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# The Measurement of the Distribution of Oxidation Power on Nickel Oxide Catalysts

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Acid strength distribution has been demonstrated to be a useful variable for the explanation of the catalytic activities on some solid acids. A similar state of affairs would also be expected in oxidation catalysis on oxides. Therefore, the present investigation was intended to provide a method for determining the distribution of oxidation power of the surface excess oxygen. This was accomplished by the combination of several aqueous reduction methods, each of which uses a certain reducing reagent having a different oxidation-reduction potential. The hydrazine method and a series of the KI(pH $x$) method with pH between 7.5 to 11.3 were used and applied to nickel oxide catalysts.

The total amount of surface excess oxygen is obtained by the hydrazine method; it decreases monotonously against the calcination temperature. The KI(pH 7.5) method provides a decreasing curve with a flat part at the range of 550–600°C. In the cases of the other KI(pH $x$) methods with pH above 9.3, the curves turn out to have one or two sets of maxima and minima against the calcination temperature. These characteristic behaviors are more emphasized by the excess oxygen having the higher oxidation power.

Taking account of the preliminary results on the catalytic decomposition of hydrogen peroxide, the distribution in the oxidation power seems to be a useful variable in explaining the catalytic activities on nickel oxide catalysts.

## INTRODUCTION

Various kinds of physicochemical properties have been taken into consideration in order to explain the catalytic activities of oxide catalysts. They will be classified as follows:

(1) Structure-insensitive properties of compounds or elements composing the catalysts, e.g., the heat of formation of oxides (*1*), the *d* character of metal ions.

(2) Rates of test reactions, e.g., the equilibration rate of the isotopic mixture of oxygen (*2*), the oxidation rate of carbon monoxide (*3*).

(3) Structure-sensitive properties determined by observing the catalysts themselves, e.g., the excess oxygen (*4–6*), the surface potential, the heat of adsorption, the semiconductive properties.

Several authors have previously pointed out that the amount of excess oxygen is a useful parameter for catalytic activities (*4–6*). In all these investigations, the excess oxygen was determined by reduction with $Cl^-$ or $I^-$ ion in strongly acidic solutions (*8, 9*); the reduction was, however, not restricted to the surface excess oxygen but extended to the bulk oxygen, since the catalysts were fully or partially dissolved in the solution. However, the essential excess oxygen for the description of the catalytic activities should primarily be that on the surface. Following this idea, we have developed a method of reduction with hydrazine for determining the total surface excess oxygen and have applied it to

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a series of nickel oxide catalysts in the previous study (*10*).

Recently, one of the present authors (Y. Y.) proposed regional analysis and reported that the catalytic activities of some solid acids were duly represented by a linear combination of the acid strength distribution of the catalysts (*7*). Similar treatment may be possible in oxidation catalysis on oxides. The primary intention of the present investigation is, therefore, to provide a new and practical method for determining the distribution of the oxidation power of the surface excess oxygen on nickel oxides; this distribution should be useful as a variable for the regional analysis over oxide catalysts. The principle of the measurement of the distribution consists in combining several methods, each of which uses a certain reducing reagent having a different oxidation-reduction potential.

## FUNDAMENTAL CONCEPTS FOR THE PRESENT METHODS

In the previous report (*10*), a certain distribution was suggested to exist in the oxidation power of the excess oxygen of nickel oxides. Let us consider schematically such a distribution curve, as shown in Fig. 1. When the surface excess oxygen reacts with a particular reducing reagent to attain an equilibrium, the excess oxygen having higher oxidation power than $E_r$ (the shaded area in Fig. 1) will be reduced, where $E_r$ is the oxidation–reduction potential of the reagent. Therefore, it is possible, in principle, to obtain the distribution curve in detail by applying as many kinds of reducing reagents as one likes. The reducing reagents should react in alkaline solution in order to restrict the reduction to the surface.

