the rate of NH_3 oxidation q as a function of temperature for the catalytic oxidation in the presence of molecular oxygen; ○, 10% NH_3 in the gas phase; □, 4.5% to 16% NH_3 in the gas phase.

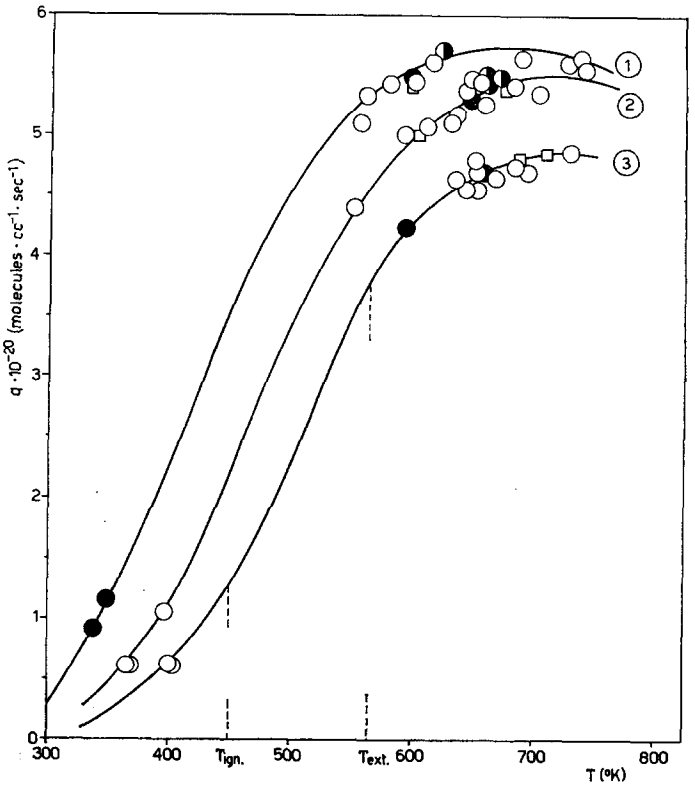

FIG. 5. A plot of the rate of NH_3 oxidation q as a function of temperature for the catalytic oxidation in the presence of oxygen atoms in the gas phase; ○, 10% NH_3 in the gas phase, power output of the microwave power source 100 W; ●, 10% NH_3, 60 W; ◐, 10% NH_3, 120–160 W; □, 4.5% to 16% NH_3, 100 W.

progress in this laboratory, on the catalytic oxidation of NH_3 on a cobalt oxide catalyst.*

The experimental points represented by squares in Fig. 4 and in Fig. 5 have been calculated from the rates measured at NH_3 concentrations ranging from 4.5 to 16%. It was assumed in the calculations that the reaction is first order in the NH_3 concentration.

The catalytic oxidation in the presence of oxygen atoms. The only oxidation products were NO and water; no N_2 has been detected in the experiments at 100 W. The rates of oxidation have been plotted as a function of the stationary temperature of the gauze in Fig. 5.

One appreciates that in this case as well the experimental points scatter around three curves corresponding to those previously mentioned for the oxidation with molecular oxygen. The maximum rate observed corresponds to 68% oxidation.

Measurements have also been performed with a power output of 60 W both with the freshly activated and with the partially poisoned catalyst. At 60 W N_2 was occasionally present in the reacted gas and N_2 concentrations were close to those observed in the oxidation experiments with molecular oxygen. The results are given in Fig. 5. Measurements at power outputs between 120 and 160 W have also been included in Fig. 5 and refer to the freshly activated catalyst.

Homogeneous oxidation in the gas phase. It has been pointed out that when ammonia

* For a detailed study of the nature of the "activation" process of Pt wires one can refer to the article by M. Prettre *in* "Alta Tecnologia Chimica. Reazioni e Reattori," p. 223. Accademia Nazionale dei Lincei, Rome, 1962 (in French).

was injected into the $O_2 + O$ stream at temperatures below 400°K the temperature of the gauze decreased while addition of NH_3 above this temperature always increased the stationary temperature of the gauze (Fig. 3). A temperature increase above 400°K was actually observed both with the "active" gauze and with gauzes which had not been "activated" and therefore exhibited only a fraction of their maximum activity.

