BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN VOL. 40 2767—2772 (1967)

The Measurement of Surface Excess Oxygen of Nickel Oxide Catalysts by Reduction with Hydrazine

Toshio UCHIJIMA, Masamichi TAKAHASHI[*1] and Yukio YONEDA

Department of Synthetic Chemistry, Faculty of Engineering, The University of Tokyo, Hongo, Tokyo

(Received June 12, 1967)

The method for the determination of the surface excess oxygen of oxides has been provided by using aqueous hydrazine solution as a reducing reagent and applied to several pure and lithium doped nickel oxide catalysts, calcined at various temperatures from 350 to 900°C. Two different kinds of procedures, *i. e.,* titration of the amount of hydrazine consumed and volumetric measurement of gaseous nitrogen evolved, have been employed. A satisfactory agreement is obtained between both methods, which affirms that the following reaction is taking place.

$$N_2H_4 + 2O(S) \rightarrow N_2 + 2H_2O$$

The amount of the surface excess oxygen decreases monotonously with increasing calcination temperature and also with increasing concentration of the lithium oxide additives. From comparison of these results with those due to acidic chloride and iodide methods, most of the excess oxygen is concluded to exist on the surface of the oxides and, furthermore, a certain distribution in the oxidation power of the excess oxygen is suggested to exist.

Many physico-chemical properties of the oxide catalysts have been taken into consideration in order to find the explanation of their catalytic activities. Among them, the amount of excess oxygen has been found to be a useful variable to

---

[*1] Present address: Research and Development Center, Nippon Rayon Co., Ltd., Uji, Kyoto.

represent their activities; for example, in the oxidation of ammonia on nickel oxide, cobalt oxide and manganese oxide catalysts,1) and the decomposition of hydrogen peroxide on nickel oxide3) and chromia catalysts,2) a good correlation has been revealed between their catalytic activities and their amounts of excess oxygen. In these studies, the excess oxygen was determined by the Bunsen-Rupp's method4) or a similar method proposed by Voltz and Weller,5) which consists in reducing the excess oxygen of catalysts with Cl^- or I^- ion in strongly acidic solution. Since the catalysts are fully or partially dissolved into the solution under these conditions, these methods measure not only the surface excess oxygen but also the bulk one.

It is believed that the important properties for heterogeneous catalysis are necessarily not of the bulk, but of the surface. Therefore, it is aimed in the present investigation to provide a practical method for the determination of the surface excess oxygen. Aqueous hydrazine solution, an alkaline and strongly reducing reagent, has been adopted for the selective reduction of the surface excess oxygen. Thus, it is examined how the amount of the surface excess oxygen changes with the calcination temperature and with the concentration of doped lithium oxide.

In addition, we have made the measurements of the excess oxygen according to the conventional procedures, that is, the reaction of the catalysts with Cl^- or I^- ion in strongly acidic media. We will compare and discuss the results obtained by the hydrazine method and the conventional ones.

Experimental

Catalysts. As catalysts, a series of pure nickel oxides and Li_2O-doped ones were used. Pure nickel oxides were prepared by the calcination of commercial nickel carbonate (G. R.) at 350—900°C in air. In the preparation of Li_2O-doped nickel oxides, the nickel carbonate was mixed with an appropriate amount of lithium carbonate solution and evaporated in a porcelain dish over a water bath. Subsequently, the residue was dried at 100°C and calcined in a muffle furnace at 900°C in air. The catalysts are designated as shown in Table 1, where Ni-2-350-8 means a nickel oxide prepared by calcining the starting material of batch number 2 at 350°C for 8 hr in air and Ni-2-Li-0.5-900-8 means Li_2O-doped NiO obtained by calcining the same raw material at 900°C for 8 hr in air after mixing with lithium carbonate at the concentration of 0.5 atom% Li.

The Determination of Surface Excess Oxygen Using the Hydrazine Method. This method consists in reducing the surface excess oxygen of nickel oxide catalysts with hydrazine in a dilute aqueous solution and in measuring the amount of either hydrazine consumed or nitrogen gas evolved. The amount of the surface excess oxygen can be calculated in the unit of meq/g, assuming the following chemical equation.

$$N_2H_4 + 2O(S) = N_2 + 2H_2O \tag{1}$$

Two different procedures were applied on the basis of the same reaction (1); the one was the titration method and the other the volumetric method.

