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Catalytic Oxidation of Ammonia

N.I.Il'chenko

Data on the catalytic properties of various substances (metals, their alloys, simple and complex oxides, and zeolites containing metal cations) in the oxidation of ammonia are described systematically and reviewed. The kinetics and mechanism of the reaction are discussed and the factors determining the activity and selectivity of the catalysts are identified. Fundamental relations between the physicochemical and catalytic properties of substances of different types are formulated and the relations between the oxidation of ammonia and the selective oxidation reactions of organic substances are analysed.
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I. INTRODUCTION

The catalytic oxidation of ammonia is one of the most interesting and important heterogeneous catalytic processes. It can proceed in the following three principal ways:

$$2NH_3 + 1\frac{1}{2}O_2 = N_2 + 3H_2O + 151 \text{ kcal}, \quad (I)$$

$$2NH_3 + 2O_2 = N_2O + 3H_2O + 132 \text{ kcal}, \quad (II)$$

$$2NH_3 + 2\frac{1}{2}O_2 = 2NO + 3H_2O + 108 \text{ kcal}. \quad (III)$$

In the presence of many catalysts, all three nitrogen-containing products (N_2, N_2O, and NO) are formed simultaneously at 400–500°C in various proportions. On the other hand, in the presence of selective catalysts and when the process is carried out under specific conditions (mainly at specific temperatures), one of the reactions (I)–(III) takes place preferentially. In the presence of platinum or cobalt oxide catalysts at 750–900°C, the main product is nitric oxide. The oxidation of ammonia in the presence of platinum catalysts (they usually consist of platinum–rhodium or platinum–rhodium–palladium alloy gauze) constitutes the basis of the modern industrial manufacture of nitric acid[1]. In the presence of manganese oxide catalysts at lower temperatures (300–400°C), nitrous oxide is formed in fairly high yields[2]; this product is a valuable anaesthetic used in medicine. In the presence of vanadium pentoxide at 500–600°C, ammonia is oxidised only to molecular nitrogen, the process being of practical interest for aviation[3]. Thus each of reactions (I)–(III) is of practical value.

The catalysts of these reactions described above have been discovered empirically. The improvement of the existing catalysts for the oxidation of ammonia and the search for new, more reactive catalysts require the development of scientific principles of the selection of catalysts for this process. This necessitates a systematic arrangement and classification of the available experimental data, a detailed study of the reaction mechanism, and a study of the relation between the catalytic and physicochemical properties of substances.

Very many studies have been made on the catalytic oxidation of ammonia[1,2]. Most of them concern the reaction in the presence of industrial platinum (and certain oxide) catalysts for the synthesis of NO operating at high temperatures under diffusional conditions. The main feature of this review, which distinguishes it from other surveys dealing with the catalytic oxidation of ammonia, is that attention is concentrated on the experimentally proved detailed mechanism and chemical kinetics of the reaction and also on the problem of the relation between the catalytic and physicochemical properties of the relevant substances. These problems were hardly considered in previous studies because the principal experimental and theoretical investigations on these lines have been carried out only in recent years.

The elucidation of the characteristics of the catalytic oxidation of ammonia is important not only from the standpoint of the practical selection of process catalysts but is also of general theoretical interest for the solution of fundamental problems of oxidative heterogeneous catalysis.

The reaction occupies in some respects an exceptional position among other oxidative processes. On the one hand, it has much in common with the oxidation reactions of other inorganic substances (hydrogen, carbon monoxide, etc.) for which the problem of the prediction of catalytic activity is of primary significance. On the other hand, in the oxidation of ammonia there arises the problem of the selectivity of catalytic action, which makes this process similar to many oxidation reactions of organic substances.

In organic catalysis, it is usual to distinguish the products of mild and extensive oxidation. The latter are characterised by a relatively high atomic fraction of oxygen. In the series of ammonia oxidation products N_2–N_2O–NO, the atomic fraction of oxygen rises from zero to 1/2. The degree of oxidation of nitrogen and the number of O_2 molecules required to oxidise one NH_3 molecule increase in the same sequence [see reactions (I)–(III)]. It is therefore natural to assume that molecular nitrogen is a mild oxidation product, while nitrogen oxides are products of the extensive oxidation (NO is a more oxidised species than N_2O).

At the same time, there is a difference between the ammonia and organic substance oxidation reactions,

involving their thermodynamics. In the oxidation of organic compounds, the products of extensive oxidation are thermodynamically more resistant to further oxidation than the mild oxidation products. In the oxidation of ammonia, the opposite situation obtains, as can be seen from a comparison of the standard heats of reactions (I) to (III) (when the entropy change is taken into account, the situation does not change). This feature of the thermodynamics of the reactions is manifested by the fact that completion of the oxidation of a mild oxidation product by molecular oxygen involves a consecutive reaction mechanism in the oxidation of organic substances, while in the oxidation of ammonia the reduction of the product of extensive oxidation by the initial oxidisable substance proceeds via this mechanism:

$$2NH_3 + 3N_2O = 4N_2 + 3H_2O, \quad (IV)$$

$$2NH_3 + 8NO = 5N_2O + 3H_2O, \quad (V)$$

$$2NH_3 + 3NO = 2\frac{1}{2}N_2 + 3H_2O. \quad (VI)$$

This feature has a significant influence on the process kinetics.

The data discussed in this review have been divided on the basis of the principal types of ammonia oxidation catalysts (metals, their alloys, simple oxides, complex and promoted oxide catalysts, zeolites). The usefulness of such subdivisions follows from the fact that the most clear-cut relations between the catalytic and physicochemical properties of the relevant substances are to be expected within a group of similar catalysts for this process. Each section is arranged as follows: data on the catalytic properties (activity and selectivity series) are considered first, next the chemical kinetics and reaction mechanism are discussed, and finally the problem of the relation between the catalytic and physicochemical properties of substances of the given type is analysed on this basis.

II. OXIDATION OF AMMONIA IN THE PRESENCE OF VARIOUS CATALYSTS

1. Oxidation of Ammonia in the Presence of Metals

The catalytic properties of various metals in the oxidation of ammonia under kinetic conditions have been investigated[4,5]; the experiments were carried out at low temperatures (up to 370°C), where the reaction products are N_2 and N_2O. Table 1 shows that at 300°C the specific catalytic activity of metals for the overall process decreases in the sequence†

$$Pt > Pd > Cu > Ag > Ni > Au > Fe > W > Ti.$$

In general, there is a similarity between this series and the series observed in the oxidation of hydrogen[6] (Pt > Pd > Ni > Fe > Cu > Ag > Au > Ti), gas containing SO_2[7] (Pt > Pd > Au > W), and lower olefins[8] (Pt > Pd > Au > W). At high temperatures (500–700°C), the activity of platinum in the oxidation of ammonia exceeds those of rhodium, palladium, and iridium[9].

An effect of the reaction medium on copper, titanium, and tungsten, leading to partial oxidation of these metals, has been noted[5]. At high temperatures, this effect is intensified and platinum and other metals become susceptible to it[1]. The oxidation of ammonia in the presence of platinum begins at temperatures of the order of 150 to 200°C. Under these conditions, the only nitrogen-containing reaction product is molecular nitrogen. With increase of temperature, nitrous oxide appears in the products, its yield passing through a maximum. At temperatures of the order of 300°C, nitric oxide begins to form; its yield increases with temperature and can reach 90% at 700 to 1000°C. Under conditions favourable for the synthesis of NO, the reaction takes place under diffusion-limited conditions[1,2].

Table 1. The oxidation of ammonia in the presence of metals*.[4,5]

Catalyst	r, mol. cm^{-1} s^{-1} (at 300°C)	E, kcal mole^{-1}	Temperature of onset of formation, °C	
			N_2	N_2O
Pt	$1.70 \cdot 10^{17}$	27	195	215
Pd	$2.69 \cdot 10^{16}$	5	100	150
Cu	$3.31 \cdot 10^{15}$	12	175	260
Ag	$2.52 \cdot 10^{15}$	15	200	210
Ni	$1.23 \cdot 10^{15}$	12	210	270
Au	$8.32 \cdot 10^{14}$	4	180	300
Fe	$6.76 \cdot 10^{14}$	9	230	270
W	$5.90 \cdot 10^{14}$	13	225	300
Ti	$2.24 \cdot 10^{14}$	5	180	**

*Composition of reaction mixture: $p_{NH_3} = 0.1$ atm; $p_{O_2} = 0.9$ atm.

**Up to 370°C, nitrous oxide is not formed.

A similar behaviour has been observed also in the presence of other metallic catalysts. Table 1 shows that, for each metal, nitrogen begins to form at a lower temperature than nitrous oxide. NO is formed at still higher temperatures[1].

At low temperatures (Table 1), the process takes place under kinetic conditons and the ammonia oxidation products in the presence of various metals are N_2 and N_2O. Under these conditions, the selectivity with respect to nitrous oxide increases with temperature[4,5]. In the presence of transition metals, the selectivity with respect to this product increases in the sequence

$$Pt, Pd > Ni > Fe > W > Ti,$$

i.e. the selectivity in relation to the extensive oxidation of ammonia varies in parallel with the catalytic activity in the overall process[5]. Experimental studies on the mechanism of the oxidation of ammonia in the presence of metals have been carried out mainly in recent years. In previous studies, a multiplicity of hypothetical mechanisms were put forward, postulating the intermediate formation of species such as NH_2OH, HNO, NH, and others (see the review of Dixon and Longfield[2]). However, these mechanisms were not supported by experimental evidence, which is the reason for their abundance.

In order to elucidate the composition of the intermediate surface complexes formed in the catalytic oxidation of ammonia, the composition of the species generated when the NH_3–O_2 mixture interacts with metals and the species desorbed from their surface following the application of a strong electric field was investigated[10] by autoionisation mass-spectrometry. The experiments were performed using emitters in the form of a platinum needle and a

†Below 250°C, palladium is more active than platinum.[5]

tungsten filament; some of the experiments were performed using ammonia labelled with ^{15}N. Apart from the ions corresponding to the starting materials and the final reaction products, those of the intermediate HNO and NH (nitroxyl and imide) formed on the surface were also detected.

The kinetics of the oxidation of ammonia on massive platinum have been studied[4] by the flow method (for conversions not exceeding 15%) and by the flow-circulation method at atmospheric pressure. The experiments were performed under conditions where the products were N_2 and N_2O. The partial pressure of ammonia in the reaction mixture (p_{NH_3}) was varied in the range 0.05–0.20 atm and the partial pressure of oxygen (p_{O_2}) was varied in the range 0.20–0.95 atm; the ratio p_{O_2}/p_{NH_3} was varied from 1 to 18.9. The results refer to the steady state of the catalyst. The study of the temperature variation of the reaction rate revealed a sharp and abrupt increase of the rate on reaching 240°C. This was accompanied by a rapid and marked increase in the catalyst temperature. Such effects were observed for different compositions of the reaction mixtures, different flow rates, and in experiments using both the flow and flow-circulation methods. The results discussed below[4] refer to the temperature range where the above complications are absent.

