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The interaction of alkaline earth cations with metal–oxygen cluster compounds and the implications for their use as heterogeneous catalysts

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The magnesium, calcium, strontium and barium salts of 12-tungstophosphoric and 12-molybdophosphoric acids have been prepared. Evidence of the presence of the Keggin anion (primary structure) was obtained from infrared spectroscopic measurements but powder X-ray diffraction and differential thermal analysis measurements indicated that changes to the secondary structure had occurred. BET surface areas were small for all of the materials studied and no dependence on the cation radius was observed. A crystallographic investigation demonstrated that divalent cations were not incorporated into the lattice suggesting that materials believed to be divalent 12-heteropoly salts are mixtures of the parent acid and a divalent cation salt.

Keywords: Metal–oxygen cluster compounds; heterogeneous catalysts; alkaline earth cations

1. Introduction

The use of metal–oxygen cluster compounds in heterogeneous catalytic reactions is now well established as attested to by the large number of reactions that are effectively catalyzed by this family of solid acids and related compounds [1]. The unique structural characteristics of metal–oxygen cluster compounds with anions of Keggin structure make them attractive materials for the study of model reactions and in addition, several industrial processes use these solids as catalysts. Briefly, the anions of Keggin structure can be represented by the stoichiometric formula $XM_{12}O_{40}^{y-}$. A central atom, X (usually P, Si or As), is surrounded by a tetrahedron of oxygen atoms. This tetrahedral unit is in turn

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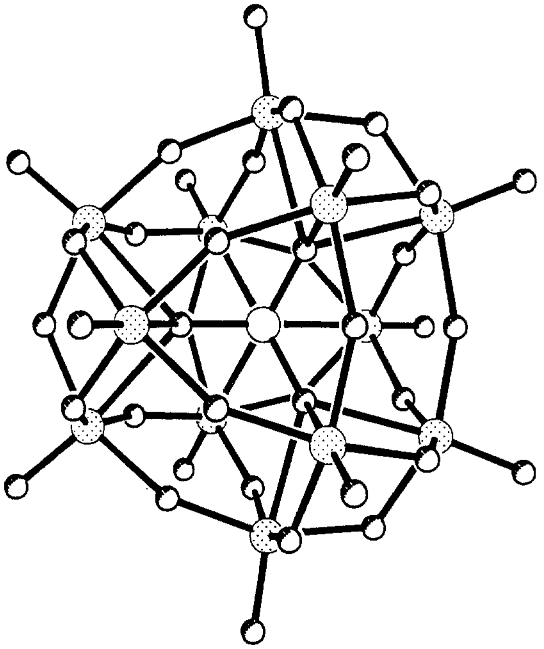

Fig. 1. Representation of a Keggin anion, $XM_{12}O_{40}^{y-}$.

surrounded by twelve octahedra of oxygen atoms which are bonded to the central unit as well as to one another. Peripheral metal atoms, M (usually W, Mo or V), are located near the centres of the octahedral unit. As fig. 1 demonstrates, the anion is highly symmetric (T_d symmetry) and possesses oxygen atoms at the surface which are available to participate in catalytic reactions. In the solid state, metal–oxygen cluster compounds form three-dimensional crystalline materials in which the anions are bonded through hydrated protons or monovalent cations to form a semi-rigid lattice which has been shown to contain a microporous network for several monovalent salts [2–4].

The catalytic activity of the metal–oxygen cluster compounds (MOCC) is determined by the combination of peripheral and central atoms as well as by the choice of cations. The peripheral atoms most strongly influence the catalytic activity of the anions and it has been shown that, whereas materials with tungsten peripheral atoms exhibit stronger Brønsted acidity and catalyze the methanol to hydrocarbon process [5,6] and hexane cracking [7], molybdenum containing acids and salts are more effective catalysts for redox processes such as the selective oxidation and dehydrogenation of aldehydes [8] and carboxylic acids [9] and the partial oxidation of methane [10]. In fact, for the isobutyric acid to methacrylic acid process, the mixed peripheral atom catalysts containing molybdenum and vanadium were found to be the most effective [11]. The effect of the central atom appears to be less important since isostructural phosphorus and silicon containing compounds are similarly effective for a variety of reactions including the methanol to hydrocarbon process [12]. Recent studies concerned with monovalent cation effects in MOCC have shown that the microporous structure can be retained as the cation composition of the catalyst is modified [13,14]. In addition, the catalytic activity of the $NH_4^+/Cs^+/PMo_{12}/O_{40}^{3-}$ system in the oxidative dehydrogenation of isobutyric acid to methacrylic acid process was found to be strongly influenced by the relative quantities of the two cations [15].

