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Catalysis by Heteropoly Compounds. XVIII.[†] Oxidation of Methacrylaldehyde over 12-Molybdophosphoric Acid and Its Alkali Salts

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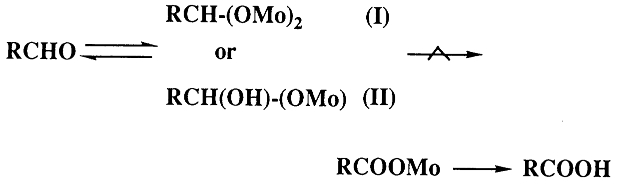
The reaction scheme for the methacrylaldehyde oxidation over heteropoly compounds proposed previously (M. Misono et al., Proc. 7th Intl. Congr. Catal., 1980) was confirmed by ^{18}O tracer experiments using the Pulse-MS method (combination of pulse reactor/mass spectrometer). The occurrence of direct and rapid oxygen exchange between methacrylaldehyde and the polyanion of $M_xH_{3-x}PMo_{12}O_{40}$ (M=Na, Cs, x=0—3.15) was verified under the reaction conditions. The results also suggested that this reaction is catalyzed by Brǿnsted acid sites of the catalysts via such intermediates as (I) and/or (II) in scheme 1. It was shown that the methacrylaldehyde oxidation is a surface-tyepe reaction and the catalytic activity is controlled by the oxidizing ability of the catalyst surface.

The selective oxidation of methacrylaldehyde to methacrylic acid has recently been industrialized by utilizing 12-molybdovanadophosphates,1) although improvements in the selectivity and durability are still desirable. As for the reaction mechanism, we previously proposed the following scheme.2)



$$RCHO \rightleftharpoons \begin{matrix} RCH\text{-}(OMo)_2 \quad (\mathrm{I}) \\ \text{or} \\ RCH(OH)\text{-}(OMo) \quad (\mathrm{II}) \end{matrix} \xrightarrow{\wedge} RCOOMo \longrightarrow RCOOH$$

Scheme 1.

We also showed that the oxygen atoms of the polyanion and/or water are directly incorporated into the products in accordance with the scheme, and that the oxygen in the feed gas reoxidizes the reduced polyanion (i.e., a redox mechanism). In this mechanism, such intermediates as (**I**) and (**II**), having C–O–Mo bonds, are assumed to exist. Isopoly compounds having partial structures similar to (**I**) and (**II**) have been synthesized,3) and it was suggested that they are the intermediates in the oxidation of aldehydes.3,4) If (**I**) and (**II**) are indeed the intermediates and the first step of Scheme 1 is rapid, direct exchange of oxygen must proceed rapidly between 12-molybdophosphoric acid and aldehyde. We actually found rapid oxygen isotopic exchange among aldehyde, water, and the catalyst in the case of acrylaldehyde oxidation over 12-molybdophosphoric acid.2) However, in that case it was not clear whether the exchange proceeds directly between the catalyst and aldehyde, or via oxygen exchange with water.

A direct exchange would be good evidence for the existence of (**I**) or (**II**). In view of this, we investigated in the present work the oxygen exchange between methacrylaldehyde and 12-molybdophosphates. The factors controlling each step of Scheme 1 have also been examined. If the second step is rate-limiting, the oxidizing ability of catalysts should control the overall rate. Further, attempts were made to clarify whether the methacrylaldehyde oxidation belongs to a bulk (**II**)-type or surface-type reaction.5,6)

Experimental

Catalysts and Reagents. 12-Molybdophosphoric acid ($H_3PMo_{12}O_{40}\cdot 27.4H_2O$, abbreviated as PMo_{12}) was commercially obtained. The Na and Cs salts ($M_xH_{3-x}PMo_{12}O_{40}$, M=Na, Cs, x=0—3.15) were prepared with Na_2CO_3 and Cs_2CO_3 by a method described previously.6) The surface areas of catalysts were measured by the BET method based on N_2 adsorption after the same pretreatments as those for the reactions.

