EXCHANGE OF OXYGEN ATOMS BETWEEN GASEOUS OXYGEN AND CHROMIUM OXIDE CATALYST

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Introduction

Exchange reactions of solid oxides with gaseous oxygen and other gaseous oxygen-compounds have been studied from various view-points[1)2)] and many metallic oxides have been proved to be exchangeable with their oxygen atoms. In our recent researches[3)4)] where we studied the rates and the mechanisms of the catalytic exchange reaction of oxygen atoms between gaseous oxygen and water vapor in flow systems, we did not take into account the effect of these kinds of exchanges of oxygen atoms between reactants and oxide catalysts. As the quantity of reactants which we used in these experiments was much larger than the amount of catalyst used, this omission should not significantly affect the results of our researches. However, at this stage, verification of the possibility and of the extent of exchange of oxygen atoms between catalysts and gaseous reactants was needed to justify our postulate and to have some knowledge of the processes on the catalysts. This paper fills, in part, such requirements.

Experimental Method

The chromium oxide catalyst used is the same as that used in previous experiments.[3)] It consists of cylindrical pellets of 2 mm in both length and diameter, having a BET surface area of 33.1 m^2/g as determined by low-temperature nitrogen adsorption isotherm.

A glass tube, inside diameter 25 mm, in vertical position was used as the reactor and 21.6 g of the catalyst was packed at random to the height of 60 mm. The reactor was heated in fused tin metal-bath by an electrical heater with a regulator. All the experiments were carried out at 450° C. As pretreatment of the catalyst, standard oxygen gas (see below) was forced at a rate of 21.0 cc (S.C.)/min through the reactor for 15 hrs at 470° C followed by one hour at 450° C and then purified nitrogen gas was introduced at the same rate for 3 hrs at 450° C. Continuing this pretreatment, oxygen gas sample enriched in heavy oxygen content was forced through at a rate of 14.0 cc (S.C.)/min. The oxygen from the reactor was introduced over charcoal in a quartz tube heated to red heat. Carbon dioxide formed was condensed at intervals by cooling with liquid air and then evaporated into gas samplers for mass-spectrometric analysis.

Two kinds of oxygen samples (I and II) were prepared from heavy-oxygen waters obtained by fractional distillation. Their concentration in heavy oxygen was determined by combining the gaseous samples with standard hydrogen and

converting to waters. Using the temperature-float method we measured the excess densities of the waters by comparing them with normal water. The relative concentrations of O^{17} and O^{18} were calculated from their concentrations in normal water and from the relative volatilities of H_2O^{17} and H_2O^{18} each compared with H_2O^{16}. They were 4.8 γ and 109.4 γ for Sample-I and 5.9 γ and 141.8 γ for Sample-II in terms of excess density of water compared with normal water.

Oxygen in cylinder was used as the standard oxygen gas. The excess concentration in O^{18} was 10.0 γ. Carbon dioxide in cylinder was also used as standard. The excess concentration in O^{18} was 8.2 γ.

Mass-spectrometric measurements were done with Hitachi Type-RM-A Mass-spectrometer, adapted to a variable scanning speed and range system by condenser charge-up method, at Nihon Oil and Fat Co. Ltd., Taketoyo. Operational conditions were: Ion accelerating voltage 730 V, total emission 200 μA, impact electron voltage 100 V. All the measurements were done by converting oxygen into carbon dioxide. The height of peak of mass-46 from the deflection of high-sensitive galvanometer was compared with the height of peak of mass-44 from the deflection of low sensitive galvanometer. Sensitivity and reproducibility were sufficient for even such relative low concentrations of heavy oxygen in samples mentioned above, as shown by the following measurements.

Sensitivity of Mass-Spectrometer

1. Sample-I was compared with standard carbon dioxide. Heights of peaks in cm were

Mass	46	44	Ratio 46/44
Sample-I	0.312	4.807	0.0649
Standard carbon dioxide	0.245	5.341	0.0459

Therefore based on the mass-spectrometric data, the ratio of O^{18} concentration in Sample-I to that in standard carbon dioxide was

$$0.0649/0.0459 = 1.41_4$$

This ratio can also be calculated from the excess density from temperature-float method noted above, i.e.

$$(109.4 + 224.7)/(8.2 + 224.7) = 1.435$$

Here 224.7 γ is O^{18} concentration of normal water.[5] Coincidence of the two results, one from mass-spectrometric and the other from densitometric, is good for the relative low concentration of O^{18}. The difference between the two results corresponds to $(0.021/0.42) \times 100 = 5\%$ of the excess density (109.4 γ) of the Sample I compared to normal water, and this is about 5 γ.

