

## The Activity of Transition Metal Oxides for Cyclohexane Dehydrogenation

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The dehydrogenation of cyclohexane has been studied in a flow reactor on a number of oxide catalysts. Rate constants and apparent activation energies were determined in the temperature range 400–465°C, and it was shown that the reaction is essentially first order with respect to cyclohexane pressure. Comparison of the rate constants at 450°C for the oxides studied indicates that the catalytic activity is determined by the  $3d$  electron configuration of the metal ion. Highest activity was associated with the  $d^3$ ,  $d^2$ , and  $d^1$  configurations, while low activity was associated with the more stable  $d^0$ ,  $d^5$ , and  $d^{10}$  configurations. The results support previous studies of hydrogen and hydrocarbon reactions at oxide surfaces and can be discussed in terms of the application of crystal field theory to the formation of surface complexes.

### INTRODUCTION

Studies of reactions of hydrogen and hydrocarbons at transition metal oxide surfaces have indicated that the catalytic activity is determined by the  $3d$  electron configuration of the metal ion, rather than by considerations of semiconductivity. The work of Dowden, McKenzie, and Trapnell (1) on hydrogen–deuterium equilibration showed a twin-peaked activity pattern across the first period of transition metal oxides, with maxima at  $\text{Cr}_2\text{O}_3$  and  $\text{Co}_3\text{O}_4$ , separated by a minimum at  $\text{MnO}$  and  $\text{Fe}_2\text{O}_3$ . High activity was associated with the  $3d^3$ ,  $3d^6$ ,  $3d^7$ , and  $3d^8$  electronic configurations, while low activity was associated with the more stable  $3d^0$ ,  $3d^5$ , and  $3d^{10}$  configurations. The importance of the oxygen ion environment was shown by Brennan (2), who found that the corresponding halides did not have the same activity pattern for hydrogen–deuterium equilibration. Dowden and Wells (3) have interpreted this twin-peaked activity pattern in terms of the effect of the crystal field of the oxide ions on the  $3d$  electron orbitals of the metal ions. Similar activity patterns were later found for the disproportionation and dehydrogenation of cyclohexene (4) and ethylene hydrogenation

(5). From an investigation of hydrogen–deuterium equilibration and complementary studies of magnetic susceptibility, on the isomorphous oxides  $\text{Ti}_2\text{O}_3$ ,  $\text{V}_2\text{O}_3$ , and  $\text{Cr}_2\text{O}_3$ , De, Rossiter, and Stone (6) concluded that the catalytic activity was determined by the availability of  $d$  electrons, released from metal–metal bonding, for covalent bond formation with chemisorbed hydrogen.

Comparative studies of hydrogen and hydrocarbons on oxides are difficult because of the intrinsic low activity, because some oxides reduce under reaction conditions to the metal or a lower oxide, and because of coke formation causing substantial changes in catalyst activity during the course of an experiment. For these reasons and in order to investigate all of the first period transition metal oxides the studies described above were carried out at relatively low temperatures, and it was not possible to directly compare the activities of the various oxides at one temperature. It was considered of interest to acquire further data on reactions of this type catalyzed by oxides. The dehydrogenation of cyclohexane was therefore studied in the temperature range 400–465°C; below 400°C the oxides are too inactive to give measurable conversion and

the reverse reaction should be taken into account, while above 465° experiment showed that the catalyst became poisoned. The relatively high temperature range made it impossible to study all the oxides of the first transition period, due to reduction, but enabled an investigation to be made of the factors governing catalytic activity in a hydrocarbon reaction at temperatures higher than previously used for most of the oxides. While several studies have been made of the dehydrogenation of cyclohexane on individual oxides (7-11) no comparative study under the same experimental conditions has been made. The present work includes the dehydrogenation of cyclohexane on  $\text{Al}_2\text{O}_3$ ,  $\text{MgO}$ , and  $\text{CaO}$  as a comparison between the transition and non-transition metal oxides.

