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Catalytic Oxidation of Ammonia

II. Relationship Between Catalytic Properties of Substances and Surface Oxygen Bond Energy. General Regularities in Catalytic Oxidation of Ammonia and Organic Substances

N. I. IL'CHENKO AND G. I. GOLODETS

The L. V. Pisarzhevskii Institute of Physical Chemistry of the Academy of Sciences of the Ukrainian SSR, Kiev, USSR

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Catalytic activity and selectivity of oxides of cobalt, manganese, copper, iron, vanadium and molybdenum with respect to ammonia oxidation to N_2 and N_2O have been studied. The activity decreases in the above-mentioned sequence of oxides. The specific activity of metallic platinum is much higher than that of the most active oxide catalysts. Generally, the selectivity towards mild oxidation (the formation of N_2) increases with decreasing activity of oxides.

On the basis of the reaction mechanism proposed in the previous paper (Part I) the relationship between surface oxygen bond energy, q_s, and catalytic behavior of oxides has been deduced theoretically. Catalytic activity, r, is expected to pass through a maximum which corresponds to low values of q_s. For the majority of catalysts the activity must decrease with increasing q_s. At the same time the selectivity for the formation of N_2 must increase while the selectivity for N_2O must fall. The experimental data obtained confirm these conclusions. In accordance with the theory, for the high temperature oxidation of ammonia to NO the selectivity in NO decreases with increasing q_s.

The following rule has been stated: more oxygen–catalyst bonds are broken in the formation of the activated complex of a stage leading to a deep oxidation product than in the formation of a mild oxidation product. This gives rise to an increase in selectivity in mild oxidation with q_s. The above rule has been shown to be rather general and also applicable to the oxidation of organic substances. Thus, the similarity between selective oxidation of ammonia and organic molecules has been found. Some general regularities concerning heterogeneous catalytic oxidation are formulated.

INTRODUCTION

In the first part of this work (*1*) the mechanism of the catalytic oxidation of ammonia was studied. In the present paper this mechanism is used for deducing the relationship of the catalytic activity and selectivity to the chemical nature of catalysts. Our approach is based on the principle of the relationship between catalytic and thermodynamic properties of substances.

Experimental study was carried out using the procedure described in Part I (*1*). Under the investigated conditions ammonia is oxidized into N_2 and N_2O.

RESULTS AND DISCUSSION

Catalytic Properties of Substances in Respect to Ammonia Oxidation

Figure 1 presents the Arrhenius plot for the temperature dependence of rates of the

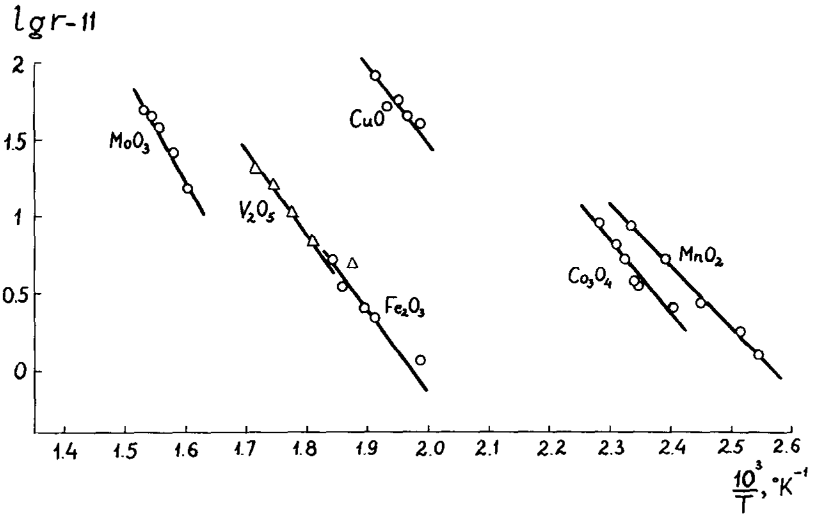

Fig. 1. Arrhenius plot for rates of the overall process over various catalysts. Rates are expressed in molecules $N_2 + N_2O/cm^2$ sec; reaction mixture composition: $P_{NH_3} = 0.1$ atm, $P_{O_2} = 0.9$ atm.

overall process of ammonia oxidation, r, over various catalysts. The reaction rates were measured with an excess of O_2 in the reaction mixture.

Table 1 shows specific catalytic activities in ammonia oxidation to decrease in the range: Co_3O_4, $MnO_2 > CuO > Fe_2O_3 > V_2O_5 > MoO_3$. Similar patterns have been observed in the oxidation of hydrogen and different organic molecules (*2*). Activation energies E for ammonia oxidation increase in the order: $MnO_2 < Co_3O_4 < CuO < Fe_2O_3 < V_2O_5 < MoO_3$.

TABLE 1

CATALYTIC ACTIVITY OF SUBSTANCES IN AMMONIA OXIDATION

Catalyst	$\log r - 11$[a]	E (kcal/mole)
Pt (wire)	4.67	
Co_3O_4	2.35	22
MnO_2	2.35	18
CuO	1.60	23
Fe_2O_3	0.07	24
V_2O_5	−0.16	26
MoO_3	−1.50	33

[a] r denotes rate of the overall process (in molecules $N_2 + N_2O/cm^2 \cdot sec$) at 230°C and for the reaction mixture composition: $P_{NH_3} = 0.1$ atm, $P_{O_2} = 0.9$ atm.

Figure 2 demonstrates the temperature dependence of rates of ammonia oxidation to N_2 and N_2O (r_{N_2} and r_{N_2O}). Selectivities in the mild oxidation of ammonia (the formation of N_2) increased in the following sequence: $MnO_2 < Co_3O_4 < Fe_2O_3 < CuO < MoO_3 < V_2O_5$. Generally, this sequence is the inverse of that of catalytic activities. Similar sequences have been found for the partial oxidation of propylene (*3*), methanol (*4*) and other organic substances.