At temperatures up to 230°C, the rates of reactions (I) and (II) and selectivity are independent of contact time (for virtually constant p_{NH_3} and p_{O_2}). This implies that nitrogen and nitrous oxide are formed simultaneously under these conditions. At the same time it also follows that the reaction products whose concentration varies severalfold do not influence the rate of oxidation of ammonia.

The variation of the rate of the overall process and of the rates of formation of the individual products (r_{N_2} and r_{N_2O}) with p_{NH_3} and p_{O_2} is described by hyperbolic curves. For low values of p_i, the rates are proportional to the p_i (first-order reaction), while, for high values of p_i, the rates are virtually independent of the latter (zero-order reaction). The attempts to describe the observed variation by kinetic equations of the Langmuir–Hinshelwood type were unsuccessful. Taking into account the results of a mass-spectrometric study of the composition of the intermediates formed on the surface of platinum and tungsten during the catalytic oxidation of ammonia[10] and data on the sorption of oxygen on platinum, the authors[4,11] proposed the following reaction mechanism‡:

	$N^{(I)}$	$N^{(II)}$
1) $O_2 + (\ ) \rightarrow (O_2) \xrightarrow[\text{fast}]{(\ )} 2\,(O)$	$1\frac{1}{2}$	2
2) $NH_3 + (O) \rightarrow (NH) + H_2O$	2	2
3) $(NH) + (O) \rightleftarrows (HNO)$	1	2
4) $(NH) + (HNO) \rightarrow N_2 + H_2O + 3(\ )$	1	0
5) $(HNO) + (HNO) \rightarrow N_2O + H_2O + 4(\ )$	0	1

(VII)

$$N^{(I)}: 2NH_3 + 1\frac{1}{2}O_2 = N_2 + 3H_2O$$

$$N^{(II)}: 2NH_3 + 2O_2 = N_2O + 3H_2O$$

The reaction proceeds via two kinetically independent routes $N(I)$ and $N(II)$, the corresponding sets of the stoichiometric numbers of the stages being shown on the right-hand side of scheme (VII) and the overall chemical equations (I) and (II). The first stage of the process involves the chemisorption of oxygen with intermediate formation of the anion $(O^2)^-$; on the basis of the available data[12], it is suggested that the adsorption of O_2 on platinum at 200–250°C leads ultimately to the formation of atomic oxygen ions (O) having a negative charge. This stage is irreversible. In the second stage, ammonia molecules react with the surface coated by oxygen and form adsorbed species (NH), which are converted in the third (quasi-reversible) stage into the surface nitroxyl (HNO). Analysis of the kinetic data[13] suggests that the (NH) species occupies one elementary surface site and the (HNO) species two such sites. Since the catalyst gives up electrons to the adsorbed oxygen in the first stage, it is natural to assume that, in the interaction of ammonia with platinum coated by oxygen, electrons are transferred from ammonia to the catalyst. The final reaction products in the last two stages are N_2 from (NH) and (HNO), on the one hand, and N_2O from two nitroxyls, on the other.

The following kinetic equations for the rate of the overall process r, the steady-stage degree of surface coverage by atomic oxygen θ, and the selectivities with respect to N_2 and N_2O (S_{N_2} and S_{N_2O}) correspond to the above process mechanism[13]:

$$r = \frac{1}{2}k_2 p_{NH_3}\theta = \frac{1}{2}\frac{k_1 k_2 p_{O_2} p_{NH_3}}{k_1 p_{O_2} + \bar{\nu} k_2 p_{NH_3}}, \quad (1)$$

$$\theta = \frac{k_1}{k_2}\frac{p_{O_2}}{p_{NH_3}}\Big/\left(\frac{k_1}{k_2}\frac{p_{O_2}}{p_{NH_3}} + \bar{\nu}\right), \quad (2)$$

$$S_{N_2} = \frac{\mu}{\mu + \theta}, \quad (3)$$

$$S_{N_2O} = \frac{\theta}{\mu + \theta}, \quad (4)$$

where

$$\mu = k_4/k_5 K_3. \quad (5)$$

In these equations, k_i are the rate constants for the various stages, K_3 is the equilibrium constant for the first stage, and $\bar{\nu}$ is a stoichiometric coefficient showing how many O_2 molecules are consumed on average in the oxidation of one NH_3 molecule; the experimental value[4] is $\bar{\nu} = 0.78 \pm 0.02$. Eqns. (1)–(4) have been derived on the assumption that the reaction proceeds in an ideal monolayer and that the degree of surface coverage by atomic oxygen is much greater than the coverage by other species.

Fig. 1 shows that Eqn. (1), according to which the relation between p_{O_2}/r and p_{O_2}/p_{NH_3} should be linear, describes satisfactorily the variation of r with the composition of the reaction mixture. The slope of the straight line is $2/k_2$ and its intercept on the ordinate axis is $2\bar{\nu}/k_1$. Hence k_1 and k_2 were calculated. The temperature variation of these constants obeys the Arrhenius equation and the heats of activation for the first two stages are $E_1 = E_2 = 32$ kcal mole^{-1}.

Eqns. (3) and (4) show that, at a constant temperature, the selectivity of the given catalyst should be determined by the degree of surface coverage by oxygen θ, which depends in its turn on the mixture composition, i.e. on the ratio p_{O_2}/p_{NH_3}. It follows from Eqn. (2) that θ increases with increase of p_{O_2}/p_{NH_3} ($\theta \rightarrow 0$ when $p_{O_2}/p_{NH_3} \rightarrow 0$ and $\theta \rightarrow 1$ when $p_{O_2}/p_{NH_3} \rightarrow \infty$). It is expected that, with increase of p_{O_2}/p_{NH_3}, i.e. with the increase of θ, the selectivity with respect to the mild oxidation product (nitrogen) should fall continuously [$dS_{N_2}/d\theta = -\mu/(\mu + \theta)^2 < 0$] and that the selectivity with respect to the extensive oxidation product (nitrous oxide) should increase ($dS_{N_2O}/d\theta = -dS_{N_2}/d\theta > 0$). Eqns. (3) and (4) predict that when $\theta \rightarrow 0$, i.e. when $p_{O_2}/p_{NH_3} \rightarrow 0$,

‡Here and henceforth the symbols for substances enclosed in brackets denote surface species, while brackets enclosing a blank space denote free surface sites.

S_{N_2} tends to unity and S_{N_2O} tends to zero. When $\theta \to 1$ (for high values of p_{O_2}/p_{NH_3}), S_{N_2} and S_{N_2O} tend to constant values, which are respectively $\mu/(\mu + 1)$ and $1/(\mu + 1)$. The quantity μ can be calculated from the values of S_i and p_{O_2}/p_{NH_3} for a single experiment by Eqn. (3) or (4) [taking into account Eqn. (2)] and then the variation of the selectivity with θ (or with p_{O_2}/p_{NH_3}) may be calculated for a wide range of compositions of the reaction mixture. The results of such calculations are presented in Fig. 2 (in the form of continuous curves). The satisfactory agreement with experiment (circles in Fig. 2) demonstrates the validity of Eqns. (3) and (4).

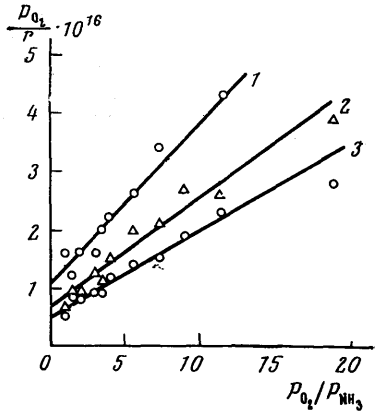


Figure 1. Variation of p_{O_2}/r with p_{O_2}/p_{NH_3} in the presence of a platinum catalyst [4] at different temperatures (°C): 1) 220; 2) 225; 3) 230.

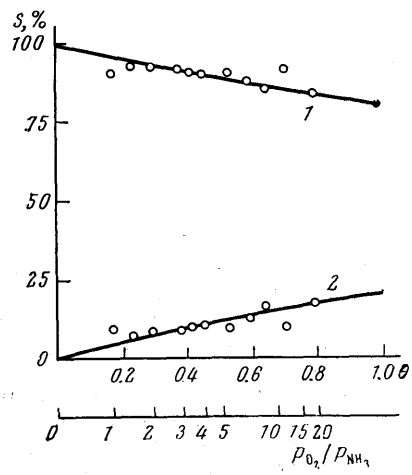


Figure 2. Variation of the selectivity with respect to N_2 (line *1*) and N_2O (line *2*) with p_{O_2}/p_{NH_3} and θ at 230°C on a platinum catalyst [4] ($\mu = 3.8$; $k_1/k_2 = 0.2$).

Thus the experimental kinetic data agree with scheme (VII). Hence it follows that this scheme reflects the essential features of the reaction mechanism on the platinum catalyst.

With increase of temperature, the parallel-reaction mechanism of the oxidation of ammonia is converted into a parallel-consecutive-reaction mechanism; at 235°C, an increase in contact time entails a decrease of selectivity with respect to N_2O. This has been explained [4] by the fact that, for fairly high values of p_{N_2O}, in addition to reactions (I) and (II), reaction (IV) also occurs, leading to the conversion of a definite proportion of the nitrous oxide formed into nitrogen. The probable process mechanism under these conditions can be described as follows [4]:

	$N^{(I)}$	$N^{(II)}$	$N^{(IV)}$
1) $O_2 + (\,) \xrightarrow[\text{fast}]{} (O_2) \xrightarrow[\text{fast}]{(\,)} 2\,(O)$	$1\frac{1}{2}$	2	0
2) $NH_3 + (O) \to (NH) + H_2O$	2	2	2
3) $(NH) + (O) \rightleftarrows (HNO)$	1	2	1
4) $(NH) + (HNO) \to N_2 + H_2O + 3\,(\,)$	1	0	1
5) $(HNO) + (HNO) \to N_2O + H_2O + 4\,(\,)$	0	1	0
6) $N_2O + (\,) \to (O) + N_2$	0	0	3

(VIII)

$$N^{(I)}: 2NH_3 + 1\frac{1}{2}O_2 = N_2 + 3H_2O\ ;$$

$$N^{(II)}: 2NH_3 + 2O_2 = N_2O + 3H_2O\ ;$$

$$N^{(IV)}: 2NH_3 + 3N_2O = 4N_2 + 3H_2O\ .$$

The reaction proceeds via three fundamental routes, $N^{(I)}$, $N^{(II)}$, and $N^{(IV)}$, to which the overall Eqns. (I), (II), and (IV) correspond. Scheme (VIII) is obtained from scheme (VII) when the latter is supplemented by a sixth stage, in which nitrous oxide is irreversibly converted on the surface into adsorbed oxygen and N_2. The (O) atoms formed in this stage subsequently react with NH_3, together with the (O) atoms generated in the first stage as a result of the adsorption of molecular oxygen. It has been shown [4] that, under the experimental conditions used in the oxidation of ammonia, the rate of desorption of oxygen formed in stages (1) and (6) can be regarded as extremely small compared with the rates of the forward reactions in these stages.