#### EXPERIMENTAL

**1. Materials.**  $\text{TiO}_2$ ,  $\text{Cr}_2\text{O}_3$ ,  $\text{ZnO}$ ,  $\text{MgO}$ ,  $\text{Al}_2\text{O}_3$ , and  $\text{CaO}$  were purchased from the Baker Chemical Company and used as supplied. X-Ray powder diffraction showed that  $\text{TiO}_2$  was in the anatase form and that  $\text{Al}_2\text{O}_3$  was in the  $\alpha$ (corundum)-form.  $\text{Ti}_2\text{O}_3$  was prepared by the reduction of  $\text{TiO}_2$  in a stream of hydrogen and  $\text{TiCl}_4$  at 750°C, as described by Friedel and Guerin (12). X-Ray diffraction showed the product to be  $\text{Ti}_2\text{O}_3$  and there were no lines corresponding to  $\text{TiO}_2$  or  $\text{TiO}$ .  $\text{V}_2\text{O}_3$  was prepared in the reactor by the reduction of  $\text{V}_2\text{O}_5$  in hydrogen at 750°C, the structure being confirmed by X-ray diffraction.  $\text{MnO}$  was prepared in the reactor by the reduction of  $\text{MnO}_2$  in hydrogen at 600°C.  $\text{Fe}_3\text{O}_4$  was prepared in the reactor by the reduction of  $\text{Fe}_2\text{O}_3$  in hydrogen at 600°C, the structure being confirmed by X-ray diffraction. Surface areas of the catalysts were determined by the BET method using krypton adsorption at 77°K ( $\sigma_{\text{kr}} = 18 \text{ \AA}^2$ ). Analytical data supplied by the manufacturer and checked by emission spectroscopy showed that all catalysts were of high purity.

$\text{V}_2\text{O}_5$ ,  $\text{MnO}_2$ ,  $\text{Fe}_2\text{O}_3$ ,  $\text{CoO}$ , and  $\text{NiO}$  powders purchased from the Baker Chemical Company were tested as catalysts and were found to reduce in the bulk under the reaction conditions. These oxides cannot

therefore be considered as catalysts for the reaction and were not studied further.

Cyclohexane (99.5 wt %) was purchased from the Phillips Petroleum Company and was carefully purified using the distillation method described by Ward (13). No impurities were detectable by vapor-phase chromatography as used in the experiments.

**2. Apparatus and procedure.** The kinetics of the dehydrogenation of cyclohexane were studied by a flow method. The reactor consisted of a fused quartz tube 2 cm in diameter and 30 cm in length, enclosed in a furnace controllable to within 1°C. The catalyst was centrally located in the reactor, supported on a bed of fused quartz wool, and the temperature of the catalyst bed was measured using a single chromel-alumel thermocouple attached to the external wall of the reactor. Nitrogen carrier gas, admitted to the system through a constant pressure valve at 1 psig, was purified by passing over copper turnings at 300°C and silica gel and was saturated with cyclohexane vapor by bubbling through a reservoir of cyclohexane at a given temperature. The resulting feed passed through a calibrated flow meter and to the reactor. The whole system was grease and mercury free, and Tygon stop-cocks were employed. The gases entering and leaving the reactor were analyzed using a Perkin-Elmer vapor-phase chromatograph fitted with a gas-sampling valve and directly connected to the system. The chromatograph was calibrated by injecting known volumes of cyclohexane with a precision syringe.