Selectivities in the formation of NO change parallel to catalytic activities. At high temperatures (700–800°C) when NO is the predominant product of deep oxidation the following sequence of selectivities in NO has been obtained (*5*): $Co_3O_4 > MnO_2 > Fe_2O_3 > CuO > ZnO > MoO_3$, WO_3, TiO_2. It is similar to the pattern of selectivities in N_2O at lower temperatures.

Initial Theoretical Propositions

According to Part I (*1*), experimental data on the catalytic oxidation of ammonia at lower temperatures can be interpreted using the following reaction mechanism (parentheses designate an adsorbed state

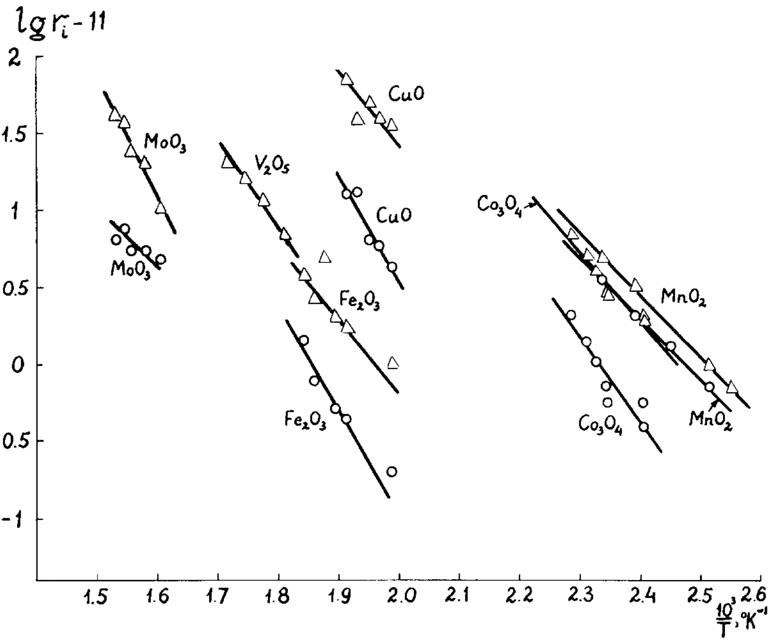

FIG. 2. Arrhenius plot for rates of formation of N_2 (△) and N_2O (○). Reaction mixture composition: $P_{NH_3} = 0.1$ atm, $P_{O_2} = 0.9$ atm.

and empty parentheses a vacant surface site):

	Stoichiometric nos. $N^{(I)}$	$N^{(II)}$
1. $O_2 + (\ ) \to (O_2) \xrightarrow[\text{fast}]{(\ )} 2(O)$	1.5	2
2. $NH_3 + (O) \to (NH) + H_2O$	2	2
3. $(NH) + (O) \rightleftarrows (HNO)$	1	2
4. $(NH) + (HNO) \to N_2 + H_2O + 3(\ )$	1	0
5. $(HNO) + (HNO) \to N_2O + H_2O + 4(\ )$	0	1

$N^{(I)}$: $2\ NH_3 + 1.5\ O_2 = N_2 + 3\ H_2O$, (I)

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

This mechanism leads (*1*) to the following equations for the oxygen coverage θ, rate of the overall process r, rates of reactions (I) and (II) (r_{N_2} and r_{N_2O}) and selectivities in N_2 and N_2O (S_{N_2} and S_{N_2O}), other symbols are as before (*1*):

$$\theta = \frac{1}{1 + \{\nu/[(k_1/k_2)(P_{O_2}/P_{NH_3})]\}}, \qquad (1)$$

$$r = {}^1\!/\!_2 k_2 P_{NH_3}\theta = \frac{{}^1\!/\!_2\, k_1 k_2 P_{O_2} P_{NH_3}}{k_1 P_{O_2} + \nu k_2 P_{NH_3}}, \qquad (2)$$

$$r_{N_2} = \frac{\mu}{\mu + \theta} \cdot r, \qquad (3)$$

$$r_{N_2O} = \frac{\theta}{\mu + \theta} \cdot r, \qquad (4)$$

$$S_{N_2} = \frac{\mu}{\mu + \theta}, \qquad (5)$$

$$S_{N_2O} = \frac{\theta}{\mu + \theta}, \qquad (6)$$

where

$$\mu = \frac{k_4}{k_5 K_3}. \qquad (7)$$

As already indicated (*1*), the above scheme can be used as the basis for searching for the relationship of the activity and selectivity of catalysts with their chemical nature, a problem of principal importance in the prediction of catalytic action.

Under definite experimental conditions (temperature, reaction mixture composition) differences in catalytic behavior of substances are caused by differences in values of constants of Eqs. (2)–(6). The value of ν, being determined by the stoichiometry of reactions (I) and (II) and by the selectivities, usually changes in a narrow range. For the catalysts MnO_2 and V_2O_5 which differ significantly in their selectivity the values of ν are 0.86 and 0.75, respectively, so that in our discussion ν can be considered as a constant. The dependence between the rate constants of the stages, k_i, and the thermodynamic characteristics of catalysts is expressed by the well-known Brønsted–Temkin relation:

$$k_i = g_i K_i^{\alpha_i} = g_i \exp\frac{\alpha_i \Delta S_i^0}{R} \exp\frac{\alpha_i q_i}{RT}, \qquad (8)$$

where K_i is the equilibrium constant for stage i, q_i is its heat effect, ΔS_i^0 is the standard entropy change; g_i and α_i are constants for a series of catalysts of the same type. For this series the values of ΔS_i^0 can also be considered as approximately constant (*6*).

