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LASER RAMAN AND DTA/TGA STUDY OF $H_{3+n}PV_nMo_{12-n}O_{40}$ HETEROPOLYACIDS PURE AND SUPPORTED ON $K_3PMo_{12}O_{40}$

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According to TGA/DTA data thin layers of $H_{3+n}PV_nMo_{12-n}O_{40}$ heteropolyacids impregnated on $K_3PMo_{12}O_{40}$ support display increased thermal stability. Raman spectroscopy proves that these deposited, catalytically significant, acid layers represent a new structural quality and tend to retain certain number of crystallization water molecules. It is argued that the acids become stabilized due to the epitaxial relationship with the support, and the isomorphous acid layers are tenatively described as hexahydrates of the respective acids.

1. Introduction

Recently it was demonstrated that the catalytic performance and thermal stability of heteropolyacids with the Keggin structure can be enhanced by their impregnation onto insoluble, thermally resistant heteropolysalts such as $K_3PMo_{12}O_{40}$ [1–3]. In the case of $H_3PMo_{12}O_{40}$ heteropolyacid supported on its potassium salt the electron microscope analysis [1] allowed to deduce that the stabilization occurs due to the formation of an epitaxial acid layer on the surface of the cubic support.

Structural isomorphism between the surface deposit and the support makes the conventional techniques for structural analysis unsuitable to study the nature of such a layer.

On the other hand, Raman spectroscopy was shown to be sensitive not only to the primary Keggin structure, but also to the type of the secondary structure of heteropolyacids and to the nature of the countercation [4–8]. Additionally, analysis of the scattered radiation enhances information from the surface and near-to-surface layers of the catalyst.

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For this reason, in the present work, we chose this technique to follow changes in the secondary structure of the $H_{3+n}PV_nMo_{12-n}O_{40}$ ($n = 0, 1, 2, 3$) series of heteropolyacids occurring upon interaction with the $K_3PMo_{12}O_{40}$ support and to elucidate the nature of the surface acid coat formed under such conditions. TGA/DTA was chosen as a complementary technique to investigate thermal properties of the deposited acid layers.

2. Experimental

2.1. MATERIALS

The $H_{3+n}PV_nMo_{12-n}O_{40}.xH_2O$ ($n = 0, 1, 2, 3$) heteropolyacids were prepared according to the method of Tsigdinos and Hallada [9]. The exact water content of the crystalline acid hydrates was found to be $H_3PMo_{12}O_{40}.28H_2O$, $H_4PVMo_{11}O_{40}.32H_2O$, $H_5PV_2Mo_{10}O_{40}.31H_2O$ and $H_6PV_3Mo_9O_{40}.30H_2O$, as determined from TGA. These samples are further referred to as H_3, H_4, H_5 and H_6. The $K_3PMo_{12}O_{40}$ support, abbreviated K_3, was prepared by the method described by Tsigdinos [10] from the stoichiometric quantities of $H_3PMo_{12}O_{40}$ and K_2CO_3. Its BET surface area was 160 m^2/g. On the assumption that one Keggin anion occupies 144 Å, catalysts corresponding formally to 1 monolayer coverage with the acid component, denoted hereinafter H_3/K_3, H_4/K_3, H_5/K_3 and H_6/K_3, were prepared by impregnation of the support with the desired quantity of aqueous solution of the respective acid, as described previously [3], and their specific areas were 20–30 m^2/g, e.g. significantly lower than that of the pure support. All catalysts, pure and supported, were subjected to the thermal treatment in air at 623 K for 3 hours which reduced their specific surface. After calcination the BET surface area of the pure acids was 1–3 m^2/g, of the supported samples 5–8 m^2/g, and of the support, 70 m^2/g.

2.2. TECHNIQUES

Laser Raman spectroscopy. Raman spectra were acquired on a DFS-24 spectrometer equipped with an ILA-120 ($\lambda = 647$ nm, linear polarisation) laser source. The laser power of 22 mW and spectral slit width of 0.5–0.7 mm were usually employed. Powdered samples were pressed into an open sample holder made of organic glass. Standard calcining treatment (see previous section) applied to all samples before the Raman experiment reduced the possibility of laser-induced changes in the state of the catalysts.

Differential thermal analysis. DTA measurements were carried out in static air in a Setaram Micro ATD M5 thermal analyser. Samples of around 15 mg were heated at 5 K per minute up to 873 K.

Thermogravimetric analysis. TGA measurements were carried out in flow of air in a Mettler thermal analyser. Samples of ca. 50 mg (pure acids) and 150 mg (supported acids) were heated at 5 K per minute up to 873 K.