In an experimental run the catalyst was placed, or prepared, in the reactor and was outgassed for 15 hr at a given temperature in a stream of oxygen-free dry nitrogen. The nitrogen-cyclohexane feed was then passed over the catalyst at the reaction temperature. For all catalysts, except  $\text{Cr}_2\text{O}_3$ , the flow rate was held constant at 8.6  $\text{cm}^3$  (STP)  $\text{min}^{-1}$ . Because of the higher activity of  $\text{Cr}_2\text{O}_3$  a constant flow rate of 33.2  $\text{cm}^3$  (STP)  $\text{min}^{-1}$  was used. In all experiments the partial pressure of cyclohexane in the feed remained essentially constant at 75 torr and the total pressure in the reactor was 760 torr. After 1 hr analyses were made of

the gases entering and leaving the reactor, using the vapor-phase chromatograph. In no case were products other than benzene detected. Runs were made in the temperature range 400–465°C, the temperature order being chosen at random, and not made in any specific increasing or decreasing sequence. Between runs pure nitrogen was passed over the catalyst. A small amount of coke was deposited on the catalyst in most cases but resulted in no irreproducibility in catalytic activity during the time of the experiment. Preliminary experiments established good reproducibility for analyses for a given catalyst run and from sample to sample of a given oxide. It was shown by experiment that there was no thermal decomposition to give benzene or other liquid products in the reactor containing only fused quartz wool at 600°C.

### RESULTS

Following the nomenclature of Bridges and Houghton (11) and assuming that the rate of reaction is much greater than the rates of longitudinal and radial diffusion in the gas phase, the rate of reaction  $r$  in a flow reactor can be expressed by the equations

$$rdA = Fdx_\alpha \quad (1)$$

$$r = k_n p^n \quad (2)$$

where  $A$  is the surface area of catalyst;  $F$ , the feed rate, mass per unit time;  $x_\alpha$ , moles of reactant  $\alpha$ -converted per unit mass of feed;  $n$ , the order of reaction;  $k_n$ , the rate constant; and  $p$ , the partial pressure of reactant  $\alpha$ . The partial pressure,  $p$ , is given by the equation

$$p = \frac{P(n_{\alpha 0} - x_\alpha)}{(n_0 + \delta x_\alpha)} \quad (3)$$

where  $n_{\alpha 0}$  is moles of reactant  $\alpha$  per unit mass of feed;  $n_0$ , moles of feed per unit mass of feed;  $\delta$ , the increase in the number of moles in the reacting system per mole of  $\alpha$  converted; and  $P$ , the total pressure. From Eqs. (1), (2), and (3) an expression for the rate constant can be derived

$$k_n = \frac{F}{A} \int_0^x \alpha \left[ \frac{(n_0 + \delta x_\alpha)}{P(n_{\alpha 0} - x_\alpha)} \right]^n dx_\alpha \quad (4)$$

This equation can be integrated for assumed

values of  $n$ , the order of reaction. For the case where  $n = 0$

$$k_0 = F y n_0 x / A \quad (5)$$

For the case where  $n = 1$

$$k_1 = (-F n_0 / AP) [x y \delta + (1 + y \delta) \ln(1 - x)] \quad (6)$$

where  $x$  is the fraction of reactant  $\alpha$  converted; and  $y$ , the mole fraction of reactant  $\alpha$  in the entering feed.

These equations express the rate constant in terms that can be measured or calculated from flow rates and analyses using the calibrated vapor-phase chromatograph.

The apparent activation energy of the reaction can be determined from a plot of rate constant against  $1/T$  (°K). However a linear plot will only be obtained where the correct equation, depending on the order of the reaction, is chosen for calculation of the rate constant. In the present case rate constants were calculated from both zero order and first order equations and plotted against  $1/T$  (°K). It was found in every case that plots using the first order rate constant  $k_1$  were linear, whereas those using the zero order rate constant  $k_0$  were not. It may be noted that consideration of the linearity of Arrhenius plots may have limited validity for the determination of reaction orders and cases are known where Arrhenius plots are not linear. This effect may be due to surface nonuniformity or to a change in the mechanism of the reaction at different temperatures. In the present case the reaction has been studied over a relatively small temperature range under the same reaction conditions, and there seems little possibility that these effects occur. It is considered that the observation of linear first order Arrhenius plots for every oxide studied is significant, and that the procedure adopted is adequate for the present purpose of comparing the activities of the various oxides for the dehydrogenation of cyclohexane. Arrhenius plots for  $\text{Cr}_2\text{O}_3$  and  $\text{TiO}_2$ , typical of those observed throughout the present work, are shown in Fig. 1. Values for the rate constant at 450°C were interpolated from the graph and the apparent activation energy determined from the slope.

