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RAPID EXCHANGE OF OXYGEN-18 BETWEEN WATER VAPOR AND HETEROPOLY COMPOUNDS BY DIFFUSION OF CRYSTAL WATER

Kanji SAKATA, Mokoto MISONO, and Yukio YONEDA
Department of Synthetic Chemistry, Faculty of Engineering,
The University of Tokyo, Hongo, Bunkyo-ku, Tokyo 113

By means of *in situ* IR measurement, it was found that rapid and reversible ^{18}O-exchange took place between all bulk oxygen atoms, but P-O oxygen, of 12-molybdophosphoric acid and water vapor, maintaining the Keggin structure. The rapid exchange is likely due to the rapid diffusion of water molecules in the bulk.

Heteropoly compounds have recently been studied intensively as catalysts for selective oxidation of methacrolein to methacrylic acid as well as for hydration and esterification reaction.[1] In industrial gas-solid processes, they are often used in the presence of water vapor. We have proposed an idea that water plays essential roles in the catalytic action of heteropoly compounds,[2-4] in addition to the roles ordinarily suggested in selective oxidation processes. We already reported in the case of 12-molybdophosphoric acid and its salts the reversible and rapid change of the surface structure by dehydration-rehydration,[2] the increased stability of the Keggin structure in the presence of water,[3] and the effect of water on the oxidation of methacrolein.[4]

By investigating the ^{18}O-exchange between 12-molybdophosphoric acid, $H_3PMo_{12}O_{40} \cdot nH_2O$ (abbreviated hereafter as HPA) and $H_2^{18}O$ vapor by means of *in situ* IR measurement, we found that the bulk oxygen atoms of HPA participated in the reversible ^{18}O-exchange with $H_2^{18}O$, the Keggin structure (primary structure) being maintained, at a much greater rate than ordinary metal oxide catalysts. The results are reported here together with a probable mechanism of the exchange. It has already been reported that the ^{18}O diffusion in the bulk was rapid during the reduction-oxidation by H_2 and $^{18}O_2$ in the case of Ag salt.[5]

HPA was prepared from MoO_3 and H_3PO_4 according to the method described by Tsigdinos,[6] of which surface area and catalytic activity (isomerization of butenes, oxidation of acrolein) were close to those of HPA used previously.[2-4] Cu salt (CuPA) was prepared from $CuCO_3 \cdot Cu(OH)_2 \cdot H_2O$ and HPA. The samples subjected to the IR measurement were HPA and CuPA (3-5 mg) dispersed on thin silicon plates. They were treated and recorded of IR spectra in an *in situ* IR cell[7] connected to a closed circulation system. By winding up or down a Pt wire suspending the sample holder, the samples were lifted up to the heating portion for various treatments and brought down into the optical path (kept at room temperature) for recording IR spectra. The Fourier transform IR spectrometer and conditions for the IR measurement were the same as before.[2-4] The ^{18}O-enriched water (99 %) was purchased from Japan Radioisotope Association.

^{18}O-Exchange Between H_2O Vapor and HPA Measured by IR Spectroscopy. Figure shows typical IR spectra of HPA before and after the ^{18}O-exchange. After the sample was treated in 10 Torr of H_2O for 30 min at 150 °C, spectrum 1-a was recorded. The typical absorption pattern of Keggin structure of HPA is seen. Each band is assigned according to the literature[8] as follows: 1060 cm^{-1}(P-O streching), 970 cm^{-1} (Mo=O streching), 880 and 790 cm^{-1}(Mo-O-Mo bending). The other two small bands at 1100 and 620 cm^{-1} are due to silicon plate (probably surface oxide). Then, sample was evacuated at 150 °C for 30 min and subsequently exposed to 6 Torr of $H_2^{18}O$ at 150 °C for 30 min. After the sample was brought down into the optical path (room temperature) within 1 min and allowed to stand for 30 min, the spectrum 1-b was recorded. A new band developed near 930 cm^{-1} and the band due to the Mo-O-Mo were shifted to lower wave number. These changes were more clearly observed after exposing the sample for 1 h at 150 °C to an increased $H_2^{18}O$ pressure of 12 Torr (the spectrum 1-c). It was confirmed that there was little change in the spectra when kept at room temperature in the $H_2^{18}O$ vapor.

