Oxygen Equilibrium Pressure as a Measure of Oxygen Binding Energy in The V_2O_{5-x} System

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Using the redox mechanism of vanadia catalyst action as a starting point, oxygen binding energy and its measurement have been discussed. Experimental results on the equilibrium oxygen pressure are presented and two types of equilibrium are distinguished: chemisorbed and redox. It has been shown that univariant redox equilibrium is appropriate for characterizing vanadia catalysts.

Introduction

Vanadium pentoxide is the basis of various catalysts for oxidation of olefins and aromates. In the Mars–van Krevelen mechanism the participation of lattice oxygen anions has been assumed in one of the steps of organic molecule oxidation (*1*). Then the catalysts should be reoxidized by gaseous oxygen. This idea for vanadia catalysts was confirmed by Vrbaski and Mathews (*2*) by the oxidation of *o*-tolualdehyde over V_2O_5 even in the absence of gaseous oxygen where the catalyst was partly reduced. Other evidence was provided by Hirota *et al.* (*3*) by the transfer of the ^{18}O indicator from the catalyst lattice to catalytic oxidation products.

In the V_2O_5 structure (*4*) the strongly distorted VO_6 octahedra form warped layers in which oxide anions are shared by adjacent octahedra. The two remaining O^{2-} in VO_6 are between these layers, but each of them is more strongly bonded to the nearer vanadium atom (1.586 Å) than to the farther one (2.788 Å). Such a structure makes the diffusion of oxygen in the bulk of the oxide easier. According to

Gillis (*5*) there are vacant passages 2 Å in diameter suitable for oxygen transport.

The removal of oxygen from the V_2O_5 lattice may cause only the formation of point defects or may cause the formation of Wasdley's phases described by the formula $V_{2n}O_{5n-2}$. Fiermans and Vennik (*6*), using LEED, observed that during the course of oxygen removal the (010) face of V_2O_5 changes to the V_6O_{13} face. The presence of this oxide on the surface of active vanadia catalysts was even suggested by Simard (*7*).

Oxygen Binding Energy and Its Measurement

The Mars–van Krevelen mechanism has raised interest in oxygen transfer processes (gas–oxide catalyst). Many kinetic measurements of both oxidation and reduction of oxide catalysts as well as $^{18}O/^{16}O$ isotopic exchange have been performed up to present.

Following the suggestions of Boreskov *et al.* (*8*) and Sachtler *et al.* (*9*) the partial decomposition enthalpy of an oxide catalyst into lower oxide and free oxygen is generally accepted as a measure of the oxygen binding

energy. Therefore, measurement of the oxygen equilibrium pressure may be used and, indeed, often has been.

There are, however, some interpretative peculiarities of this equilibrium. Boreskov *et al.* (*8, 10, 11*) assumed, and it has become generally accepted, that in the course of equilibrium pressure measurements, as well as during catalytic reactions, oxygen is desorbed only from the chemisorbed layer. These assumptions are rather contradictory to the Boreskov–Sachtler definition of the oxygen binding energy and to the Mars–van Krevelen mechanism. But they are virtually in agreement with another mechanism of catalytic action, as suggested by Roiter (*12*) and Margolis (*13*). According to the latter a hydrocarbon molecule is oxidized by a species of oxygen chemisorbed on the oxide surface, e.g., O^-.

The next peculiarity concerns the mode of application of the equilibrium oxygen pressure. The results of the measurements were introduced to the Claussius–Clapeyron equation and the heat of oxygen desorption was calculated. If we assume, after Boreskov, that no new oxide phase is formed during the experiments, the system should be bivariant. Nevertheless, the possibility of using the Claussius–Clapeyron equation is justified by Boreskov by the fact that only a very small part of the oxygen from the adsorbed layer is removed in the course of measurements.

In consequence, the appropriate experimental conditions during the equilibrium pressure measurements were established. The measurements were carried out using the largest possible samples. Their surfaces were first cleaned under conditions that were not severe and only a small number of molecules, was desorbed in the course of measurements. All precautions were taken in order to maintain the one-phase system.

Review of Oxygen Pressure Measurements and Discussion

By applying such experimental conditions many measurements of oxygen pressure have been performed on a number of metal oxides.