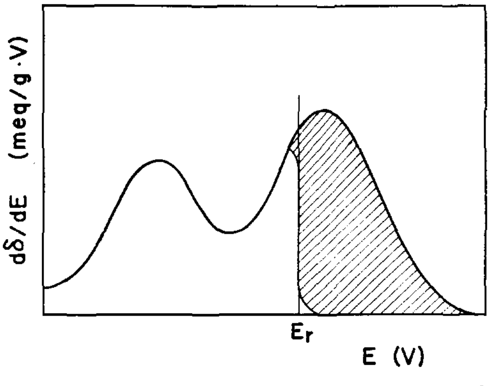

FIG. 1. Schematic distribution curve of the oxidation power. $E$ represents the oxidation–reduction potential of the excess oxygen and $\delta$ the amount of the excess oxygen.

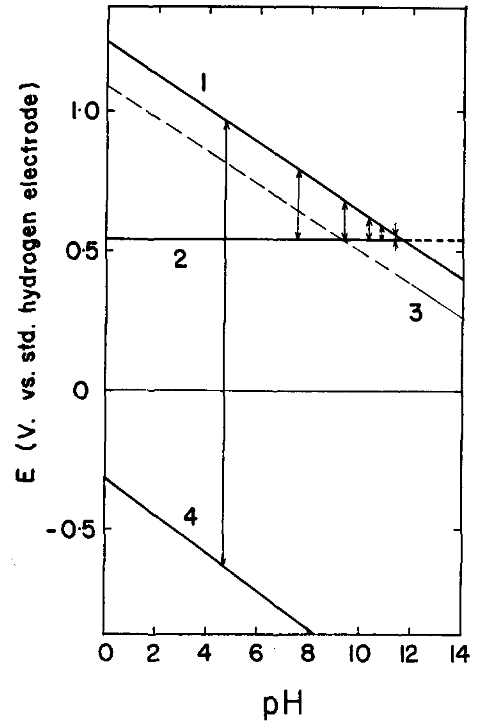

FIG. 2. Diagram of the oxidation-reduction potential as a function of pH: line 1, $O_2/OH^-$ system; 2, $I_3^-/I^-$ system; 3, $IO_3^-/I^-$ system; 4, $N_2/N_2H_4$ system.

In the present study, both potassium iodide solutions of various pH and hydrazine solution were employed as reducing reagents. The oxidation–reduction potentials of these reducing reagents, $E_r$, and that of one atmospheric oxygen, $E_{O_2}$, as a reference, are shown as a function of pH in Fig. 2. Lines 1, 2, 3, and 4 correspond to the reactions (1), (2), (3), and (4), the oxidation–reduction potentials of which are expressed by Eqs. (1a), (2a), (3a), and (4a), respectively.

$$\tfrac{1}{2}O_2 + 2H^+ + 2e \rightleftharpoons H_2O \qquad (1)$$

$$E_{O_2} = E_{O_2}{}^\circ + \frac{RT}{2F} \ln \frac{(p_{O_2})^{1/2}(a_{H^+})^2}{(a_{HO_2})} \qquad (1a)$$

$$I_3^- + 2e \rightleftharpoons 3I^- \quad (2)$$

$$E_2 = E_2^\circ + \frac{RT}{2F} \ln \frac{(a_{I_3^-})}{(a_{I^-})^3} \quad (2a)$$

$$IO_3^- + 6H^+ + 6e \rightleftharpoons I^- + 3H_2O \quad (3)$$

$$E_3 = E_3^\circ + \frac{RT}{6F} \ln \frac{(a_{IO_3^-})(a_{H^+})^6}{(a_{I^-})(a_{H_2O})^3} \quad (3a)$$

$$N_2 + 4H^+ + 4e \rightleftharpoons N_2H_{4aq} \quad (4)$$

$$E_4 = E_4^\circ + \frac{RT}{4F} \ln \frac{(p_{N_2})(a_{H^+})^4}{(a_{N_2H_4})} \quad (4a)$$

Here, $E_{O_2}^\circ$ is equal to 1.226 V, $E_2^\circ$ to 0.536 V, $E_3^\circ$ to 1.09 V, and $E_4^\circ$ to −0.332 V (*11*). The lines in Fig. 2 are given for the simplified cases where activities are unity, except $a_{H^+}$.

