© 1990 The Chemical Society of Japan Bull. Chem. Soc. Jpn., 63, 590—591 (1990) [Vol. 63, No. 2

Reducibility of Metal Oxides in Hydrogen and Strength of Oxygen Bond in Their Surface Layer

D. Klissurski* and R. Dimitrova†
Institute of General and Inorganic Chemistry, Bulgarian Academy of Sciences, Sofia 1040, Bulgaria
†Faculty of Chemistry, University of Sofia, 1126, Bulgaria
(Received March 20, 1989)

A distinct correlation between the reducibility of metal oxides in hydrogen and the strength of the oxygen bond in their surface layer has been found. Simultaneously it has been shown that the widely accepted concept for a correlation between the melting points of oxides and their reducibility needs a critical reconsideration.

The initial stages of interaction play an important role in the reduction of metal oxides. Their studies are associated with a series of problems such as the chemical compatibility of the metal oxides and the elucidation of the kinetics and mechanism of reduction processes. In this connection, special attention is paid to the initial temperature of reduction of metal oxides, which is regarded as an important characteristic of their activity.[1,2]

In previous papers the initial temperature of reduction was compared with the melting points of the oxides, with the transition point doped to intrinsic conductivity, and with the width of the forbidden zone of semiconducting oxides.[3,4]

Some authors[5,6] have used the initial temperature of reduction as a measure of the strength of oxygen bond in metal oxides. In a paper of ours[7] a satisfactory correlation between these quantities was found. However, the data available permitted a semiquantitative comparison only.

Very reliable data are obtained during the recent years on the temperatures at which close rates of the initial reduction of oxides of the 1st transition metal series with hydrogen are achieved.[8]

It is of interest to find a correlation between these data and the results on the binding energy of oxygen in the surface layer of metal oxides. For that purpose, we used the values of the bonding energy of oxygen in the surface layer of metal oxides obtained by the method of oxygen isotopic exchange.[9,11] The exchange of gas-phase oxygen with the oxygen of metal oxides is a subject of numerous studies.[7,9,12] As is known the homomolecular oxygen isotopic exchange may obey one of three mechanisms depending upon the nature and pretreatment procedure of oxides;

I. Without the participation of oxygen from the oxide surface.

II. With the participation of one atom of the surface oxygen in each act of displacement.

III. With the participation of two atoms of surface oxygen of the oxide in each act of exchange.

It has been established by numerous studies that in the cases when the 3rd mechanism of exchange is obeyed the activation energies of exchange practically coincide with the energies of oxygen bonding to the oxide surface.[13,14] This was confirmed also by adsorption-calorimetric and other independent measurements of the bonding energy of oxygen in the surface layer of different metal oxides.[14] Simultaneously we took into consideration that in the study of the two processes (the reduction with hydrogen and the oxygen isotopic exchange) the oxides are subjected to similar treatments. As was already noted in our previous papers,[7] this method of determination of the bond energy of surface oxygen (q_s') has some advantages and belongs to the most reliable methods (10). The reciprocal value of the temperature at which a definite rate of the reduction with hydrogen $R_{H_2}=1/T_r$ is achieved is taken as measure of the oxides reducibility. The values of q_s' and R_{H_2} for oxides of the metals of the 4th Period of the Periodic Table are compared in Fig. 1. Obviously, there is a clearly expressed correlation. Figure 2 shows that there is also a satisfactory correlation between the oxygen bonding energies of the oxides and the initial activation energy of their reduction. This leads to the supposition that during the reduction of the oxides with hydrogen a simple correlation of the type of the Brϕnsted-Polanyi relationship[12] is followed; i.e.;

$$E_a = E_o + \beta q_s' \qquad (1)$$

where β is a proportionality coefficient which depends

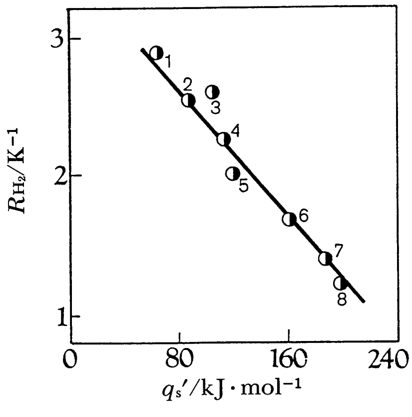

Fig. 1. Relationship between the binding energy of the surface oxygen in metal oxides (q_s') and the reciprocal temperature at which a given rate of reduction is attained, R_{H_2}.
1, Co_3O_4; 2, MnO_2; 3, CuO; 4, NiO; 5, Fe_2O_3; 6, ZnO; 7, V_2O_5; 8, TiO_2.