TABLE I

RESULTS OF THE DIRECT MEASUREMENTS OF EQUILIBRIUM OXYGEN PRESSURE ABOVE V_2O_5 AND COMPLEX OXIDE SYSTEMS

Reference	Temperature (°C)	P (Torr)	Sample	x_{max} in formula V_2O_{5-x}
14	370–465	0.005–0.125	V_2O_5	?
15	320–350	0.005–0.038		
	350–380	0.028–0.1	V_2O_5	0.001
	390–425	0.06–0.13		
16	340–535	0.001–0.22	V_2O_5	0.0001
17	370–485	0.0006–0.2	V_2O_5–TiO_2	0.0001
9	275–500	0.03–0.60	V_2O_5–SnO_2 (3 g)	0.02
	350–500	0.50–1.80	V_2O_5–SnO_2 (5 g)	0.006
18	358	1–0.002		0.0008
	382	1–0.009	V_2O_5–SiO_2	0.0016
	513	1.5–0.2		0.004
19	320–390	0.0015–0.5		0.0005
	415–500	0.001–1.0	V_2O_5	0.001
	500–635	0.001–0.95		0.002
20	600	0.00062	V_2O_{5-x} (V_2O_5–V_6O_{13})	0.02–0.43
	600	>0.00062		<0.02
21	575–615	0.0002–0.0011		0.10–0.35

Among them, the experiments done on vanadium pentoxide and systems containing V_2O_5 make up the greatest part. The results of the direct measurements are shown in Table I.

There are, in fact, some other works on this subject, particularly those published by Boreskov *et al.* Unfortunately, these other authors frequently give only the values of oxygen binding energy calculated on the basis of the Claussius–Clapeyron equation.

The amounts of oxygen removed from the samples in most of the measurements were small. The highest amounts were the basis of computing the values of x_{max} in the formula V_2O_{5-x}. As stated in a previous paper (20) such low values of x correspond to the bivariant equilibrium in the V_2O_{5-x}–O_2 system. On the other hand, if one accepts the assumption of Boreskov *et al.* (8, 10, 11) that in the course of experiments the processes occurred only on the surface, one may also expect the bivariant equilibrium. In such cases an infinite number of values P for a given T should be observed.

Variations of oxygen pressure dependent on experimental conditions have been frequently reported. Sachtler *et al.* (9) observed differences in oxygen pressure caused by changes in the sample amounts. Mishtchenko *et al.* (15) obtained various pressure values according to the temperature at which the series of measurements was started. More recently, Figueras and associates (18) and Joly (19) have studied pressure decreases as a function of the desorption degree as defined by the oxygen monolayer fraction. Such effects have been interpreted by the authors of (8–11, 15, 18) as the result of an increase of adsorption heat when desorption extents are greater.

On the other hand, Joly (19) interprets them in a different way, basing his computation on a simulation model of oxygen adsorption and desorption. Joly showed (22) that the dissociative oxygen adsorption observed on the oxide surface causes instability of oxygen pressure in relation to the surface coverage and even causes deviation from the linear dependence of log P versus $1/T$. Then, in the case of V_2O_5, the heat of oxygen adsorption is constant.

In the present author's opinion the problem is much more complicated. It was found in an earlier study using the temperature-programmed desorption (TPD) method that two oxygen forms are released during desorption (23). One of them originates in the adsorbed layer and the other among the lattice anions. The amounts of desorbed loosely bonded oxygen gradually decrease in subsequent runs, when separated by oxidizing of the sample, until this form disappears completely.

Owing to these facts one may expect two different types of equilibrium between oxygen and V_2O_5. A chemisorption equilibrium appertains to the monolayer chemisorbed on the surface, while a "redox" equilibrium corresponds to the subsurface multilayer or to the bulk of the sample. With the gradual removal of oxygen the transition from chemisorption to the "redox" equilibrium should be expected. This may account for the great increase of oxygen adsorption heat—from 10 to 60 kcal/mole—which has frequently been observed.

The TPD experiments cited above also showed that if the samples formed thick layers considerable difficulties in outgassing them were observed. This would leave in question the purity of the gaseous and solid phases, especially in the case of layers that were some centimeters thick. The use of such large samples was the result of Boreskov's assumption, as stated above.

In view of what has been stated so far it may be appropriate at this point to formulate one or two general questions. Are pressure measurements of the chemisorption equilibrium an appropriate measure for determining the lattice oxygen bonding energy? And, which value from among the many possible values of oxygen pressure of bivariant equilibrium at a given temperature should be used to calculate the oxygen binding energy?

Activation and catalytic action of vanadia

catalysts cause considerable reduction of the oxide system, which may be described by the formula V_2O_{5-x}. Chemical analysis of such catalysts often showed $0.1 < x < 0.3$ and sometimes even more drastic reduction. In connection with this one may formulate further questions. Are the oxygen equilibrium pressures measured at very small values of x (see the table) an appropriate basis for characterizing vanadia catalysts? Would it not be more useful to use the oxygen pressure values referring to the greater x values, as they appeared in active catalysts?

It would seem that in the case where lattice oxygen participates in a catalytic process only the measurements of "redox" equilibrium pressure within the appropriate range of x can be the basis for determining oxygen bond energy. Proper experiments should be carried out after previous cleaning of a sample's surface and removal of chemisorbed oxygen.