A common feature of all the stages under consideration is the formation or the breaking of oxygen–catalyst bonds. Because of that, catalytic activity and selectivity must essentially depend on the energy of this bond (*2,7*); a measure of the latter can be the heat q_s of the process of binding of oxygen to a surface (*7*): $\frac{1}{2}O_2 + (\ \ ) = (O)$. At the same time during the reaction the bonds of the catalyst with other atoms (with nitrogen and probably hydrogen) are formed and destroyed. Our approximation requires that the energies of the latter bonds change much less than the values of q_s in going from one catalyst to another. Some evidence in favor of this assumption is the fact that metal–oxygen energies depend much more on the chemical nature of metals than do the energies of metal–nitrogen and metal–hydrogen bonds (*8*). In addition, because the typical value of α_i in Eq. (8) is 0.5 (*6*), the magnitudes of α_i for different stages will be taken as equal to the same value, α, which simplifies our analysis.

Dependence Between Catalytic Activities and Surface Oxygen Bond Energy

The character of the dependence between catalytic activity, r, and q_s is reflected by

$$\rho = \left(\frac{\partial \ln r}{\partial q_s}\right)_{T,P_i},$$

where r is determined by Eq. (2). Differentiating Eq. (2) and taking Eq. (8) into account (as well as the fact that $q_1 = 2\,q_s$ and $q_2 = q_2' - q_s$ where q_2' unites quantities which do not depend on q_s in our approximation) we obtain

$$\rho = \frac{\alpha}{RT}(2 - 3\theta). \qquad (9)$$

Besides,

$$\theta = \frac{1}{1 + \dfrac{\nu}{A \exp(3\alpha/RT)\, q_s}}, \qquad (10)$$

where

$$A = \frac{g_1}{g_2} \cdot \frac{P_{O_2}}{P_{NH_3}} \exp\frac{\alpha}{R}(\Delta S_2^0) \times \exp\left(-\frac{\alpha}{RT} q_2'\right);$$

A is constant at a given temperature and reaction mixture composition.

Equation (10) shows that θ increases with q_s, θ approaching unity. With a rather wide range of the q_s change the dependence of ln r on q_s passes through a maximum because $\rho > 0$ at $\theta \to 0$ and $\rho < 0$ at $\theta \to 1$. The position of the maximum corresponds to $\rho = 0$, from which on the basis of Eq. (9) we have $\theta_{\text{optim}} = \frac{2}{3}$. This means that in a series of systems of the same type the highest catalytic activity (at a given temperature and reaction mixture composition) is exhibited by the catalyst for which q_s corresponds to $\theta = \frac{2}{3}$.

When θ is close to unity for all the catalysts being compared (this is probable for our experiments made in a great excess of O_2) the dependence of ln r on q_s must be expressed by a straight line with a negative slope

$$\rho = -\frac{\alpha}{RT}, \qquad (11)$$

i.e., the specific activity must progressively fall with increasing q_s. Figure 3 shows this to be true. It follows from Eq. (2) that in this region $r \approx \frac{1}{2}k_2P_{NH_3}$, so the decrease in activity with increasing q_s is due to the fact that the rate is determined by the second stage in which the oxygen–catalyst bond is broken.

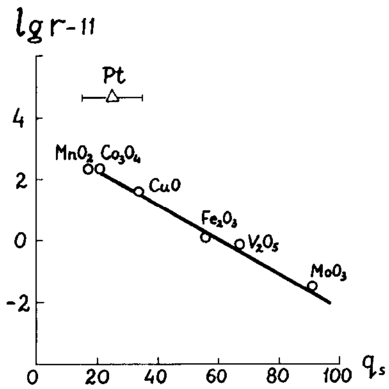

FIG. 3. The relationship between specific catalytic activities in ammonia oxidation and surface oxygen bond energies [q_s (kcal)(7)]. The specific activity, r, is expressed in molecules $N_2 + N_2O/cm^2$ sec; $t = 230°C$; reaction mixture composition: $P_{NH_3} = 0.1$ atm, $P_{O_2} = 0.9$ atm.

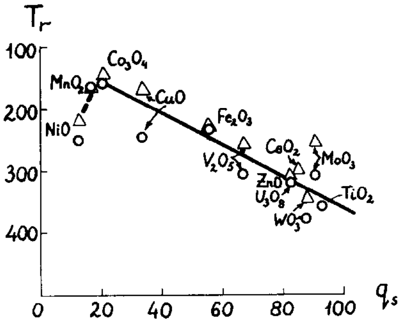

FIG. 4. The relationship between the activities of oxides in ammonia oxidation and surface oxygen bond energies. T_r is the temperature of attaining 1% conversion (△) (9) or 8% m^{-2} conversion (○) (*10*).

The observed dependence log r vs q_s for ammonia oxidation is similar to those obtained earlier (*2,7*) for the oxidation of hydrogen, carbon monoxide and organic compounds.

Figure 4 also presents the relation between q_s and catalytic activity of oxides; the measure of the latter was the temperature T_r of attaining equal reaction rates [according to literature data (*9,10*)]. The observed correlation is qualitatively similar to that obtained on the basis of our experimental data. The greater scatter of points may be due to the fact that the surface areas of samples in (*9*) were different. Besides, the cited data (*9,10*) refer to less excess O_2 in the mixture (10% NH_3, ~ 20% O_2). This might result in partial reduction of catalysts.

The following fact is noteworthy. As in hydrogen oxidation (*7,11*), the absolute catalytic activity of platinum in ammonia oxidation is much higher than that of the optimum oxide catalyst (Fig. 3). This suggests that in ammonia oxidation metals and metal oxides belong to different types of catalysts. It is probable that on platinum and other transition metals ammonia and hydrogen are activated easier than on oxide surfaces (i.e., the N–H bond rupture is facilitated) which causes higher values of g_2 in Eq. (8) for transition metals in comparison with oxides.

At $\theta \approx 1$ the activation energy E for the overall process is close to the activation energy for the second stage, E_2. According to the Polanyi relation, $E_2 = A_2 - \alpha q_2$ ($A_2 = \text{const}$), so that

$$E \approx E_2 = A_2 - \alpha q_2' + \alpha q_s = A_2' + \alpha q_s \tag{12}$$

(A_2' is a new constant). Thus, in the considered case one should expect E to increase with q_s. This agrees with experiment (Fig. 5). The physical sense of this relation and the relation log r vs q_s is evidently the same: since in the second stage the oxygen–catalyst bond is broken, the activation energy increases with the strengthening of this bond. Similar dependences have been found for the oxidation of hydrogen and some organic substances (*2*).