Since the nickel oxide catalysts have been prepared by calcining in air, the surface excess oxygen is believed to have a certain oxidation power broadly distributed below line 1, if the chemical processes occurring on the surface are only those accompanying the negative changes in the free energy. However, taking account of the possible occurrence of some metastable states on a part of the active sites, the oxidation power may also be distributed slightly above line 1.

The oxidation potential of the excess oxygen, having a specific fugacity, decreases as a linear function of pH according to Eq. (1a), whereas that of the $I_3^-/I^-$ system does not depend on pH. Employing potassium iodide solutions of various pH's as reducing reagents, one can provide a series of the relative reduction power against oxygen. This method will be named, hereafter, as the KI(pH $x$) method, where $x$ is for the pH value of the solution. The lengths of the arrows extended from lines 2 or 4 to line 1 in Fig. 2 correspond to the approximate values of the reduction power involved in the KI(pH $x$) or hydrazine method. At the higher pH value in a series of KI (pH $x$) systems, the reduction is naturally restricted to the region of the stronger oxidation power.

Strictly speaking, not only the value of pH but also the term $[I_3^-]/[I^-]^3$ must be maintained constant in all measurements, because the reduction potential of a specific KI(pH $x$) system is defined by Eq. (2a). However, it is difficult to satisfy this requirement completely in the experiment, since the amount of iodine may vary at each measurement. Fortunately, the variation of $[I_3^-]$ affects the potential to a smaller extent than that of $[H^+]$ or $[I^-]$ according to Eqs. (1a) and (2a). In actual measurements, the condition was chosen so as to maintain $[I_3^-]$ as constant as possible within a specific KI(pH $x$) system.

It has been known that the equilibrium of the $I_3^-/I^-$ system passes into that of $IO_3^-/I^-$ (line 3, in Fig. 2) with increasing pH of the solution. If this change might occur at higher pH, the relative reduction power of iodide against the oxygen would not depend on pH, since line 3 is parallel to line 2 in Fig. 2. In order to ascertain this ambiguity, the electrochemical potentials of the iodine/iodide solutions of various pH's at the concentrations ($10^{-3}$ $N$ $I_2$ and 10% KI) similar to the actual experimental conditions were measured using a platinum wire as an electrode for at least 10 hr in a nitrogen atmosphere. The constant values were obtained within the range of pH from 7 to 12, independent of both the pH values and the standing period, although the potential decreased gradually along the time at pH of 13.2. Furthermore, the potential values assured that the equilibrium of the iodine/iodide system was surely realized at least below 12 in pH. Thus, Eq. (2a) is reasonably employed for calculating the oxidation power of the surface excess oxygen.

In the present investigation, five KI(pH $x$) methods were employed, with $x$ values of 7.5, 9.3, 10.3, 10.8, and 11.3.

## EXPERIMENTAL

**1. Catalysts.** The same lots of catalysts as described previously (*10*), i.e., a series of pure nickel oxide and $Li_2O$-doped catalysts, were used. In the designation of the catalysts as shown in Table 2, Ni-2-350-8, for example, means a nickel oxide prepared by calcining the nickel carbonate of batch number 2 at 350°C for 8 hr in air; Ni-2-Li-0.5-900-8 means $Li_2O$-doped nickel oxide obtained by calcining the same raw material at 900°C for 8 hr in air after

