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CATALYTIC ACTIVITY PATTERNS AND REDOX PROPERTIES OF $H_3PMo_{12}O_{40}$ AND ITS ALKALI SALTS

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Redox processes (reductions by H_2 and CO, and reoxidation by O_2) over $M_xH_{3-x}PMo_{12}O_{40}$ (x=0-3, M=Na, Cs) were classified into two groups. This classification was important in catalytic oxidations of H_2 and CO, which proceeded by redox mechanism.

We reported previously that oxidation reactions (not catalytic) by heteropoly compounds were divided into two groups.[1)] In the first group (oxidative dehydrogenation), bulk polyanions take part through rapid migration of protons and electrons. In the second group (oxygen-addition reaction), polyanions only near the surface are utilized due to slow diffusion of oxygen. In this letter, we report experimental facts which confirm the existence of the two processes and wish to demonstrate the importance of this concept in catalytic oxidations which proceed by redox mechanism.

$M_xH_{3-x}PMo_{12}O_{40}$ (x=0-3, M=Na, Cs), which will be abbreviated as PMo_{12} (x=0) and M_xPMo_{12} ($x \neq 0$), were prepared as described before.[1-3)] The reduction and reoxidation of the catalysts and catalytic oxidation of H_2 and CO were carried out by use of a closed circulation system (ca. 250 cm^3). The standard pretreatment was as follows; the catalysts (500 mg) were treated at 350 °C for 2 h in circulating O_2 (50 Torr; 1 Torr=133.3 Pa) with a dry ice-ethanol trap. Then the catalysts were evacuated for 5 min, and reduced by H_2 or CO at 350 °C. After the reduction, the reduced catalysts were evacuated for 5 min and then reoxidized by O_2. Initial pressures were about 100 Torr for H_2 and CO, and 50 Torr for O_2. The rates of the reactions were measured by the pressure decrease, where H_2O was condensed by a liquid nitrogen trap or a dry ice-ethanol trap and CO_2 was condensed by a liquid nitrogen trap. The rates of H_2-reduction, CO-reduction and O_2-reoxidation will be abbreviated as $r(H_2)$, r(CO), and $r(O_2)$, respectively. In the catalytic oxidation, after the standard pretreatment, H_2-O_2 or CO-O_2 mixture (98 and 50 Torr) was introduced and the pressure decrease was followed, H_2O or CO_2 being trapped.

Figure 1 shows the time course of reductions of PMo_{12} by H_2 and CO, and its reoxidation by O_2. The anion was prereduced on average by H_2 by 1 electron/anion. At the dotted lines in Fig. 1, reoxidation was interrupted, by evacuating the system and keeping the sample in a vacuum for 3 h. After the interruption, $r(O_2)$ was measured again. It was noted that r(O_2) became more than ten times greater than that just before the interruption (line 1 in Fig. 1). Similar increase was observed in the reduction step by CO (line 2). In contrast, no change of the rate was observed in the reduction by H_2 (line 3). This contrast observed in the effect of interruption confirms the idea$^{1,2)}$ that redox processes are divided into two groups, and is explained as follows. In the case of reduction by CO and reoxidation by O_2, polyanions only near the surface are mainly involved in the reactions, because the diffusion of oxygen which is necessary for polyanions in the bulk to take part is slow. In this case, during the period of interruption, the surface anions were reoxidized by the polyanions in the bulk through the migration of oxide ion, so that r(CO) and r(O_2) after the interruption became much greater. In contrast, bulk polyanions can be used in the case of H_2-reduction, since oxygen diffusion is not necessary and rapid migration of proton and electron into the bulk keeps the oxidation state of the surface polyanions high. In other words, whole anions were reduced more or less homogeneously, so that the interruption did not affect r(H_2) as shown in Fig. 1. The existence of two redox processes (r(CO), r(O_2), vs. r(H_2)) is further confirmed by the contrast observed in the dependencies of r(H_2) and r(CO) on the alkali contents. The contrast was the same as found between the reactions of isobutyric acid and methacrolein.$^{1)}$ Faster decrease of r(CO) than r(H_2) with increasing extent of reduction is also consistent with the above idea.