The temperature decrease observed below 400°K implies that an appreciable fraction of the O atoms (of the order of 50%) was consumed before reaching the gauze. This observation suggests that an appreciable oxidation of ammonia by oxygen atoms is apparently taking place homogeneously in the space between the injection point and the gauze. The homogeneous gas-phase oxidation of ammonia in a stream of $O_2 + O$ has recently been investigated (*4*). Measurements carried on in the apparatus of Fig. 1, with the Pt–Rh gauze removed, agree with previous data in showing that approximately eight oxygen atoms are consumed per molecule of ammonia consumed (chain reaction) and that NO and water are the main oxidation products.

The amount of ammonia that could be oxidized within the contact time in the volume above the gauze can be calculated from the rate constants of the homogeneous reaction previously determined. However it turns out that the amount of NH_3 oxidized should correspond to about 0.2% of the injected ammonia, i.e. to a consumption of oxygen atoms of only about 1.5%.

The observed temperature drop of the gauze therefore implies that the contact time in the volume above the gauze is larger than calculated from the known flow rates. This is possible due to the geometry of the system and is confirmed by the observation that the glow which is emitted in the homogeneous $O + NH_3$ (*5*) reaction extends upstream *r* 1 cm from the injection point.

At initial temperatures of the gauze above 400°K the observed increase of the stationary temperature could be easily explained in the case of the "active" gauzes. In fact the high activity of the gauze for the heterogeneous oxidation could compensate for the loss of oxygen atoms in the gas phase. However, a temperature increase was also observed with nonactivated gauzes whose activity was less than 10% of the maximum activity, and comparable with the activity of the "active" gauzes below 400°K.

Furthermore the glow due to the homogeneous $O + NH_3$ reaction, which had been observed at temperatures below 400°K, was practically absent under these conditions.

These observations are a strong indication that at initial temperatures above 400°K the homogeneous reaction is actually suppressed, even in the presence of unactive gauzes. In the presence of active gauzes the homogeneous contribution should become still smaller due to the depletion of NH_3 from the gas phase (see below). No corrections for the homogeneous contribution have therefore been applied for initial temperatures above 400°K.

The reasons for the suppression of the homogeneous reaction should be sought in heterogeneous chain-breaking mechanisms, both on the walls and on the gauze, the rates of which increase with increasing temperature.

No correction has been applied for the homogeneous contribution in the space downstream from the gauze in that the recombination of oxygen atoms on the catalyst and the depletion of NH_3 make this contribution very small as witnessed by the absence of the $O + NH_3$ glow in this space.

A correction should, however, be applied for the homogeneous contribution in the space above the gauze at temperatures below 130°C, but this correction is difficult to calculate. From the temperature drop of the gauze one can estimate that about 5–8% of the injected ammonia should have been oxidized in the gas phase. It is found that a correction of 7% applied to the data below 400°K will bring all the points on the q/T curves calculated from the high temperature data, as discussed below (see Fig. 5).

Diffusional kinetics. The shape of the q vs. T curves (Figs. 4 and 5) and the abrupt change of the stationary temperature of the catalyst when plotted as a function of the initial temperature (Fig. 3) suggest that in the temperature range investigated there is

a passage of the oxidation reaction from a kinetic region into a diffusional region.

The experimental results will, therefore, be treated according to the theory of diffusional kinetics (*6*).

The treatment is simplified because the reaction appears to be approximately first order in the NH_3 concentration (square points of Figs. 4 and 5) and there is practically only one over-all oxidation reaction, leading to NO and water.

The reaction rate q for a first order reaction is given by the equation

$$q = [k\beta/(k + \beta)]c \qquad (1)$$

where k is the first order rate constant of the catalytic reaction, β is the diffusional rate constant, which is defined by the geometry of the system and by the conditions of convection, and c is the NH_3 concentration in the gas phase. Equation (1) reduces to $q = kc$ in the kinetic region where $\beta \gg k$ and to $q = \beta c$ in the diffusional region where $k \gg \beta$.

The temperature dependence of k should be expressed by an Arrhenius equation $k = k_0 \exp(-E/RT)$, while the dependence of β on the temperature is determined by the conditions of diffusion and convection and should be in any case rather small.