TABLE 1
REACTION CONDITIONS OF THE KI(pH $x$) METHODS

| Method | Buffer solution | pH | | Reaction period (hr) |
|---|---|---|---|---|
| | | Initial | Steady state | |
| KI(pH 7.5) | 0.2 $M$ $KH_2PO_4$ (160 ml) + $H_2O$ (540 ml) + 0.2 $N$ NaOH (107 ml) | 7.49 | 7.49 | 6 |
| KI(pH 9.3) | 20 g $Na_2B_4O_9 \cdot 10H_2O$/liter | 9.29 | 9.35 | 4 |
| KI(pH 10.3) | satd. $Na_2B_4O_9$ (200 ml) + 0.1 $N$ NaOH (472 ml) | 10.55 | 10.30 | 8.5 |
| KI(pH 10.8) | 0.1 $M$ $Na_2HPO_4$ (400 ml) + $H_2O$ (320 ml) + 0.1 $N$ NaOH (80 ml) | 11.30 | 10.80 | 8 |
| KI(pH 11.3) | 0.1 $M$ $Na_2HPO_4$ (400 ml) + $H_2O$ (200 ml) + 0.1 $N$ NaOH (215 ml) | 11.80 | 11.29 | 9.5 |

mixing with lithium carbonate at the concentration of 0.5 atom % Li.

**2. The determination of the surface excess oxygen using the KI(pH *x*) methods.** A weighed amount of the catalyst (0.1–2 g) and 1.0 g of KI with 10.0 ml of a buffer solution, given in Table 1, were introduced into a conical flask under a nitrogen flow and then the flask was stoppered tightly. The mixture was allowed to react for a certain period under vigorous shaking. Then, the suspension was filtered by means of suction and washed with 20 ml of methanol and, subsequently, 40 ml of distilled water. All these steps were carried out carefully without exposure to air. After adding 2 ml of 1.2 $N$ HCl to the filtrate and allowing it to stand for 2 min, the iodine formed was titrated with a standard sodium thiosulfate solution (0.004 $N$), with starch as an indicator.

The amount of iodine produced was so small ($1–2 \times 10^{-2}$ meq) that a correction was made for the sensitivity of starch and for the incomplete recovery of iodine. These corrections were mostly lower than 6% of every titer.

The reaction conditions of these methods are tabulated in Table 1. The reaction periods were chosen so as to attain a steady state, where the concentration of iodine did not increase with further extention of the reaction time.

Moreover, the present methods are intended to involve not the bulk but only the surface excess oxygen. In this respect, it was ascertained by a test with dimethylglyoxime that no $Ni^{2+}$ ion was found in solution after the reaction.

## RESULTS AND DISCUSSION

In Fig. 3, the amount of the surface excess oxygen is plotted against the reaction period. The reaction proceeds rapidly at first, followed by slow progress and finally by a steady state after 4–5 hr without further increase of iodine. This steady state is assumed tentatively to be an apparent equilibrium, established by reactions (1) and (2).

The results concerning the surface excess oxygen obtained by the series of the KI(pH $x$) methods are summarized as a function of the calcination temperature and the concentration of doped lithium ion in Figs. 4 and 5. The hydrazine method

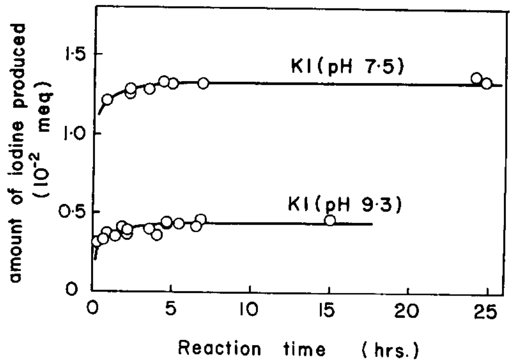

FIG. 3. The variation of the amount of iodine produced vs. the reaction time. Catalyst; Ni-2-350-16.