The application of the theory of complex steady-state reactions [14] to scheme (VIII) taking into account the postulates noted above leads to the following selectivity equations [4]:

$$S_{N_2} = \frac{r_{N_2}}{r} = \frac{r^{(I)} + 4r^{(IV)}}{r} = \frac{\mu}{\mu + \theta} + \frac{2\bar{\nu}k_6}{k_1}\frac{p_{N_2O}}{p_{O_2}}\ , \qquad (6)$$

$$S_{N_2O} = \frac{r_{N_2O}}{r} = \frac{r^{(II)} - 3r^{(III)}}{r} = \frac{\theta}{\mu + \theta} - \frac{2\nu k_6}{k_1}\frac{p_{N_2O}}{p_{O_2}}\ , \qquad (7)$$

where $r^{(I)}$, $r^{(II)}$, and $r^{(IV)}$ are the rates of the reactions via routes $N^{(I)}$, $N^{(II)}$, and $N^{(IV)}$, while the remaining quantities have the previous significance. The expressions for r and θ are again determined by Eqns. (1) and (2).

By oxidising ammonia using the flow-circulation method with virtually constant p_{NH_3}, p_{O_2}, and θ but significantly variable values of p_{N_2O}, the authors [4] established that the selectivity with respect to N_2O decreases linearly with increase of p_{N_2O}, which confirms the validity of Eqns. (6) and (7). The latter equations can be put in the form

$$S_{N_2} = (S_{N_2})_0 + \Delta,$$
$$S_{N_2O} = (S_{N_2O})_0 - \Delta, \qquad (8)$$

where $(S_{N_2})_0$ and $(S_{N_2O})_0$ are the selectivities with respect to N_2 and N_2O when the reaction proceeds exclusively via the parallel-process mechanism [Eqns. (3) and (4)] and

$$\Delta = \frac{2\bar{\nu}k_6 p_{N_2O}}{k_1 p_{O_2}} = \frac{2\bar{\nu}r_6}{r_1} \qquad (9)$$

reflects the change in selectivity caused by the appearance of the consecutive-reaction mechanism (IV); this quantity

is determined by the ratio of the rates of the sixth and first stages. Eqn.(9) shows that the higher the rate of decomposition of N_2O compared with the rate of absorption of O_2, the greater the contribution to the observed selectivity by the consecutive-reaction scheme; in this case, the dominant source of adsorbed oxygen is N_2O and not O_2. A decrease of contact time leads to a decrease of p_{N_2O}, so that, when $\tau \to 0$, i.e. when $p_{N_2O} \to 0$, Δ tends to zero—the parallel-reaction mechanism obtains exclusively [Eqns.(6) and (7) are identical with Eqns.(3) and (4)].

As mentioned above, when the temperature is raised appreciably, NO appears in the reaction products in addition to N_2 and N_2O, i.e. all three processes (I)–(III) take place at once. At temperatures in the range 700 to 1000°C in the presence of platinum catalysts, mainly NO is formed. At the same time, the process is inhibited by diffusional factors, since the overall rate of reaction increases sharply. For the stoichiometric [in relation to reaction (III)] $O_2 : NH_3$ ratio, the observed rate of oxidation of ammonia is determined by the rate of diffusion of oxygen to the outer surface of the massive catalyst (gauze); in the presence of an excess of oxygen relative to stoichiometry of more than 30%, the diffusion of ammonia is rate-limiting[1].

As a result of macrokinetic inhibition of this kind, the kinetics and mechanism of the reaction at high temperatures, i.e. under conditions where reaction (II) also occurs, have been scarcely investigated experimentally. One can only mention one study[15] where the oxidation of ammonia was investigated on platinum at low pressures (where the diffusion of gases if facilitated) and it was shown that the rate of the overall process is described by the first-order equation

$$r = k p^1_{NH_3} p^0_{O_2}. \qquad (10)$$

Despite the lack of the necessary experimental data (which will evidently become available in the future), it is useful to discuss the problem of the probable behaviour which may be expected when reactions (I)–(III) occur simultaneously under kinetic conditions and provided that a parallel-process and purely heterogeneous mechanism operates. In this case the following mechanism can be postulated[13]:

		$N^{(I)}$	$N^{(II)}$	$N^{(III)}$
1) $O_2 + (\ )$	$\to (O_2) \xrightarrow[\text{fast}]{(\ )} 2(O)$	$1\frac{1}{2}$	2	$2\frac{1}{2}$
2) $NH_3 + (O)$	$\to (NH) + H_2O$	2	2	2
3) $(NH) + (O)$	$\rightleftarrows (HNO)$	1	2	2
4) $(NH) + (HNO)$	$\to N_2 + H_2O + 3(\ )$	1	0	0
5) $(HNO) + (HNO)$	$\to N_2O + H_2O + 4(\ )$	0	1	0
6) $2(HNO) + (O)$	$\to 2NO + H_2O + 5(\ )$	0	0	1

(IX)

$$N^{(I)}: 2NH_3 + 1\,\frac{1}{2}\,O_2 = N_2 + 3H_2O;$$

$$N^{(II)}: 2NH_3 + 2O_2 = N_2O + 3H_2O;$$

$$N^{(III)}: 2NH_3 + 2\,\frac{1}{2}\,O_2 = 2NO + 3H_2O.$$

Scheme (IX) is obtained from scheme (VII) when the latter is supplemented by the postulated stage (6)§, which results in the appearance of a third reaction pathway N(III) and the overall Eqn.(III) applies.

§Experimental data justifying the above formulation of stage (6) are as yet unavailable; it is possible to postulate other versions, for example (HNO) + (O) → NO + (OH) + 2 ( ) with subsequent conversion of (OH) into H_2O, etc.

Eqn.(I) for the overall rate of the process remains unchanged under these conditions. The equations for the selectivity then become

$$S_{N_2} = \frac{\mu}{\mu + \theta + \mu'\theta^2}, \qquad (11)$$

$$S_{N_2O} = 1 - \frac{\mu}{\mu + \theta + \mu'\theta^2} - \frac{\theta}{1/\mu' + \theta + \mu/\mu'\theta}, \qquad (12)$$

$$S_{NO} = \frac{\theta}{1/\mu' + \theta + \mu/\mu'\theta}, \qquad (13)$$

where μ is again defined by Eqn.(5) and $\mu' = k'_6/k_5$ [k'_6 is the rate constant for the sixth stage in scheme (IX)].

The heat of the sixth stage is significantly smaller than that of the fifth stage. Indeed the difference between the heats of these stages is $q_6 - q_5 = 2q_{NO} - q_{(O)} - q_{N_2O}$, where q_i are the heats of formation of the reactants; the difference $2q_{NO} - q_{N_2O} = -23.7$ kcal [16] is negative and, since the heat of adsorption of oxygen $q_{(O)} > 0$, the difference $q_6 - q_5$ is significantly smaller than zero. On the basis of the Brønsted–Temkin relation, the heat of activation for this stage is the higher the lower is its heat of reaction. For this reason, the heat of activation for the sixth stage is higher than for the fifth stage, so that μ' increases with temperature. If the temperature is low, μ' is close to zero; Eqn.(13) shows that, under these conditions, $S_{NO} \simeq 0$ and Eqns.(11) and (12) become identical with Eqns.(3) and (4). At high temperatures, μ' is high and S_{NO} is considerable. This is consistent with the fact that the oxidation of NH_3 to NO is as a rule carried out at high temperatures.

Eqns.(11)–(13) have the following consequences. For mixtures rich in ammonia (when $p_{O_2}/p_{NH_3} \to 0$ and $\theta \to 0$), $S_{N_2} \to 1$ and S_{N_2O} and S_{NO} tend to zero. With increase in the excess of oxygen in the reaction mixture (with increase of θ), S_{N_2} falls, tending to the constant value $\mu/(\mu + 1 + \mu')$ (when $\theta = 1$), while S_{NO} increases, tending to the corresponding limit $\mu'/(\mu + 1 + \mu')$. The variation of S_{N_2O} with θ is more complex: for fairly large values of μ', it passes through a maximum. To illustrate all these findings, Fig.3 presents the results of a model calculation of the variation of the selectivity with θ and p_{O_2}/p_{NH_3} when $\mu' = 100$ (continuous curves) and $\mu' = 10$ (dashed curves); it was assumed in both cases that $k_1/k_2 = 1$, $\bar{\nu} = 1$, and $\mu = 1$. Evidently, the higher the value of μ', the higher the selectivity with respect to NO, and the lower the selectivity with respect to N_2 and N_2O.

In order to test the theoretical calculations, it is necessary to investigate the kinetics of the oxidation of ammonia at elevated temperatures under conditions ruling out the influence of transport processes and of consecutive reactions of the products. The theoretical and experimental data can already be compared to some extent. Thus Eqn.(10) for the rate of the overall process, corresponding to high temperatures of the catalytic reaction on platinum[15], is the same as Eqn.(1): with $k_1 p_{O_2} \gg \bar{\nu} k_2 p_{NH_3}$, Eqn.(1) becomes identical with Eqn.(10). The dependence of the selectivity with respect to NO on p_{O_2}/p_{NH_3} observed at 900°C on platinum[1] is very close to that illustrated in Fig.3. Since the process is distorted by the influence of external diffusion under these conditions, the above comparison is not rigorous, but can nevertheless serve as an argument in support of Eqn.(13).

For a complete description of the reaction kinetics under conditions corresponding to the formation of N_2, N_2O, and NO, it is necessary to take into account the

interaction of NH_3 with NO, i.e. reactions (V) and (VI), in addition to reactions (I)–(IV). The kinetics of the platinum-catalysed reaction (VI) have been investigated[17] and it has been shown that the reaction is strongly inhibited by oxygen. The mechanism of reactions (V) and (VI) on platinum has been studied by the isotopic tracer method[18]. The authors[18] concluded that, in the course of the above reactions at 200°C, NH_3 molecules dissociate on the surface of platinum with formation of the (NH_2) species, which then react with NO, yielding N_2 and H_2O. At high temperatures, further dissociation of (NH_2) with formation of (NH) is postulated.

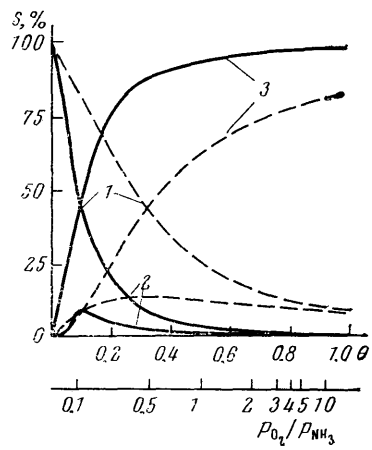


Figure 3. Variation of S_{N_2} (curve *1*), S_{N_2O} (curve *2*), and S_{NO} (curve *3*) with mixture composition[13,46].