(a) Titration Method for the Determination of Hydrazine Consumed. Flowing nitrogen gas through a reaction vessel, a weighed amount (0.1—0.3 g) of a catalyst and 5 m*l* of distilled water free from oxygen were introduced therein, then a known excessive amount of N_2H_4 (0.06 N) was added. After the mixture was allowed to react with each other at least for 20 min*2 under shaking, the dark green suspension was filtered by means of suction and washed with water. During these procedures, the mixture was always maintained in nitrogen atmosphere. By means of a conventional iodometric titration for hydrazine remaining unchanged in the filtrate, the amount of hydrazine consumed is determined, which should be equal to that of the surface excess oxygen.

(b) Volumetric Method for the Determination of Nitrogen Gas Evolved. A weighed amount of a catalyst (0.5—2 g) and 15 m*l* of distilled water were introduced into a reaction vessel, at the top of which there were equipped a capillary manometer and a small side tube. This side tube, inverted L-shaped, could rotate around a glass joint connecting the tube and the vessel. Subsequently, 1 m*l* of 0.3 N N_2H_4 solution was introduced into the side tube. The closed reaction system with total volume of 28 m*l* was fixed in a thermostat and maintained at a constant temperature of 30.0±0.1°C. When the constant pressure was attained, the catalyst system was mixed with the N_2H_4 solution by rotating the side tube in an inverted position and then the suspension was stirred with a magnetic stirrer. Simultaneously, the increase of the pressure due to the liberation of nitrogen was followed with a running microscope, until the constant pressure was again obtained which confirmed the completion of the reaction. As will be described later, the existence of gaseous oxygen in the reaction vessel does not affect the result.

From the difference in pressures at the steady states before and after the reaction, the amount of nitrogen gas evolved can be calculated in a usual way. This value should be related to the amount of the surface excess oxygen according to Eq. (1).

The Determination of the Excess Oxygen with Cl^- and I^- in Acidic Media. For the sake of comparison with the above method, the excess oxygen of nickel oxide catalysts was measured by using the two conventional methods and a modification of them, which were designated here as the HCl (concd.) method (the Bunsen-Rupp's method4)), the KI (2 N HCl) method (the Voltz-Weller's method5)) and the KI (0.12 N

---

1) V. W. Krauss, *Z. Elektrochem.*, **53**, 320 (1949).

2) S. E. Voltz and S. W. Weller, *J. Am. Chem. Soc.*, **76**, 1586 (1954): Y. Matsunaga, This Bulletin, **30**, 984 (1957); J. Deren, J. Haber, A. Podgorecka and J. Burzyk, *J. Catalysis*, **2**, 161 (1963); J. Deren and J. Haber, *ibid.*, **4**, 22 (1965).

3) I. Maxim and T. Braun, *J. Phys. Chem. Solids*, **24**, 537 (1963).

4) A. Bielanski, J. Deren, J. Haber and J. Sloczynski, *Trans. Faraday Soc.*, **58**, 166 (1962).

5) S. W. Weller and S. E. Voltz, *J. Am. Chem. Soc.*, **76**, 4695 (1954).

[*2] The reaction period of 20 min was ascertained to be long enough to attain a constant value.

HCl) method, respectively. These methods cover the excess oxygen existing on the surface and even in a part or the whole of the bulk phase. The HCl (concd.) method and KI (2 N HCl) method were applied following the procedures as reported previously.[4,5] The KI (0.12 N HCl) method was applied as follows. A weighed amount of a catalyst (0.1—0.8 g), 1.0 g of KI and 10 m*l* of 0.12 N HCl were introduced into a conical flask in nitrogen atmosphere and then the flask was stoppered tightly. The mixture was allowed to react for 4 hr under shaking. Then, the suspension was filtered by means of suction and washed with 20 m*l* of methanol and then with 40 m*l* of distilled water. All these steps were conducted without exposing the mixture to air. The filtrate containing iodine was titrated with a standard sodium thiosulfate solution.