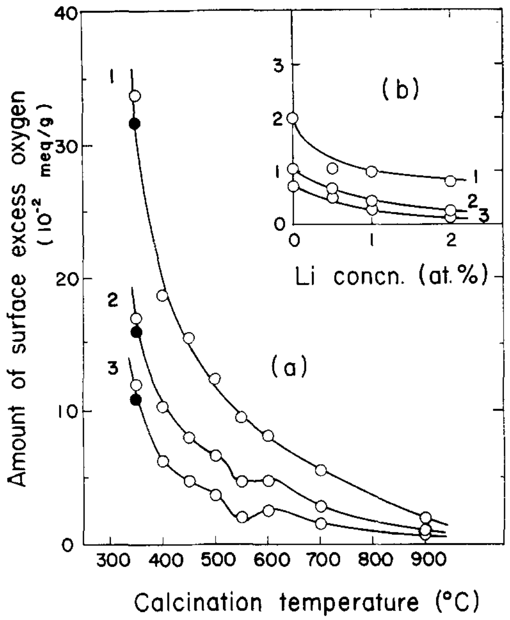

FIG. 4. The amount of the surface excess oxygen due to the hydrazine and KI(pH $x$) methods as a function of the calcination temperature (a) and the concentration of doped lithium ion (b): 1, hydrazine method; 2, KI(pH 7.5) method; 3, KI(pH 9.3) method. Solid points mean the catalyst was calcined for 16 hr.

(volumetric) (*10*) is also included in Fig. 4.

It is to be noted that a characteristic behavior is recognized for the surface excess oxygen against the calcination temperature. While the hydrazine method gives a monotonously decreasing curve against the calcination temperature, the KI(pH 7.5) method provides a decreasing curve with a flat part at the range of 550–600°C. In the cases of the KI(pH 9.3) and especially of the KI(pH 10.3) method, the curves are characterized by a maximum at 600°C and a minimum at 550°C. Furthermore, the KI (pH 10.8) and KI(pH 11.3) methods give two maximum points at 500° and 600°C and two minimum points at 400° and 550°C. There is a continuous change among the curves from the hydrazine method to the KI(pH 11.3) method. This phenomenon should be caused by the variation of the oxidation power distribution of the surface excess oxygen in a series of calcining temperatures. This characteristic behavior was confirmed even with another set of nickel oxide catalysts calcined at the corresponding temperatures.

One of the main aspects of these methods is that the reduction is made under conditions where not any amount of the catalyst is dissolved. Therefore, the reduction should clearly be restricted at most to the thin uppermost surface layers in contrast to the conventional methods which involve the partial or complete dissolution of the catalysts. As for the case of the hydrazine method, furthermore, it has been concluded that no penetration of the reduction takes place (*10*). In the case of the KI methods, much weaker reducing reagents than hydrazine are used at relatively low temperature and the amount of the reduction is much lower than a monolayer coverage, as will be shown in the following discussion. Moreover, as seen in Fig. 3, the almost instantaneous reduction occurs within a short

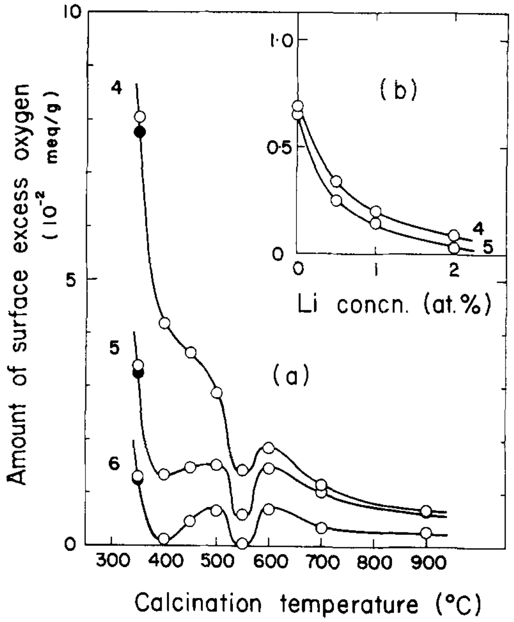

FIG. 5. The amount of surface excess oxygen due to the KI(pH $x$) methods as a function of the calcination temperature (a) and the concentration of doped lithium ion (b): 4, KI(pH 10.3) method; 5, KI(pH 10.8) method; 6, KI(pH 11.3) method. Solid points mean the catalyst calcined for 16 hr.