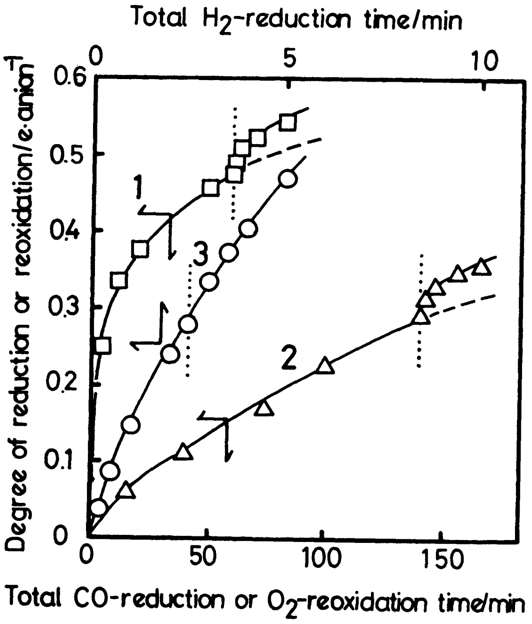

Fig. 1. Reductions of $H_3PMo_{12}O_{40}$ by H_2 (line 3) and CO (line 2), and its reoxidation by O_2 (line 1) at 350 °C.
At the dotted line reduction or reoxidation was interrupted (see text). This period is not included in the reduction or reoxidation time given on the abscissa. Broken lines indicate time course without above treatment.

Figure 2 shows the relative rates of catalytic oxidation of H_2 to H_2O and CO to CO_2 over $M_xH_{3-x}PMo_{12}O_{40}$ at 350 °C. The rates over PMo_{12} are taken as unity. The rate of catalytic oxidation of H_2 normalized to catalyst weight decreased monotonously with the alkali content except for an increase with $Cs_{2.85}PMo_{12}$ (Fig. 2a). However, in the case of catalytic CO-oxidation, there is no simple or monotonous relationship between the rate and the amount of alkali (Fig. 2b). Moreover, the rate over Na_2PMo_{12} varied from one catalyst lot to another, while the rate of

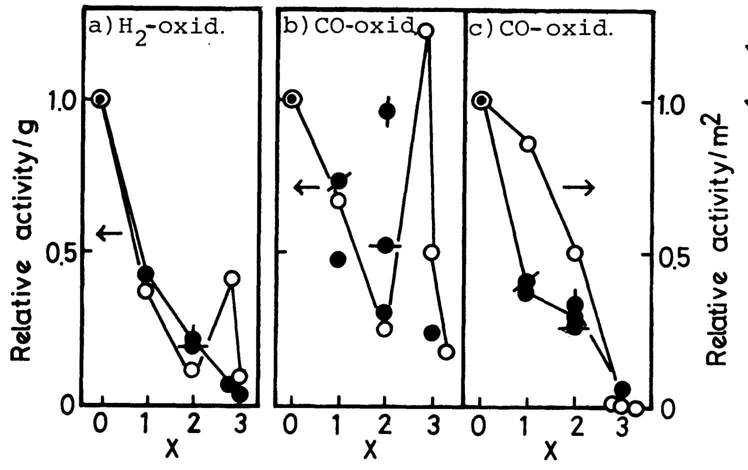

Fig. 2. Relative rates of catalytic oxidations of H_2 and CO over $Cs_xH_{3-x}PMo_{12}O_{40}$ (○) and $Na_xH_{3-x}PMo_{12}O_{40}$ (● ; flags attached indicate different lots) at 350 °C.

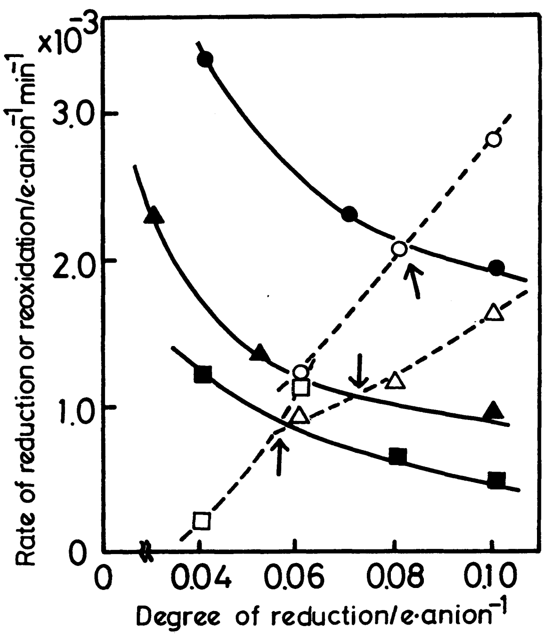

Fig. 3. Rates of reduction by CO (solid line) and reoxidation by O_2 (broken line) as a function of degree of reduction (350 °C).

