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REDUCTION-OXIDATION MECHANISM OF OXIDE CATALYSTS.
OXYGEN DIFFUSION DURING REDOX CYCLES

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A new method was developed to determine under the conditions close to the reaction conditions whether or not the redox cycle of bulk metal oxide proceeds by the diffusion of lattice oxygen, and was applied to two examples; γ-Fe_2O_3 and $La_{0.8}Sr_{0.2}CoO_3$. It has been demonstrated that iron in stead of oxygen diffuses rapidly with γ-Fe_2O_3 and oxygen rapidly diffuses with $La_{0.8}Sr_{0.2}CoO_3$.

Direct involvement of lattice oxygen has been pointed out for several metal oxides in the selective oxidation of olefins.$^{1)}$ In some cases,$^{2)}$ rapid migration of lattice oxygen seems prime factor of the selective oxidation, in which metal oxides are subjected to rapid reduction-oxidation cycles. Therefore, the reduction-oxidation mechanism of bulk metal oxide may be very important in relation to the catalytic activity and selectivity. We have developed a new method which is able to determine whether or not the rapid redox cycles are made possible by the rapid diffusion of lattice oxygen. It is advantageous that this method is applied under the conditions close to the reaction conditions and to fine particle samples. Two examples of application will be reported here; γ-Fe_2O_3 and $La_{0.8}Sr_{0.2}CoO_3$.

We previously found high selectivity and activity of γ-Fe_2O_3 for oxidative dehydrogenation and suggested that diffusion of lattice oxygen does not accompany the redox cycles, but that iron ion migrates.$^{3)}$ By the present method, the suggested mechanism was confirmed. Another example is $La_{0.8}Sr_{0.2}CoO_3$, a perovskite-type mixed oxide, which was shown to be a good oxidation catalyst.$^{4)}$

Method and Procedure. In this method, a sample of metal oxide is first partially reduced (pre-reduction, A→B in Fig. 1), and then re-oxidized by $^{18}O_2$ to the initial oxidation state (re-oxidation, B→C in Fig. 1). It is important in this

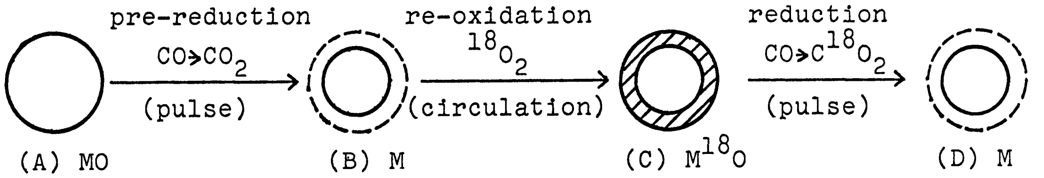

Fig. 1. Schematic description of the procedure.
Changes of one sample particle are schematically drawn. Shaded area is the layer formed by re-oxidation, which is eliminated by reduction.

method to confirm the structure of metal oxide before and after reduction or re-oxidation. When this ^{18}O-labelled metal oxide, $M^{18}O$, is gradually reduced by CO with the procedure mentioned below (reduction, C→D in Fig. 1), ^{18}O recovery, which is defined as

$$\frac{2\times[^{18}O\ \%\ \text{in}\ CO_2\ \text{produced during the reduction by CO}]}{^{18}O\ \%\ \text{in}\ O_2\ \text{used for the re-oxidation}}$$

is expected to be as follows, depending on the rate of oxygen diffusion. (1) If lattice oxygen does not migrate at all during $^{18}O_2$ re-oxidation and the subsequent CO reduction, ^{18}O should be uniformly contained only in the surface layer formed by the re-oxidation, the ^{18}O content being identical to that in $^{18}O_2$ used for the re-oxidation. Therefore, differential ^{18}O recovery, which is defined as the ^{18}O recovery for small increment of CO reduction, should be 100% until the $M^{18}O$ is reduced to the state of the pre-reduction, and null on further reduction (Fig. 2, full line). (2) If lattice oxygen diffuses very rapidly (complete mixing of lattice oxygens), the differential ^{18}O recovery is constant and is equal to the amount determined by the reaction stoichiometry and experimental conditions: 11% for γ-Fe_2O_3 and 16% for $La_{0.8}Sr_{0.2}CoO_3$ (Fig. 2, broken line). Thus the ^{18}O recovery reflects the change in the ^{18}O concentration from the surface to the center and, therefore, the rate of diffusion of oxide ion.