3. Results

Figure 1a–e shows the most characteristic fragments of the Raman spectra of the pure acids, and of the support itself. The bands observed in the low wavenumber range are caused by deformational vibrations both of the terminal M=O groups and of the entire framework and are sensitive to the cationic surrounding of the Keggin unit [4–8]. The other characteristic fragment of the spectrum falls in the range 900–1100 cm^{-1} where the valence vibrations of the individual M=O groups, the PO_4 and the pulsation vibrations of all 12 M=O groups are expected [4–8].

The characteristic feature of the K_3 spectrum (fig. 1e) is a split band in the 230–250 cm^{-1} region and maxima at 973 and 987 cm^{-1}.

All spectra of the calcined acids show common features (fig. 1a–d) visible even in the rather poor spectrum obtained for the H_6 sample. The worse quality of the latter is due to the dark colouration of the sample resulting in low intensity of sacttered radiation. All spectra differ from that of the support in both regions. In the 230–250 cm^{-1} range the band around 245 cm^{-1} becomes relatively less intense and appears only as a shoulder. In the 900–1100 cm^{-1} region the maximum is shifted towards 1010–1012 cm^{-1}. Similar shift was observed by others on thermal treatment of the acid hydrates and was assigned to an anhydrous form of the acid [5,7]. No such shift was observed for thermally treated insoluble salts [8].

The Raman spectra of the supported acids, shown in fig. 2a–d, in the low wavenumber range resemble those of the acids, whereas the 900–1100 cm^{-1} bands are similar to those observed for the K_3 support. On the whole they resemble the spectra of solid acid hydrates or their water solutions [5,7,8].

Differential thermal analysis is a convenient technique for determination of the thermal stability of the acids. From the previous studies [9,11] it is known that after the final loss of constitutional water, an exothermic peak appears around 700 K, associated with the irreversible destruction of the Keggin units. According to DTA the decomposition temperatures of pure acids of the investigated series, determined from the position of the peak maximum, are following: H_3–706 K, H_4–715 K, H_5–685 K, and H_6–669 K. For each member of the supported acid series a distinct shift of the exothermic peak position towards higher temperatures is visible, i.e. H_3/K_3–727 K, H_4/K_3–733 K, H_5/K_3–725 K, and H_6/K_3–700 K (fig. 3).

Comparison of the TGA profiles for the pure and the supported acids shows that in the latter case the initial loss of weight due to the evolution of water of

