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Nature of the Effect of Counter Cations on the Redox Property of 12-Molybdophosphates

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The role of counter cations of 12-molybdophosphates in determining the redox property of the catalysts has been studied systematically. It is suggested that the electronegative cations act as large electron reservoirs to facilitate electron transfer in the redox process, as supported by the XPS results.

It is well known that the high activity of heteropoly acids in many oxidation processes is due to their property to be reduced and reoxidized easily, so-called the redox property. In this study, the 12-molybdophosphoric acid, to be denoted as 12-MoP acid hereafter, and its metal salts have been prepared according to the procedures of Tsigdinos,1) and their redox property has been investigated. The prepared samples have exhibited the characteristic redox property of heteropoly acids as described below.

We have measured the reduction rate of the 12-MoP, either supported or unsupported, when the reduction proceeds in CO or H_2 stream. In the CO stream, the rate is higher for the supported sample than for the unsupported one. This is an obvious result because CO reduces only the catalyst surface and the supported catalyst has higher surface area than the unsupported. In the H_2 stream, however, the reduction rate is the same for both cases despite of the difference in the surface areas. This is because oxygen in heteropoly acid is loosely bound in the lattice enough to be reduced easily by H_2 even to the bulk phase. It is known that the reducible oxygen species is the bridged-bonded one in the Mo-O-Mo structure,2) and this has been confirmed by IR observation in this study. The reduced acid and its metal salts have been reoxidized easily, the amount of reoxidation being proportional to those of the initial reduction.

The reducibility and the reoxidizability, accordingly the redox power, of the 12-MoP acid may be changed by replacement of proton with various counter cations. In fact, it is by this method that the heteropoly acid catalysts may be modified to have the proper activity and selectivity in various oxidation processes.3)

As to the role of the counter cations in changing the redox power of the 12-MoP acid, various explanations as well as correlations have been suggested so far although there is not yet an unequivocally accepted one.

Simple explanations such as surface area or structural modification by the cation exchange are easily ruled out due to the following experimental observation in this study. The redox power of the Cs-exchanged salt, which has relatively high surface area (217 m^2/g), is an order of magnitude lower than that of the low area samples such as Bi-(4.3 m^2/g) and Fe-exchanged (3 m^2/g) salts. Also, the X-ray and IR observations show that the Keggin structure characteristic to the heteropoly acid is not altered by the cation substitution.

Correlating the redox power to the acidic property of the 12-MoP salts is not successful for general application, although a case has been demonstrated by Ai[4)] for olefin oxidation. This conclusion is supported by the following results of this study. The peaks of pyridine desorption from the Na- and Fe-exchanged 12-MoP salts are smaller and shifted to lower temperatures than those from the unsubstituted 12-MoP acid. This indicates that the amount and the strength of the acidic sites are simultaneously reduced by the cation exchange. Contrary to this, the reducibility, hence the oxidizing power, of the salts increases with the amount of the Fe-cation exchange whereas it decreases with that of the Na or Cs exchange (Fig. 1). Accordingly, no correlation is observed between the acidic and the redox property of the above salts.

Other parameters used for the correlation are 1) the heat of oxide formation,[4)] 2) ionic potential,[5)] and 3) the electronegativity of the counter cations.[4)] Among them, the electronegativity defined by Tanaka[6)] is used most frequently. We also have plotted the extents of reduction and reoxidation of the samples prepared in this study versus the electronegativity of cations. Although the data in Fig. 2 are somewhat scattered from the correlation curve, it is apparent that the redox power increases in parallel with the electronegativity of the counter cations. Similar correlation is observed when the rates of MEK (methylethyl ketone) oxidation on various 12-MoP salts are plotted against the electronegativity of the cations (Fig. 3).

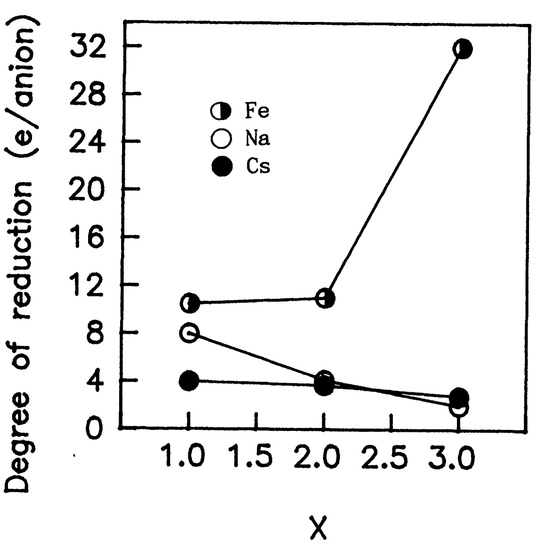

Fig. 1. Changes in the percentage reduction of 12-molybdophosphoric acid salts ($M_xH_{3-x}PMo_{12}O_{40}$) for different M and X, when the salts are reduced at 300 °C in H_2 for 1 h.

Since the redox mechanism of the heteropoly acids involves transfer of electrons between the molybdenum ion and the adsorbed hydrogen or oxygen,[7)] a measure to facilitate the electron transfer between them should increase the redox power. The electron transfer will become easy when a third boby, such as the counter cations, works as an electron reservoir to provide a route for the electron transfer during the redox process.