Results and Discussion

The Surface Excess Oxygen by the Hydrazine Method. As for the case of the titration method, the amount of hydrazine consumed is plotted in Fig. 1 against the initial amount of hydrazine added. Since hydrazine is a strongly reducing reagent, its reaction with the surface excess oxygen will be completely quantitative. Accordingly, if hydrazine does only react with the excess oxygen in such a manner as the chemical equation (1), the amount of hydrazine consumed must always be a constant value, so far as the excess amount of hydrazine is present. However, the consumption of hydrazine increased slightly with the increment of its initial addition and this behavior did not change by extending the reaction period. This phenomenon may be due to the adsorption of hydrazine on the reduced oxide surface, whose amount is a function of the concentration of the remaining hydrazine. Then, the true value of the surface excess oxygen should be the maximum consumption of hydrazine in the absence of excessive hydrazine; this value is obtained from the crossing point of an extrapolated line of the observed points with a line representing the equivalence between the amount of consumed hydrazine and that of added one.

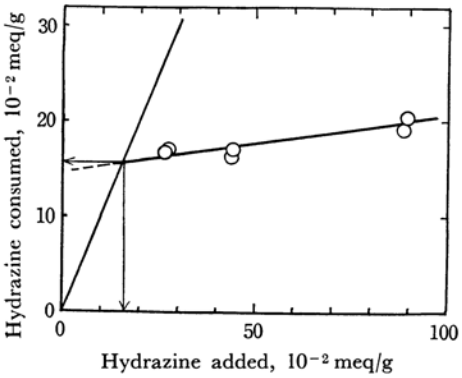

Fig. 1. The dependency of the amount of hydrazine consumed against that of hydrazine added.
Ni-2-450-8, 0.100 g

The values of the surface excess oxygen, thus obtained, are presented against the calcination temperature and the concentration of doped lithium ion in Fig. 2(a) and (b), respectively.

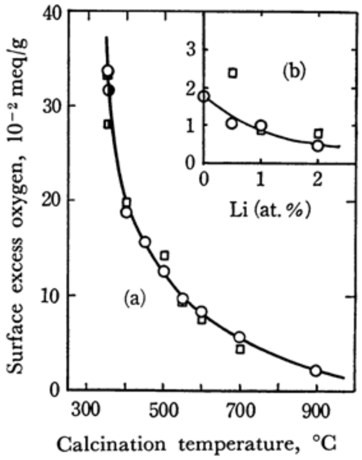

Fig. 2. The amount of the surface excess oxygen *vs.* the calcination temperature (a) or the concentration of doped lithium ion (b).
○: Volumetric method
□: Titrating method
Half-filled points are for the catalyst calcined for 16 hr.

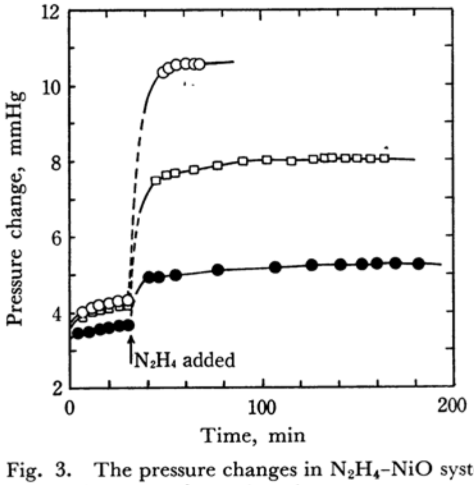

Fig. 3. The pressure changes in N_2H_4–NiO system as a function of reaction time.
○: Ni-2-350-16, 0.562 g
□: Ni-2-500-8, 0.903 g
●: Ni-2-900-8, 2.225 g

In Fig. 3, there are shown some examples of the kinetic curves of the liberation of nitrogen measured by the volumetric method. The amount of the surface excess oxygen can be derived from the volume of nitrogen which is calculated from the