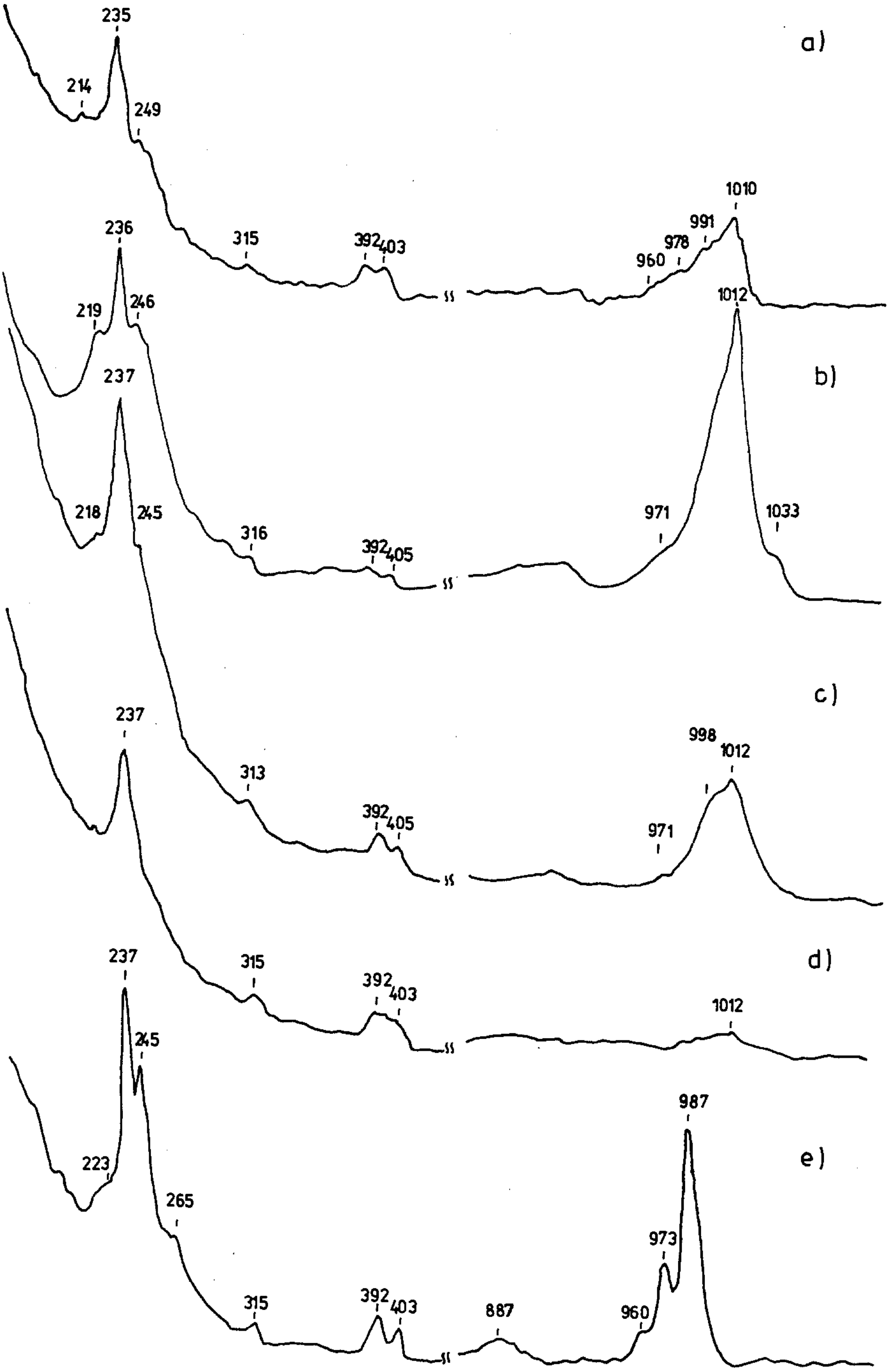

Fig. 1. Laser Raman spectra of a) H_3, b) H_4, c) H_5, d) H_6 and e) K_3, calcined at 623 K.