The second stage in schemes (VII)–(IX), reflecting the interaction of NH_3 with adsorbed oxygen, is probably in reality more complex than would follow from the equation quoted for this stage. Possibly the formation of the (NH) species from NH_3 and (O) is preceded by the activation of the ammonia molecules on the metal surface free from oxygen[4,5]. This hypothesis is confirmed by the finding that mechanical admixtures of platinum to cobalt, manganese, and vanadium oxides accelerate their reduction by ammonia[19]. The activation of NH_3 molecules on the surface of platinum and other transition metals may involve the dissociation (or marked weakening) of the N–H bond. As pointed out by the present author and Golodets[4,5], this is supported by the fact that transition metals actively catalyse the NH_3–D_2 exchange, although this happens at temperatures lower than those corresponding to the oxidation of NH_3: the exchange between NH_3 and D_2 involves an intermediate stage with partial dissociation of ammonia molecules[20]. As mentioned above, it is natural to suppose that ammonia behaves as an electron donor in its reaction with (O). The conclusion that electrons are transferred from the adsorbed ammonia molecules to the metal follows from a study[21] where the adsorption of NH_3 on gold was investigated by electrophysical methods.

All the schemes described presuppose a purely heterogeneous mechanism of the oxidation of ammonia. Many investigators have considered the possibility of a heterogeneous-homogeneous mechanism of this reaction on platinum, particularly at high temperatures[1,2]. It has been concluded[22,23] that this process is transferred to the bulk phase. It was mentioned above that an abrupt acceleration to the process on platinum has been observed[4] on reaching 240°C. Similar "critical" phenomena have been observed in another investigation[24]. One of their likely causes, according to the present author and Golodets[4], is the transfer of the process to the bulk phase, where the reaction proceeds via a radical-chain mechanism. On the other hand, other investigators (see, for example, Epshtein[25] and Nutt and Kapur[26]) reject a heterogeneous-homogeneous mechanism of the oxidation of ammonia. Thus Nutt and Kapur[26], using mass-spectrometric analysis, failed to detect the presence in the gas phase of unstable intermediate species which might serve as the active centres for the bulk-phase chains in the catalytic oxidation of ammonia; they carried out the catalytic process on platinum at low pressures over a wide range of temperatures (up to 1300°C).

Evidently the discrepancies between the conclusions reached in different investigations can be largely attributed to different experimental conditions. The problem of the role of bulk-phase chains in the mechanism of the catalytic oxidation of ammonia requires further study under conditions as close as possible to the usual conditions in the catalytic process.

We shall now consider the problem of the relation between the catalytic properties of metals in the oxidation of ammonia and their physicochemical (thermodynamic) properties. The discussion may be based[27,28] on mechanism (VII) and the corresponding kinetic equations (1)–(4).

It is natural to suppose that the mechanisms of reactions occurring on different transition metals are similar. This is indicated, in particular, by the finding that the compositions of the intermediate nitrogen compounds desorbed from the platinum and tungsten surfaces after the catalytic process are similar[10]. The differences between the catalytic activities and selectivities of different metals for a constant composition of the reaction mixture and temperature are determined by the differences between the constants in Eqns. (1)–(4).

The relation between the rate constants for different stages and the thermodynamic characteristics of the catalysts is given by the Brønsted–Temkin equation

$$k_i = g_i K_i^{\alpha_i} = g_i \exp\left(\frac{\alpha_i \Delta S_i^0}{R}\right) \cdot \exp\left(\frac{\alpha_i q_i}{RT}\right), \qquad (14)$$

where K_i is the equilibrium constant for the ith stage, q_i the heat of this stage, ΔS_i^0 the standard entropy of the stage, and g_i and α_i are constants for a number of similar catalysts for the given process (ΔS_i^0 in the given series may be regarded as approximately constant[29]).

A common feature of the different stages of mechanism (VII) is that they involve the formation or dissociation of the oxygen–catalyst bond. Consequently, the catalytic activity and selectivity should depend significantly on the energy of this bond, which may be measured by the heat q_S of the binding of oxygen to the surface[30]: $\frac{1}{2}O_2 + (\ ) = (O)$. At the same time, bonds between the catalyst and other atoms (for example, nitrogen) may be formed and dissociated during the reactions. The approximation employed is that the energies of these bonds change much less on passing from one catalyst to another than the q_S.[32] The fact that the energy of the metal–oxygen bond depends much more markedly on the nature of the metal than those of the metal–nitrogen and metal–hydrogen bonds is an argument in support of this hypothesis[31]. Furthermore, since the

typical value of the coefficient α in Eqn. (14) is 0.5, [29] we shall assume that the α_i for different stages are the same and equal to α, which somewhat simplifies the analysis.

The variation of the catalytic activity with q_S is described by the function $\rho = \partial \ln r/\partial q_S$ for T, p_i = const., where r is defined by Eqn. 1. On differentiating Eqn. (1)¶ and taking into account Eqn. (14) as well as the fact that $q_1 = 2q_S$ and $q_2 = q_2' - q_S$ (where q_2' is a combination of the terms of the approximation employed), we obtain

$$\rho = \frac{\alpha}{RT}(2-3\theta). \qquad (15)$$

Here

$$\theta = \left[1 + \frac{\bar{\nu}}{A}\exp\left(-\frac{3\alpha}{RT}q_s\right)\right]^{-1}, \qquad (16)$$

where A is a constant. The last equation shows that θ increases with increase of q_S, tending to unity. If the range of variation of q_S is fairly large, then the variation of ln r with q_S passes through a maximum, since $\rho > 0$ when $\theta \to 0$ and $\rho < 0$ when $\theta \to 1$. The maximum corresponds to $\rho = 0$, whence the optimum value of θ is 2/3 according to Eqn. (15). This implies that, in the group of similar catalytic systems, the catalyst for which q_S corresponds to $\theta = 2/3$ exhibits the highest specific activity at the given temperature and for the given mixture composition.

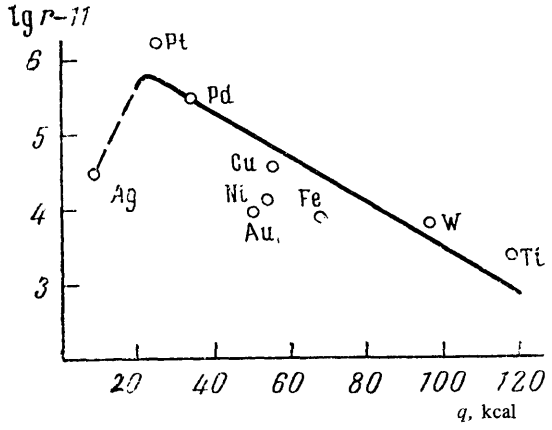


Figure 4. Variation of the specific catalytic activity of metals in the oxidation of NH_3 at 300°C with the energy q_S of the bond between the catalyst and oxygen [30]; mixture composition: p_{NH_3} = 0.1 atm; p_{O_2} = 0.9 atm. [5]

In the region where θ is close to unity (this is attained by carrying out the catalyst process in the presence of a large excess of O_2), the variation of ln r with q_S should be represented by a straight line with a negative slope:

$$\rho = -\alpha/RT, \qquad (17)$$

i.e. the specific activity should fall steadily as q_S increases.

¶ Since the coefficient $\bar{\nu}$ usually varies within narrow limits, in our discussion it is permissible to disregard this variation of $\bar{\nu}$ with q_S.

Fig. 4 shows that this is indeed observed. It follows from Eqn. (1) that in this region $r \simeq \frac{1}{2}k_2 p_{NH_3}$, i.e. the decrease of the activity with increasing q_S is caused by the fact that the rate is determined by stage (2), where the bond between oxygen and the catalyst dissociates. The observed relation between log r and q_S is analogous to corresponding relations found earlier [30] for the oxidation of hydrogen, carbon monoxide, and organic substances.

The type of variation of the selectivity with q_S is determined, as can be seen from Eqns. (3) and (4), by the dependence of θ and μ on q_S. Using Eqn. (14) to determine k_4 and k_5 and taking into account Eqn. (5), we obtain

$$\mu = B\exp\left[\frac{\alpha}{RT}(q^4 - q^5)\right]\cdot\exp\left(-\frac{q_3}{RT}\right), \qquad (18)$$

where B combines a number of constants. Assuming, as before, that on passing from one catalyst to another, mainly the values of q_S change, we have

$$q_4 = q_4' - n_{N_2}q_s, \quad q_5 = q_5' - n_{N_2O}q_s, \quad q_4 - q_5 = q' + (n_{N_2O} - n_{N_2})q_s.$$

In these equations, q_4', q_5', and q' combine terms independent of q_S and n_{N_2} and n_{N_2O} are coefficients determined by the number of oxygen–catalyst bonds dissociated in stages (4) and (5). In terms of the approximation employed, q_3 may be regarded as independent of q_S, since in the third stage the oxygen–catalyst bond is both dissociated and formed. We then obtain in place of Eqn. (18)

$$\mu = \mu_0 \exp(\alpha\,\Delta n q_s/RT), \qquad (19)$$

where μ_0 is independent of q_S and Δn is

$$\Delta n = n_{N_2O} - n_{N_2}. \qquad (20)$$

Fewer oxygen–catalyst bonds are dissociated in stage (4) than in stage (5), so that $\Delta n > 0$; consequently the coefficient μ increases with increase of q_S and so does θ [Eqn. (16)]. The selectivity with respect to N_2 should therefore increase with increase of q_S, tending to unity, while the selectivity with respect to N_2O should fall, tending to zero. Fig. 5 shows that such a relation is indeed observed.

Thus the principal cause of the increase of selectivity with respect to the mild oxidation product as q_S increases is that the formation of this product (the fourth stage) entails the dissociation of fewer oxygen–catalyst bonds than in the formation of the extensive oxidation product (the fifth stage).

This approach can be extended to a more general stage where NH_3 is oxidised to N_2, N_2O, and NO [scheme (IX), Eqns. (11)–(13)]. In this case, the behaviour expected on the basis of the theory is as follows [27,28]: with increase of q_S, the selectivity with respect to the mild oxidation product (N_2) should rise continuously and that with respect to the extensive oxidation product (NO) should fall. This is confirmed qualitatively by the observation that, at fairly high temperatures, platinum exhibits a higher selectivity with respect to NO than palladium, rhodium [9], and other transition metals [1] characterised by higher values of q_S than platinum.

On the basis of the Polanyi relation for the heats of activation and the hypothesis that the higher the degree of oxidation of the product the greater number of oxygen–catalyst bonds dissociated in the stage leading to its formation, one can show [33] that the heat of activation for the reactions under consideration (in the presence of the given catalyst) should increase in the sequence $E_{N_2} < E_{N_2O} < E_{NO}$. The temperatures of the onset of the formation of the corresponding products should therefore increase in the same sequence. This conclusion is confirmed by

the data in Table 1 and by the finding[1] that NO begins to be formed at higher temperatures than N_2O in the presence of each metal.