TABLE 1. THE SURFACE EXCESS OXYGEN MEASURED BY THE HYDRAZINE METHOD AND SOME OTHER PHYSICO-CHEMICAL PROPERTIES

Catalyst	Surface excess oxygen 10^{-2} meq/g	Surface area m^2/g	Surface coverage %	X-ray analysis Phase	a_0 (Å)*	$d_{1/2}$ (°)**	Color
Ni-2-350-8	33.8	121	8.5	NiO	4.165	1.24	Black
Ni-2-350-16	31.7	106	9.2	—	—	—	Black
Ni-2-400-8	18.67	57.6	10.0	—	—	—	Black
Ni-2-450-8	15.50	34.4	13.8	NiO	4.165	0.60	Black
Ni-2-500-8	12.43	26.1	14.6	—	—	—	Black
Ni-2-550-8	9.45	17.4	16.6	NiO	4.165	0.46	Gray
Ni-2-600-8	8.16	14.4	17.4	NiO	4.165	0.48	Gray
Ni-2-700-8	5.53	8.8	19.3	—	—	—	Dark green
Ni-2-900-8	1.98	3.7	16.5	NiO	4.166	0.28	Green
Ni-2-Li-0.5-900-8	1.05	—	—	—	—	—	Grayish-black
Ni-2-Li-1.0-900-8	0.98	—	—	NiO	4.149	0.29	Black
Ni-2-Li-2.0-900-8	0.45	—	—	—	—	—	Black

* Lattice constant
** Half width of (111) diffraction line at $2\theta=27.3°$

steady values of the pressure before and after reaction assuming the law of ideal gas. In this calculation, some corrections are made for the vapor pressure of water and the variation of the dead volume.

Moreover, it is worthy of mention that the existence of gaseous oxygen remaining in the vessel does not affect the result so far as the excess amount of hydrazine is present, since the reduced catalyst may adsorb oxygen only slowly, while this oxygen will be rapidly reduced by hydrazine, accompanying no net change of the volume.

The oxidation process of dilute aqueous hydrazine solution has been reported generally not to be a simple one as represented in Eq. (1). Hydrazine reacts with various oxidizing reagents to produce nitrogen, ammonia or hydrazoic acid, the proportions among which vary according to the reagents and the conditions employed. It is noted that some typical p-type oxides such as lead peroxide and manganese dioxide react with hydrazine almost quantitatively according to Eq. (1).[6] Therefore, Eq. (1) would be reasonably assumed in the present investigation for calculating the surface excess oxygen of the nickel oxide catalysts.

The results obtained by the volumetric method are also shown in Fig. 2(a) and (b).

A satisfactory agreement is revealed in Fig. 2 between the results obtained by the two kinds of hydrazine methods. This means either that the assumption as mentioned above is realized or that some side reactions, if any, contribute to the observation only within the accuracy.

The volumetric method appears to be simpler and more accurate than the titration method, since the latter involves many laborious steps of taking the differences between the experimental values of comparable magnitude and of extrapolating these ones.

Heretofore, the excess oxygen determined with the hydrazine method has been assumed implicitly to be restricted only to the surface. Furuichi *et al.*[7] studied the reduction of ferric oxides with more concentrated hydrazine solution (0.4 N) at 35°C. Their samples were reportedly rather amorphous and contained some water even in the bulk phase. Although they described that the reduction penetrated into the bulk phase with the rate being controlled by the bulk diffusion of H^+, the amount of the reduction after 24 hr can be easily estimated not to exceed one layer of the surface for all their samples. On the contrary, nickel oxides having more crystalline structure were used in the present study. Furthermore, as is seen in Fig. 3, the reaction of nickel oxides with dilute aqueous hydrazine solution accompanied the abrupt changes at relatively short initial period (<30 min) and no further increases could be observed. From the aspects mentioned above, it will be justified to consider the excess oxygen being restricted probably to the surface.

The amount of the surface excess oxygen, calculated as the amount per unit weight, decreases monotonously as the calcination temperature is raised. The same values recalculated as the surface coverage are shown in Table 1 (column 4) together with other physico-chemical properties of the catalysts, such as surface area, color and X-ray analysis data. The calculation of the surface coverage is based on the assumption that the

---

[6] L. F. Audrieth and B. A. Ogg, "The Chemistry of Hydrazine," John Wiley and Sons, Inc., N. Y. (1951), p. 120.