Methacrylaldehyde (MAL) from Aldrich Chem. Co., Inc. was distilled and stored at ca. 253 K. No impurity was detected in it by gas chromatography. Pyridine (Py) was used after removing water as impurity with Molecular Sieve 3A. $H_2{}^{18}O$ (^{18}O content; 98—99%, Japan Radioisotope Association) was used for the ^{18}O exchange reaction.

Reactions. ^{18}O exchange reactions were carried out at 473 K with a pulse reactor directly connected to a mass spectrometer (NEVA NAG 531) (Pulse-MS method, Figure 1). The path from the injection port at the top of the reactor up to the inlet of mass spectrometer, was heated at 423 K to suppress isotopic contamination by oxygen exchange with water adsorbed on the wall. The influence of the adsorbed water was minimized by pretreating the system properly as detailed in Results and Discussion. The ^{18}O content in each reactant was measured with the mass spectrometer directly connected to the outlet of the reactor. The weight of catalysts used was 100 mg. After exposing the catalysts to a He stream (30 cm^3 min^{-1}) at 473 K for 1.5 h, water, MAL, or Py was injected at the top of the reactor at 473 K. No

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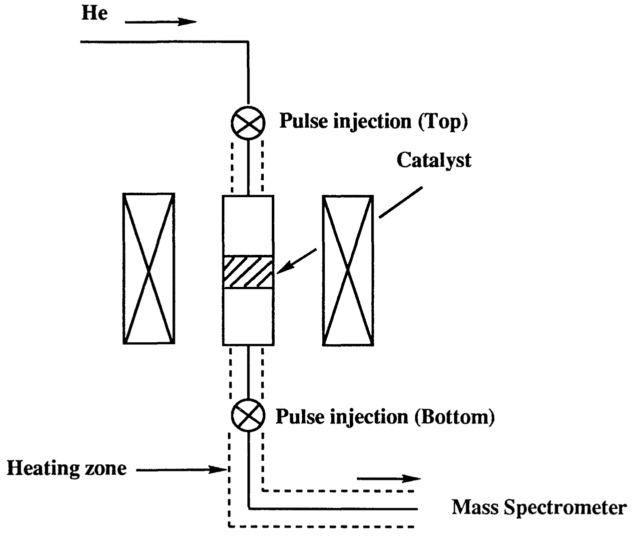

Fig. 1. Pulse-MS apparatus for the ^{18}O exchange reaction.

methacrylic acid formation took place when MAL was injected at the outlet of the reactor.

The oxidation of MAL was carried out with a conventional flow reactor as described previously.[2] The conditions were as follows; temperature, 573 K; weight of catalyst, 0.5 g; flow rate, 32.5 cm^3 min^{-1}; MAL, 2%; O_2, 12%; N_2, balance.

Results and Discussion

Direct Oxygen Isotopic Exchange between MAL and PMo$_{12}$. Table 1 summarizes the results of the ^{18}O exchange reaction among PMo$_{12}$, MAL, and water. Different run numbers denote separate experiments carried out with fresh catalysts. PMo$_{12}$ and M$_x$PMo$_{12}$, to which 3 μl of $H_2{}^{18}O$ was injected 10—14 times, are denoted as ^{18}O-PMo$_{12}$ and ^{18}O-M$_x$PMo$_{12}$, respectively. After $H_2{}^{18}O$ was injected 10—14 times, the ^{18}O content in water at the outlet of the reactor reached a constant value in a range of 90—100%. The amount of ^{18}O incorporated into the catalyst corresponded to approximately three quarters the amount of oxide ions in the whole polyanions. Therefore, the whole bulk was nearly equilibrated with $H_2{}^{18}O$; the ^{18}O content in the polyanions not only on the surface but also in the large portion of the bulk is close to 90—100%. The oxygen isotopic exchange between the polyanion and water has already been reported.[7,8]

The agreements of the ^{18}O contents in water and MAL between Runs No. 1 and 2 and among Runs No. 3—5 in Table 1 ensure a high reproducibility of the experiments. In Runs No. 2′ and 5′, the reactants were injected at the outlet of the reactor. The results were also highly reproducible. These experiments were carried out to estimate the oxygen exchange between the reactants injected and water adsorbed on the wall from the outlet of the reactor to the detector of the mass spectrometer. The ^{18}O contents in MAL in Runs No. 2′ and 5′ were less than 1%. The low ^{18}O content in MAL ($\leqslant$1%) indicates that the oxygen exchange of MAL proceeded to a small extent in the absence of the catalysts. Oxygen exchange between water and the wall proceeded to some extent.