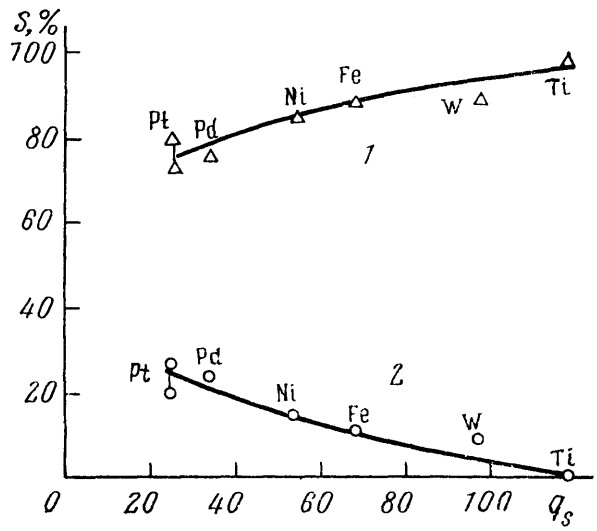


Figure 5. Variation of the selectivity of transition metals at 300°C with q_S (Il'chenko et al.[5]): 1) selectivity with respect to N_2; 2) selectivity with respect to N_2O.

The observed decrease with q_S of both characteristics—the activity r with respect to the overall process and the selectivity S_{N_2O} with respect to the extensive oxidation of NH_3 (see Figs. 4 and 5)—explains the empirical relation noted previously, namely the parallel variation of r and S_{N_2O}.

2. Oxidation of Ammonia in the Presence of Metallic Alloys

In the oxidation of ammonia to NO under industrial conditions, platinum is strongly acted upon by the reaction mixture, under the influence of which the surface of the platinum gauze is loosened, the gauze becomes brittle, and gradually breaks up. The attention of the investigators has therefore been directed to the search for additives to platinum which would improve its strength and stability without reducing its catalytic activity and selectivity. Such requirements are satisfied by platinum–rhodium alloys. In practice, one uses gauze made of 90% Pt–10% Rh alloy (owing to the high cost of rhodium, alloys containing 5–7% Rh are sometimes used). When the reaction is carried out at atmospheric pressure, platinum alloys with 4% Pd and 3.5% Rh, which are somewhat less stable but no less active than the platinum–rhodium catalysts, are employed. Other platinum (and palladium) alloys with transition metals, particularly the platinum alloy with 1% 1% Ir,[1] also exhibit a high activity in the oxidation of ammonia to NO.

Systematic studies yielding information about the specific catalytic activities of alloys and their selectivities under kinetic conditions (particularly at low temperatures) have not so far been made. The kinetics and mechanism of the oxidation of ammonia in the presence of metallic alloys have also been hardly investigated. Presumably the same behaviour should apply here as in catalysis on the pure metals.

It has been shown[34] that the catalytic activity of the 90% Pt–10% Rh alloy increases when ammonia is oxidised by the O_2–O mixture instead of molecular oxygen. The homogeneous oxidation of NH_3 by atomic oxygen was ruled out[34] and it was assumed that acceleration is achieved either owing to the increase of the concentration of adsorbed oxygen or because excited activated species appear in the purely exothermic interaction of O atoms with the surface of the catalyst. The first hypothesis is consistent with schemes (VII)–(IX), because it follows from Eqn. (1) that the rate of reaction is proportional to θ.

3. Oxidation of Ammonia in the Presence of Simple Oxide Catalysts

Quantitative data on the catalytic properties of simple oxides in the oxidation of ammonia have been obtained in a number of studies[13,35,36] (Table 2). Under the conditions of these experiments, the reaction products were N_2 and N_2O and the process occurred in the kinetic region. The steady state was usually attained rapidly, in the course of 5–10 min. A phase transformation of the oxide (with the exception of Ag_2O) was not observed. Table 2 shows that at 230°C the specific catalytic activities of the oxides decrease in the following sequence:

$$Co_3O_4,\ MnO_2 > CuO > CaO_2 > NiO > Bi_2O_3 > Fe_2O_3 > V_2O_5 > TiO_2 > \\ > CdO > PbO > ZnO > SnO_2 > ZrO_2 > MoO_3 > WO_3$$

A similar sequence was obtained in another study[37], according to which the activities of the oxides decrease as follows:

$$Co_3O_4 > Mn_2O_3 > Cr_2O_3 > Fe_2O_3 > CuO > NiO > V_2O_5 > MoO_3 > U_3O_8 > \\ > ThO_2 > WO_3 > SnO_2 > ZrO_2 > ZnO > Nb_2O_5 > Bi_2O_3 > Sb_2O_4 > Ta_2O_5.$$

However, one should note that the activity of Bi_2O_3 observed by Germain and Perez[37] is significantly lower than that found by Il'chenko et al.[36]. According to other data[38,39], lanthanide (La, Ce, Pr) oxides exhibit a low activity in the oxidation of NH_3 and the activities of Al_2O_3 and SiO_2 are very low indeed. The activity of barium peroxide approaches that of Fe_2O_3.[40]

Thus, among the simple oxides, the highest activities in the oxidation of ammonia are shown by the transition metal oxides Co_3O_4, $MnO_2(Mn_2O_3)$, Cr_2O_3, and CuO, the oxides NiO, Fe_2O_3, and V_2O_5 are moderately active, and the activities of the oxides La_2O_3, Pr_6O_{11}, CeO_2, TiO_2, ZrO_2, ThO_2, Nb_2O_5, Ta_2O_5, MoO_3, WO_3, and U_3O_8 are low. The oxides of elements in the main subgroups (except for calcium and barium peroxides) are relatively inactive. A similar behaviour has been observed in the oxidation of hydrogen[41,42], methane, benzene[41], and other inorganic and organic substances.

As in the presence of metals, the oxidation of ammonia in the presence of metal oxides results in the preferential formation of N_2 at low temperatures; on raising the reaction temperatures, nitrous oxide appears in the products, its yield passing through a maximum; at still higher temperatures (400–500°C and above), ammonia is oxidised to an even greater extent—to NO.[1,2,35–40] It has been noted[33] that, in the presence of each catalyst the temperature of the onset of formation of particular products increases in the sequence $N_2 < N_2O < NO$ (see Refs. 36, 38, 40 and Table 2).

At low temperatures and for low degrees of conversion, when only reactions (I) and (II) occur, the selectivity with respect to N_2O in the presence of the majority of oxides increases with temperature [36,40]. In this region, the selectivity with respect to N_2O falls in the sequence

$$CaO_2 > MnO_2,\ NiO > Co_3O_4 > Fe_2O_3 > SnO_2 > CdO > CuO > TiO_2 > ZnO,\ Bi_2O_3,\ PbO,\ ZrO_2,\ MoO_3,\ WO_3$$

(Table 2). Comparison of these data with other results[37,38] leads to the conclusion that the maximum selectivity with respect to N_2O (minimum selectivity with respect to N_2) is shown by the most active oxides (MnO_2, Mn_2O_3, Co_3O_4, CuO, NiO, Cu_2O, and CaO_2), so that the following tendency is observed: the selectivity with respect to mild oxidation varies in general in opposition to the catalytic activity, while the selectivity with respect to extensive oxidation varies in parallel with the activity [36].

Table 2. The oxidation of ammonia in the presence of metal oxides*. [13,35,36]

Catalyst	Specific surface, $m^2\ g^{-1}$	Sample, g	Temp. range of catalytic reaction, °C	lg r—11**	E, kcal mole^{-1}	S_{N_2O}, at 230°C, %	Temperature of onset of formation, °C	
							N_2	N_2O
Co_3O_4	5.25	11.25	130—170	2.35	22	38	130	140
MnO_2	24.60	3.625	110—160	2.35	18	43	110	120
CuO	0.92	10.79	220—260	1.60	23	11	220	230
CaO_2	3.20	8.56	200—260	0.54	15	50	<200	200
NiO	52.00	11.08	80—160	0.40	11	43****	80	105
Bi_2O_3	1.41	17.31	235—320	0.13	12	0	235	255
Fe_2O_3	22.10	6.72	220—270	0.07	24	17	220	230
V_2O_5	4.50	8.80	260—320	—0.16	26	0	260	—
TiO_2	5.71	8.23	265—320	—0.36	16	8****	265	290
CdO	10.4	16.45	205—275	—0.38	9	13	205	230
PbO	6.00	23.40	240—285	—0.64	16	0	240	260
ZnO	1.00	5.07	265—380	—0.79	31	0	265	295
SnO_2	2.53	15.69	210—260	—0.90	17	16	<210	210
ZrO_2	9.60	10.92	245—330	—0.91	18	0	245	>330
MoO_3	0.33	28.90	330—370	—1.50	33	0	330	—
WO_3	6.35	19.14	200—380	—2.22	22	0	200	>380
Ag_2O***	0 09	24.55	115—155	3.40	18	—	125	147

*Composition of reaction mixture: p_{NH_3} = 0.1 atm; p_{O_2} = 0.9 atm.

**r is the rate of the overall process (in mol.cm^{-2} s^{-1}) at 230°C.

***The oxide was reduced to the metal during the catalytic reaction.

****S_{N_2O} for NiO at 160°C and to TiO_2 at 290°C.

At high temperatures (700–800°C), reaction (III) proceeds at a high rate. Owing to the marked influence of macrokinetic factors, it is difficult to obtain rigorous quantitative selectivity data in this temperature range. Qualitative characteristics of the selectivity with respect to NO for various oxides at temperatures in the range 700–800°C have been published [43,44]. According to Kurin and Zakharov [43], the yield of NO decreases in the sequence

$$Co_3O_4 > MnO_2 > PbO > Cr_2O_3,\ Fe_2O_3 > CuO > NiO > ZnO > SnO_2,\ MoO_3,\ WO_3,\ TiO_2,\ Al_2O_3;$$

while Morozov et al. [44] obtained the sequence

$$Co_3O_4 > CuO > Cr_2O_3 > Fe_2O_3.$$

Thus, under these conditions too the selectivity with respect to the extensive oxidation products in general varies in parallel with the catalytic activity in relation to the overall process. The most active catalyst (among simple oxides), namely Co_3O_4, exhibits a fairly high selectivity with respect to N_2O at low temperatures and with respect to NO at high temperatures. This catalyst is sometimes used in practice in the oxidation of NH_3 to NO. [1]

The kinetics and mechanism of the oxidation of ammonia in the presence of oxide catalysts (Co_3O_4, MnO_2, CuO, Fe_2O_3, and V_2O_5; see Table 2) have been investigated [13,35,45,46]. The experiments were performed in a differential flow reactor (with conversions not exceeding 20%) and by the flow-circulation method. The reaction was studied at temperatures below 400°C when the products were N_2 and N_2O. The study of the variation of the rate of reactions (I) and (II) with contact time τ in the presence of the most active catalysts (Co_3O_4, MnO_2) showed that, under the chosen conditions, the values of r_i (and hence the selectivity) are independent of τ. This implies that reactions (I) and (II) take place simultaneously and are not inhibited by the products. The variation of the rate of the overall process and of specific reactions with p_{NH_3} and p_{O_2} is represented (for each catalyst) by hyperbolic curves: the reaction is of first order for low values of p_i, and of zero order for high values of p_i.

