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REDUCTION MECHANISM OF 12-MOLYBDO- AND 12-TUNGSTOPHOSPHORIC ACIDS IN THE SOLID STATE

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On the basis of the temperature programmed reduction (TPR) by hydrogen and infrared spectral changes during reversible reduction-oxidation cycle, it was concluded that 12-molybdophosphoric acid in the solid state is reduced in two steps: $H_2 \rightarrow 2H^+ + 2e \rightarrow H_2O$. Reducibility of heteropoly acids measured by TPR exhibited fair correlation with their catalytic activity for methacrolein oxidation.

Temperature programmed reduction (TPR) is the method which measures the reduction rate of a catalyst sample as a function of the temperature. The temperature is usually raised at a constant rate in the presence of a reducing agent like hydrogen. TPR has already been applied to the study of molybdenum catalysts and the relationship between the reducibility and the catalytic activity for oxidation reactions has been discussed.

Although quite a few studies have been reported on the reduction process and the structure of reduced products of heteropoly acids in solution,1) little is known for solid state. In this communication, we wish to report novel TPR results which together with IR measurement clarify the important aspect of the reduction-oxidation mechanism of 12-molybdo- and tungstophosphoric acids. To examine the relationship between the catalytic activity for oxidation and the reducibility of catalyst (in other words, oxidizing power) was also one of our aims. TPR method using hydrogen was applied to 12-molybdophosphoric acid and its salts by Niiyama et al.,2) and the role of counter cations in the activation of hydrogen molecule was pointed out.

Experimental procedures are as follows. Method [1-a]: The catalyst pretreated in the O_2 stream (60 ml min^{-1}) at 200°C for 1h was kept in the stream of H_2(10%)-N_2(balance) (flow rate: 60 ml min^{-1}) at room temperature to attain a stationary state (usually within 30 min). Then the temperature was raised at a constant rate (2°C min^{-1}) and hydrogen uptake was detected by use of a thermal conductivity cell. Method [1-b]: Procedure is the same as [1-a], except that a quadrupole mass spectrometer (NEVA NAG-531) was used for the detection of both the uptake of H_2 and the evolution of H_2O. Method [2]: Hydrogen uptake was measured at room temperature by the pressure decrease using a closed circulation system. 12-Molybdophosphoric acid (abbreviated as PMo_{12}), 12-tungstophosphoric acid (PW_{12}), and 6-molybdo-6-tungstophosphoric acid (PMo_6W_6) were prepared as before following the literature.[3] Pd-Carbon (Pd-C, Pd:5 wt%, Nippon Engelhard Inc.) was mechanically mixed with catalysts in an agate pestle and mortar. The Pd-C content was 10% to the sample.

TPR profiles obtained by means of the method [1-a] are shown in Fig. 1. Solid lines show TPR for catalysts without Pd-C. Hydrogen uptake was observed only at high temperatures which were close to the decomposition temperature of heteropoly acids. This is probably because these catalysts have little ability of hydrogen activation. When the Pd-catalyst was mixed with these compounds to accelerate the activation of H_2 and to supply atomic hydrogen, it became possible to reduce PMo_{12} and PMo_6W_6 at low temperatures (broken lines in Fig. 1) as found for MoO_3 and PMo_{12} previously.[4,5] The temperature (Ts) at which the reduction rate of Pd-C mixed heteropoly acids reaches 2 μmol min^{-1} $g\text{-}cat^{-1}$, exhibited fair correlation with the catalytic activity for methacrolein oxidation[6] and the redox potential measured in aqueous solution.[7] For example, the order of the catalytic activity was $PW_{12} \ll PMo_6W_6 < PMo_{12}$ and redox potentials are $PW_{12} < PMo_6W_6 \approx PMo_{12}$, Ts being the reverse order: $PMo_{12} \leq PMo_6W_6 \ll PW_{12}$.