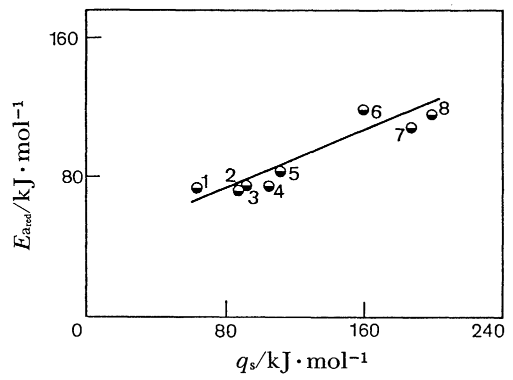

Fig. 2. Relationship between the binding energy of surface oxygen in metal oxides and the activation energy of their reduction in hydrogen, $E_{a_{red}}$ (kJ mol⁻¹).

on the nature of the reducing agent. Evidently, in this case the value of the bonding energy of surface oxygen is included in the value of the activation energy of the reduction process. It may be expected that this would also be valid for other gaseous reducing agents such as CO, hydrocarbons, alcohols, and other organic compounds, if the reduction is not complicated by secondary processes (autocatalysis, disproportionation of CO, transport phenomena etc). The presence of a correlation of the above type expressed by Eq. 1 facilitates predictions of the reducibility of metal oxides with various gaseous reducing agents. If the correlation is valid, with the change of the gaseous reducing agent the oxide reducibilities would vary in an analogous manner. Of course, other factors have also to be taken into consideration, e.g. the acidity or basicity of oxides and reducing agents, the specificity of activation of the reducing agent molecule, the possibility of blocking the oxide surfaces by the reaction products etc.

As was already pointed out, in some papers[2)] it is stated that there is a correlation between the initial temperature of reduction of metal oxides and their melting points. In some of the papers, a quantitative ratio between these parameters is found,[2,4)] which is expressed by the equation:

$$T_{\text{initial reduction}} = 0.46\, T_{\text{melting}} + 250$$

The analysis of the experimental data on metal oxides reduction gives no convincing evidence of this correlation. It suffices to note that the melting points of NiO and SiO_2 do not substantially differ from each other. At the same time, the differences between the initial temperatures of oxides reductions with gaseous reducing agents, exceeds 1000 °C. The high dissipation of the points in Fig. 3 indicates the necessity of reconsideration this widely accepted concept.[2,4)]

Finally it should be pointed out that the above examples and data agree with our opinion according

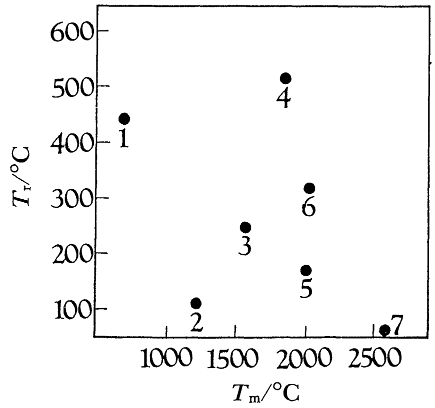

Fig. 3. Relationship between the temperature at which a given rate of reduction of metal oxides is attained T_r and their melting temperatures, T_m.
1, V_2O_5; 2, CuO(Cu_2O); 3, Fe_2O_3; 4, TiO_2; 5, NiO; 6, ZnO; 7, Co_3O_4(CoO).

to which the data on the bond strength of surface oxygen in metal oxides and in complex oxide systems can successfully be used to predict their reducibility.

References

1) S. T. Rostovtsev, "Teorya Metallurgicheskikh protsessov, Gos. Izd. Chernoi i tsetnoi metallurgii," Moskva (1956), p. 389 (Russ.).

2) V. P. Elyutin, A. V. Manukhin, and Yu. A. Pavlov, "Fizicheskaya khimia okislov metallov," Izd., "Nauka", Moskva (1981), p. 182 (Russ.).

3) V. P. Elyutin, R. F. Merkulova, and Yu. A. Pavlov, "Proizvodstvo stali i splavov," Izd, "Metallurgizdat", Moskva (1958), p. 79 (Russ.).

4) V. P. Elyutin, Yu. A. Pavlov, V. P. Pdlyakov, and S. B. Sheboldaev, "Vzaimodeistvi okisiov metallov s uglerodom," Izd. "Metallurgia", Moskva (1976), p. 359.

5) G. I. Golodets, *Teor. Exper. Khimia,* **1**, 775 (1965).

6) W. M. H. Sachtler, and J. H De Boer, Proceedings of the 3rd International Congress on Catalysis, Elsevier Publ. Co., Amsterdam, 1965, p. 252.

7) D. G. Klissurski, Proceedings 5th Ibero-American Symp. Catalysis, ed by M. Portela and C. Pulido, Qmimica, Lisbon, (1979), Vol. 1, p. 29.

8) V. V. Popovskii, G. K. Boreskov, and E. A. Mamedov, Proc. 1st Soviet-Japanes Seminar on Catalysis," ed by "Nauka," (1971), preprint No. 23.

9) G. K. Boreskov, *Adv. Catal.,* **15**, 285 (1964).

10) G. K. Boreskov, and V. S. Muzikantov, "Vsesouz. Conf. po Izotopnomu Obmenu na Tverdykh Katalizatorakh," Izd. "Nauka," Novosibirsk (1971), preprint No. 12, (Russ).

11) G. K. Boreskov, V. V. Popovskii, and V. A. Sazonov, "Osnovy Predvideniya Kataliticheskogo Deistviya," Izd. "Nauka," Moscow (1970), p. 343 (Russ.)

12) D. G. Klissurski, in press.

13) G. K. Boreskov, "Catalysis: Science and Technology," Vol. 3 (1982), p. 40.

14) G. K. Boreskov, *Kinetika i Kataliz (Russ.),* **8**, 1020 (1967).