The experimental data of Figs. 4 and 5 have been treated as follows: From Eq. (1) and the experimental values of q it is possible to derive the values of the k's at different temperatures, once the values of β are known. These values are, however, difficult to calculate for the present experimental conditions. They have, therefore, been determined by trial and error. A value of β is selected for each curve which gives the best

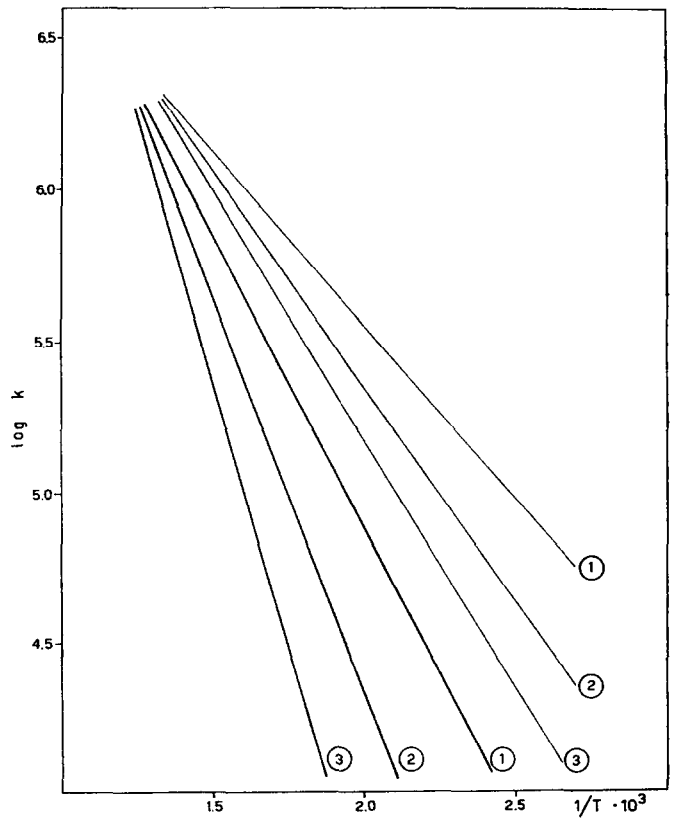

Fig. 6. Arrhenius plots of the rate constants k of the catalytic reaction in molecular oxygen (thick lines) and of the catalytic reaction in the presence of oxygen atoms (thin lines).

straight line when the calculated values of log k are plotted against $1/T$. It is assumed that β is constant in the temperature range investigated. The Arrhenius plots derived from the data of Figs. 4 and 5 are given in Fig. 6. The corresponding values of β are given in Table 1, together with the activation energies calculated from the plots of Fig. 6.

TABLE 1
DIFFUSIONAL RATE CONSTANTS β AND ACTIVATION ENERGIES E

	$\beta \times 10^{-5}$ (sec^{-1})		E (kcal/mole)	
Curve	O_2	$O_2 + O$	O_2	$O_2 + O$
1	4.2	4.3	9.0	5.3
2	3.3	4.2	12.5	6.5
3	2.5	3.7	16.0	7.5

The curves drawn through the experimental points in Figs. 4 and 5 have been calculated from the values of β and from the straight lines of Fig. 6. It appears that within the approximation of a temperature-independent diffusional rate constant, the experimental results can be represented by means of Eq. (1) and of an Arrhenius expression for the rate constants valid in the whole temperature range investigated.

It should be remarked that the values of β which are necessary to fit the experimental data for the partially deactivated catalyst are lower than those corresponding to the freshly activated catalyst, particularly so in the case of the oxidation reaction with molecular oxygen.

In the present calculations the dimensions of β are sec^{-1} in that the reaction velocity is expressed in molecules cc^{-1} sec^{-1}. To convert the values of β into the more usual units, cm/sec, one should multiply β by the contact volume* ($\simeq 10^{-2}$ cm^3) and divide by the uniformly accessible surface area. The observed differences in the β's could, therefore, be attributed to a smaller accessible area of the partially deactivated catalyst.

Another point should be examined in connection with the results of Fig. 3 and with Frank-Kamenetskii's treatment of the thermal regime of exothermic heterogeneous reactions (*6*). The transition between the kinetic region and the diffusional region of the reaction is marked by the so called "ignition temperature." Within the kinetic region the stationary temperature of the catalyst surface will be only a few degrees above the temperature of the environment. However, when the "ignition temperature" of the reaction is reached there will be a discontinuous increase of the stationary temperature of the surface and the reaction will be shifted into the diffusional region.