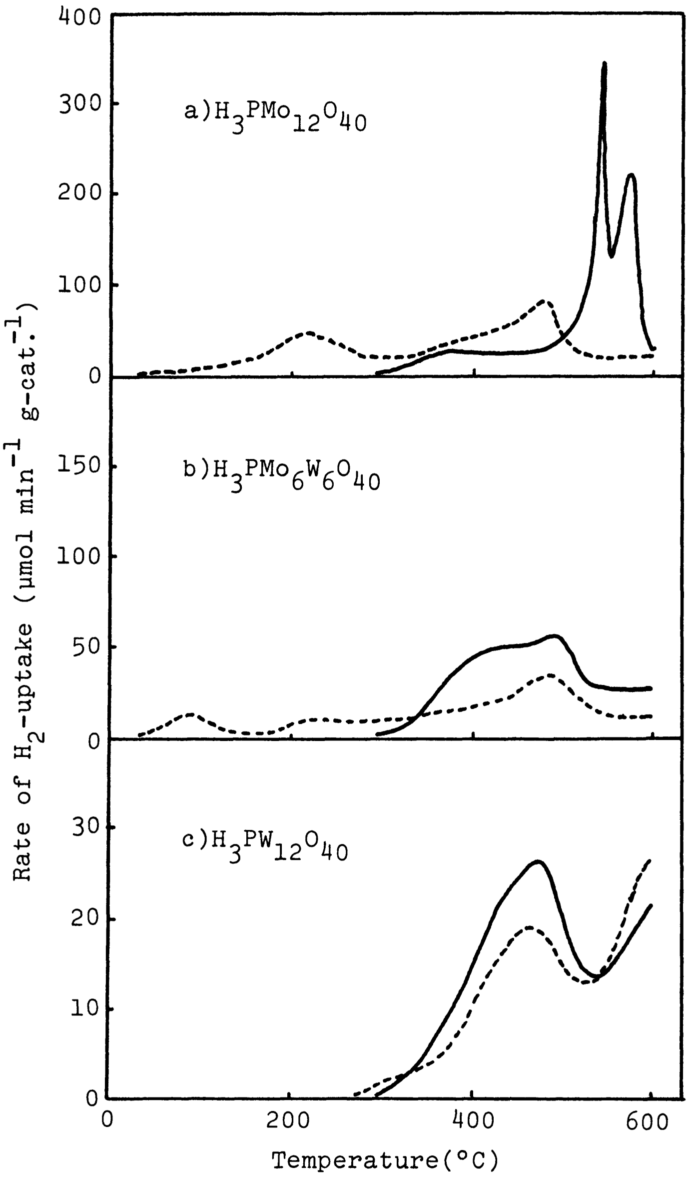


FIG. 1 TPR PROFILES
Cat.:500mg, Pd-C:50mg, β=2°C min^{-1}
10%H_2 in N_2:60ml min^{-1}
—— :Heteropoly acid (HPA) only
---- :HPA+Pd-C ground together

The hydrogen uptake was observed even at room temperature in the cases of PMo_{12} and PMo_6W_6 mixed with Pd-C when measured by the method [2]. About 3∼4 molecules of H_2 per Keggin unit were absorbed in 1h by these compounds pre-evacuated at 25°C. The rate and the amount of hydrogen uptake changed considerably depending on the water content of catalyst. For example, addition of water vapor (5∼10 mg) into the circulation system remarkably accelerated the rate of hydrogen uptake.

