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ACIDITY OF HETEROPOLY COMPOUNDS FROM XPS MEASUREMENTS

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The changes in the partial charges on oxygens in the various heteropoly salts as a result of the acidity differences have been exploited for probing the oxygen 1s and W 4f lines. The gradation of the acidity thus obtained is compared to that of the conventional method.

Heteropoly acids and their salts have been used as Bronsted acid catalysts in the conversion of methanol to hydrocarbons [1]. The Bronsted acidity of these catalysts has been probed using molecules like ammonia or pyridine [2] as well as by indicator method [3]. From the study of the acidity of a number of salts of heteropoly acids, Ghosh and Moffat [3] showed that the number of acid sites of varying acid strength decreased exponentially with the magnitude of charge on the anionic oxygen atoms. They have employed a semiempirical procedure for estimating the effect of the cation on the magnitude of the negative charge on the oxygen atoms of the anion using the equilization method [4]. In this connection it was considered worthwhile to see whether these effects will be manifested as shifts in X-ray photoelectron spectra of the salts of heteropoly acid, since these mainly contribute to the initial state properties. Incidentally, the XPS studies could be used to understand other surface properties of this interesting class of materials especially in view of their importance as catalysts for a variety of organic transformations.

The materials used in the present study namely 12-tungsto-phosphoric acid and its salts were prepared and calcined at 573 K by the methods reported in the literature [5]. Their acid strength distributions were evaluated by the procedure developed by Benesi [6] using visible Hammett indicators. The XP spectra of these samples were recorded using a ESCA LAB Mark II spectrometer with Mg K_α X-ray radiation with a background pressure of 10^{-9} Torr. The positions of the various peaks of these samples were referenced to an adventitious carbon peak in order to avoid any charging effect if present. However, the positions of the various peaks under various experimental conditions employed showed that the charging effect in these samples is almost negligible.

Table 1
Acidity distribution on 12-tungsto-phosphoric acid and its salts pretreated at 573 K in air and the partial charge on oxygen calculated by electronegativity equilization method

Catalyst	Partial charge on oxygen	Butylamine titre (mmole/g) in the H_0 range						
		+6.8 to +5.0	+5.0 to +3.3	+3.3 to +1.5	+1.5 to −3.0	−3.0 to −5.6	−5.6 to −8.2	$\geqslant -8.2$
$H_3PW_{12}O_{40}$	−0.197	0.5	0.4	0.2	1.2	0.2	0.2	0.8
$BiPW_{12}O_{40}$	−0.193	0.2	0.2	0.2	1.6	0.2	0.4	–
$AlPW_{12}O_{40}$	−0.201	0.6	0.2	0.2	1.6	0.2	0.2	–
$Zn_{3/2}PW_{12}O_{40}$	−0.198	0.4	0.2	0.4	1.3	0.1	0.2	–
$Ca_{3/2}PW_{12}O_{40}$	−0.219	1.0	0.2	0.2	0.4	0.1	0.1	–
$Mg_{3/2}PW_{12}O_{40}$	−0.213	1.2	0.2	0.2	0.2	0.2	–	–
$(NH_4)_3PW_{12}O_{40}$	−0.217	3.2	0.2	0.2	0.2	0.2	–	–
$Na_3PW_{12}O_{40}$	−0.272	0.6	0.2	0.1	0.1	–	–	–
$K_3PW_{12}O_{40}$	−0.282	0.6	0.2	0.2	0.2	–	–	–
$Cs_3PW_{12}O_{40}$	−0.288	2.1	0.1	0.1	0.2	–	–	–
$Cd_{3/2}PW_{12}O_{40}$	−0.200	1.4	0.4	0.4	0.8	–	–	–

The acid strength distribution of 12-tungsto-phosphoric acid (HPW) and its salts after pretreatment at 593 K in air for 4 h is given in table 1. It is seen that the salts like Bi, Al, Zn are strongly acidic with H_0 values lower than −5.6, while the alkali and Cd salts possess no acidic sites with H_0 values less than −3.0. The observed gradation of acidity of these salts is in general agreement with those reported by Ghosh and Moffat [3]. In view of this observed gradation in the acidity of HPW and its salts, the XP spectrum of the oxygen 1s line of these compounds was scanned. In fig. 1, the spectra obtained for the acid and the salts of Al and Na are also given. Hayashi and Moffat [7] have calculated the partial charge on oxygen (δ_0) on the metal salts of 12-tungsto-phosphoric acid using electronegativity equilization principle [7]. Similar calculations were carried out and the values of the partial charge on oxygen are also given in table 1. It is seen that the oxygen 1s peak of sodium salt is at a lower binding energy as compared to that of the free acid or the aluminium salt. It is also to be noted that the oxygen 1s peak of sodium salt is asymmetric which could be due to the contribution due to low binding energy oxygens which are more negatively charged as compared to the majority of other oxide ions of the $PW_{12}O_{40}^{3-}$ anion. Even though one could guess the least acidic nature of the sodium salt from the absolute binding energy values of the oxygen 1s peak, it is not clear whether this approach can be used for comparative evaluation of acidity of a number of salts of heteropoly acid as the observed shift and asymmetry of the oxygen 1s peak is small.