To examine the adequacy of this postulate, the electron binding energy of the

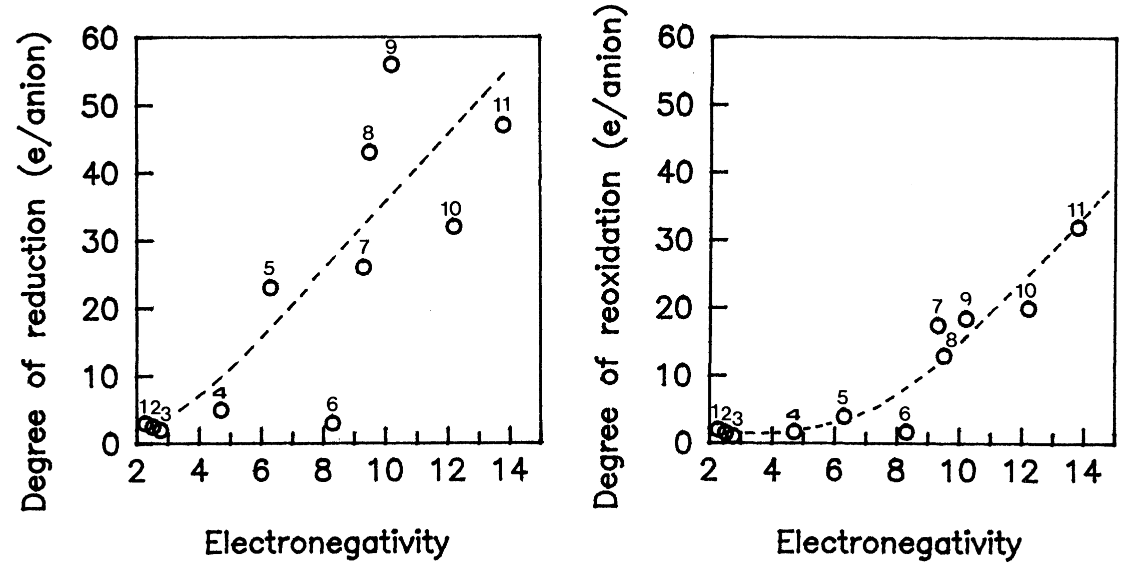

Fig. 2. Extents of reduction and reoxidation of 12-molybdophosphoric acid salts versus the electronegativity of the counter cations.
1. Cs 2. Na 3. Li 4. Sr 5. Mg 6. Zn 7. Co 8. Ni 9. Cu 10. Fe 11. Bi

molybdenum and counter cations in the 12-MoP salts has been measured by XPS before and after reduction in H_2. Table 1 shows that the binding energy of the molybdenum 3d electron in the Cs and Cu salts decreases by about 0.3 eV when the salts are reduced in H_2. Therefore, the molybdenum ion of both salts gain electrons, partially losing the valency, by the H_2 reduction.

The reduction also decreases the binding energy of the Cu 2p electron in the Cu salt by 0.6 eV, but that of the Cs 3d electron in the Cs salt is decreased only by 0.1 eV. This indicates that the Cu ion gains more electron than the Cs ion during the reduction process. Accordingly, the electrons supplied by the adsorbed hydrogen in the reduction step are distributed between the molybdenum and the counter cation such as Cu or Cs ion. During this course, the Cu ion, which is more electronegative than the Cs ion, acts as a large electron reservoir to facilitate, by

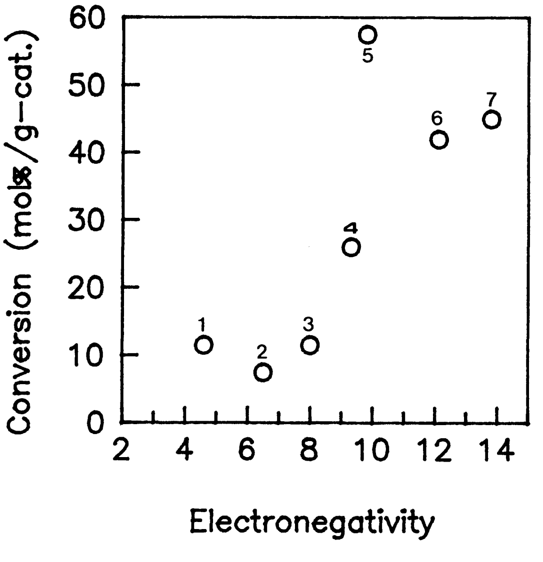

Fig. 3. Oxidation rates of MEK on various 12-molybdophosphoric acid salts.
1. Sr 2. Mg 3. Zn 4. Ni 5. Cu 6. Fe 7. Bi

Table 1. Binding energy (eV) of molybdenum and counter cations in 12-molybdophosphoric acid and its salts as observed by XPS

	Mo(3d)		Cu(2p)	Cs(3d)	
$H_3PMo_{12}O_{40}$					
(Unreduced)	239.8	236.8			
$Cu_3PMo_{12}O_{40}$					
(Unreduced)	239.8	236.8	937.1		
(Reduced)	239.5	236.8	936.5		
Δ	-0.3	0.0	-0.6		
$Cs_3PMo_{12}O_{40}$					
(Unreduced)	241.1	238.1		742.6	728.4
(Reduced)	240.8	237.8		742.5	728.3
Δ	-0.3	-0.3		-0.1	-0.1

providing a route for the electron delocalization, transfer of electrons to the molybdenum ion in the reducing environment. The less electronegative Cs ion is not so efficient in the role.

In fact, the explanation about the role of the counter cations as an electron reservoir to improve the redox power of 12-MoP has been made previously by Akimoto et al.[8,9] They observed by XPS the electron binding energy of palladium in the Pd salt, and confirmed that the binding energy decreased after reduction. However, their report did not compare quantitatively the XPS results of the salts of different counter cations, as done in this work. Accordingly, this work provides a good XPS evidence to enforce the previous suggestion that the electronegative cation acts as an electron reservoir to facilitate electron transfer in the salt.

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