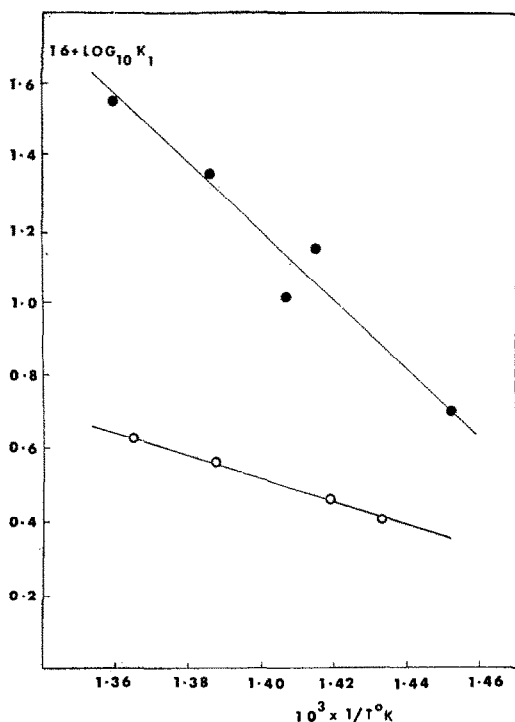


Fig. 1. Arrhenius plots for TiO<sub>2</sub> and Cr<sub>2</sub>O<sub>3</sub>: ○, TiO<sub>2</sub>; ●, Cr<sub>2</sub>O<sub>3</sub>.

The results for all the oxides studied are summarized in Table 1, together with values for specific surface areas and outgassing temperatures.

### DISCUSSION

The rate constants at 450°C are shown in Fig. 2 to represent an activity pattern for

TABLE 1  
SUMMARY OF RESULTS FOR  
CYCLOHEXANE DEHYDROGENATION

Oxide	Outgassing temperature (°C)	Specific surface area (m <sup>2</sup> g <sup>-1</sup> )	$k_1$ (moles cm <sup>-2</sup> sec <sup>-1</sup> torr <sup>-1</sup> )	$E_a$ (kcal mole <sup>-1</sup> )
TiO <sub>2</sub>	600°	7.7	$3.7 \times 10^{-16}$	15
Ti <sub>2</sub> O <sub>3</sub>	600°	1.3	$9.4 \times 10^{-16}$	42
V <sub>2</sub> O <sub>5</sub>	700°	1.6	$1.6 \times 10^{-15}$	17
Cr <sub>2</sub> O <sub>3</sub>	600°	3.5	$2.2 \times 10^{-15}$	42
MnO	600°	2.1	$7.1 \times 10^{-16}$	22
Fe <sub>3</sub> O <sub>4</sub>	600°	1.6	$4.5 \times 10^{-16}$	17
ZnO	500°	3.4	$3.2 \times 10^{-16}$	22
MgO	600°	31.8	$3.8 \times 10^{-17}$	44
Al <sub>2</sub> O <sub>3</sub>	600°	18.6	$4.7 \times 10^{-17}$	36
CaO	600°	13.9	$6.0 \times 10^{-17}$	—