Dependence Between Selectivities and Surface Oxygen Bond Energy

Equations (5) and (6) show that selectivity changes with q_s are determined by the dependence of θ and μ on q_s. Applying Eq. (8) to k_4, k_5 and taking Eq. (7) into account we have

$$\mu = B \exp\left[\frac{\alpha}{RT}(q_4 - q_5)\right] \exp\left(-\frac{q_3}{RT}\right), \tag{13}$$

where B unites constant quantities. Assuming as before that in going from one catalyst to another mainly the values of q_s are changed we will obtain

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

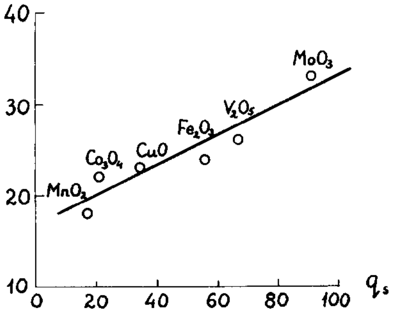

FIG. 5. The relationship between the activation energies for ammonia oxidation and q_s.

In these equations q_4', q_5' and q' unite quantities which are independent of q_s; n_{N_2} and n_{N_2O} are coefficients determined by the number of oxygen–catalyst bonds which are broken in stages (4) and (5). The value of q_3 (heat of the third stage) in a first approximation can be considered as independent of q_s since in this stage oxygen–catalyst bonds are broken as well as formed. Then instead of Eq. (13) we will have

$$\mu = \mu_0 \exp\left(\frac{\alpha}{RT} \cdot \Delta n \cdot q_s\right), \tag{14}$$

where μ_0 is independent of q_s and

$$\Delta n = n_{N_2O} - n_{N_2}. \tag{15}$$

Equation (14) shows the character of the relation between μ and q_s to be determined by the sign of Δn. Since in the fourth stage less oxygen–catalyst bonds are broken than in the fifth stage, the value of Δn is essentially positive. Consequently, μ increases with q_s. The value of θ also increases with q_s [see Eq. (10)]. This is why on increasing q_s the selectivity in N_2 grows approaching unity while the selectivity in N_2O falls approaching zero. Figure 6 shows this regularity to be the case.

Let us examine now the dependence of the rates of the formation of N_2 and N_2O on q_s. One can show that at $\theta \approx 1$

$$\rho_{N_2} = \left(\frac{\partial \ln r_{N_2}}{\partial q_s}\right)_{T,P_i} = -\frac{\alpha}{RT}\left(1 - \frac{\Delta n}{1+\mu}\right),$$
$$\rho_{N_2O} = \left(\frac{\partial \ln r_{N_2O}}{\partial q_s}\right)_{T,P_i} = -\frac{\alpha}{RT}\left(1 + \frac{\Delta n \cdot \mu}{1+\mu}\right).$$

It is easy to see that the value of ρ_{N_2O} is negative as well as ρ [Eq. (11)]. Therefore the character of the dependence of deep oxidation rates and rates of the overall

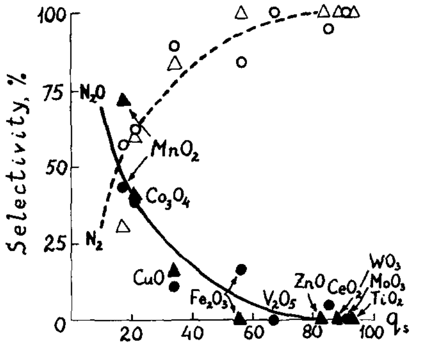

FIG. 6. The dependence of selectivities on q_s: (○,●) present work, 230°C; (△,▲) after (9), 253°C.

process on q_s should be qualitatively similar.

The difference $\rho_{N_2O} - \rho_{N_2} = -(\alpha/RT)\Delta n$ is also negative for $\Delta n > 0$. This means that deep oxidation rates should fall with increasing q_s much more sharply than mild oxidation rates. Experimental data prove this conclusion (Fig. 7). The greater q_s, the higher the contribution of r_{N_2} into the overall process rate and the higher the selectivity in mild oxidation (Fig. 6).

Thus, the main reason for the increasing selectivity in mild oxidation with q_s is the fact that in the formation of the corresponding product [stage (4)] less oxygen–catalyst bonds are broken than in the formation of the product of deep oxidation [stage (5)].

This approach can be applied to a more general situation when ammonia is oxidized to N_2, N_2O and NO. In this case the reaction follows three kinetically independent routes, $N^{(I)}$, $N^{(II)}$ and $N^{(III)}$. $N^{(III)}$ corresponds to the overall chemical equation,

$$2\ NH_3 + 2.5\ O_2 = 2\ NO + 3\ H_2O, \quad \text{(III)}$$

and can be obtained from the reaction mechanism already cited by adding a stage for the formation of NO, for example

$$6.\ 2\ (HNO) + (O) \rightarrow 2\ NO + H_2O + 5\ (\ \ ).$$

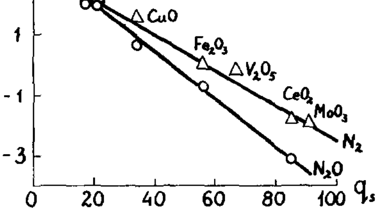

FIG. 7. The relationship between the rates of formation of N_2 (△) and N_2O (○) and q_s. The data for CeO_2 are calculated on the basis of (9).