The occurrence of direct isotopic exchange between MAL and PMo$_{12}$ can be concluded from the results of Runs No. 1, 2, and 2′, as follows. The ^{18}O content in MAL (40—44%) was greater than that in water (35—37%) in Runs No. 1 and 2, which were carried out after the system was equilibrated with $H_2{}^{18}O$. This difference is meaningful, because the isotopic exchange with water adsorbed on the wall was much slower for MAL than for water (No. 2′). Hence ^{18}O was incorporated into MAL not only from water but also directly from PMo$_{12}$, because the ^{18}O content in MAL will never exceed that in water if a direct exchange is absent.

The following explanation based on Fig. 2, which illustrates the results of Runs No. 1, 2 (top), and 3—5 (bottom), would make clearer the occurrence of direct oxygen exchange between MAL and PMo$_{12}$. The ^{18}O content in MAL at the outlet in Runs No. 3—5 (23—

Table 1. Oxygen Isotopic Exchange among Methacrylaldehyde, Water, and $H_3PMo_{12}O_{40}$ at 473 K (Pulse-MS Method)

Run	Catalyst	Reactants injected	^{18}O content in water	^{18}O content in MAL
			%	%
1	^{18}O-PMo$_{12}$ a)	$H_2{}^{16}O$(0.5)+MAL(3) b)	37	44
2	^{18}O-PMo$_{12}$ a)	$H_2{}^{16}O$(0.5)+MAL(3) b)	35	40
2′ c)	^{18}O-PMo$_{12}$ a)	$H_2{}^{16}O$(0.5)+MAL(3) b)	8	<1
3	PMo$_{12}$	$H_2{}^{18}O$(3)+MAL(3)	34	26
4	PMo$_{12}$	$H_2{}^{18}O$(3)+MAL(3)	32	23
5	PMo$_{12}$	$H_2{}^{18}O$(3)+MAL(3)	35	25
5′ c)	PMo$_{12}$	$H_2{}^{18}O$(3)+MAL(3)	86	1
6	^{18}O-PMo$_{12}$ a)	$H_2{}^{18}O$(3)+MAL(3)	78	70
7	Py-^{18}O-PMo$_{12}$ a)	$H_2{}^{18}O$(3)+MAL(3) b)	75	17
8	Py-^{18}O-PMo$_{12}$ a)	Py(2)+$H_2{}^{18}O$(3)+MAL(3)	79	3

a) Oxide ions of polyanion were fully exchanged (equilibrated) with ^{18}O of water prior to pulse. b) The value in parenthesis is the amount (μl) of reactant injected. c) Reactants were injected at the outlet of reactor.

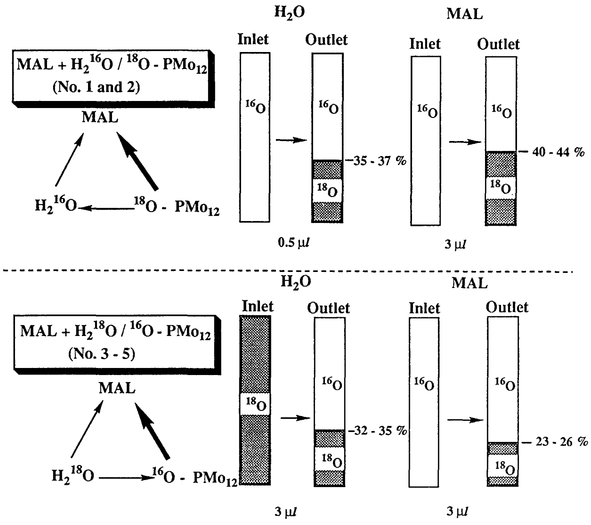

Fig. 2. Explanation of the presence of the direct ^{18}O exchange between methacrylaldehyde and $H_3PMo_{12}O_{40}$. Arrows indicate the flow of ^{18}O. Solid; indirect path, bold; direct path.