Studies of the catalytic and surface properties of heteropoly catalysts have generally been concerned with the acid form and various salts containing monovalent cations, while significantly fewer investigations of salts with multivalent cations have appeared [6,9,16]. Few, if any of these studies have been concerned with the bulk properties of these materials containing divalent cations. Consequently there is an urgent requirement for additional data which will clarify the structural and crystallographic nature of these solids. Since certain monovalent salts of the MOCC have been shown to possess microporous structures it is important to determine whether similar porous properties can be found with salts prepared from divalent cations. Further, there is evidence which suggests that the introduction of cations with oxidation numbers greater than one may advantageously alter the catalytic properties of the MOCC [6,9,16]. With the MOCC the effect of the insertion of such muitivalent cations on the structural properties has not yet been clarified. In the case of some zeolite catalysts it is possible to balance the negative charge of the framework using muitivalent cations (alkaline earth, transition metal, rare earth) as well as monovalent cations [17]. The incorporation of multivalent cations provides the opportunity to prepare zeolites with lower cage densities of cations which can significantly modify the sieving properties of the solids. In addition, the incorporation of certain multivalent cations is believed to result in the formation of additional acid sites within the porous structure.

The present investigation was initiated to address the limited data regarding the bulk and surface properties of alkaline earth salts of 12-molybdophosphoric and 12-tungstophosphoric acid. Such a study should provide insight into the effect of cation size, charge and relative numbers with regard to the formation and structure of the MOCC.

2. Experimental

The magnesium, calcium, strontium and barium salts of $H_3PW_{12}O_{40}$ and $H_3PMo_{12}O_{40}$ were prepared by adding aqueous suspensions of the appropriate alkaline earth hydroxide to a stirred solution of a stoichiometric quantity of the heteropoly acid (to nominally prepare a neutral salt that does not contain protons) at 333–343 K. The resulting homogeneous solutions were taken to dryness to isolate the desired material.

Infrared spectra were recorded on a Perkin-Elmer 983 spectrometer for samples prepared as KBr pellets. Powder X-ray diffraction patterns were recorded on a Phillips 1011/60 diffractometer using Cu Kα radiation filtered through nickel (30 mA and 40 kV). Differential thermal analysis curves were recorded on a DuPont 910 thermal analyzer at 10 K min^{-1} in flowing nitrogen to a maximum temperature of 923 K. Nitrogen adsorption–desorption isotherms were measured at 77 K using a standard glass volumetric system following pretreatment at 473 K and 10^{-5} Torr (1 Torr = 101.3 kPa).

3. Results and discussion

The infrared spectra of the divalent materials were consistent with those published previously for the MOCC of Keggin structure [18]. The fingerprint region below 1100 cm^{-1} contains the P–O ($\approx$ 1080 cm^{-1} for $PW_{12}O_{40}^{3-}$ and 1060 cm^{-1} for $PMo_{12}O_{40}^{3-}$) and M–O ($\approx$ 980 cm^{-1} for W–O and 960 cm^{-1} for Mo–O) asymmetric stretches and the M–O–M stretches of the octahedral bridges ($\approx$ 900 and 810 cm^{-1} for $PW_{12}O_{40}^{3-}$ and 880 and 800 cm^{-1} for $PMo_{12}O_{40}^{3-}$) which were in good agreement with literature values and confirmed the presence of the Keggin anion.

Although the primary structure or Keggin anion has been retained, the crystal structure or secondary structure is significantly affected by the addition of divalent cations. The powder XRD for the four alkaline earth 12-molybdophosphates and the parent acid are shown in fig. 2. Whereas the diffraction pattern for the parent acid indicates the presence of a crystalline secondary structure (Fd3m), those of the divalent materials were largely featureless. Similar differences were observed between the diffraction patterns of 12-tungstophosphoric acid and the divalent materials. This behaviour is distinctly different from that observed for salts prepared with alkali metal and ammonium cations which are highly crystalline materials and belong to the Pn3m space group [19].