At $\theta \approx 1$ the selectivities for the above mechanism [see Part I (*1*)] will be

$$\begin{aligned} S_{N_2} &= \mu/(1 + \mu + \mu'), \\ S_{N_2O} &= 1/(1 + \mu + \mu'), \\ S_{NO} &= \mu'/(1 + \mu + \mu'), \end{aligned} \qquad (16)$$

where $\mu' = k_6/k_5$. Applying the Brønsted–Temkin relation to k_6 and k_5 we will have

$$\mu' = \mu_0' \exp\left(-\frac{\alpha}{RT}\Delta n' \cdot q_s\right),$$

where μ_0' unites terms which are independent of q_s, and

$$\Delta n' = n_{NO} - n_{N_2O} \qquad (17)$$

[n_{NO} and n_{N_2O} are determined by the number of oxygen–catalyst bonds which are broken in stages (5) and (6)]. Differentiating S_{N_2}, S_{N_2O} and S_{NO} with respect to q_s we will obtain

$$\frac{\partial S_{N_2}}{\partial q_s} = \frac{\alpha}{RT} S_{N_2} [\Delta n\ (1 - S_{N_2}) + \Delta n' \cdot S_{NO}],$$

$$\frac{\partial S_{N_2O}}{\partial q_s} = \frac{\alpha}{RT} S_{N_2O} (\Delta n' \cdot S_{NO} - \Delta n \cdot S_{N_2}),$$

$$\frac{\partial S_{NO}}{\partial q_s} = -\frac{\alpha}{RT} S_{NO} [\Delta n'\ (1 - S_{NO}) + \Delta n \cdot S_{N_2}]. \qquad (18)$$

The value of $\Delta n'$ determined by Eq. (17) is positive because in the formation of NO [stage (6)] more oxygen–catalyst bonds are broken than in the formation of N_2O [stage (5)]. Since Δn, S_i and $1 - S_i$ are also positive quantities, it follows from Eq.

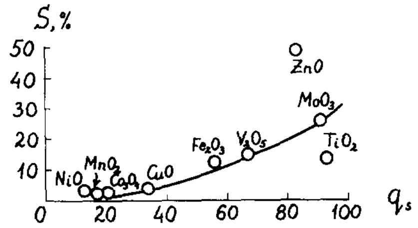

FIG. 8. The dependence of selectivities in NO (*5*) on q_s.

(18) that $\partial S_{N_2}/\partial q_s > 0$ and $\partial S_{NO}/\partial q_s < 0$; $\partial S_{N_2O}/\partial q_s$ can be positive, negative or equal to zero.

So the deduced relations predict the following: on increasing q_s the selectivity for the mild oxidation product (N_2) must progressively grow, the selectivity for the product of the most deep oxidation (NO) must fall and the selectivity for N_2O (which is intermediate in respect to the degree of oxidation) must pass through a maximum. These predictions are qualitatively proved by the fact that at rather high temperatures when reactions (I)–(III) occur together the selectivity in NO decreases with increasing q_s (Fig. 8).

Using the Polanyi relation for activation energies together with the concept that with a higher degree of oxidation of a product the more oxygen–catalyst bonds are broken in the stage leading to that product, we have shown (*12*) that activation energies for the considered reactions (over a given catalyst) must grow in the sequence $E_{N_2} < E_{N_2O} < E_{NO}$. Therefore the initial temperatures of the formation of the corresponding products must increase in the same sequence. Experimental data confirm this conclusion (Table 2).

TABLE 2

INITIAL TEMPERATURES [t_i (°C)] OF THE FORMATION OF N_2, N_2O AND NO IN AMMONIA OXIDATION (*13*)

Catalyst	t_{N_2}	t_{N_2O}	t_{NO}
MnO_2	100	140	425
MnO_2-15% KOH	130	200	330
NiO	120	135	395
Fe_2O_3	270	410	490

A correlation between the type of conductivity of oxides and their catalytic behavior in ammonia oxidation has been reported (*9*). The catalytic activity decreases in the order: *p*-semiconductors > *n*-semiconductors > insulators. In the same order the selectivity in N_2O falls and the selectivity in N_2 grows. Such a correlation can be interpreted by the fact that there is qualitative correspondence of a type of conductivity of an oxide with the energy of oxygen binding to its surface: *p*-type semiconductors (oxides of manganese, cobalt, nickel, copper) possess lower oxygen bond energies, while insulators (oxides of nontransition metals) are characterized by the highest q_s-values; *n*-type semiconductors (oxides of vanadium, molybdenum, zinc, titanum) occupy an intermediate position.

Regularities in the Oxidation of Organic Substances

Let us assume that during the oxidation of an organic molecule, R, a partial oxidation product RO and a deep oxidation product RO_2 are formed by parallel ways according to the scheme:

	$N^{(I)}$	$N^{(II)}$
1. $O_2 + (\ ) \rightarrow (O_2) \xrightarrow[\text{fast}]{(\ )} 2(O)$	0.5	1
2. $R + (O) \rightarrow (RO)$	1	1
3. $(RO) \rightarrow RO + (\ )$	1	0
4. $(RO) + (O) \rightarrow RO_2 + (\ )$	0	1

$N^{(I)}$: $R + 0.5\ O_2 = RO,$ (IV)

$N^{(II)}$: $R + O_2 = RO_2.$ (V)

The reaction follows two independent routes $N^{(I)}$ and $N^{(II)}$ which correspond to summary equations (IV) and (V). It can be shown that with the assumptions used in our analysis, rate equations for the rate *r* of the overall process, rates for the routes

$N^{(I)}$ and $N^{(II)}$ (r_{RO} and r_{RO_2}) and selectivities in RO and RO_2 (S_{RO} and S_{RO_2}) will be

$$r = \frac{k_1 k_2 P_{O_2} P_R}{k_1 P_{O_2} + \nu k_2 P_R}, \qquad (19)$$

$$r_{RO} = \frac{\mu''}{\mu'' + \theta} \cdot r, \qquad (20)$$

$$r_{RO_2} = \frac{\theta}{\mu'' + \theta} \cdot r, \qquad (21)$$

$$S_{RO} = \frac{\mu''}{\mu'' + \theta}, \qquad (22)$$

$$S_{RO_2} = \frac{\theta}{\mu'' + \theta}, \qquad (23)$$

where

$$\mu'' = \frac{k_3}{k_4} \qquad (24)$$

(P_R is partial pressure of R). The validity of equations of type (19)–(23) was shown for the catalytic oxidation of *o*-xylene (*14*).