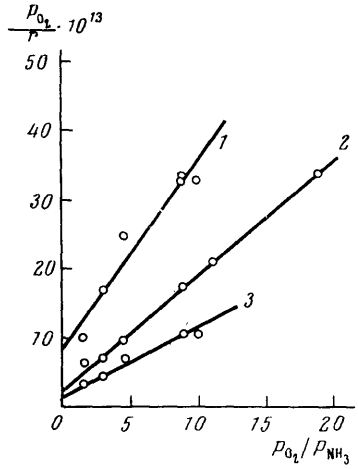


Figure 6. Variation of p_{O_2}/r with p_{O_2}/p_{NH_3} on an MnO_2 catalyst [13,46] at different temperatures (°C): 1) 135; 2) 145; 3) 155.

As in the catalytic reaction on platinum [4], mechanisms of the Langmuir–Hinshelwood type proved to be unsuitable for the interpretation of the experimental data. Scheme (VII) and the kinetic equations (1)–(4) corresponding to it proved to be the most appropriate. Figs. 6 and 7 show that these equations describe satisfactorily the experimental data for the MnO_2 catalyst. A similar result was obtained also for other oxides (Co_3O_4, CuO, Fe_2O_3, and V_2O_5). The rate constants, heats of activation, and entropies of activation for the first two stages of scheme (VII), calculated from the experimental data, have been compiled for the above catalysts [13]. The kinetic data [47] for the oxidation of ammonia in the presence of Cu_2O also agree with Eqns. (1)–(4).

The conclusion that S_{N_2O} increases with increase of θ agrees with the results of a study [40] where it was found that

the yield of nitrous oxide increases with increasing concentration of the "excess" oxygen on the surface of transition metal oxides.

According to scheme (VII), the oxygen adsorption stage is irreversible. We shall now consider[45] another extreme case, where adsorption equilibrium is established in the first stage. If such a case does indeed occur, deviations from Eqn. (1) should be observed. The selectivity equations (3) and (4) retain their previous form, but the values of θ involved in them are determined by the oxygen adsorption isotherm and not by Eqn. (2). This means that, at a given temperature, the selectivity should be independent of p_{NH_3} and, for a constant p_{O_2}, it should remain unchanged; in reality, S_{N_2O} decreases with increase of p_{NH_3} (for p_{O_2} = const.), which corresponds to Eqn. (4).

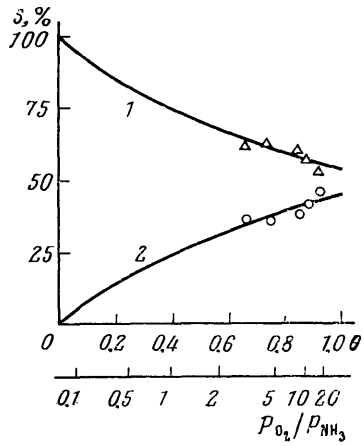


Figure 7. Variation of the selectivity with respect to N_2 (curve *1*) and N_2O (curve *2*) with p_{O_2}/p_{NH_3} and θ at 145°C on an MnO_2 catalyst[13,46] (μ = 1,2; k_1/k_2 = 0.55).

The similarity of the behaviour observed in the catalytic oxidation of ammonia and in the surface reduction of various oxides by ammonia (in the absence of O_2 from the gas phase) constitutes an independent demonstration of the involvement of the (O) species in the process and that their surface concentration θ plays a decisive role in the reaction kinetics. The following observations were made[13,35].

(1) The composition of the products in the catalytic and reduction reactions is the same (see the data of Krauss and Neuhaus[40]).

(2) The rate of the overall conversion of ammonia in the reduction process decreases with increase of the duration of reduction τ'. This result is consistent with Eqn. (1), since θ falls continuously as τ' increases. If the reduction is carried out after treating the catalyst with oxygen, whereupon the catalyst surface is fully oxidised in the initial state (θ is a maximum), then the initial rate of reduction is higher than the steady-state rate of the catalytic reaction. After a specific time τ', the rate of reduction becomes equal to the rate of the catalytic reaction; at this point, the values of θ for the catalytic and reduction reactions are the same. If the reduction is carried out immediately after the catalytic experiment, then the initial rate of reduction is close to the steady-state rate of the catalytic reaction.

(3) In conformity with Eqns. (3) and (4), the selectivity with respect to N_2 increases and that with respect to N_2O falls as τ' increases, i.e. as θ decreases.

The similarity of the characteristics of the catalytic oxidation of ammonia and of the surface reduction of oxides by ammonia shows that, in the interaction of NH_3 with the surface [the second stage in scheme (VII)], electrons are transferred from the ammonia molecule to the catalyst, i.e. NH_3 behaves as an electron donor. This is consistent with the results of studies[47,48] where the catalytic properties of oxides in the oxidation of ammonia were compared with their semiconductor properties.

It is natural to assume that the abstraction of hydrogen from the NH_3 molecule proceeds simultaneously with electron transfer from NH_3 to the catalyst and is completed gradually, in several stages: the formation of the final products from NH_3 and O_2 in a single stage would require the simultaneous collision of many species, which is unlikely. In order to demonstrate the involvement of (NH) and (HNO) species and possibly of other surface complexes in the process, it is necessary to employ physical research techniques. In this connection, we may note that the most probable product of the reaction between NH_3 and the surface oxygen of iron(III) oxide at low temperatures has been shown by infrared spectroscopy to consist of species of the nitroxyl type[49].

It has been shown by ESR[50] that, in the adsorption of ammonia at room temperature on partly reduced vanadium pentoxide deposited on silica gel, the NH_3 molecule enters into the first coordination sphere of the tetrahedrally coordinated V^{4+} ion. This results in a rearrangement of the coordination sphere and in the formation of a shortened vanadium–oxygen bond, characteristic of vanadyl ions. Thus formation of an unstable coordination compound may be the primary step in the activation of NH_3 during the catalytic process, facilitating the next electron transfer stage. This hypothesis appears probable, bearing in mind the tendency of transition metal cations to form complexes with ammonia, a molecule having a lone electron pair.

In the subsequent stages of the catalytic process, the (NH) and (HNO) species behave as electron donors, like ammonia. When these species are converted into the reaction products (N_2, N_2O, and H_2O), electrons are liberated. The reduced form of the catalyst cations M^{n+}_{red}, capable of giving up electrons, therefore corresponds to the free surface sites, appearing as a result of the fourth or fifth stages of scheme (VII).

In the adsorption of electron-accepting oxygen molecules on these centres, electrons combine with the O_2 molecules, forming negatively charged atomic ions (O) bound to the oxidised form of the cations M^{m+}_{ox}. Hence it follows that the surface concentration of the (O) species, equal to θ, is proportional to $[M^{m+}_{ox}]$, while the concentration of free sites ( ), equal to $1 - \theta$, is proportional to $[M^{n+}_{red}]$; the ratio of the concentrations of the oxidised and reduced forms $\gamma = [M^{m+}_{ox}]/[M^{n+}_{red}]$ will be proportional, under steady-stage conditions of the catalytic reaction, to $\theta/(1 - \theta)$. According to Eqn. (2), this implies that γ is proportional to p_{O_2}/p_{NH_3}, i.e. the degree of oxidation of the surface is determined by the ratio of the partial pressures of oxygen and ammonia in the reaction mixture.

The same quantity determines the catalytic selectivity (at a given temperature). The higher the value of p_{O_2}/p_{NH_3}, the higher the degree of surface coverage by

oxygen θ. Since the activated complex in the stage leadng to the formation of N_2O incorporates a larger number of oxygen atoms than the activated complex in the stage leading to the formation of N_2 (see the fourth and fifth stages), an increase of p_{O_2}/p_{NH_3} tends to increase the selectivity with respect to the more oxidised product—nitrous oxide.

The kinetics and mechanism of the reaction in the presence of oxides at elevated temperatures have not been investigated. Presumably schemes of types (VIII) and (IX), taking into account the parallel-reaction oxidation of NH_3 to NO and the consecutive-reaction reduction of nitrous oxide by ammonia [here it is also necessary to take into account reactions (V) and (VI)], are valid for these conditions.

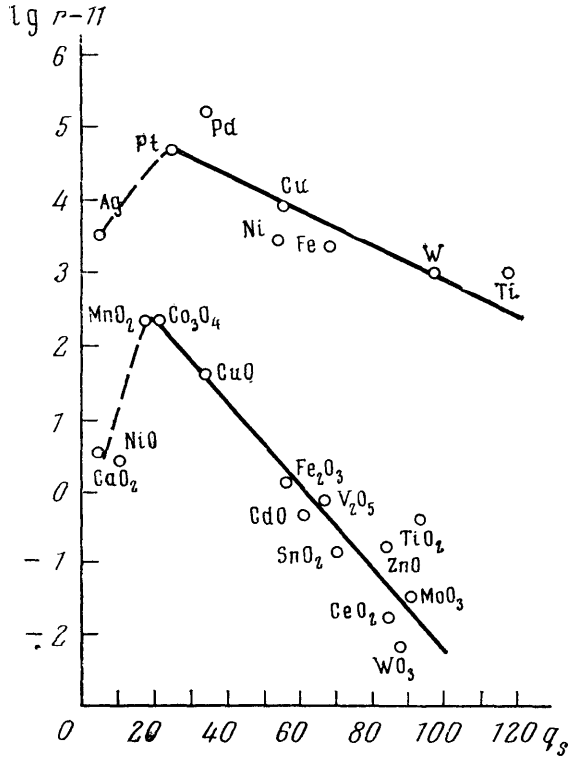


Figure 8. Variation of the specific catalytic activity of metals and oxides in the oxidation of NH_3 at 230°C with q_S; mixture composition: $p_{NH_3} = 0.1$ atm; $p_{O_2} = 0.9$ atm.[36]

The results of the theoretical analysis carried out above in relation to metallic catalysts (section II, subsection 1) can be usefully employed in the discussion of the problem of the relation between the catalytic and physicochemical properties of oxide catalysts. Such an examination, which has been carried out in a number of studies[27,28,36], is based on the hypothesis that the oxygen–catalyst bond energy q_S plays a decisive role. Arguments in support of this hypothesis have been obtained[36] by quantum-chemical calculations on complexes simulating the surface compounds of the oxidised and reduced forms of various oxide catalysts with oxygen and the NH species.

Fig. 8 shows that the correlation predicted by Eqn. (15) does indeed occur between q_S and the specific catalytic activity of the oxide. The correlation is analogous to that observed for transition metals. At the same time, it is seen that, under identical conditions, the absolute activity of metals exceeds considerably that of oxides[4,36]. The cause of the difference should probably be sought in the fact that, in the presence of transition metals, the preliminary activation of NH_3 molecules takes place on a metallic surface free from oxygen and leads to the dissociation (or considerable weakening) of the N–H bond (see section II, subsection 1); because of this, the absolute values of k_2 for metals are higher than for oxides[4]. Similar relations between the absolute catalytic activities of metals and oxides have been observed in the oxidation of hydrogen and certain organic substances[30].