[7] R. Furuichi, N. Sato and G. Okamoto, *Kogyo Kagaku Zasshi (J. Chem. Soc. Japan, Ind. Chem. Sect.)*, **69**, 1010 (1966); R. Furuichi, N. Sato and G. Okamoto, *ibid.*, **69**, 1014 (1966).

surface consists of (100) and (110) crystal faces existing in an equal proportion and one oxygen atom (2 equivalents) is coordinated on a nickel atom of these crystal faces. The amount of the surface excess oxygen per unit area is not large enough to cover more than 10—20% of the surface, showing a broad mountain-like curve against the calcination temperature with its maximum at 700°C.

It is noted from Fig. 2(b) that the amount of the surface excess oxygen measured by the hydrazine method decreases slightly with increasing concentration of the Li_2O-additives for the doped catalysts. Bielanski *et al.*⁴⁾ investigated the excess oxygen extensively on a series of nickel oxide by using the Bunsen-Rupp's method and determined separately the excess oxygen near the surface and in the bulk phase according to the measurements on the sample with or without evacuation at 400°C. They described, as a result, that the amount of the excess oxygen near the surface increased with the increment of the doped lithium oxide. Their results do not coincide with the present results. This conflict will be probabyl due to the inadequacy of their method for distinguishing the surface and the inner lattice oxygen.

The Excess Oxygen by the Acidic Cl^- and I^- Method. The results, obtained by the HCl (concd.), the KI(2 N HCl) and the KI(0.12 N HCl) methods, are plotted against the calcination temperature and the concentration of the doped lithium oxide in Fig. 4(a) and (b), respectively.

As for the HCl (concd.) method, the catalysts are dissolved completely by heating in concentrated HCl solution and, therefore, this method will give the total excess oxygen existing both on the surface and in the bulk phase. In this method, evolved chlorine is carried away from the reaction system by the nitrogen stream. Therefore, the oxidation-reduction potential of this system is controlled by the ratio of the concentration, Cl_2/Cl^-, which depends on the dynamic conditions during the reaction and accompanies the ambiguity in this sense; however, the reduction power will be much weaker than that of any KI methods.

In the KI (2 N HCl) and the KI (0.12 N HCl) methods, the catalysts are partially dissolved and the degree of their dissolution is more severe in the former method. Although the reduction power of I^-, the reacting species, does not depend on the concentration of proton, $[H^+]$, the potential of the surface oxygen increases with $[H^+]$ as follows. The oxidation-reduction potential of the surface excess oxygen, E_{O_s}, should be equal to that of the hypothetical gaseous oxygen, $E_{O_2}{}^{he}$, that is in a hypothetical equilibrium with the former (a superscript "he" in $E_{O_2}{}^{he}$ designates a hypothetical equilibrium). Thus, E_{O_s} is expressed in the following equation, no matter what sort of chemical species of oxygen may exist on the nickel oxide surface, *i. e.*, ionic or neutral species of either molecular or atomic oxygen.

$$E_{O_s} = E_{O_2}{}^{he} = E_{O_2}{}^{0} + \frac{\boldsymbol{RT}}{4\boldsymbol{F}} \times \ln\frac{(f_{O_2}{}^{he})\times(a_{H^+})^4}{(a_{H_2O})^2} \qquad (2)$$

where $f_{O_2}{}^{he}$ represents the hypothetical fugacity of the gaseous oxygen molecule in equilibrium with the surface excess oxygen and $E_{O_2}{}^{0}$ is the standard single electrode potential of gaseous oxygen. Therefore, the relative reduction power of I^-, towards the oxygen having the same fugacity, is larger in more acidic media, where E_{O_s} has a more noble value. As the result, when the solution is more acidic, the excess oxygen measured must be extended to those existing in the more inner part of the lattice, and also even to those having still lower oxidation power if they have some distribution in its free energy. Actually, the amount of excess oxygen is found reasonably larger by the KI (2 N HCl) method than by the KI (0.12 N HCl) method for all the catalysts investigated as is noted in Fig. 4.