Since Eqs. (19) and (2) as well as the physical meaning of their constants are similar, the dependences ln r vs q_s for the oxidation of ammonia and organic substances must be similar. This is the case, as was noted above.

The relation between μ'' and q_s can be presented as

$$\mu'' = \mu_0'' \exp\left(\frac{\alpha}{RT}\,\Delta n'' \cdot q_s\right), \qquad (25)$$

which is similar to Eq. (14). In Eq. (25) μ_0'' unites the terms which are independent of q_s and

$$\Delta n'' = n_{RO_2} - n_{RO},$$

where n_{RO_2} and n_{RO} are quantities determined by the number of oxygen–catalyst bonds broken in stages (4) and (3), respectively. It is evident that $n_{RO_2} > n_{RO}$ so that $\Delta n'' > 0$ and μ'' increases with q_s. Since θ also increases with q_s [see Eq. (10)] the selectivity in mild oxidation must grow and the selectivity in deep oxidation must fall with increasing q_s ($\partial S_{RO}/\partial q_s > 0$, $\partial S_{RO_2}/\partial q_s < 0$). This regularity is actually observed for the oxidation of many organic substances (*2–4,15,16*) (see, for example, Fig. 9).

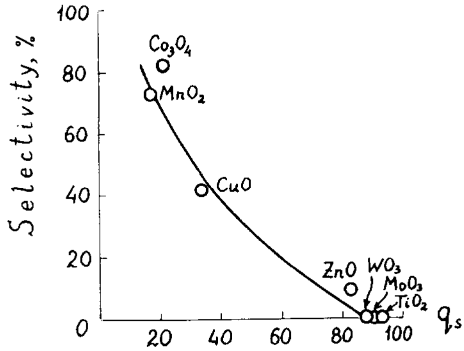

FIG. 9. The dependence of selectivities in the allylic oxidation of propene (*3*) on q_s.

On increasing q_s the rate of deep oxidation of the organic molecule decreases much more sharply than that of mild oxidation (Fig. 10). The difference of negative slopes of the curves log r_{RO_2} vs q_s and log r_{RO} vs q_s can be shown to be $-(\alpha/4.575\,T)\,\Delta n''$ which is essentially a negative value because $\Delta n'' > 0$.

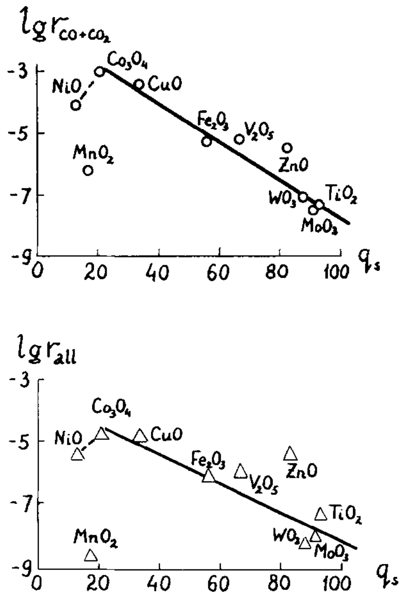

FIG. 10. The dependence of rates (mole/m^2 sec) of the deep oxidation (r_{CO+CO_2}) and the allylic oxidation (r_{all}) of propene (*3*) on q_s.

General

Similarity Between Processes of Catalytic Oxidation of Ammonia and Organic Substances. General Regularities in Selective Catalytic Oxidation

The results obtained show ammonia oxidation to be a suitable system for elucidating general regularities in selective catalytic oxidation. Under controlled conditions the mechanism of this reaction is similar in many significant aspects not only to the mechanism of oxidation of inorganic molecules (H_2, CO) but also to the mechanism of oxidation of organic substances (*12*).

The oxidation of ammonia and organic molecules can be presented as the sequence of two main steps: (1) oxygen adsorption to form negative ions of adsorbed oxygen (oxidation of a surface) and (2) the reaction between an oxidized molecule and adsorbed oxygen to form final reaction products (reduction of a surface). The latter step consists of several stages involving the formation of a range of surface complexes with progressively increasing degrees of oxidation. As a result of desorption (or more complicated transformations) these complexes are converted into corresponding reaction products. So, for example, in ammonia oxidation (*1*) hydrogen abstraction from NH_3 and the formation of final products (N_2, nitrogen oxides) occur gradually: at first, (NH) species are formed from NH_3 and adsorbed oxygen, the former are converted into (HNO) species by way of further reaction of (NH) with adsorbed oxygen. Similarly, in *o*-xylene oxidation (*14*) hydrogen abstraction from methyl groups and their oxidation also proceeds gradually: at first, *o*-xylene and adsorbed oxygen give a surface complex (X_1) which is then converted into more oxidized surface species (X_2), etc. As a result of desorption (or other reactions) of complexes (X_1), (X_2), . . . final products (*o*-toluic aldehyde, *o*-toluic acid, phthalide, phthalic anhydride) are formed.

Such similarity in the mechanism is clearly reflected by the kinetics of the reactions. Thus, rate equations for the overall oxidation of *o*-xylene (*14*) and ammonia (*1*) are similar. In the oxidation of *o*-xylene (*14*) and butene-1 (*17*), the selectivity for mild oxidation decreases with increasing ratio P_{O_2}/P_R in a reaction mixture; this is like ammonia oxidation where the selectivity for N_2 formation decreases with increasing P_{O_2}/P_{NH_3} (*1*).

The mechanism of oxidation of such inorganic substances as hydrogen (*18*) or carbon monoxide (*19*) is also similar to the mechanism of ammonia oxidation because the nature of transient chemical interaction in the course of these reactions over the majority of studied catalysts is similar. But in hydrogen or carbon monoxide oxidation only one final product (H_2O or CO_2) is formed, and the problem of selectivity does not appear here. Because of that the similarity between the oxidation of ammonia and organic substances is more interesting.