Difference spectrum 1-d [=(1-b)-(1-a)] demonstrates clearly the changes by the ^{18}O-exchange even at the initial stage. The bands which increased appears above the

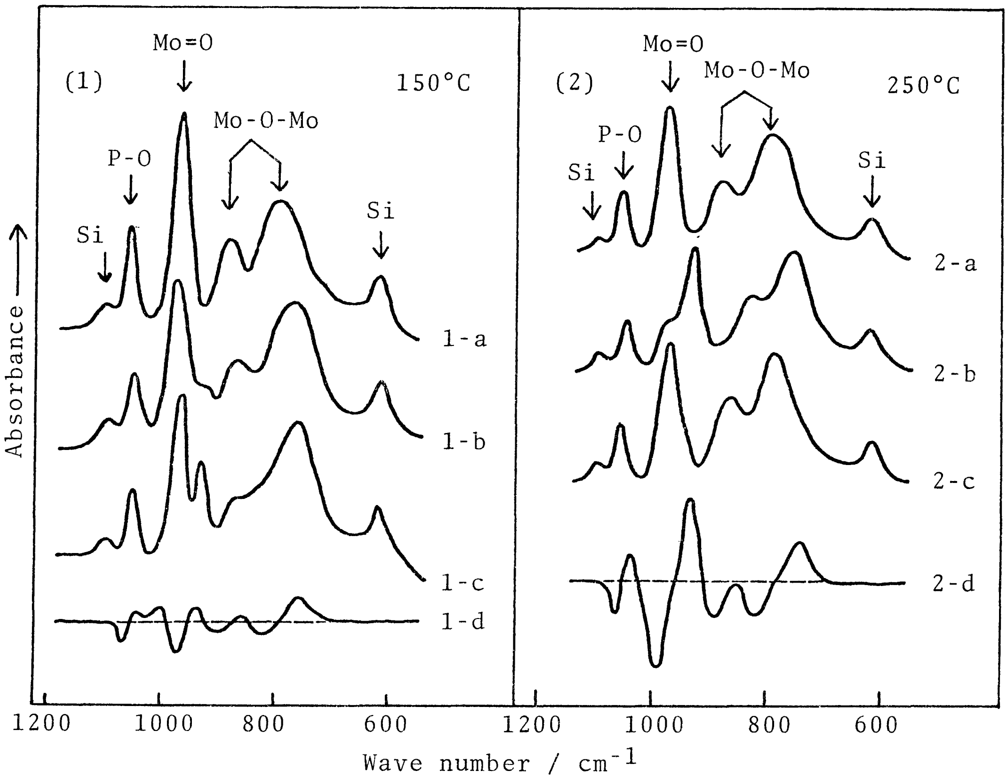

Fig. IR spectra of HPA in the ^{18}O-exchange with $H_2^{18}O$ at (1) 150°C and (2) 250°C. Spectra were recorded in the presence of water vapor after

(1) (1-a): 150°C, $H_2^{16}O$ 10 Torr, (1-b): $H_2^{18}O$ 6 Torr, 30 min after (1-a),and (1-c): $H_2^{18}O$ 12 Torr, 1 h after (1-b). (1-d): Difference spectrum [(1-b)−(1-a)].

(2) (2-a): evac. at 250°C, (2-b): $H_2^{18}O$ 22 Torr, 1 h after (2-a), and (2-c): $H_2^{16}O$ 22 Torr, 3 h after (2-b). (2-d): Difference spectrum [(2-b)−(2-a)].

base line and the bands which decreased below the base line. The shifts of each band upon the ^{18}O-exchange were thus determined as follows: P - O (1060 → 1050 cm^{-1}), Mo = O (970 → 930 cm^{-1}), Mo-O-Mo (880, 790 → 840, 750 cm^{-1}). The isotope shifts (40 cm^{-1}) observed for the Mo=O and Mo-O-Mo bands agree with those reported for ^{18}O-labeled $Ag_3PMo_{12}O_{40}$, although they observed a smaller isotope shift for the P - O band.5)

At 250°C and 22 Torr of $H_2^{18}O$, the ^{18}O-exchange occurred much more rapidly throughout the HPA bulk as shown by the spectrum 2 - b. The extent of the ^{18}O-exchange calculated from the changes in the Mo=O band intensity was 80%. The isotope shifts seen in difference spectrum 2 - d [=(2 - b) - (2 - a)] are in agreement with those in the spectrum 1 - d.