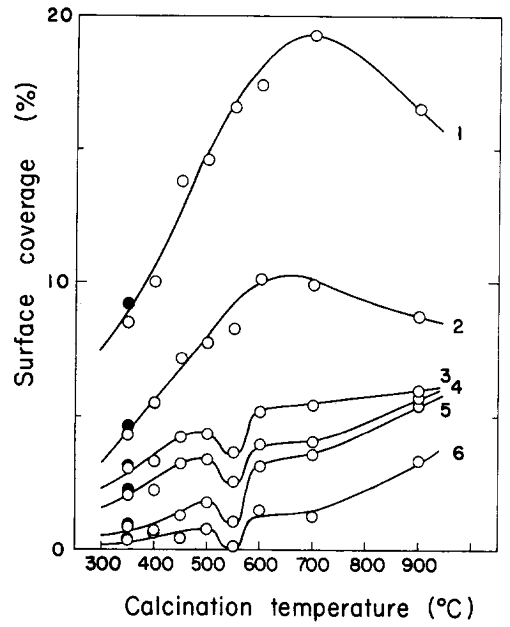

FIG. 6. The surface coverage, calculated from the results as shown in Figs. 4 and 5, as a function of the calcination temperature: 1, hydrazine method; 2, KI(pH 7.5) method; 3, KI(pH 9.3) method; 4, KI(pH 10.3) method; 5, KI(pH 10.8) method; 6, KI(pH 11.3) method. Solid points mean the catalyst calcined for 16 hr.

initial period; no gradual increase of the reduction is observed even by further extention of the reaction period, which may imply no penetration of the reduction. From the aspects mentioned above, it may be justified to assume that the reduction is probably restricted to the surface.

The amount of surface excess oxygen is represented as the surface coverage in Fig. 6. The surface coverage was calculated on the assumption that the surface was made of (100) and (110) crystal faces in an equal proportion and that one oxygen atom (2 equivalents) adsorbed on one Ni site of these crystal faces. According to both the hydrazine and the KI(pH 7.5) methods, the surace coverage increases with the calcination temperature up to the maximum at 700° or 600°C and then decreases slowly. On the other hand, the KI methods at higher pH than 9.3 give monotonous curves with a depression at 550°C. At present, the reason is not clear why the oxidation power is distributed as such with the calcination temperatures, as is shown in Figs. 4–6.

It is possible to represent the distribution of the oxidation power as regional quantities, by taking differences between the values of the neighboring methods. There are presented in Table 2 the regional quantities, $\delta_i$, of the surface excess oxygen from the first to the sixth region. The oxidation power of the regional surface excess oxygen is selected as increasing in order from the first to the sixth region. In Table 2 are represented the values of the free energy of