26%) was lower than those for Runs No. 1 and 2 (40, 44%), although the ^{18}O content in water which was in contact with MAL during the passage of the pulse through the catalyst bed was much greater for Runs No. 3—5 (100% at the inlet to ca. 35% at the outlet, bottom in Fig. 2) than for Runs No. 1 and 2 (0 to ca. 35%, top in Fig. 2). If the oxygen of MAL was exchanged with that of PMo_{12} only via water (absence of the direct path, bold arrows in Fig. 2), the ^{18}O content in MAL should be higher for Runs No. 3—5 than that for Runs No. 1 and 2. However, the experimental observations were definitely opposite. In addition, this would favor a conclusion that the amount of water injected in Runs No. 3—5 was larger than that in Runs No. 1 and 2. Therefore, these findings evidence the occurrence of "direct" oxygen exchange between MAL and the polyanion of PMo_{12}.

The occurrence of direct oxygen exchange demonstrates the formation of such intermediates as (**I**) and (**II**), which possess direct bonds between PMo_{12} and MAL (i.e., C–O–Mo bond), and supports the mechanism of Scheme 1.

Roles of Water Vapor and Acidity in Isotopic Exchange. The quantity of MAL pulsed in the present study was 3 μl (36 μmol). This corresponds to ca. three times and 2%, respectively, of those of surface and bulk oxide ions of PMo_{12} (12 μmol surface oxide ions and 1.7 mmol bulk oxide ions for 0.1 g of PMo_{12} (3.8 m^2 g^{-1})). If the oxygen exchange between MAL (^{16}O) and ^{18}O–PMo_{12} proceeds only on the surface of PMo_{12}, the ^{18}O content in MAL at the isotopic equilibrium would never exceed 25%. Therefore, the ^{18}O content greater than 25% in the presence of $H_2{}^{16}O$ (in Runs No. 1 and 2) demonstrates that the oxide ion of the polyanion in the catalyst bulk was transferred to MAL. The acceleration of the ^{18}O incorporation into MAL by water (^{16}O) (No. 1 and 2) may be due to the promotion of oxide ion diffusion from the bulk in the form of water molecules or hydroxide ions, as was suggested previously.[2,5,6]

On the other hand, when MAL (^{16}O, 3 μl) was injected without water onto ^{18}O–M_xPMo_{12}, the ^{18}O content in MAL at the outlet was only 8—10%. Therefore, the exchange of oxygen between MAL and PMo_{12} in the absence of water probably proceeds on the surface alone. This is consistent with a view that aldehyde oxidation is a surface-type reaction.

The results from Runs No. 6—8 show the effects of Py poisoning on the oxygen isotopic exchange. ^{18}O–PMo_{12}, to which 2 μl of Py was injected 7 times, is denoted as Py–^{18}O–PMo_{12}. The amount of Py absorbed corresponded to 2.7 molecules•anion^{-1}. The extent of ^{18}O exchange of MAL decreased from 70% (No. 6) to 17% (No. 7) when Py was pre-absorbed. Further, the ^{18}O content in MAL dramatically decreased to 3% when Py was co-pulsed with MAL over Py–^{18}O–PMo_{12} (No. 8). The inhibition of ^{18}O exchange by Py suggests that the oxygen exchange between MAL and the polyanion directly (first step in Scheme 1) and/or indirectly via water is catalyzed by Brønsted acid sites as was previously suggested.[2] This is probably not due to a decrease in the absorptivity of water or MAL by the salt formation of PMo_{12} with Py.