The values obtained by the HCl(concd.) method are larger than those by the two acidic KI methods for the oxides calcined below 500°C, but are nearly the same for above 550°C. Thus, the HCl(concd.) method does not necessarily give the largest value among these methods, in spite of its covering the excess oxygen in the whole lattice. This fact may

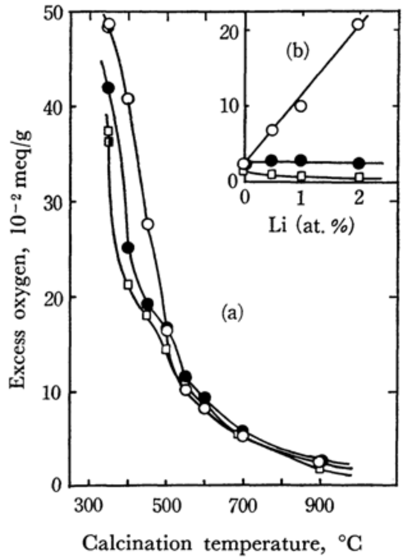

Fig. 4. The amount of the excess oxygen obtained by the acidic Cl^- and I^- method *vs.* the calcination temperature (a) or the concentration of doped lithium ion (b).
○: Concd. HCl method
●: KI (2 N HCl) method
□: KI (0.12 N HCl) method
Half-filled points are for the catalyst calcined for 16 hr.

be accounted for by the existence of the distribution in the oxidation power of the excess oxygen in cooperation with the difference in the reduction power among each method.

All results obtained by these acidic methods show the similar curves against the calcination temperature as those by the hydrazine method. It is interesting that these acidic methods give the larger excess oxygen than the hydrazine method throughout the catalysts investigated.

On the contrary, doping effects of lithium oxide on the amount of the excess oxygen are different among these methods. The values by the KI (0.12 N HCl) method decrease slightly with the concentration of lithium, and the KI (2 N HCl) method gives almost constant values, while the values of excess oxygen obtained by the HCl (concd.) method increase linearly. Then, it may be concluded that the excess oxygen is introduced mainly into the lattice with the addition of lithium oxide. However, as is shown in Table 2, the values determined by the HCl(concd.) method are nearly equal to or slightly smaller than those calculated from the amount of lithium ion incorporated on the basis of the following equation.

$$\frac{1}{2}\delta \mathrm{Li_2O} + (1-\delta)\mathrm{Ni^{II}O} + \frac{1}{4}\delta \mathrm{O_2} \rightarrow \mathrm{Li_\delta Ni^{II}_{1-2\delta} Ni^{III}_\delta O}$$

This fact will suggest that the excess oxygen produced by the doping of lithium oxide has high oxidation power which can be measured even by the HCl(concd.) method.

TABLE 2. COMPARISON BETWEEN THE OBSERVED VALUES AND THE CALCULATED VALUES OF THE TOTAL EXCESS OXYGEN IN Li_2O-DOPED NiO

Catalyst	Amount of the total excess oxygen	
	Calcd., meq/g	Obsd., meq/g
Ni-2-Li-0.5-900-8	6.7×10^{-2}	6.9×10^{-2}
Ni-2-Li-1.0-900-8	13.5×10^{-2}	10.1×10^{-2}
Ni-2-Li-2.0-900-8	27.1×10^{-2}	20.9×10^{-2}

Conclusion

The surface excess oxygen can be measured by using hydrazine as a reducing reagent. Both techniques of titrating hydrazine consumed and of measuring the volume of nitrogen evolved are found to be useful. The reaction of hydrazine with the surface excess oxygen proceeds according to Eq. (1). In addition, a certain distribution of the oxidation power of the excess oxygen is suggested to exist from the comparison of the values obtained by the HCl (concd.), KI (2 N HCl) and KI (0.12 N HCl) methods.

Valuable informations will be obtained by developing quantitative methods for determining the distribution of the oxidation power. This problem will be soon reported in near future.

The authors wish to express their sincere thanks to Mr. H. Matsumoto and Mr. K. Kojima for their contribution to the preliminary research, and to Mr. N. Nojiri and Mr. K. Kurokawa for their kind help in the course of this experiment. The expenses of the work were partly defrayed by a grant-in-aid for Developmental Research, Ministry of Education, to which their thanks are due