The presence of an ignition temperature for the oxidation reaction, both in O_2 and in $O_2 + O$ is clearly shown by the curves of Fig. 3, which confirms previous results by Buben (*7*) for the NH_3 oxidation in molecular oxygen. According to Frank-Kamenetskii the occurrence of the critical conditions of ignition and of extinction (i.e., the discontinuous passage from the diffusional into the kinetic region) is determined by the behavior of the function: $\delta = \theta(\mu + e^{-\theta})$ where

$$\theta = (E/RT_0^2)(T - T_0) \quad \text{and} \quad \mu = (k_0/\beta)\,(\exp - E/RT_0)$$

T_0 is the temperature of the medium surrounding the catalyst. If this function has extreme values, the extreme points correspond to the critical conditions of ignition and of extinction. If the function is monotonous there will be no critical conditions.

In Fig. 7 the values of δ have been plotted against the corresponding values of θ for curves 3 of Figs. 4 and 5. The values of T_0 are 515°K and 400°K, respectively, for the oxidation in molecular oxygen and in the presence of oxygen atoms (see Fig. 3). The critical temperatures of ignition and of extinction calculated from these curves are $T_{ign} = 550$°K and $T_{ext} = 665$°K for the molecular oxidation and $T_{ign} = 450$°K and $T_{ext} = 565$°K for the reaction in the presence of oxygen atoms. For the latter reaction the ignition temperature is therefore 100° below the ignition temperature for the reaction in molecular oxygen. The critical temperatures are also shown in Figs. 4 and 5. Their position on these curves is consistent with the

* Volume of contact zone = 2 × (diameter of gauze wire) × (total cross section of the gauze) − 2 × (volume of wire of the gauze).

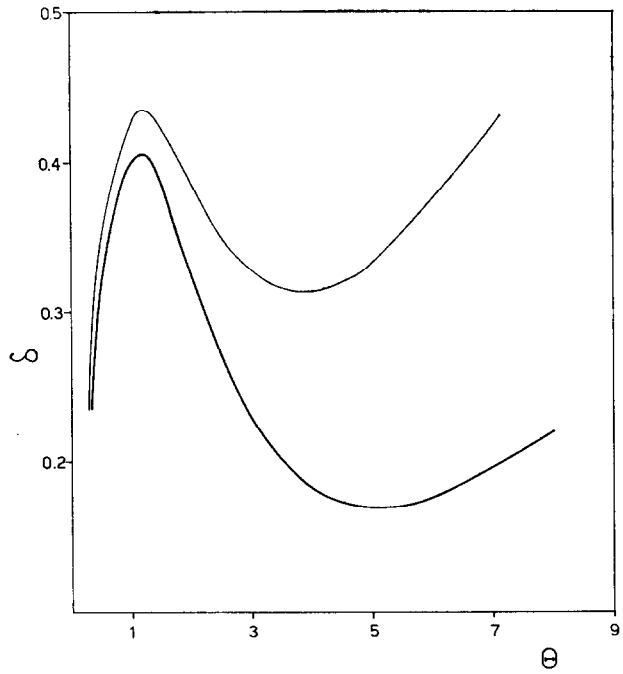

FIG. 7. Plots of δ as a function of θ for the reaction in molecular oxygen (bottom line) and for the reaction in the presence of oxygen atoms (top line).

theory of the thermal regime (*6*) and with the results of Fig. 3.

DISCUSSION

The influence of oxygen atoms in the gas phase on the kinetics of the catalytic oxidation of ammonia is apparent from Fig. 6 and Table 1. The activation energies of the process are significantly lower in the presence of atoms. Within the accuracy of the method there is practically no influence on the nature of the oxidation products.

One also appreciates from Fig. 6 that the Arrhenius plots for the oxidation in molecular oxygen merge at a common temperature as well as the plots for the reaction in the presence of atoms.

The relationship, $\ln k_0 = \ln B + E/RT_c$, between pre-exponential factor k_0 and activation energy E which seems to be of a rather general validity in catalytic processes (*8*, *9*), is therefore obeyed in the present case as well. The values of B and T_c for the oxidation in molecular oxygen are $B = 2.5.10^6$, $T_c = 820°K$. The corresponding values for the reaction in the presence of atoms are: $B = 3.6.10^6$, $T_c = 860°K$ where the B's are given in sec^{-1} units.