(●,○): PMo_{12}, (▲,△): Cs_1PMo_{12}, (■,□): Cs_2PMo_{12}. Reoxidation was carried out for the samples which had been prereduced by 0.3 e/anion except for Cs_2PMo_{12} (0.13 e/anion).

H_2-oxidation little varied. In Fig. 2c, the rates are normalized to the surface area of each catalyst and replotted against x. In this case, the scattered data for Na_1PMo_{12} and Na_2-PMo_{12} agreed respectively, showing that the rates were proportional to the surface area, and the rates decreased monotonously as in Fig. 2a. This indicates that in the catalytic oxidation of CO the number of surface polyanions is an important factor besides the oxidizing ability of each polyanion, while the latter which seems to decrease with x is predominant in the catalytic oxidation of H_2. Reoxidation rates probably differ significantly depending on the surface area also in the catalytic oxidation of H_2, but owing to the fact that the reduction rates were little depending on the surface area, the crosspoints in Fig. 3 (see below) did not change much. These trends are in good agreement with those found for non-catalytic reactions, that is, $r(H_2)$$^{2)}$, r(CO) in the present work, and also reductions by isobutyric acid and methacrolein.$^{1)}$ Thus, the classification of redox processes into two groups is an important concept not only in the stoichiometric redox reactions,$^{1,2)}$ but also in catalytic oxidations. Greater rate observed for $Cs_{2.85}PMo_{12}$ is likely due to its very high surface area. The effect was much greater for $r(O_2)$ and CO-oxidation than $r(H_2)$, as expected.

Since the redox processes are closely related to the catalytic oxidation, rates of redox processes measured in the present work ($r(H_2)$, r(CO), and $r(O_2)$) may explain the rates of catalytic oxidations (r(cat)). The oxidation reactions proceeded at

Table 1. Rates of Catalytic Oxidation of CO and the Degrees of Reduction at the Stationary State (350 °C)

		PMo_{12}	Cs_1PMo_{12}	Cs_2PMo_{12}	$Cs_{2.85}PMo_{12}$	Cs_3PMo_{12}
r(cat)[a]		2.4×10^{-3}	1.6×10^{-3}	6.0×10^{-4}	2.9×10^{-3}	1.2×10^{-3}
r=r(CO)=r(O_2)[a]		2.1×10^{-3}	1.1×10^{-3}	9.0×10^{-4}	3.1×10^{-3}	–
Degree of reduction ($e \cdot anion^{-1}$)	obsd[b]	0.038	0.064	0.065	0.050	0.054
	calcd[c]	0.081	0.072	0.057	0.043	–

a) electrons·anion^{-1}min^{-1}. b) Experimental. c) Crosspoints in Fig. 3.

nearly constant rates for a prolonged period due to small pressure changes, after an initial rapid reduction of catalyst to a stationary oxidation state. So we regard these states as stationary states in the present work. In Fig. 3, r(CO) and r(O_2), which were calculated from the slopes of the pressure vs. time curves of reduction and reoxidation as in Fig. 1, are plotted against the degree of reduction of catalyst. If the catalytic oxidation proceeds by the repetition of reduction and reoxidation of catalyst, namely "redox mechanism", r(cat), to the first approximation, agrees with the rate at the crosspoints of reduction and reoxidation curves in Fig. 3 (r=r(CO)=r(O_2)).

r(cat) and r=r(CO)=r(O_2) are summarized in Table 1. The two values agreed well, although the surface and bulk were not in the same oxidation states in the measurements of r(CO). The degrees of reduction of catalysts were measured by reversible reoxidation after the stationary state of catalytic oxidation was attained, and compared with those estimated from the crosspoints in Fig. 3 (abscissa). The agreement was good as well. Therefore, it may be concluded that the catalytic oxidation of CO over alkali salts of 12-molybdophosphoric acid proceeded by the redox mechanism. This conclusion was confirmed by the fact that r(CO) and r(O_2) of Cs_2PMo_{12}, which were measured after the catalyst attained stationary oxidation state (reduced homogeneously by 0.065 e/anion), almost agreed with each other and were close to r(cat). Redox mechanism has previously been suggested by Niiyama et al.[4] for heteropoly compounds to explain the effect of Ag^+ and Cu^{2+}.

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