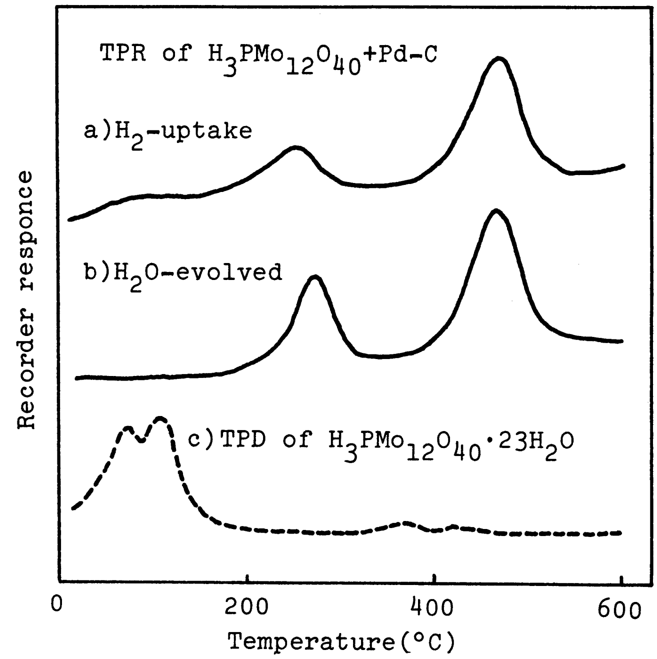
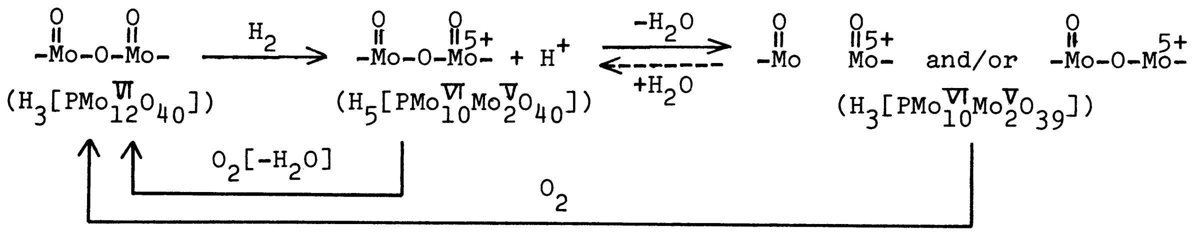


FIG. 2 H_2-UPTAKE AND H_2O-EVOLVED IN TEMPERATURE PROGRAMMED REDUCTION BY H_2 MEASURED BY THE METHOD [1-b]

Aqueous solutions of the samples which absorbed hydrogen at 25°C were dark blue indicating the reduction to Mo^{5+} or W^{5+}. On the other hand, PW_{12} did not absorb hydrogen at this temperature. It was confirmed that in the absence of Pd-C there was little hydrogen uptake and that the amount of hydrogen consumed by Pd-C itself was negligible.

Figure 2 shows the TPR profiles of PMo_{12} (Pd-C added) obtained by means of the method [1-b]. We found previously that, in the H_2-reduction and O_2-reoxidation cycle, water was evolved in both reduction and oxidation steps, and therefore proposed that reduction by H_2 occurred in two steps8): $H_2 \longrightarrow H^+ \longrightarrow H_2O$. The results in Fig. 2 provide important evidence to support this reduction mechanism. Hydrogen uptake (Fig. 2-a) started at about 30°C (certain amount of hydrogen was already consumed at room temperature without water evolution before the TPR profiles were recorded), but water evolution (Fig. 2-b) was not observed until 200°C, which was close to the temperature of the first peak of hydrogen uptake. Since the removal of crystal water completed at about 200°C (Fig. 2-c), the possibility that water was formed during the hydrogen uptake, but was not evolved at low temperatures being held in the bulk as crystal water would be eliminated.