Taking the above-mentioned profound similarity between different processes of heterogeneous catalytic oxidation into account, certain general regularities essential for catalyst selection can be formulated. Some of them were found earlier (this is specially noted), while other ones directly follow from the present work. We must recall that those conditions of selective catalytic oxidation are being considered under which products are formed only by parallel ways. The rules are:

1. Catalytic *activity* of substances of the same type (for instance, metal oxides) with respect to overall conversion of various molecules is mainly determined by the surface oxygen bond energy of a catalyst, q_s, the optimum corresponding to small values of q_s. This regularity is valid for the oxi-

dation of hydrogen, carbon monoxide, various organic molecules (*2,7*) and ammonia (data of the present work).

As a result of this, catalytic activity patterns for different oxidation processes are similar and their optimum catalysts have similar chemical composition. Among individual substances these catalysts are usually Pt, Pd, Co_3O_4, MnO_2.

2. Absolute catalytic activity of metals is essentially higher than that of oxides so that metal and metal oxide catalysts of a process belong to different types. Earlier this fact was noted for the oxidation of hydrogen and hydrocarbons (*7,11*); as we saw, this is also valid for ammonia oxidation. A possible reason for this peculiarity is a different ability of metals and oxides to activate an oxidized molecule.

3. There is a definite correspondence between the degree of oxidation of a product and the composition of the activated complex of the stage leading to this product (*12*). *In the formation of deep oxidation products (CO, CO_2 in the oxidation of organic substances; N_2O, NO in the oxidation of ammonia) more oxygen–catalyst bonds are broken than in the formation of mild oxidation products (aldehydes, ketones, etc., in organic catalysis; N_2 in the oxidation of ammonia).* Because of that, on increasing q_s the rate of mild oxidation decreases less sharply than the rate of deep oxidation.

4. As a consequence of the previous rule, *selectivity* in mild oxidation increases with oxygen–catalyst bond energy. This is observed in the oxidation of methanol (*4,16*), propene (*3,15*), butene (*20*); we have also found this to be valid for ammonia oxidation.

5. From the above rules it follows that high selectivity in deep oxidation is attained when catalysts with small q_s values are used which coincides with the conditions of the highest activity. That is why the best catalysts for the oxidation of NH_3 into NO and those for full combustion of organic substances (Pt, Co_3O_4) are at the same time the most active catalysts.

6. Catalytic activity, like selectivity in deep oxidation, usually falls with increasing q_s. This explains the fact that the patterns of activity and selectivity in deep oxidation are similar while the sequences of selectivity in mild oxidation are the reverse of the activity sequences.

7. High selectivity in mild oxidation is attained when catalysts with rather high values of q_s are used, which corresponds to the low catalytic activity region. The similarity between the mild oxidation of organic molecules and ammonia is displayed by the fact that in both cases similar catalysts are employed (Table 3).

8. In the selection of an optimum catalyst for mild oxidation it is reasonable to use the following considerations. Equa-

TABLE 3
CATALYSTS FOR MILD OXIDATION

Reagent	Product	Catalyst	Refs.
Propene	Acrolein	Bi_2O_3–MoO_3	(*21*)
Benzene	Maleic anhydride	V_2O_5–MoO_3	(*21*)
Naphthalene	Phthalic anhydride	V_2O_5–K_2SO_4–SiO_2	(*21*)
Benzaldehyde	Benzoic acid	V_2O_5–SnO_2	(*25*)
Methanol	Formaldehyde	Fe_2O_3–MoO_3	(*21*)
Ammonia	Nitrogen	V_2O_5	Present work
		Molybdates of Bi, Mn, Fe, Co	(*22*)

tions (5),(14) and (22),(25) show that at $\theta \approx 1$ the dependence of selectivity in mild oxidation (S_m) on q_s is expressed by a relation of the type

$$S_m \approx \frac{\mu_0 \exp [(\alpha/RT)\, \Delta n \cdot q_s]}{1 + \mu_0 \exp [(\alpha/RT)\, \Delta n \cdot q_s]};\ n > 0.$$

At high values of q_s the term μ_0 exp $[(\alpha/RT)\, \Delta n \cdot q_s]$ becomes much higher than unity so that S_m approaches 1. Let us suppose that at a certain value of q_s which is equal to q_s' the selectivity $S_m = 95\%$. Further increasing of q_s will lead to a rather small increase in S_m, which amounts to only several percent since in the region of higher values of q_s the magnitude of S_m is increasing with q_s slowly (see Figs. 6, 8 and 10). But simultaneously catalytic activity will fall sharply because Eq. (11) gives

$$\ln r = \text{const} - \frac{\alpha}{RT} \cdot q_s.$$

The latter equation shows that a 10 kcal increase in q_s is accompanied (at 500°K and $\alpha = 0.5$) by a decrease of more than 2 orders of magnitude in activity, so that a small increment in selectivity is conjugated with a very sharp loss in the overall rate r which results in a great decrease in the rate of mild oxidation, $r_m = rS_m$. Thus, a suitable catalyst for mild oxidation should be sought among those substances with higher q_s which provide a necessary level in selectivity. But the value of q_s should not be too high since the overall activity of the catalyst must not be low.

9. In general, the mild oxidation *rate* (as well as that of deep oxidation) contrary to selectivity decreases with increasing q_s (see Figs. 7 and 9). Hence, under the conditions of the parallel scheme of mechanism the most *active* catalysts for mild oxidation and for deep oxidation are similar. So, at lower temperatures with low contact times when consecutive reactions of products are still negligible the highest rate of propene mild oxidation is reached with Co_3O_4 and CuO (*23*), and the highest rate of ammonia oxidation to N_2 is attained on Co_3O_4 and MnO_2 (see Fig. 7). Usually these oxides are considered to be typical catalysts for deep oxidation. It follows from this that a routine classification of catalysts for mild and deep oxidation is rather conventional and it is always necessary to determine the criteria of the classification.