TABLE 2
REGIONAL AMOUNT OF SURFACE EXCESS OXYGEN DETERMINED BY THE PRESENT METHOD ON A SERIES OF NICKEL OXIDES

| | Regional amount of surface excess oxygen (meq/g) | | | | | |
|---|---|---|---|---|---|---|
| $-\Delta G$ (kcal/mole): | $\delta_1$ 141.5–29.9 | $\delta_2$ 29.9–19.8 | $\delta_3$ 19.8–14.6 | $\delta_4$ 14.6–12.6 | $\delta_5$ 12.6–11.1 | $\delta_6$ <11.1 |
| Ni-2-350-8 | 16.8 | 5.0 | 3.96 | 4.65 | 2.07 | 1.32 |
| Ni-2-350-16 | 15.7 | 5.1 | 3.15 | 4.50 | 2.01 | 1.24 |
| Ni-2-400-8 | 8.37 | 4.06 | 2.07 | 2.84 | 1.21 | 0.12 |
| Ni-2-450-8 | 7.48 | 3.29 | 1.10 | 2.17 | 0.99 | 0.47 |
| Ni-2-500-8 | 5.83 | 2.93 | 0.79 | 1.36 | 0.86 | 0.66 |
| Ni-2-550-8 | 4.76 | 2.62 | 0.64 | 0.84 | 0.54 | 0.05 |
| Ni-2-600-8 | 3.42 | 2.31 | 0.58 | 0.39 | 0.76 | 0.70 |
| Ni-2-700-8 | 2.70 | 1.28 | 0.39 | 0.14 | 0.67 | 0.35 |
| Ni-2-900-8 | 0.93 | 0.33 | 0.03 | 0.04 | 0.37 | 0.28 |
| Ni-2-Li-0.5-900-8 | 0.37 | 0.17 | 0.17 | 0.09 | 0.25 | |
| Ni-2-Li-1.0-900-8 | 0.54 | 0.16 | 0.08 | 0.06 | 0.14 | |
| Ni-2-Li-2.0-900-8 | 0.21 | 0.11 | 0.04 | 0.06 | 0.03 | |

adsorption ($-\Delta G$) involved in the formation of the surface excess oxygen, with 1 atm of oxygen being taken as a standard. These are calculated from the oxidation–reduction potential of the excess oxygen by assuming the equations (1a) and (2a).

Physicochemical properties such as surface area, color, and X-ray spectra were found to exhibit monotonous changes (*10*) against the calcination temperature, although the particular behavior was found for the distribution of the surface excess oxygen.

It is an important problem whether or not the distribution of the oxidation power is a useful variable for the catalytic activities. In order to examine this problem, preliminary experiments were carried out for the catalytic decomposition of hydrogen peroxide by using the same nickel oxide catalysts as employed in the present study. The catalytic activities showed a very similar behavior against the calcination temperature to the surface excess oxygen obtained by the KI(pH 10.3) method. The details of this subject will be reported later.

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## REFERENCES

*1.* MOROOKA, Y., AND OZAKI, A., *J. Catalysis* **5,** 116 (1966); MAKISHIMA, S., YONEDA, Y., AND SAITO, Y., *Actes Congr. Intern. Catalyse, 2ᵉ, Paris, 1960* **1,** 617 (Editions Technip, Paris, 1961).

*2.* BORESKOV, G. K., *Advan. Catalysis* **15,** 286 (1964).

*3.* PARRAVANO, G., *J. Am. Chem. Soc.* **75,** 1452 (1953).

*4.* KRAUSS, V. W., *Z. Elektrochem.* **53,** 320 (1949).

*5.* VOLTZ, S. E., AND WELLER, S. W., *J. Am. Chem. Soc.* **76,** 1586 (1954); MATSUNAGA, Y., *Bull. Chem. Soc. Japan* **30,** 984 (1957); DEREN, J., HABER, J., PODGORECKA, A., AND BURZYK, J., *J. Catalysis* **2,** 161 (1963); DEREN, J., AND HABER, J., *ibid.* **4,** 22 (1965).

*6.* MAXIM, I., AND BRAUN, T., *J. Phys. Chem. Solids* **24,** 537 (1963).

*7.* YONEDA, Y., *J. Catalysis,* **9,** 51 (1967).

*8.* BIELANSKI, A., DEREN, J., HABER, J., AND SLOCZYNSKI, J., *Trans. Faraday Soc.* **58,** 166 (1962).

*9.* WELLER, S. W., AND VOLTZ, S. E., *J. Am. Chem. Soc.* **76,** 4695 (1954).

*10.* UCHIJIMA, T., TAKAHASHI, M., AND YONEDA, Y., *Bull. Chem. Soc. Japan* **40,** 2767 (1967).

*11.* LATIMER, W. M., "The Oxidation States of the Elements and Their Potentials in Aqueous Solutions," p. 99. Prentice-Hall, Englewood Cliffs, New Jersey, 1964.