Figure 3 shows the change in the IR spectra of PMo_{12} accompanying the reversible redox cycle. In a separate experiment which was carried out under the same conditions, reduction and oxidation took place by 2 electrons per Keggin unit in the redox cycle.6) After the reduction by H_2, the Mo=O band little changed (decrease in absorbance was less than 1%), but the absorbance of the Mo-O-Mo and P-O bands decreased by ca. 5%. Upon reoxidation, IR spectra identical to that of the original oxidized state was obtained in a reversible way. On the basis of the present findings, we propose the following redox cycle for PMo_{12}.



$$\underset{(H_3[PMo^{VI}_{12}O_{40}])}{-\overset{O}{\overset{\|}{Mo}}-O-\overset{O}{\overset{\|}{Mo}}-} \xrightarrow{H_2} \underset{(H_5[PMo^{VI}_{10}Mo^{V}_{2}O_{40}])}{-\overset{O}{\overset{\|}{Mo}}-O-\overset{O}{\overset{\|5+}{Mo}}- + H^+} \underset{+H_2O}{\overset{-H_2O}{\rightleftarrows}} \underset{(H_3[PMo^{VI}_{10}Mo^{V}_{2}O_{39}])}{-\overset{O}{\overset{\|}{Mo}}\quad \overset{O}{\overset{\|5+}{Mo}}- \text{ and/or } -\overset{O}{\overset{\|}{Mo}}-O-\overset{5+}{Mo}-}$$

In the first step, a hydrogen molecule becomes protons and electrons. Electrons formed are trapped by heteropoly anions, converting a part of Mo^{6+} to Mo^{5+}. Little change in the Mo=O band indicates that Mo-OH is not formed from Mo=O. Protons may be weakly hydrogen-bonded to oxygen of Mo-O-Mo or Mo=O. We previously observed a shift of ca. 15 cm^{-1} for the interaction of Mo=O with H_2O.[6)] The H-D exchange and the ^{18}O exchange between H_2O and PMo_{12} were much faster than H_2-uptake[8)] and electron migration is probably very rapid, so that the reduction proceeds uniformly throughout the bulk.

In the second step, protons react with oxygen atoms of heteropoly anion (probably with bridging oxygen[9)]) and are evolved as water. Lower symmetry of heteropoly anion caused by the elimination of the bridging oxygen may explain the change of IR spectra in the P-O region. The same structural change may also explain a part of the change in the Mo-O-Mo bands. However, further examination is needed to clarify the details of these changes of the IR spectra. The redox cycle of PMo_{12} given above operates during the catalytic oxidation of methacrolein which was reported before.[6)] A similar mechanism may be applied to PW_{12}, if it could be reduced at a low temperature.

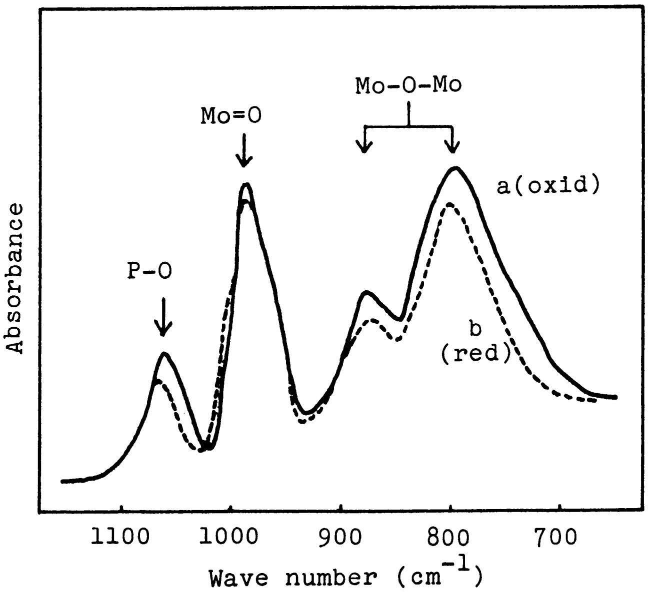


FIG. 3 IR SPECTRAL CHANGE OF PMo_{12} WITH REDUCTION

a: The original oxidized state and after reoxidation

b: After the reduction of ca. 2 electrons per Keggin unit at 250°C

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9) H. Tsuneki, H. Niiyama, and E. Echigoya, Chem. Lett., 1978, 1183. Figure 3 in this communication also suggests that bridging oxygen is more reactive.

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