cyclohexane dehydrogenation. It is seen that for the transition metal oxides Cr<sub>2</sub>O<sub>3</sub> is of highest activity, V<sub>2</sub>O<sub>5</sub> and Ti<sub>2</sub>O<sub>3</sub> are intermediate, and TiO<sub>2</sub>, MnO, Fe<sub>3</sub>O<sub>4</sub>, and ZnO are of lower activity. There is therefore a correlation of catalytic activity with the 3*d* electron configuration of the metal ion, in that low activity is associated with the stable 3*d*<sup>0</sup>, 3*d*<sup>5</sup>, and 3*d*<sup>10</sup> configurations, while oxides with the 3*d*<sup>1</sup>, 3*d*<sup>2</sup>, and 3*d*<sup>3</sup> configurations are progressively more active. The position of Fe<sub>3</sub>O<sub>4</sub> in the activity pattern is anomalous and this will be discussed later. By comparison with the transition metal oxides, MgO, Al<sub>2</sub>O<sub>3</sub>, and CaO are of much lower activity. The outer electronic states of MgO and Al<sub>2</sub>O<sub>3</sub> are 2*s*<sup>2</sup>2*p*<sup>6</sup>, and of CaO are 3*s*<sup>2</sup>3*p*<sup>6</sup>, and the stability of these filled orbitals and the absence of any possible contribution from *d* orbitals are considered to be responsible for the low catalytic activity. The activity pattern found here for cyclohexane dehydrogenation is identical, for the oxides studied, with those found for hydrogen-deuterium equilibration (1), cyclohexene disproportionation (4), ethylene hydrogenation (5), and there is no correlation with the semiconducting properties of the oxides (1, 6). It should be noted that the activity pattern found for cyclohexane dehydrogenation has been made from a comparison of rate constants at a single reaction temperature, and avoids possible errors due to extrapolation of Arrhenius plots. Unfortunately, it was not possible to study those oxides which in previous studies have represented the second peak of activity, due to reduction to a lower oxide or to the metal under reaction conditions. The above facts indicate that the metal ions are the active sites for dehydrogenation, and cyclohexane is chemisorbed by covalent bonding rather than by complete electron transfer between gas and solid to give any ionic surface species. Dowden and Wells (3) have interpreted the correlation of catalytic activity in hydrogen-deuterium equilibration with the 3*d* electron configuration, in terms of crystal field effects and the formation of surface complexes. It would seem that this approach can be applied to the dehydrogenation of cyclohexane.

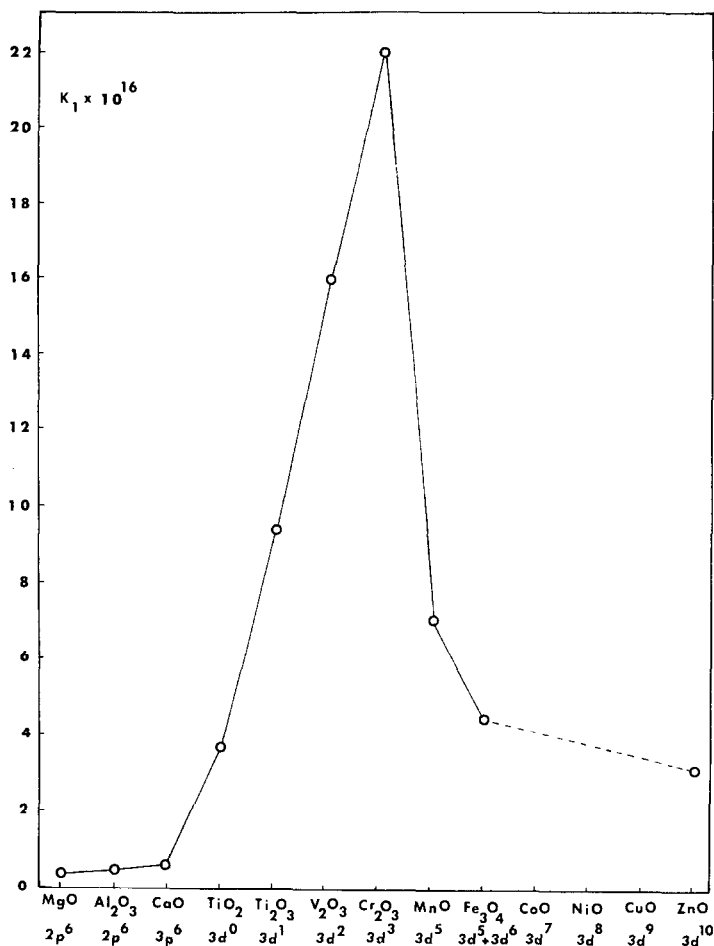


FIG. 2. Activity pattern of oxides in cyclohexane dehydrogenation at 450°C.