2. Sample-II was compared with standard oxygen gas. Heights of peaks in cm were

Mass	46	44	Ratio 46/44	Mean
Sample-II	0.665	5.093	0.1306	0.1338
	0.670	5.025	0.1333	
	0.668	4.890	0.1366	
	0.670	4.968	0.1349	
Standard Oxygen	0.476	5.574	0.0854	0.0868
	0.481	5.458	0.0881	

The probable error or reproducibility limit of the ratio 46/44 from mass-spectrometric method is about 1.5%, which corresponds to about 5 γ error in O^{18} concentration which is of the same order as in the first experiment. The ratio of O^{18} concentration in Sample-II to that of standard oxygen gas is

$$0.1338/0.0868 = 1.54_1$$

This ratio is to be compared with the ratio from densitometric values, i.e.

$$(141.8 + 224.7)/(10.0 + 224.7) = 1.562$$

The difference between them is also of the same order, and mass-spectrometric values are always somewhat smaller than densitometric values.

Results and Discussion

Results are tabulated in Table 1, where t is the time of sampling from the first appearance of carbon dioxide at the outlet of the reactor, ϕ_t is the mass-spectrometric ratio 46/44 in the sampled oxygen at time t, and x is the fractional conversion given by

$$x = (\phi_o - \phi_t)/(\phi_o - \phi_s) \tag{1}$$

Here ϕ_o is the value of ϕ of heavy-oxygen sample, and ϕ_s is that of standard oxygen and is assumed to be equal to the original value of ϕ of the oxygen of the oxide catalyst.[6] With the object of finding the functional relation between x and t, we set it tentatively as logarithmic, i.e.

$$\log x = a + bt$$

TABLE 1

t in min	ϕ_t	x
5	0.1116	0.472
7	0.1189	0.316
11	0.1152	0.395
14	0.1197	0.300
26	0.1202	0.289
40	0.1289	0.104
110	0.1292	0.097

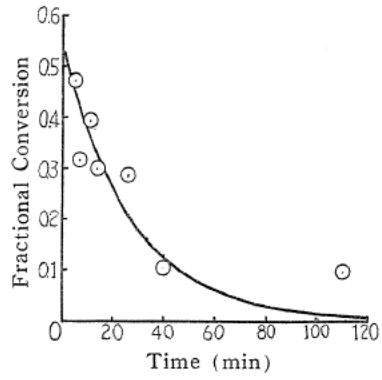

FIG. 1

Inserting experimental values of Table 1 into this relation, the values of constants a and b were determined as

$$a = -0.278, \qquad b = -0.0156$$

and therefore

$$x = 0.527(0.965)^t \tag{2}$$

This relation well represents experimental values as shown in Figure 1.

The net number of atoms of O^{18} transferred from flowing gaseous oxygen to catalyst in an infinitesimal time dt is given from material balance by

$$(u_o - u_t)\,F dt$$

where u_o and u_t are respectively the fractional concentrations of O^{18} in the flowing gaseous oxygen at the inlet and outlet of the reactor, and F is the flow rate of gaseous oxygen in atoms per unit time. This number divided by $(u_\cdot - u_{st})\,dt$, where u_{st} is the average fractional concentration of O^{18} of the catalyst at time t, gives from probability consideration[3] the total number of exchange of oxygen atoms between flowing gaseous oxygen and catalyst per unit time, assuming no isotopic effect. This rate, denoted as R, is constant during the exchange reaction. Then the value of x extrapolated to time zero, i.e. $x = 0.527$ from Eq. (2), multiplied by F gives R because we have the relation

$$\frac{u_o - u_{t=0}}{u_o - u_{so}} F = \frac{\phi_o - \phi_{t=0}}{\phi_o - \phi_s} F = x_{t=0} F$$

The feed rate 14.0 cc (S.C.)/min gives $F = 1.25(10)^{19}$ atoms/sec. Then

$$R = 6.6(10)^{15} \text{ atoms/sec.}$$

This rate is divided by the total volume of catalyst bed 29.4 cc, or by the total area of the catalyst $7.15(10)^6$ cm^2, then

$$\begin{aligned} R &= 2.24(10)^{17} \text{ atoms/sec·cc of catalyst bed} \\ &= 9.2(10)^{11} \text{ atoms/sec·cm}^2 \end{aligned}$$

In the earlier research,[3] done with the same catalyst (chromium oxide) at the same temperature (450° C) and in the same volume of catalyst bed (25 mm dia., 60 mm height) as this research, the rate of exchange of oxygen atoms between gaseous oxygen and water vapor was $3.28(10)^{17}$ and $2.10(10)^{17}$ atoms/sec·cc, differing in flow rate of reactants. The coincidence between these rates and the rate obtained above is rather striking.