The tungsten 4f level was scanned for all these salts and the free acid and are shown in fig. 2. The peak separation between $4f_{7/2}$ and $4f_{5/2}$ is of the order of

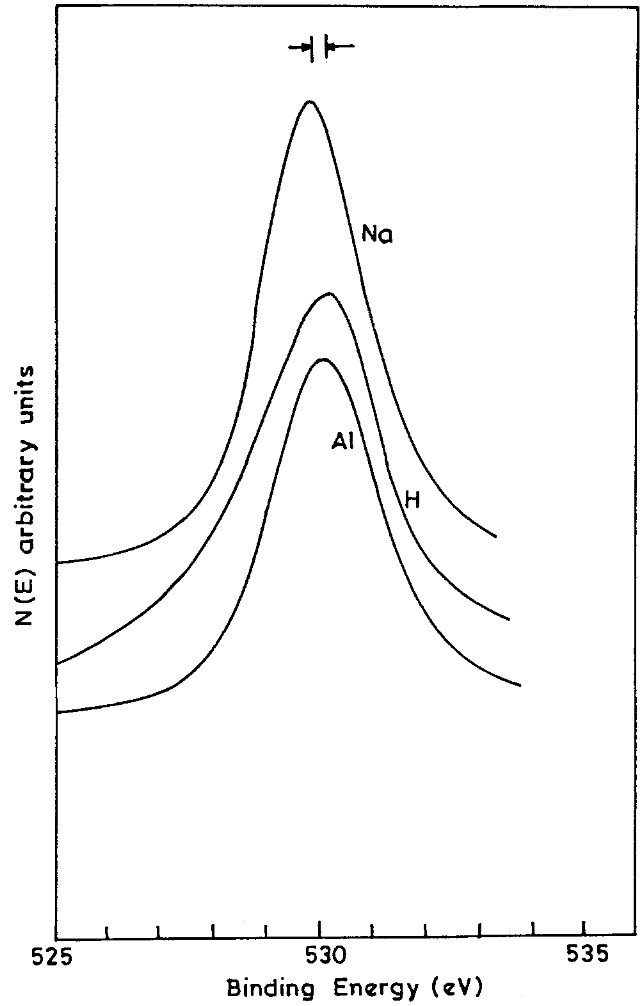

Fig. 1. XP spectrum of oxygen 1s level for 12-tungsto-phosphoric acid and typical salts like sodium and aluminum.

1.9 eV corresponding to what is reported for elemental tungsten. It is seen that it is also showing the same order of difference namely 0.1 to 0.2 eV between the sodium salt and the other acidic salts like that of aluminum or the free acid itself. Similar differences in the binding energy values of tungsten 4d are also noticed. The phosphorus 2p level is observed around 133.8 eV for the acid salts though for the sodium salt this is observed at 134.4 eV. The reason for this shift is not clear at present.

Therefore, it can be concluded that though in principle the relative acidity of the salts of heteropoly acids should be reflected in the binding energy shifts of the cation of the salt and oxide ions, these shifts are too small to be monitored directly. The relative acid strength distribution between the various salts can

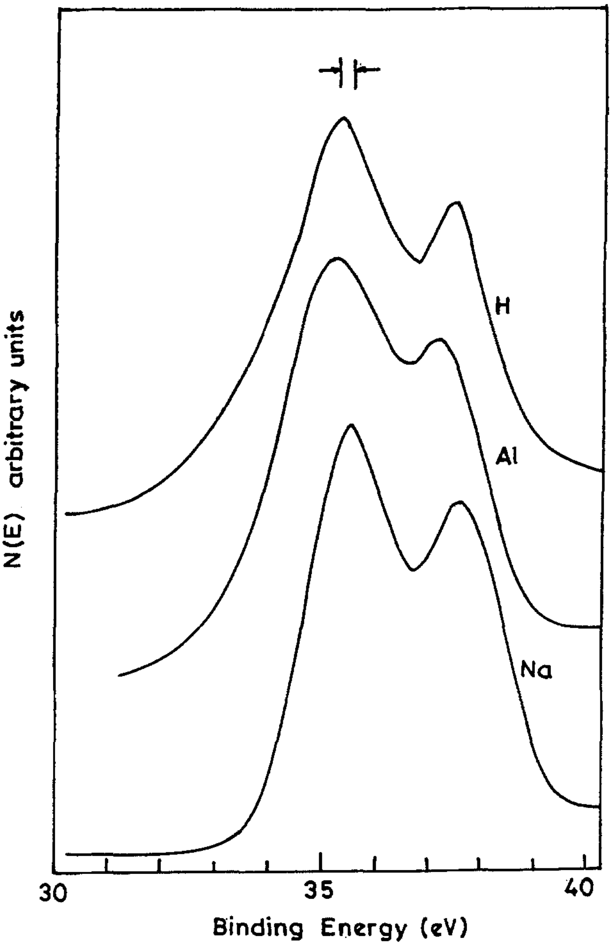

Fig. 2. XP spectrum of W 4f line for 12-tungsto-phosphoric acid and typical salts like sodium and aluminum.

probably be deduced from XPS measurements only when one can consider the difference between the peak positions of the cation and anion. The difference between the oxygen 1s line and the tungsten 4f line was found to be 495.5 eV for the free acid, 495.4 eV for the aluminum salt and 495.1 eV for the sodium salt which reflects the order of the acidity of these substances.

We have also attempted to identify the active sites of these salts in alcohol conversion reactions by monitoring these XPS lines on the spent systems used for the conversion of isopropyl alcohol into propane. The only consistent observation was that the binding energy values of all the lines probed (W $4f_{7/2}$, P 2p, O 1s) were shifted to higher values. Therefore, it is deduced that though the specific reaction might be taking place at the Bronsted acid sites, the net effect is felt in all the surroundings of the anion and hence direct deduction of the nature of the active site involved in hydrocarbon conversion reaction cannot be deduced by

XPS measurements alone. However, it may be possible to make intelligent guesses on the nature of the surface species formed from monitoring the carbon 1s peak of the adsorbed species. From the observation of carbon deposit on the spent acidic salts, it was deduced in an earlier communication [8] that the nucleophilic attack of hydride ion on the dehydration product or the alcohol itself is the preferred route for the formation of saturated hydrocarbons.

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