Differential thermal analysis curves were recorded to investigate the thermal behaviour of the divalent materials. The patterns for the parent acids were in good agreement with previously published curves [20]. Introduction of the divalent cations significantly alters the thermal behaviour of the materials (fig. 3 and table 1). Whereas the decomposition temperatures for the anions remained relatively stable (exothermic transition), several additional endothermic transitions were observed, particularly for the 12-molybdophosphate materials. The presence of the additional endothermic transitions suggests that there is a perturbed interaction between the divalent cation and the MOCC anion.

BET surface areas for all of the divalent materials were less than 20 m^2 g^{-1} and showed no dependence on the diameter of the divalent cation. This behaviour is in marked contrast to that observed for the monovalent salts of

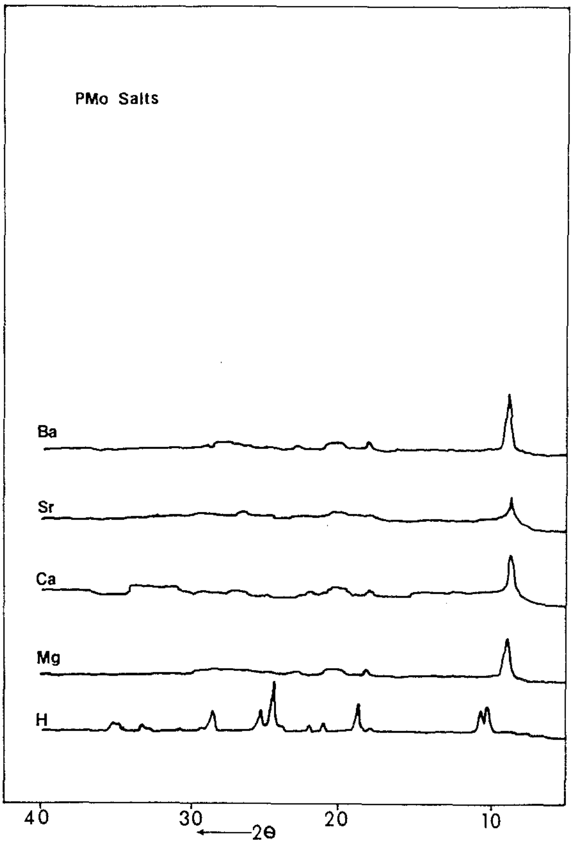

Fig. 2. Powder X-ray diffraction patterns for $H_3PMo_{12}O_{40}$ and the alkaline earth 12-molybdophosphates.

these two anions for which a definite dependence of surface area and micropore volume as a function of the cation diameter has been observed [2–4].

The unexpected differences between the 12-heteropoly compounds formed with monovalent and divalent cations suggests that the divalent materials were not formed, but rather the resulting system was a mixture of the MOCC acid and a divalent cation salt. During the preparation of the divalent compounds, homogeneous solutions of the cation and the heteropoly acid were formed which suggested that single crystals could be prepared and isolated. The $Ba^{2+}/PMo_{12}O_{40}^{3-}$ system was chosen for the crystallographic study because of the similarity between the cation radii of Ba^{2+} and K^+ and the fact that potassium 12-molybdophosphate is known to be a microporous solid. The solutions were prepared as previously described and allowed to stand in air until crystallization commenced. Crystals were grown and studied in Lindemann tubes to circumvent the problem of rapid desolvation of the crystals. A full description of the experimental procedures and crystallographic results will be published elsewhere [21].

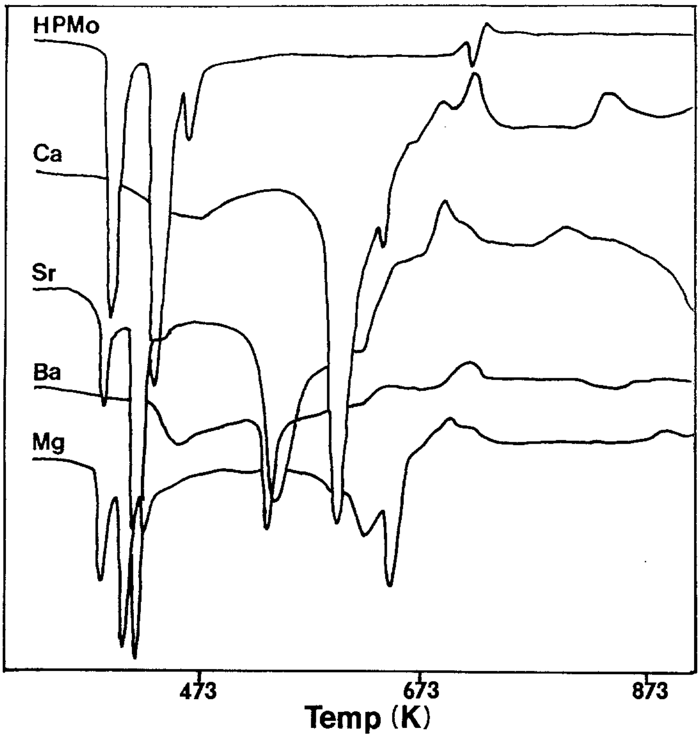

Fig. 3. Differential thermal analysis curves for $H_3PMo_{12}O_{40}$ and the alkaline earth 12-molybdophosphates.