Finally, the number of oxygen atoms of the catalyst exchangeable with flowing gaseous oxygen was calculated by the method described in an ealier paper.[7] By assuming constancy of the number of the exchangeable oxygen atoms of the catalyst and assuming complete serial mixings of oxygen atoms with each part of flowing gaseous oxygen, the mean of the fractional decrease of concentration of O^{18} in the gaseous oxygen after reaction from time zero to t is given by

$$(M/N)\,[1 - \exp(-N/M)]$$

where M is the number of exchangeable oxygen atoms of the catalyst and N is the total number of oxygen atoms of gaseous oxygen flowed during the time t. This quantity is equal to the mean value of x from time zero to t i.e.

$$\bar{x} = \left(0.527\int_0^t 0.965^t\,dt\right)/t = 14.7_7(1-0.965^t)/t$$

Calculated values are tabulated in Table 2.

TABLE 2

t in min	$\bar{x}$	N/M	$N(10)^{-22}$	$M(10)^{-21}$
5	0.484	1.68	0.375	2.23
20	0.378	2.39	1.50	6.27
50	0.246	4.00	3.75	9.38
100	0.144	6.98	7.50	10.72
∞	0	∞	∞	11.08

Inconstancy of the calculated values of M means that the two assumptions made above do not hold. First, the constancy of M is incorrect because there is diffusion of O^{18} into the bulk of catalyst, and secondly the exchange of oxygen atoms between gaseous oxygen and catalyst, even if confines to the easily exchangeable oxygen on the surface, will be neither complete nor homogeneous. However, these incorrectnesses will become smaller as t becomes larger, because the diffusion will becomes more difficult as it proceeds and because the surface concentration of O^{18} will approach homogeneity as it approaches equilibrium with gaseous oxygen. Formally, values of M calculated by the above method converge to a definite value for large value of t. For large value of t, where N is also large, above calculation gives

$$\lim_{t\to\infty} M = (14.77/t)(Ft)$$
$$= (14.77)(7.50)(10)^{20} = 1.108(10)^{22}$$

where $F = 7.50(10)^{20}$ atoms/min. This limiting value should not be much different from the number of atoms of catalyst easily exchangeable with gaseous oxygen. This value corresponds to $1.55(10)^{15}$ atoms/cm^2. If we assume that one oxygen atom on the surface of chromium oxide occupies 6.8 A^2 as closed packed oxide ion, then the number of oxygen ion is $1.47(10)^{15}$ atoms/cm^2. Thus, if we consider that all the surface of the catalyst is covered with chromium oxide, the number of exchangeable oxygen atoms corresponds to just one layer of the catalyst and if we consider the catalyst as a homogeneous mixture of chromium oxide and kaolin of 1 : 3, the number of exchangeable oxygen atoms corresponds to two layers of the catalyst.

The total amount of exchangeable oxygen obtained above is relatively so small that the oxygen atoms of catalyst will not give any serious effect on the results obtained in the exchange reactions of oxygen atoms between gaseous oxygen and water vapor catalyzed by chromium oxide. In those catalytic exchange reactions, catalyst was pretreated with reacting gaseous mixture for several ten-minute periods before each experiment and subsequently, the reaction was conducted with high

feed rate of reacting gases, i.e. about 60 cc(S.C.)/min. These conditions will minimize the effect of exchange between reactants and catalyst.

Under a small flow rate of reacting gaseous oxygen as applied here the apparent rate of reaction may be influenced by the mixing effect in the gaseous phase, and the true rate may be somewhat larger than the rate observed.[3] However, this effect does not change greatly the rate and the coincidence of the observed rate of the exchange reaction of oxygen atoms between chromium oxide catalyst and gaseous oxygen with that between gaseous oxygen and water vapor catalyzed by chromium oxide supports our conclusion on the mechanism of the catalytic exchange reaction.[4]

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