One can, therefore, conclude that the presence of atoms increases the rates of the catalytic reaction particularly at low temperatures. However, as a consequence of compensation effects, between pre-exponential factors and activation energy, the rates become approximately equal around the compensation temperatures T_c which are very close for the two reactions. It could now be questioned whether the increased activity determined in the presence of atoms could not be attributed to the simultaneous presence of the normal catalytic oxidation in molecular oxygen and of an additional oxidation reaction occurring homogeneously in the gas phase. The homogeneous oxidation could be either the $O + NH_3$ reaction previously discussed or some homogeneous process originating from radicals emitted from the catalytic surface. The contribution from the homogeneous $O + NH_3$ reaction has already been examined. The following

argument should however apply to all possible homogeneous reactions, and seems to rule out the possibility of a homogeneous contribution: the ignition temperature of the reaction is determined by a balance between heat input to the catalyst surface, due to the exothermic catalytic process, and heat exchange with the surrounding medium. Oxidation processes occurring in the gas phase cannot contribute to the heat input to the surface and are, therefore, unlikely to alter the ignition temperature appreciably. However, the ignition temperature observed in the presence of atoms is 100° lower than the ignition temperature in molecular oxygen.

It therefore appears that the reasons for the increased activity in the presence of oxygen atoms should be sought in a specific influence of the atoms on the catalytic process itself.

(a) The first possibility to consider is that of a reaction between chemisorbed NH_3 fragments and gaseous oxygen atoms. A process of this kind should be approximately first order with respect to the concentration of oxygen atoms. The results obtained at different power outputs of the microwave generator do, however, show that the experimental points scatter around the same curves (Fig. 5). This points to an approximately zero order dependence of the rates on the concentration of oxygen atoms, at least within the limited range of concentrations obtainable with the technique employed (Fig. 2). This appears to be true even in the kinetic region where diffusion of two reactants is unlikely to complicate the dependence of the rate on concentration (*6*).

This type of contribution of the oxygen atoms does not seem, therefore, to be substantiated by the experimental results.

(b) The mechanism of the catalytic oxidation of ammonia on Pt–Rh in the presence of molecular oxygen is complex and there is some controversy about the possible steps of the heterogeneous reaction (*10*).

However, all the proposed schemes assume that the primary step of the oxidation is the reaction between NH_3 and chemisorbed oxygen, with the formation of either hydroxylamine or NH radicals:

$$NH_3 + O_{ads} \rightarrow NH_2OH \quad (2)$$

$$NH_3 + O_{ads} \rightarrow NH + H_2O \quad (3)$$

If this is also the rate-determining step the influence of oxygen atoms might well be that of increasing the concentration of adsorbed oxygen (*1*). An increased surface coverage is, furthermore, likely to cause a significant drop in the heat of adsorption thus making the adsorbed oxygen more reactive toward NH_3, by lowering the activation energy of the surface reaction. The assumption that Reaction (2) (or 3) may be an important rate-determining step appears to be substantiated by the observation that *p*-type oxides are more active for the catalytic oxidation than either *n*-type or insulating oxides (*10, 11*).

The observation that the rates are independent of the O-atom concentration would in this case mean that the surface coverage with oxygen atoms cannot increase above the value corresponding to the minimum concentration of gaseous oxygen atoms present in our experiments, i.e. the surface is saturated with oxygen atoms under the present experimental conditions.

(c) The third possibility of an activating influence of the atoms, which has been mentioned in the introduction, should also be examined. Under the conditions of the present experiments a rapid recombination of the oxygen atoms is occurring on the catalyst surface. The liberation at the surface of the heat of recombination of the atoms represents an additional heat input to the surface. This situation is likely to modify the energy distribution within the chemisorbed layer with respect to the distribution present in the absence of atoms in the gas phase.

A modification of the energy distribution within the chemisorbed layer is in fact likely to occur if the solid cannot accommodate the additional energy at a sufficient rate. If this is the case, part of the additional energy can be taken up by the adsorbed molecules in the form of internal modes.

A number of recent observations seem to indicate that energy accommodation by solids under conditions similar to those of the present experiments is not sufficiently rapid.

As a consequence adsorbed molecules might leave the surface with an excess of energy.

It has been observed (*12*) that when a stream of N and O atoms strikes a metallic surface (Ag, Co, Ni) a luminosity is observed extending for a few millimeters from the metal surface into the gas phase. The interpretation of this observation, based on the spectral analysis of the emitted light, was that the metal surface catalytically recombines the atoms to give N_2 and NO molecules which leave the surface in an electronically excited state. This observation implies that the energy set free by the recombination of the atoms cannot be completely accommodated by the metal. Part of this energy is taken up by the adsorbed species which are then desorbed as electronically excited molecules.