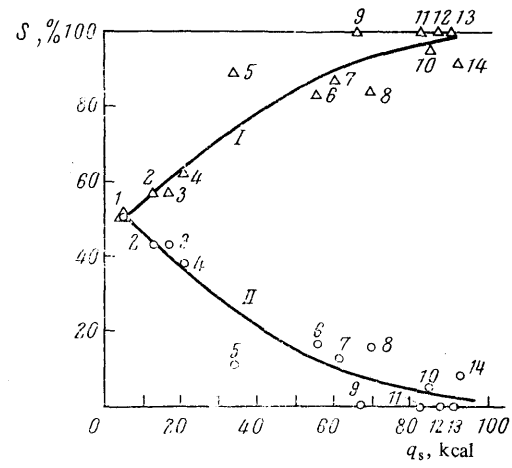


Figure 9. Dependence of the selectivity of oxides with respect to N_2 (curve *1*) and N_2O (curve *2*) on q_S at 230°C: 1) CaO_2; 2) NiO; 3) MnO_2; 4) Co_3O_4; 5) CuO; 6) Fe_2O_3; 7) CdO; 8) SnO_2; 9) V_2O_5; 10) CeO_2; 11) ZnO; 12) WO_3; 13) MoO_3; 14) TiO_2.[36]

Fig. 9 shows that the selectivity of the process with respect to N_2 increases with increase of q_S, while the selectivity with respect to N_2O falls. Such variation of selectivity follows from Eqns. (3), (4), (19), and (20). In addition to the above analysis, we shall consider[27,28] the variation of the rates of formation of N_2 and N_2O with q_S. It can be shown that, when $\theta \simeq 1$, we have

$$\rho_{N_2} = \frac{\partial \ln r_{N_2}}{\partial q_s} = -\frac{\alpha}{RT}\left(1 - \frac{\Delta n}{1+\mu}\right),$$

$$\rho_{N_2O} = \frac{\partial \ln r_{N_2O}}{\partial q_s} = -\frac{\alpha}{RT}\left(1 + \frac{\Delta n \mu}{1+\mu}\right).$$

It is readily seen that ρ_{N_2O} is negative like ρ [see Eqn. (17)]; the type of variation of the rate of extensive oxidation and of the overall rate of the process with q_S should therefore be qualitatively the same. The difference $\rho_{N_2O} - \rho_{N_2} = -\alpha\Delta n/RT$ is likewise negative, which implies that the rate of extensive oxidation should decrease with increase of q_S more rapidly than the rate of mild oxidation. Experiment confirmed this inference (Fig. 10).

The higher the value of q_S, the greater the contribution of r_{N_2} to the overall rate and the higher the selectivity with respect to the mild oxidation product (Fig. 9).

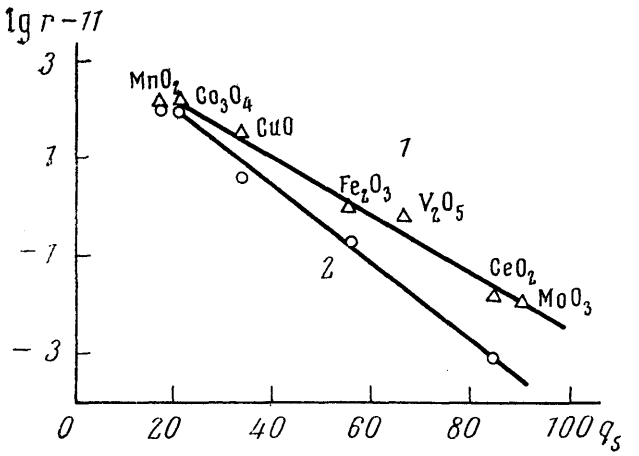


Figure 10. Variation of the rates of formation of N_2 (line *1*) and N_2O (line *2*) with q_S.[27]

This shows clearly that the principal cause of the increase of the selectivity with respect to the mild oxidation product with increase of q_S is that the formation of this product entails the dissociation of fewer oxygen–catalyst bonds than the formation of the extensive oxidation product[33].

When the above approach is extended to a more general case, where reactions (I)–(III) occur simultaneously, one may conclude that at high temperatures the selectivity with respect to NO should decrease with q_S. Fig. 11 shows that this inference is likewise fulfilled. The observed decrease with q_S of the catalytic activity in relation to the overall process and of the selectivity with respect to the extensive oxidation product explains the empirical observations noted above—the parallel variation of these quantities for a series of oxide catalysts.

The increase of the heats of activation in the sequence $E_{N_2} < E_{N_2O} < E_{NO}$ predicted by the theory[33] also agrees with experiment, since, in the presence of each oxide catalyst, the temperatures of the onset of formation of particular products increase in the sequence $N_2 < N_2O <$ NO (see Table 2 and the data in Refs. 36, 38, 40).

A correlation between the type of conductivity of the oxides and their catalytic properties in the ammonia oxidation reaction has been noted in a number of investigations[2,38,43]. The catalytic activity decreases in the sequence *p*-type semiconductors > *n*-type semiconductors > insulators; the selectivity with respect to N_2O (and NO) increases in the same sequence while that with respect to N_2 diminishes. The above correlation can be explained by the fact that there is a qualitative correspondence between the semiconductor properties of the oxides and the energy of the bond between oxygen and their surfaces[51]; *p*-type semiconductors (MnO_2, Co_3O_4, NiO, and CuO) have the smallest values of q_S, insulators (aluminium, silicon, and other oxides) are characterised by the highest values of q_S, while *n*-type semiconductors (V_2O_5, MoO_3, ZnO, TiO_3, etc.) occupy an intermediate position.

4. Oxidation of Ammonia in the Presence of Complex and Promoted Oxide Catalysts

Complex oxide catalysts based on MnO_2 exhibit a high activity in relation to the low-temperature oxidation of ammonia and at the same time a high selectivity with respect to N_2O. The temperature dependence of the yields of N_2, N_2O, and NO in the presence of these catalysts is of the same type as in the presence of simple oxide catalysts[1,2,40,52]. In the reaction involving the oxidation of NH_3 to N_2O at 200–300°C, MnO_2 with added Bi_2O_3 is extremely effective[2,39,53]. The studies discussed in the preceeding subsection showed that nickel(II) oxide is fairly active in relation to the overall reaction and selective with respect to the formation of N_2O. According to Giordano et al.[48], small amounts of lithium and sodium oxides added to this catalyst increase while added aluminium and iron oxides decrease the activity and selectivity, i.e., in this case, the activity and selectivity in relation to extensive oxidation vary in parallel.

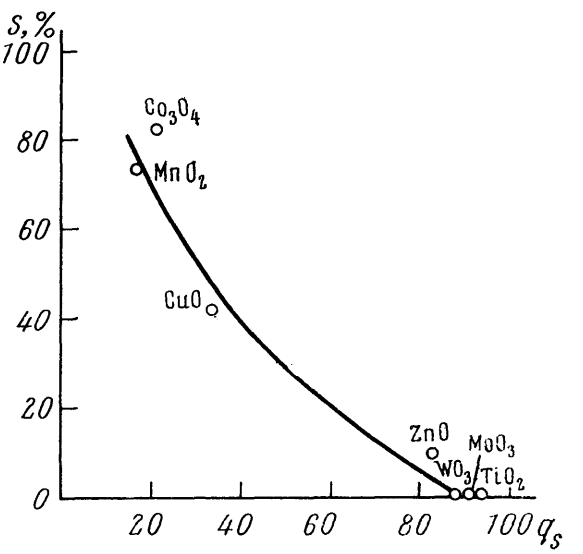


Figure 11. Dependence of the selectivity of oxides with respect to NO on q_S.[27]

In the high-temperature oxidation of ammonia, a high selectivity with respect to NO is shown mainly by complex catalysts, the chemical composition of which resembles that of the effective catalysts of the synthesis of N_2O at low temperatures. It has been shown[44] that, in the presence of cobalt oxide catalysts containing added copper, chromium, zinc, nickel, magnesium, iron, and silver oxides as well as copper and zinc chromites, the yield of NO attained at 700°C is 90–95%; best results are obtained in the presence of pure Co_3O_4. The 85% Co_3O_4–15% Al_2O_3 catalyst is sometimes used in practice[1]. In the presence of manganese oxide catalysts containing added chromium and copper oxides, the yield of NO is 60–80%.[44] The Fe_2O–MnO_2–Bi_2O_3 catalyst is fairly active (but is operation is unstable); complex iron oxide–chromium oxide catalysts are more stable and are used as the second component in two-component catalysts (platinum catalysts are used as the first component)[1].

In contrast to the catalysts based on Co_3O_4, MnO_2, and Fe_2O_3, accelerating the extensive oxidation of ammonia, which were discussed above, complex oxide catalysts based on MoO_3 catalyse, like MoO_3 itself, virtually only the mild oxidation of NH_3 (only to N_2).[54,55] Nitrogen oxides are obtained in very significant amounts in the presence of bismuth molybdate[54] and other molybdates[55]. The activity of such systems decreases in the sequence[55]

$$Bi—Mo—O\ (Bi : Mo = 1) > Fe—Mo—O > Mn—Mo—O > Co—Mo—O >$$
$$> Bi—Mo—O\ (Bi : Mo) = 2) > MoO_3 > Ca—Mo—O,\ Tl—Mo—O,\ Pb—Mo—O.$$

The kinetics and mechanism of the oxidation of ammonia in the presence of complex oxide catalysts and the factors governing their selection have been little investigated. Nevertheless the isolated facts available suggest that this instance constitutes an analogy with catalysis by simple oxides:

(1) The kinetics of the overall process in the presence of MnO_2–Bi_2O_3 catalyst are said to be described[39] by the relation $r = kp_{NH_3}\theta$, i.e. Eqn. (1).

(2) In the presence of complex catalysts, the same relations are observed between the temperatures of the onset of the formation of N_2, N_2O, and NO as in the presence of simple oxide catalysts.

(3) The qualitative composition of the products in the surface reduction of complex oxides by ammonia and in the catalytic reaction is the same[40,55], as for simple oxides.

(4) Since complex catalysts based on Co_3O_4 and MnO_2 have a much lower oxygen binding energy than the catalysts based on MoO_3, presumably the same relations between q_S and the activity and selectivity are valid qualitatively for complex catalysts as for simple oxides: the first group of catalysts (based on Co_3O_4 and MnO_2) are active and selective in relation to the extensive oxidation of ammonia, while the activity of the second group (based on MoO_3) is low, but the catalysts are selective in relation to the mild oxidation. The validity of relations of this kind for complex oxide catalysts too provides a natural explanation of the opposite variation of r and S_{N_2} observed for such catalysts.

Thus, by altering the oxygen–oxide catalyst bond energy as a result of the introduction of additives, it is possible to regulate the activity and selectivity of the catalyst in the oxidation of ammonia.