De, Rossiter, and Stone (6) have pointed out the importance in studies of this nature of using oxides of the same crystal structure. In the present work four of the oxides—Al<sub>2</sub>O<sub>3</sub>, Ti<sub>2</sub>O<sub>3</sub>, V<sub>2</sub>O<sub>3</sub>, and Cr<sub>2</sub>O<sub>3</sub>—have the corundum structure and it cannot be considered that the rise in activity to a maximum at Cr<sub>2</sub>O<sub>3</sub> is due to any changes in the crystal field of the metal ion. Their work also showed that, for hydrogen–deuterium equilibration on Ti<sub>2</sub>O<sub>3</sub> and V<sub>2</sub>O<sub>3</sub>, the nominal 3d electron configuration was of less importance than the availability of d electrons, released from metal–metal bonding, for covalent bond formation with hydrogen. In the present study this is not likely to be a significant factor as the reaction

temperatures are considerably higher than those at which metal–metal bonding breaks down (6).

The position of Fe<sub>3</sub>O<sub>4</sub> in the activity pattern is of interest. McIver and Tobin (14) have shown that in Co<sub>3</sub>O<sub>4</sub> the Co<sup>3+</sup> ion (3d<sup>6</sup> configuration) is much more active than the Co<sup>2+</sup> ion (3d<sup>7</sup> configuration) for hydrogen–deuterium equilibration. It might therefore be expected that the presence of Fe<sup>2+</sup> ions (3d<sup>6</sup>), as well as Fe<sup>3+</sup> ions (3d<sup>5</sup>), would lead to some catalytic activity of Fe<sub>3</sub>O<sub>4</sub> in cyclohexane dehydrogenation. This is clearly not the case. Both Co<sub>3</sub>O<sub>4</sub> and Fe<sub>3</sub>O<sub>4</sub> have the inverse spinel structure but differ in that Fe<sub>3</sub>O<sub>4</sub> is strongly ferromagnetic, whereas Co<sub>3</sub>O<sub>4</sub> is paramagnetic (15). It is

suggested that the low activity of  $\text{Fe}_3\text{O}_4$  is due to the electronic exchange interactions that lead to ferromagnetism.

The slight catalytic activity of  $\text{TiO}_2$ , which in the stoichiometric form has no 3d electrons, is probably due to the presence of a number of  $\text{Ti}^{3+}$  ions which are associated with anion vacancies formed during outgassing. Similarly, the activity of  $\text{ZnO}$ , which has the  $d^{10}$  configuration, is probably due to the presence of defects generated during outgassing. Such defects may be anion vacancies or interstitial Zn atoms.

While the present investigation does not represent a detailed kinetic study of cyclohexane dehydrogenation, it has been found that in every case the reaction is essentially first order with respect to cyclohexane pressure, indicating that only a small fraction of the surface is covered with adsorbed cyclohexane. This suggests that a relatively large fraction of the surface cations may be available as active sites, rather than only a small fraction of the surface being catalytically active, as is often the case for oxides. This may arise by the removal of a large fraction of the surface hydroxyl groups during outgassing, and which would otherwise prevent chemisorption of cyclohexane on the cations.