The results of the crystallographic study appear to have important ramifications regarding the use of MOCC salts prepared with divalent cations. At no point in the refinement of the crystal structure was the existence of the barium

Table 1
Thermal transitions [a] (DTA) for divalent 12-heteropoly salts

Compound	Endotherm (K)	Exotherm (K)
$H_3PW_{12}O_{40}$	548 s	863 m
$Mg^{2+}/PW_{12}O_{40}^{3-}$	583 w, 608 m	868 s
$Ca^{2+}/PW_{12}O_{40}^{3-}$	518 m	833 s
$Sr^{2+}/PW_{12}O_{40}^{3-}$	563 m, 613 m	828 m
$Ba^{2+}/PW_{12}O_{40}^{3-}$	528 m, 558 s	833 w, 873 m
$H_3PMo_{12}O_{40}$	433 s, 463 w	723 w
$Mg^{2+}/PMo_{12}O_{40}^{3-}$	403 m, 423 w, 598 w 628 w, 648 m	703 w, br
$Ca^{2+}/PMo_{12}O_{40}^{3-}$	473 w, 598 s, 638 w	693 w, 718 m, 838 w, br
$Sr^{2+}/PMo_{12}O_{40}^{3-}$	413 s, 438 w, 543 m, br	698 m, 803 w
$Ba^{2+}/PMo_{12}O_{40}^{3-}$	458 w, br, 536 m	723 w, br

[a] s, m, w and br denote strong, moderate, weak and broad peaks.

cation observed. In fact, the refined structure was that of 12-molybdophosphoric acid. These results appear to explain in part the results described earlier. The featureless powder XRD patterns are believed to be the result of the presence of a mixture of the parent acid and a second phase containing the divalent cation. Once again, the infrared results confirmed the presence of the Keggin anion, suggesting that a diffraction pattern for one of the known crystallographic structures of one of the several hydrates of $H_3PMo_{12}O_{40}$ should have been observed. A recent study of the powder X-ray diffraction patterns of different hydrates of $H_3PW_{12}O_{40}$ has demonstrated that the intensity of the diffraction peaks and the space group are dependent on the degree of hydration [22]. This suggests that in the present study the diffraction patterns were recorded for hydrated forms of the acid with intrinsically weak diffraction peaks that were further obscured by the presence of the second phase in the mixture.

With regard to the question of the formation of the salts containing divalent cations, it is useful to consider the results of an ion exchange study of divalent cations with MOCC salts [23]. The conclusion of this study was that for divalent cations to exchange on $(NH_4)_3PMo_{12}O_{40}$ the solution pH must be > 4. If one assumes that the same conditions are required to form salts with divalent cations from the parent acids then it is apparent that the formation is not possible. $H_3PMo_{12}O_{40}$ and $H_3PW_{12}O_{40}$ are only stable in strongly acidic solutions and at pH 4 the major MOCC anion species will be the lacunary anions $PW_{11}O_{39}^{7-}$ and $PMo_{11}O_{39}^{7-}$ [24]. It therefore appears to be impossible to prepare the salts with divalent cations under these conditions. This does not preclude the eventual formation of salts with divalent cations, but apparently the standard published methods are not adequate and it suggests that a detailed investigation of the preparations with particular emphasis on the solution pH may be beneficial in clearing up the discrepancies.

From the results of the present study it appears, for 12-molybdophosphoric acid and 12-tungstophosphoric acid, that alkaline earth salts are not formed but instead mixtures of the MOCC acid and alkaline earth materials evidently coexist. This being the case it is believed that catalytic results obtained using MOCC catalysts prepared with alkaline earth cations should be interpreted with caution since it is conceivable that differences in the catalytic behaviour are the result of the divalent cation present in the mixture, rather than the divalent salt of the MOCC.

Acknowledgement

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