More recently it has been shown (*13*) that when metal filaments are exposed to a flux of H atoms only a fraction of the energy liberated at the surface by recombination can be accommodated by the metal. The remaining fraction is apparently carried away by the desorbing H_2 molecules. Hydrogen molecules formed by surface recombination are not in thermal equilibrium with the catalytic surface and are, therefore, desorbed with an excess of energy in the form of internal and of translational modes.

The idea that adsorbed molecules might not be in thermal equilibrium with the catalytic surface even under usual working conditions in the presence of gaseous molecular species was put forward some years ago (*9*) to account for the relation: $\ln k_0 = \ln B + E/RT_c$ between the pre-exponential factor k_0 of the Arrhenius equation and the activation energy E of the catalytic process. In cases where the slow step of the catalytic process is likely to be the desorption of the product molecules it was assumed that a temperature-dependent fraction of the heat of desorption can be provided by the rapid liberation at the surface of the heat of adsorption of the reactant molecules.

The possibility that the rapid energy input which is present during adsorption might lead to nonequilibrium conditions on the surface has recently been invoked to interpret the kinetics of hydrogen chemisorption on ZnO semiconductors (*14*).

The possible consequence of the presence of atoms in the gas phase on the course of a catalytic reaction is, therefore, the following: If under stationary conditions the rate of energy accommodation by the catalyst is not sufficiently rapid, higher vibrational levels of the adsorbed species might become more populated. This is equivalent to saying that the observed activation energy is decreased by an amount corresponding approximately to the increase of the average vibrational energy of the adsorbed species which take part in the slow step of the reaction. In the case of the ammonia oxidation this would correspond to a lowering of the activation energy of the reaction $NH_3 + O_{ads} \rightarrow$ products. The essential difference between this interpretation of the observed effects and the interpretation given under (b) is, therefore, the following: Under (b) the lowering of the activation energy is attributed to a decrease of the heat of adsorption of oxygen as a consequence of a possible increase of surface coverage. According to (c), and if one restricts the attention only to chemisorbed oxygen, the lowering of the activation energy is attributed to the fact that the average vibrational energy of the oxygen-to-surface bond is higher in the presence of oxygen atoms in the gas phase. The situation is schematically illustrated in Fig. 8.

Conclusions

The influence of gaseous oxygen atoms on the activation energy of the catalytic reaction can be interpreted on the assumption of an increased coverage of the surface with oxygen atoms. It should however be pointed out that a mechanism of energy transfer to the chemisorbed layer, competing with the energy transfer to the solid lattice, can also account for the results. A mechanism of this kind is suggested by previous results of a rather different nature (*9*, *12–14*). Increased surface coverage and increased population of higher energy levels could actually occur simultaneously, but the two contributions are difficult to disentangle.

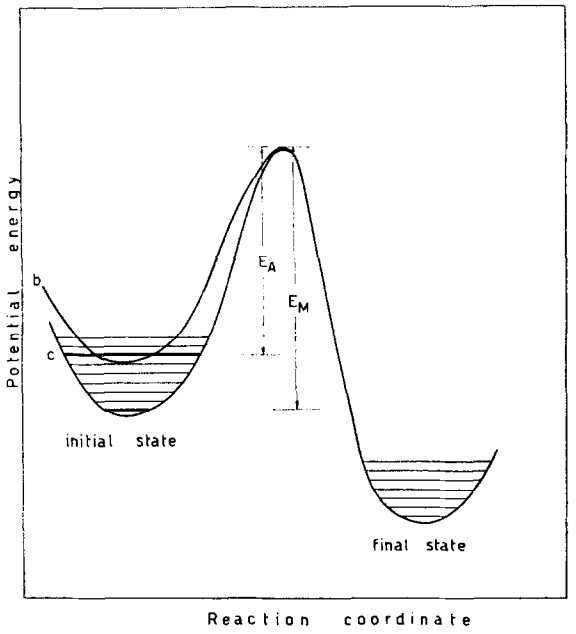

FIG. 8. Potential energy curves showing the activation energy E_M for the reaction in molecular oxygen and the activation energy E_A for the reaction in the presence of oxygen atoms, according to (b) and (c) (see text).

The possibility that exothermic steps of a catalytic reaction might assist other endothermic steps, or steps requiring an activation energy, has not been duly considered in the theory of the rates of heterogeneous catalytic reactions. It is however felt that a deeper understanding of this problem might significantly contribute to the elucidation of the dynamics of heterogeneous processes.

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