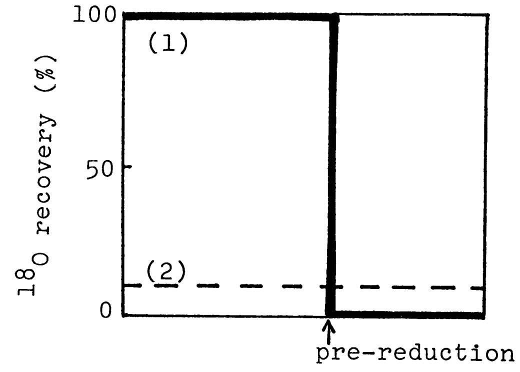

Fig. 2. ^{18}O recovery (differential) for the process C→D in Fig. 1 for two extreme cases.
(1) no oxygen diffusion,
(2) rapid oxygen diffusion.

α-Fe_2O_3 (BET surface area, 10 m^2g^{-1}) was prepared from $Fe(NO_3)$.[3)] $La_{0.8}Sr_{0.2}CoO_3$ (BET surface area, 4.3 m^2g^{-1}) was prepared from acetates of La, Sr, and Co, and finally calcined at 850°C. The structure of $La_{0.8}Sr_{0.2}CoO_3$ was confirmed by X-ray powder diffraction analysis to have perovskite structure.[4)]

Metal oxide catalyst (MO) charged in the reactor was reduced by CO pulses after standard O_2 treatment at 300°C in the pulse system. The extent of reduction of metal oxide was determined by GC analysis of the amount of CO_2 formed or CO converted. The reactor which contained this reduced catalyst (M) was removed from the pulse system and attached to the closed circulation system without exposing the oxide to the air. Then, re-oxidation by $^{18}O_2$ (^{18}O: 70 atom %) was carried out to prepare ^{18}O labelled metal oxide ($M^{18}O$) at 200°C for γ-Fe_2O_3 and 300°C for $La_{0.8}Sr_{0.2}CoO_3$, respectively. This $M^{18}O$ was reduced incrementally by CO pulses to recover ^{18}O into CO_2 again in the pulse system at 300°C. $C^{18}O_2$ produced was collected with a trap kept at liquid-nitrogen temperature and its ^{18}O content was analyzed with the aid of a mass spectrometer as a function of the extent of reduction. During this redox cycle, stoichiometry of reduction and oxidation agreed very well. The reason why CO reduction was carried out with a pulse system is that CO reduction of iron oxide in a closed circulation system leads to partial formation of Fe metal and Fe carbide.

<u>γ-Fe_2O_3</u> γ-$Fe_2{}^{18}O_3$ was prepared by reducing α-Fe_2O_3 to Fe_3O_4(x=0.33, Fe_2O_{3-x})

with CO pulses, followed by re-oxidation with $^{18}O_2$. With a pulse system, the reduction and subsequent re-oxidation of

$$\alpha\text{-}Fe_2O_3 \xrightarrow{CO} Fe_3O_4 \xrightarrow{O_2} \gamma\text{-}Fe_2O_3$$

was confirmed at each step by the stoichiometry and also by the X-ray powder diffraction and Mössbauer spectroscopy.3) Formation of Fe_3O_4 after reduction of γ-Fe_2O_3 was also confirmed by X-ray powder diffraction. BET surface area little changed by the redox cycle. The ^{18}O content of O_2 in the gas phase for re-oxidation did not vary before and after re-oxidation. The results are shown in Fig. 3-a, where the differential ^{18}O recovery for the reduction (C → D in Fig. 1) is given. The ^{18}O recovery was 91% at the extent of reduction of x=0.25 and after then decreased to 49% at x=0.33 (Fe_3O_4). The mobility of lattice oxygen seems to increase slightly with the increasing extent of reduction. However, total ^{18}O recovered by the reduction of γ-Fe_2O_3 to Fe_3O_4 was 82% (83% after correction for the oxygen isotope exchange between CO_2