At elevated temperatures and higher contact times a parallel reaction scheme usually becomes a parallel-consecutive one. Here certain differences between the oxidation of ammonia and organic substances appear. They are due to the thermodynamics of the processes. In the oxidation of organic molecules the products of deep oxidation are more stable than those of mild oxidation while in the oxidation of ammonia the situation is reverse. Hence in the former case a product of mild oxidation (aldehyde, ketone, anhydride of organic acid, etc.) is usually sought while in the latter case one seeks to increase the yield of deep oxidation products (NO or N_2O). This is natural because the advantage of catalysis is the possibility of obtaining products which are less stable thermodynamically. This peculiarity of the thermodynamics of the compared reactions is displayed by the fact that the consecutive scheme in the oxidation of organic substances corresponds to the further oxidation of mild oxidation products while in ammonia oxidation this scheme involves the reaction between a deep oxidation product and an initial oxidized substance:

$$2\, NH_3 + 3\, N_2O \overset{\text{cat}}{=} 4\, N_2 + 3\, H_2O, \qquad \text{(VI)}$$

$$2\, NH_3 + 3\, NO \overset{\text{cat}}{=} 2.5\, N_2 + 3\, H_2O. \qquad \text{(VII)}$$

Qualitatively many of the above formulated regularities keep their validity also under the conditions of a parallel-consecutive scheme.

Thus, as regards the catalytic activity

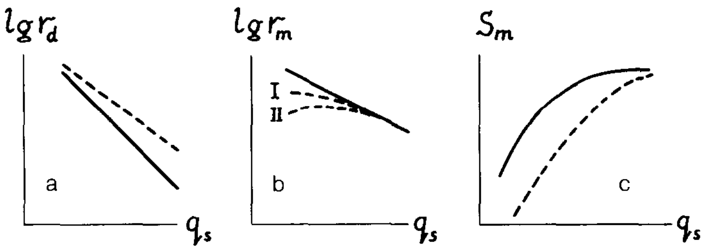

Fig. 11. The relation between q_s and catalytic properties in the oxidation of an organic substance: (a) deep oxidation rates, (b) mild oxidation rates, (c) selectivities in mild oxidation. (—) Related to a parallel scheme of the reaction mechanism; (--) a parallel-consecutive one.

with respect to overall process, we note that in retaining the same elementary mechanism, Eqs. (2) and (19) for the rate of the overall process are valid also under the conditions of consecutive reactions of products. Because of that, the relations ln r vs q_s should be similar for different reaction conditions.

In the oxidation of organic substances when further oxidation of mild oxidation products takes place, the observed rate of deep oxidation will be higher than that for the purely parallel scheme (under the same conditions) (Fig. 11a). The same character for the correlation between q_s and deep oxidation rates will be retained. On the other hand, on active catalysts an observed rate of mild oxidation will fall, so that the character of the correlation between q_s and mild oxidation rates will essentially change (Fig. 11b). For instance, in butene oxidation over metal oxides (*24*) the dependence between the oxygen–catalyst bond energy and the activity in respect to the formation of butadiene passes through a maximum (like curve II, Fig. 11b) whereas the deep oxidation rate progressively decreases with an increase in this energy.

The general character of the dependence of selectivities on q_s is therefore expected to be kept but because of further oxidation of products the magnitudes of selectivities will be lower than under the conditions of the purely parallel scheme; this decrease will be higher for lower q_s (Fig. 11c).

In ammonia oxidation a consecutive scheme leads to elevated rates of mild oxidation [the formation of N_2, reactions (VI) and (VII)] and to lower observed rates of deep oxidation. Therefore changes in the dependences of rates and selectivities on q_s for this reaction will be the reverse of those expected for the oxidation of organic molecules (Fig. 12).

The approach which we used for establishing the relation between catalytic behavior and chemical structure of substances involves certain limitations.

A more strict treatment should take energetic nonuniformity of surface oxygen into account (*25*). The importance of this factor for a given catalyst may be similar

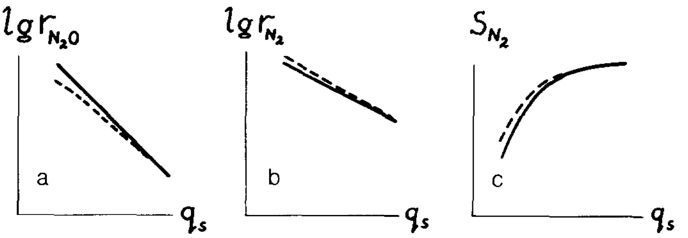

Fig. 12. The relation between q_s and catalytic properties in the oxidation of ammonia: (a) deep oxidation rates, (b) mild oxidation rates, (c) selectivities in mild oxidation. (—) Related to a parallel scheme of the reaction mechanism, (--) a parallel-consecutive one.

to the significance of the change in oxygen bond energy on going from one catalyst to another.

Another simplification is due to the assumption that in a range of catalysts under consideration only oxygen–catalyst bond energies alter significantly. A more precise approach should examine changes in other catalyst bond energies (*2*). This factor should be treated in a rather wide sense involving the formation of coordination compounds by means of π-bonding, etc., and the formation of salt-like surface species. In the latter case acid–base properties of catalysts are of great importance (*26*).

Moreover, one can suppose that in the oxidation of complex organic molecules a geometric factor would be of certain significance (e.g., the necessity of multipoint adsorption).

The results of the present work suggest acid–base and other properties of a catalyst in ammonia oxidation to be of much less importance than in the oxidation of organic compounds, so that in the former case a governing role of the surface oxygen bond energy is revealed rather clearly. In this respect ammonia oxidation is similar to the oxidation of such inorganic molecules as H_2 or CO.

Finally, let us point out that the correlations between catalytic properties of substances and oxygen bond energies are reasonable only within series of the same type catalysts of a reaction for which values of each constant in the Brønsted–Temkin type relations are close (*11*). The existence of different types of catalytic systems (for example, metals and metal oxides) can be caused by their different ability to activate an oxidized molecule (*11*) or by a different polarity of the oxygen–catalyst bonds (*27*).

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