Studies carried out in this manner (20, 21) have shown that the equilibrium

$$V_6O_{13} + O_2 = 3 V_2O_5 \qquad (1)$$
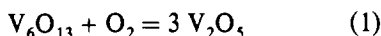
is reached. This is a univariant equilibrium because only one value of oxygen pressure at a given temperature is observed. This value of the equilibrium oxygen pressure is then a univocal parameter for determining the oxygen binding energy.

The enthalpy of reaction (1) obtained from the equilibrium pressure measurements is -63.5 kcal/mole of O_2 (21). The measurements were carried out on the V_2O_{5-x} oxide system which has been produced by thermal decomposition of NH_4VO_3. The V_2O_5 and V_6O_{13} phases formed spontaneously in the solid product decomposition. At high temperature equilibrium between them was reached.

This enthalpy is similar to the initial re-oxidation heat of the vanadia molybdena catalysts measured by Pankratyev and Tichy (24). Activation and work at steady state of catalytic acrolein oxidation caused the degree of the catalysts' reduction within the range of x mentioned above.

For $x < 0.02$ at $600°C$ the V_6O_{13} phase vanishes and consequently the oxygen pressure greatly increases with the subsequent decrease of x (20). The observed variation in oxygen pressure is characteristic of the solid solution of oxygen vacancies in the V_2O_5 lattice. This bivariant equilibrium can be obtained at an infinite number of values P for a given T. The majority of the measurements presented in the table refer to this equilibrium or even to the chemisorption one.

The thermodynamics of the V_2O_{5-x} oxide system are the subject of another paper (21).

References

1. J. MARS AND D. W. VAN KREVELEN, Chem. Eng. Sci. Suppl. 3, 41 (1954).
2. TH. VRBASKI AND W. K. MATHEWS, J. Catal. 5, 125 (1966).
3. K. HIROTA, Y. KERA, AND S. TERATANI, J. Phys. Chem. 72, 3133 (1968).
4. H. BACHMANN, F. R. AHMED, AND W. H. BARNES, Z. Krist. 115, 110 (1961).
5. E. GILLIS, Compt. Rend. 258, 4765 (1964).
6. L. FIERMANS AND J. VENNIK, Surface Sci. 9, 187 (1968).
7. G. L. SIMARD, Ind. Eng. Chem. 47, 1424 (1955).
8. G. K. BORESKOV, V. V. POPOVSKII, AND V. A. SAZONOV, "Proceedings, 4th International Congress on Catalysis (Moscow, 1968)," Vol. 1, p. 439, Akademiai Kiado, Budapest (1971).
9. W. M. SACHTLER, G. J. W. DORGELO, J. FAHRENFORT, AND R. J. H. VOORHOEVE, "Proceedings, 4th International Congress on Catalysis (Moscow, 1968)," Vol. 1, p. 454, Akademiai Kiado, Budapest (1971).
10. V. A. SAZONOV, V. V. POPOVSKII, AND G. K. BORESKOV, Kinetika i Kataliz 9, 307, 312 (1968).
11. G. K. BORESKOV, Kinetika i Kataliz 8, 1020 (1967); 14, 7 (1973).
12. V. A. ROITER, Kinetika i Kataliz 1, 63 (1960).
13. L. YA. MARGOLIS, "Geterogennoe Kataliticheskoe Okislenie Uglevodorov," p. 123, Izd. Khimiya, Leningrad (1967).
14. V. V. SPITZIN AND L. G. MAIDANOVSKAYA, Zh. Fiz. Khim. 33, 180 (1959).
15. YU. A. MISHTCHENKO, N. D. GOLDSTEIN, AND A. I. GELBSTEIN, Zh. Fiz. Khim. 47, 511 (1973).
16. V. I. MARSHNEVA, G. K. BORESKOV, AND V. D. SOKOLOVSKII, Kinetika i Kataliz 14, 210 (1973).
17. V. I. MARSHNEVA AND G. K. BORESKOV, Reaction Kinetics Catal. Lett. 1, 15 (1974).

18. F. Figueras, M. Forissier, L. de Mourgues, J. L. Portefaix, and M. Rossa-Brussin, *Kinetika i Kataliz* **14**, 25 (1973).

19. J. P. Joly, *J. Chem. Phys.* **72**, 1019 (1975).

20. R. Dziembaj and J. Piwowarczyk, *J. Solid State Chem.* **21**, 387 (1977).

21. R. Dziembaj, *J. Solid State Chem.* **26**, 159 (1978).

22. J. P. Joly, *J. Chim. Phys.* **72**, 1013 (1975).

23. R. Dziembaj, *Bull. Acad. Polon. Sci., Ser. Sci. Chim.* **24**, 965 (1976).

24. Yu. O. Pankratyev and J. Tichy, *Reaction Kinetics Catal. Lett.* **2**, 319 (1975).