The following observations are also in line with a view that the first step in Scheme 1 is catalyzed by a Brønsted acid. When MAL was injected to ^{18}O–M_x-PMo_{12} at the inlet of the reactor, the ^{18}O content in MAL divided by the surface area of catalyst decreased with x as seen in Fig. 3. Since the amount of water

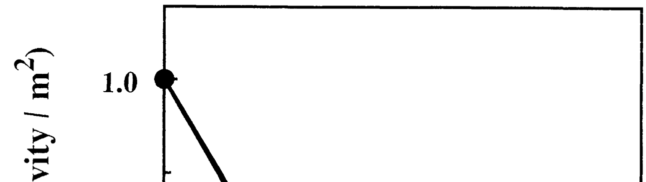

Fig. 3. Effect of alkali content on the ^{18}O exchange between methacrylaldehyde and $M_xH_{3-x}PMo_{12}O_{40}$. ●: $Cs_xH_{3-x}PMo_{12}O_{40}$. ○: $Na_xH_{3-x}PMo_{12}O_{40}$. The activity of $H_3PMo_{12}O_{40}$ was taken as unity.

evolved was only 0.04—0.05 μl, the ^{18}O exchange between water evolved and MAL could be ignored in this case and the ^{18}O content in MAL may be considered as a measure of the catalytic activity for direct oxygen exchange between MAL and the polyanion. A similar dependence of the amount of Brønsted acid sites on the Na or Cs content was observed.[3]

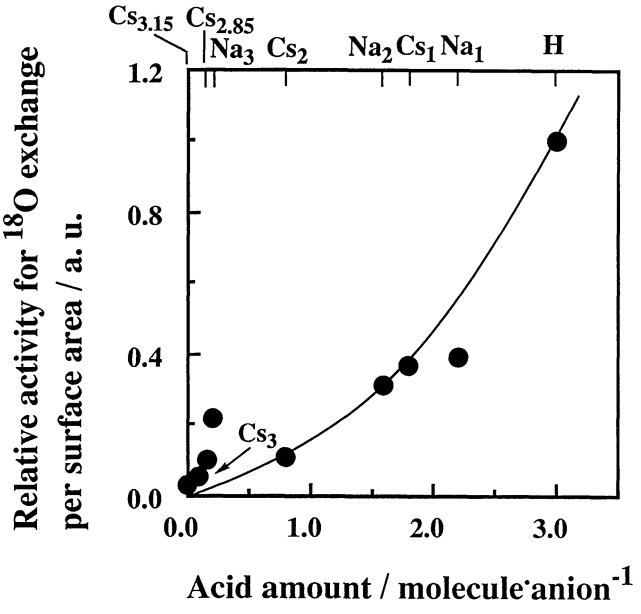

Fig. 4. Dependency of the catalytic activity for the ^{18}O exchange on the amount of Brønsted acid measured by the amount of pyridine absorbed or adsorbed. H and M_x denote $H_3PMo_{12}O_{40}$ and $M_xH_{3-x}PMo_{12}O_{40}$, respectively. The relative activity for the ^{18}O exchange per surface area of $H_3PMo_{12}O_{40}$ was taken as unity.

Figure 4 shows the correlation between the amount of Brønsted acid sites of 12-molybdophosphates measured by Py uptake (taken from Ref. 9) and their relative activity for oxygen exchange between MAL and the polyanion. The relative activity increased with an increase in the amount of Brønsted acid sites. This result would indicate that direct oxygen exchange between MAL and the polyanion, namely the first step in scheme 1 is catalyzed by a Brønsted acid.

Type of Catalysis and Factors Controlling the Rate. We previously reported that there are two different groups of reactions as classified by the dependency of the rate of non-catalytic reduction of 12-molybdophosphates on the specific surface area.[6,9] One is the oxidative dehydrogenation reaction, for which the rate per unit weight of catalyst does not depend on the specific surface area. H_2, isobutyric acid, and cyclohexene are typical reactants. In this case, rapid migration of protons and electrons leads to reduction of the whole solid.