In no case were liquid products other than benzene detected, which is consistent with previous studies on oxides, and is expected on thermodynamic grounds (16, 17). The dehydrogenation of cyclic hydrocarbons on metals has been discussed by Balandin (17, 18) in terms of a sextet mechanism involving planar adsorption of the cyclohexane molecule on six metal atoms. An alternative mode of adsorption is that shown on a silica-supported nickel catalyst, involving adsorption on four nickel atoms with the cyclohexane molecule in the boat conformation (19, 20). On oxides it is usually considered (7, 17) that the sextet mechanism does not apply and that reaction proceeds by a mechanism involving edge-wise adsorption of cyclohexane on two cations, with stepwise abstraction of hydrogen, the rate-determining step being the formation of monoolefin. Balandin and his associates have considered dehydrogenation

on oxides in terms of the multiplet theory, and Tolstopyatova, Naumov, and Balandin (21) have found a correlation between the activation energy of the reaction and the ionic radius of the cation. Such a correlation is not supported using the apparent activation energies determined in the present work. However it should be noted that the activation energy is known to depend strongly on the method of preparation of the catalyst (21). It is suggested that the correlation of catalytic activity in the dehydrogenation of cyclohexane with the 3d electron configuration of the cations observed in the present study offers a more useful and fundamental criterion for catalytic activity in this reaction.

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#### REFERENCES

1. DOWDEN, D. A., MCKENZIE, N., AND TRAFNELL, B. M. W., *Proc. Roy. Soc. (London)* **A237**, 245 (1956).
2. BRENNAN, D., *Discussions Faraday Soc.* **28**, 219 (1959).
3. DOWDEN, D. A., AND WELLS, D., *Actes Congr. Intern. Catalyse, 2<sup>e</sup>, Paris, 1960* **2**, 1499 (1961).
4. DIXON, G. M., NICHOLLS, D., AND STEINER, H., *Proc. Intern. Congr. Catalysis, 3rd, Amsterdam, 1964* **1**, 815 (1965).
5. HARRISON, D. L., NICHOLLS, D., AND STEINER, H., *J. Catalysis* **7**, 359 (1967).
6. DE, K. S., ROSSITER, M. J., AND STONE, F. S., *Proc. Intern. Congr. Catalysis, 3rd, Amsterdam, 1964* **1**, 512 (1965).
7. HERINGTON, E. F. G., AND RIDEAL, E. K., *Proc. Roy. Soc. (London)* **A190**, 289, 309 (1947).
8. TOLSTOPYATOVA, A. A., KONENKO, I. R., AND BALANDIN, A. A., *Bull. Acad. Sci. USSR (English Transl.)*, p. 1945 (1960).
9. BALANDIN, A. A., AND SOKOLOVA, N. P., *Bull. Acad. Sci. USSR (English Transl.)*, p. 370 (1960).
10. ROZHDESTVENSKAYA, I. D., AND BALANDIN, A. A., *Bull. Acad. Sci. USSR (English Transl.)*, p. 1824 (1961).

11. BRIDGES, J. M., AND HOUGHTON, G., *J. Phys. Chem.* **81**, 1334 (1959).
12. FRIEDEL, C., AND GUERIN, J., *Ann. Chim. (Paris)* **8**, 38 (1876).
13. WARD, H. K., *J. Chem. Phys.* **2**, 153 (1934).
14. McIVER, D. S., AND TOBIN, H. H., *J. Phys. Chem.* **65**, 1665 (1961).
15. SELWOOD, P. W., "Magnetochemistry," 2nd ed. Interscience, New York, 1956.
16. TAYLOR, H. S., *J. Am. Chem. Soc.* **60**, 627 (1938).
17. TRAPNELL, B. M. W., *Advan. Catalysis* **3**, 1 (1951).
18. BALANDIN, A. A., *Advan. Catalysis* **10**, 96 (1958).
19. GALWEY, A. K., AND KEMBALL, C., *Trans. Faraday Soc.* **55**, 1959 (1959).
20. SELWOOD, P. W., *J. Am. Chem. Soc.* **79**, 4637 (1957).
21. TOLSTOPYATOVA, A. A., NAUMOV, V. A., AND BALANDIN, A. A., *Russian J. Phys. Chem. (English Transl.)* **38**, 879 (1964).