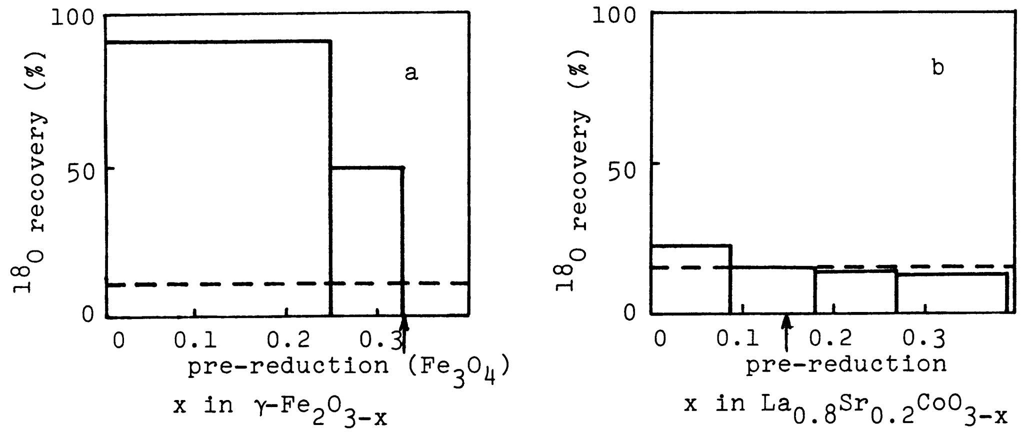

Fig. 3. ^{18}O recovery (differential) for the process C→D in Fig. 1.
a: γ-Fe_2O_3, b: $La_{0.8}Sr_{0.2}CoO_3$
----; expected for the case of complete mixing of lattice oxygen

produced and iron oxide), which is very high as compared with that expected for complete mixing of lattice oxygen (11%). This result demonstrates that the redox cycle of γ-Fe_2O_3 bulk proceeds by the migration of Fe ion instead of lattice oxygen. If one takes into account the fact that γ-Fe_2O_3 has a spinel structure with cation vacancies and the packing structure of oxide ion is identical to that of Fe_3O_4, it seems very probable that the redox cycle between γ-Fe_2O_3 and Fe_3O_4 proceeds by the elimination and addition of oxide layer on the surface accompanied by the migration of Fe ion through the cation vacancy to compensate the charge. This rapid diffusion of Fe ion makes the redox cycle easy. The very slow diffusion of oxygen is in accordance with the fact that the amount of lattice oxygen of γ-Fe_2O_3 participating in CO oxidation or oxygen isotope exchange with CO_2 is at most less than one surface layer.5)

$La_{0.8}Sr_{0.2}CoO_3$ Fig. 3-b shows the results of $La_{0.8}Sr_{0.2}CoO_3$. The X-ray powder diffraction pattern and BET surface area of $La_{0.8}Sr_{0.2}CoO_3$ did not change in the redox cycle. In re-oxidation step, oxygen isotope exchange between gaseous O_2 and catalyst occurred considerably, as the ^{18}O content in O_2 decreased from 71 to 18%. The ^{18}O recovery was about 20% until $La_{0.8}Sr_{0.2}CoO_3$ was reduced to the state of pre-reduction. On further reduction the differential ^{18}O recovery was 12-15%, as shown in Fig. 3-b. Since, in the absence of oxygen diffusion, $La_{0.8}Sr_{0.2}CoO_3$ must contain ^{18}O only in 6.5 surface layers (100% relative to the ^{18}O content of O_2 used for re-oxidation), this low ^{18}O recovery shows high mobility of lattice oxygen in this mixed oxide at 300°C. The mobility of lattice oxygen in $La_{0.8}Sr_{0.2}CoO_3$ was so high as to mix nearly completely, and was much higher than γ-Fe_2O_3. Although the mobility of cation in $La_{0.8}Sr_{0.2}CoO_3$ can not be estimated by the present method, it is very probable that rapid diffusion of lattice oxygen makes the redox cycle very easy.

It has been demonstrated with the present method that the rapid redox cycle of γ-Fe_2O_3 bulk proceeds through the migration of Fe ion instead of lattice oxygen, and with $La_{0.8}Sr_{0.2}CoO_3$, in contrast to γ-Fe_2O_3, rapid diffusion of lattice oxygen accompanies the redox cycle. Although the re-oxidation temperature was lower for iron oxide, this difference does not seem to affect much the ^{18}O recovery of iron oxide. High ^{18}O recovery of about 70% was also obtained for iron oxide, even when re-oxidation temperature was 300°C. In this experiments the reduction by CO was carried out in a circulation system, so that partial reduction to iron metal or carbide took place and should have lowered the ^{18}O recovery. Therefore, the contrast in redox mechanism between γ-Fe_2O_3 and $La_{0.8}Sr_{0.2}CoO_3$ must be intrinsic.

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