The other is the oxygen-addition reaction, for which the rate is proportional to the surface area, presumably because the redox carrier is oxide ion with slow diffusion.

We also reported that the catalyst oxidizing ability as assayed with CO (a surface-type reductant) represents the oxidizing ability of catalyst surface, and is correlated with such surface-type catalysis as oxidations of acetaldehyde and CO.[5,6] Here, we will extend this

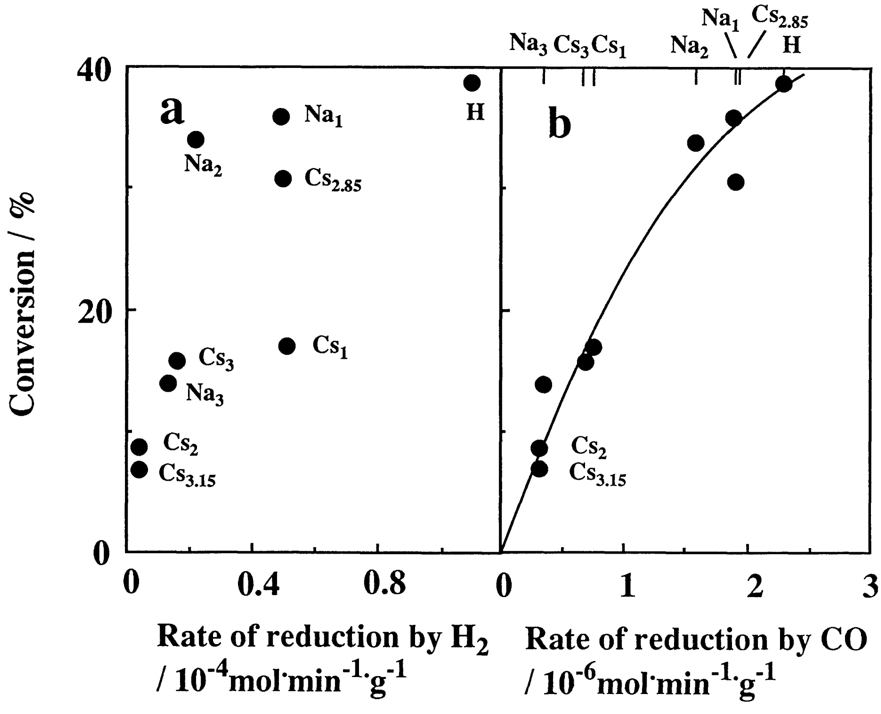

Fig. 5. Correlations between the conversion of methacrylaldehyde and the rate of reduction of catalyst by H_2 (a) or CO (b).

classification to the catalytic oxidation of MAL.

The main products of the oxidation of MAL over M_xPMo_{12} were methacrylic acid, acetic acid, CO, and CO_2. Since they all are oxygenated products, the reaction would belong to the surface-type.5,10) The selectivities to methacrylic acid, acetic acid, and CO_x ($CO+CO_2$) are slightly different among the M_xPMo_{12} catalysts.

Figure 5 shows a correlation between the % conversion of MAL and the rates of non-catalytic reduction of catalysts by H_2 or CO. In Fig. 5, the results of oxidation reactions in the absence of water vapor are displayed, because the presence of water would make a surface-type reaction behave like a bulk-type reaction.5) A good correlation exists between the catalytic activity (conversion of MAL) and the rate of catalyst reduction by CO (Fig. 5b), while the correlation is poor between the catalytic activity and the rate of catalyst reduction by H_2 (Fig. 5a).

These results are very similar to those observed for other surface-type reactions such as the oxidation of acetaldehyde and CO.5,6) The good correlation noted in Fig. 5b not only confirms that the oxidation of MAL (in the absence of water vapor) is a surface-type reaction, but also indicates that the catalytic activity is controlled by the oxidizing ability of catalysts. The formation of methacrylate by oxidative dehydrogenation in scheme 1 is most probably the rate-determining step.

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