A fundamentally new method for the selection of a low-temperature catalyst for the synthesis of nitrous oxide from ammonia was used by the present author[19]. The idea is as follows. Since we have seen that a high selectivity with respect to N_2O is achieved on oxides with low values of q_S, oxides such as MnO_2 and Co_3O_4 can be used as a basis for the above catalyst. Next, it is necessary to increase the activity of these without altering q_S, since otherwise the selectivity would fall. Such a method of increasing the activity is provided by the dissimilarity (noted above) of transition metals and their oxides, associated with the higher rate of activation of ammonia on metallic surfaces. When small amounts of platinum or palladium are introduced into the oxide, then q_S for the oxide remains unchanged, but the rate of oxidation of ammonia should increase owing to its activation on the metal. Using this procedure, it was indeed possible to obtain new extremely active and selective catalysts for the oxidation of NH_3 to N_2O (cobalt or manganese oxide promoted by platinum). In the presence of these catalysts at low temperatures (of the order of 200°C), ammonia can be fully converted, the selectivity with respect to N_2O being 60–80%.[19]

The study of the reaction kinetics in the presence of the above promoted catalysts showed that the same Eqns. (1) to (4) are valid for them as for the unpromoted oxides. This demonstrates that the introduction of additives does not cause a fundamental change in the reaction mechanism but there is an appreciable increase of the rate of reaction of ammonia with the surface oxygen of the oxide. This is proved by the observed acceleration of the surface reduction of cobalt and manganese oxides by ammonia in the presence of small amounts of added platinum[19].

A similar promotion effect was demonstrated previously in the oxidation of hydrogen on vanadium pentoxide[56]. We may note that the reactivity of ammonia in its oxidation on metal oxides is close to the reactivity of molecular hydrogen[36].

5. Oxidation of Ammonia on Zeolites Containing Transition Metals

The oxidation of ammonia on a type Y zeolite containing Mn^{2+}, Fe^{3+}, Co^{2+}, Ni^{2+}, Cu^{2+}, Cr^{3+}, and Ag^+ cations has been investigated[57] by a pulse method ($O_2 : NH_3 = 3 : 1$). The cations were introduced into the initial NaY zeolite by ion exchange from solutions of the metal nitrates. The degree of exchange (%) was 70.5 for CuY, 50.0 for FeY, 55 for CoY, 80.4 for CrY, 48.0 for NiY, 56 for MnY, and 51.7 for AgY. After the exchange, the colour of the zeolite corresponded to the colour of the cations in the aqueous solution. The aluminosilicate crystal structure of the NaY specimen was retained in the exchange reaction. It also remained unchanged after the specimens had been heat-treated at temperatures up to 600°C. The only exception was the chromium catalyst in which the formation of a α-Al_2O_3–Cr_2O_3 solid solution was observed.

The catalytic activity was characterised by the degree of conversion of ammonia for the same weight of the metal in the zeolite. The following activity series was established:

$$CuY > CrY > AgY > CoY > FeY > NiY,\ MnY.$$

The reaction product was molecular nitrogen in the presence of all the above catalysts. A fairly small amount of nitrous oxide was also formed in the presence of the chromium- and silver-zeolites; in the presence of AgY, the selectivity with respect to N_2O at 400°C was approximately 25%. On other zeolites, the selectivity with respect to this product was 1–5%. The authors[57] believe that the process proceeds via a parallel-consecutive reaction mechanism, the N_2O formed being converted into N_2 via reaction (IV). A high rate of this reaction at the temperatures of the catalytic oxidation of ammonia has been demonstrated for the CuY catalyst.

The study of the alternate oxidation of the catalysts by oxygen pulses and of the reduction of the oxidised specimen by ammonia showed that N_2 is formed on reduction in the presence of the FeY, CuY, and CrY zeolites, which absorb O_2; the MnY and CoY catalysts do not absorb oxygen. The adsorption of ammonia on the CuY catalyst at room temperature leads to a change in the colour of the latter, which becomes blue, i.e. is characteristic of the coordination compounds of NH_3 and Cu^{2+}. There is a simultaneous change in the ESR spectrum of the specimen. The adsorbed ammonia is removed by evacuation (at 60°C), whereupon the specimen returns to the initial state. The adsorption of O_2 at 385°C does not change the ESR spectrum of the zeolite. When ammonia is readmitted at 385°C, some of the Cu^{2+} ions are reduced; the copper atoms formed can be reoxidised by oxygen.

A different behaviour is observed in the presence of the MnY zeolite: the ESR spectrum changes only when NH_3 is adsorbed at room temperature. The retention of the ESR signal following the interaction of the zeolite with O_2 and NH_3 at elevated temperatures suggests that in this case the valence state of the manganese in the zeolite remains unaltered. X-Ray diffraction studies of all the zeolites after exposure to a stream of ammonia at 500°C failed to reveal any changes relative to the initial state, which indicates the absence of a metallic phase.

Comparison of the metal cations shows that the above zeolite activity series differs significantly from the corresponding series obtained for oxide catalysts (see subsection 3 of this section). This is evidently associated with the fact that the intermediate chemical interaction in the catalytic process on the zeolite is of the local type and involves a single catalyst cation, while in catalysis on solid oxides collective interactions due to the presence of the crystal lattice also play a significant role.

The authors[57] suggest that a mechanism involving the alternate reduction and oxidation of the catalyst cations is possible on the CuY and FeY zeolites, while in the presence of the MnY, CoY, and NiY zeolites, where the valence state of the metal is stabilised, a mechanism involving the simultaneous interaction of the catalyst with NH_3 and O_2 is probable.

III. THE ANALOGY BETWEEN THE SELECTIVE OXIDATION REACTIONS OF AMMONIA AND ORGANIC SUBSTANCES[27,28]

The oxidation of ammonia is a convenient reaction for the elucidation of the general characteristics of selective catalytic oxidation. In many significant respects, the mechanism of this reaction is similar to that of the oxidation of organic substances. The similarity is manifested in the kinetics. Thus the kinetic equations for the overall oxidation of *o*-xylene[58] and ammonia are analogous. In the oxidation of *o*-xylene[58], but-1-ene[59], and other substances (R), the selectivity with respect to the mild oxidation product increases with increase of the ratio p_R/p_{O_2} in the reaction mixture, as has been observed in the oxidation of NH_3, where the selectivity with respect to nitrogen increases with p_R/p_{O_2}.

The catalytic activity in the oxidation of both ammonia and organic substances is determined primarily by the energy of the bond formed by oxygen with the catalyst surface, the optimum corresponding to low values of q_S. The similarity of the mechanisms of these reactions is responsible for the analogous variation of the catalytic activity as a function of q_S. This explains the finding that the most active catalysts for the oxidation of NH_3 and organic substances are the same (Co_3O_4, MnO_2, and platinum).

The general rule whereby one can understand the nature of the variation of selectivity as a function of q_S is that the formation of the extensive oxidation products (CO and CO_2 in the oxidation of organic substances and N_2O and NO in the oxidation of ammonia) involves the dissociation of a larger number of oxygen–catalyst bonds than the formation of the mild oxidation products (aldehydes, ketones, etc. in organic catalysis and N_2 in the oxidation of NH_3). As a result of this, the selectivity with respect to the mild oxidation products increases and that with respect to the extensive oxidation products decreases with increase of q_S. This implies that a high selectivity with respect to the extensive oxidation products is attained on catalysts with low values of q_S, in agreement with the condition for the highest activity of the catalyst, and explains why the best catalysts for the oxidation of NH_3 to NO and for the complete combustion of organic substances are usually Co_3O_4 and platinum.

Experiments have shown that the optimum values of q_S for the mild oxidation reactions of organic substances is close to the value of q_S for V_2O_5 and for complex catalysts based on V_2O_5 and MoO_3, because the latter are used to accelerate these reactions. The similarity of the mild oxidation reactions of organic substances and ammonia is manifested by the fact that the same catalysts are used also in the mild oxidation of NH_3.

There are also definite differences between the oxidation reactions of organic substances and ammonia. These involve primarily the thermodynamics of the reactions. In the oxidation of organic substances, the extensive oxidation products are thermodynamically more stable than the mild oxidation products, while in the oxidation of ammonia the opposite behaviour is observed (see Section I). In the former case, the mild oxidation product is desired and in the latter the aim is to obtain the extensive oxidation product. This is reasonable, since the advantage of catalysis are reflected in the possibility of obtaining thermodynamically less stable products. The above feature of the thermodynamics of the reactions compared is manifested by the finding that, in the oxidation of ammonia (in contrast to the oxidation of organic substances), an enhanced rate of formation of the mild oxidation product and a reduced observed rate of extensive oxidation correspond to the consecutive reaction scheme.

One must note that the approach used above to establish a relation between the catalytic properties and chemical structures of substances has certain limitations. In a more rigorous treatment, it is necessary to take into account the energy inhomogeneity of the surface oxygen[60], which can play the same role on a given catalyst as the changes in the oxygen binding energy on passing from one catalyst to another. Another simplification is associated with the hypothesis that only the energy of the oxygen–catalyst bond changes significantly from one catalyst to another. In a more exact analysis, one must take into account also the changes in the energies of other bonds formed with the catalyst[32]. Allowance for the energies of other bonds should be understood in a fairly broad sense, including the formation of coordination compounds via π bonding, etc. as well as salt-like surface complexes. In the latter case, the acid–base properties of the catalyst play a significant role[61]. One can also suppose that, in the oxidation of complex organic molecules, the geometrical factor should have a definite importance (the requirement for multipoint adsorption).

It follows from the results discussed that, in the oxidation of ammonia, the acid–base and other properties of the catalysts play an appreciably smaller role than in the oxidation of organic substances, so that the decisive importance of the energy of the bond between oxygen and the surface is shown much more distinctly. In this respect, the oxidation of ammonia is closer to the oxidation reactions of inorganic molecules such as H_2 or CO_2.

IV. CONCLUSION

The analysis carried out in this review has shown that the kinetic method combined with physical research techniques can be employed to establish important features of the mechanism of the oxidation of ammonia under

conditions where the oxidation products are nitrogen and nitrous oxide. It follows from the available data that the mechanism is qualitatively similar for metallic and oxide catalysts. The observed differences are largely quantitative and are caused by the specific features of the interaction of the oxidised molecule with the metallic surface. The mechanisms examined, considered in conjunction with the Brønsted–Temkin relation, serve as a fruitful basis for the determination of a relation between the thermodynamic properties of substances and their activities and selectivities in the oxidation of ammonia.

At the same time, one should note many unsolved problems, which include the kinetics and mechanism of the reaction at high temperatures, where NO is formed, the catalytic properties of complex catalysts in the kinetic region, the nature of the intermediate chemical interaction at elevated temperatures, and the role of homogeneous stages in the mechanism of the oxidation of ammonia. The solution of these problems will accelerate progress in the practical selection of new effective catalysts for this most important catalytic reaction.

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Pisarzhevskii Institute of Physical Chemistry, Academy of Sciences of Ukrainian SSR, Kiev