Quantitative comparison of the spectra 2-a and 2-b reveals that there is little difference in the relative changes in the P-O, Mo=O, and Mo-O-Mo band intensities (80-90% of each band shifted by the ^{18}O-exchange). Therefore, although the small shift (5-10 cm^{-1}) of the P-O band could be due to indirect influence caused by the exchange of the outer oxygen atoms in the Keggin unit as suggested by Tsuneki et al.5), it is obvious that most of the oxygen atoms (at least 36 out of 40 in the Keggin unit) of the whole bulk exchanged rapidly and nearly equally. This ^{18}O-exchange proceeded reversibly, retaining the Keggin structure: the spectrum 2-c, which was obtained by re-exchange with $H_2^{16}O$, was identical with the initial spectrum (2-a).

The rates of exchange calculated from the absorbance, A, of the Mo=O bands (970 and 930 cm^{-1}), placing the ^{18}O fraction equal to $A_{930}/(A_{970} + A_{930})$, are far greater than other metal oxide catalysts. For example, it has been reported that, in 100 min of reaction period, only the following percentages of the whole oxygen atoms are exchanged : 0.4% for MoO_3 at 440°C and 3% for Fe-Mo oxide at 200°C9). These are in contrast to 80% in 60 min for HPA at 250°C. The exchange rates of the bulk oxygen are two or three orders greater for HPA. It is noted that the rate increased nearly proportionally to the H_2O pressure (150°C).

Consequently, the ^{18}O-exchange between $H_2^{18}O$ vapor and HPA bulk takes place rapidly and the whole oxygen atoms (except P-O) in the HPA bulk participate in the exchange. Tsuneki et al. reported that rapid ^{18}O-exchange took place in the case of Ag salt of HPA during the reduction-oxidation by H_2 and $^{18}O_2$.5) However, the present study demonstrates that the rapid exchange throughout the bulk is possible even in the absence of reduction process. The exchange was also rapid for CuPA.

Mechanism of the ^{18}O-Exchange Between HPA and $H_2^{18}O$. We presume that the rapid ^{18}O-exchange with H_2O, which was much greater than that with $C^{18}O_2$10) or $^{18}O_2$, is closely related to the structural characteristics of HPA2-4): the arrangement of the primary structure (Keggin units) easily changes in the presence of water, and water molecules rapidly enter into and go out of the HPA bulk. It is, therefore, probable that ^{18}O in H_2O vapor is rapidly brought into the bulk as H_2O or OH^-. This speculation may be confirmed by the following. (1) H-D exchange between water vapor and crystal water of HPA or 12-tungstophosphoric acid is rapid even at room temperature as revealed from the bending mode of crystal water (complete exchange in less than 1 min). Thus, H^+ (or D^+) migration is rapid in the HPA bulk.11) (2) Diffusion of water in the bulk is also rapid since absorption and desorption of water is a rapid process even at room temperature. At 300°C, 10.8 cm^3(STP)/g-HPA of water was absorbed (or adsorbed) and reached equilibrium within 1 min. This amount is equivalent to ca. 14 adsorbed layers, so that this is a process of H_2O absorption into the bulk (ca. 1 x H_2O/Keggin unit (bulk)).

Furthermore, the ^{18}O-exchange is more rapid than the reduction of HPA by H_2[4] or the oxidation of methacrolein.[4] It appears quite possible that some reactions take place not only on the surface but also in the bulk near the surface, as we suggested previously.[4] We already reported that organic molecules like acetone, alcohols, and pyridine penetrate readily into the bulk of heteropoly acids.[4,11]

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