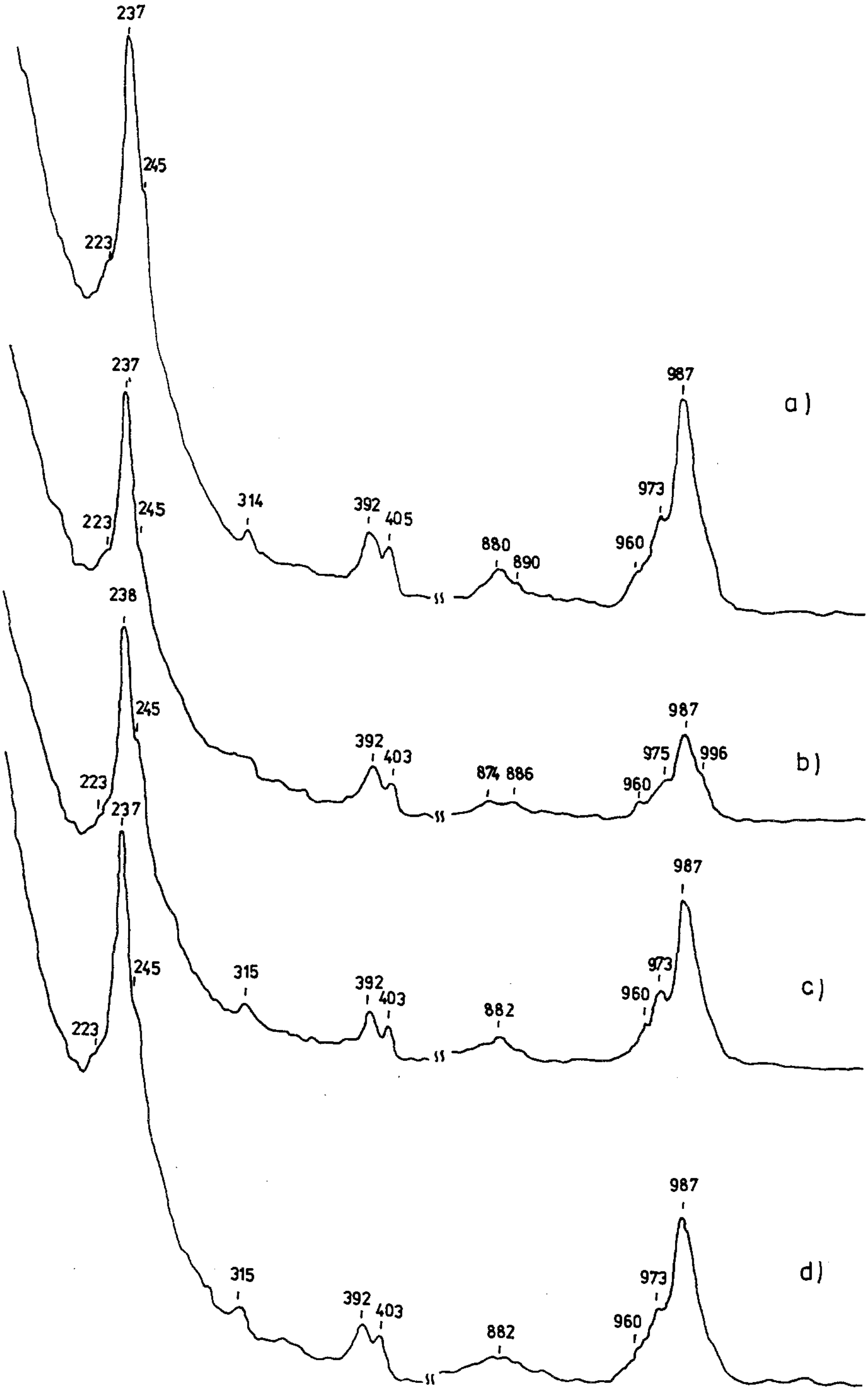

Fig. 2. Laser Raman spectra of a) H_3/K_3, b) H_4/K_3, c) H_5/K_3 and d) H_6/K_3, calcined at 623 K.

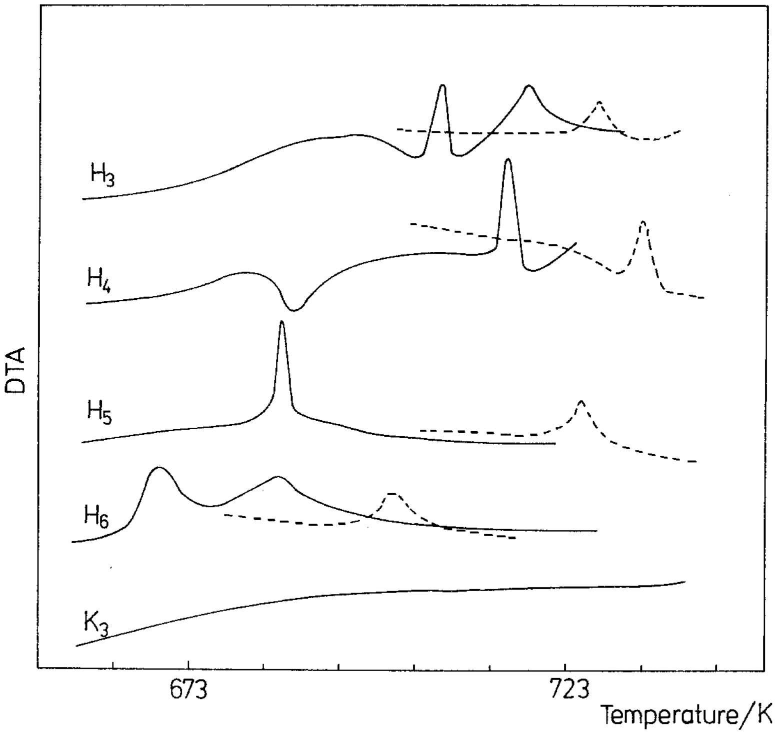

Fig. 3. DTA of pure (———) and supported (- - - - -) acids, and of the K_3 support.

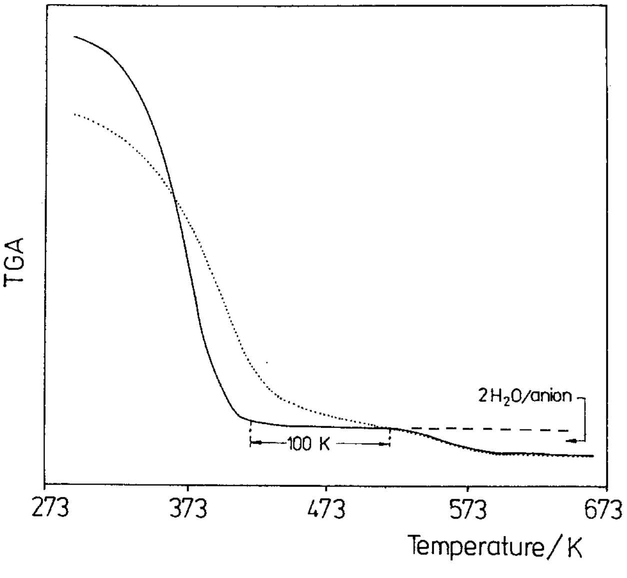

Fig. 4. TGA of H_4 (———) and H_4/K_3 (· · · · · ·). Both samples contain about the same amount of acid component.

crystallization proceeds at much lower rate, as shown in the example presented in fig. 4. For H_4 and H_4/K_3 samples, taken in amounts containing about the same quantity of acid phase, the TGA curve of the supported specimen reaches the value characteristic of the acid that lost all of its water of crystallization but retained still the constitutional protons (corresponding, according to the stoichiometry of H_4, to 2 H_2O molecules/Keggin anion) at temperatures by ca. 100 K higher than in the case of pure acid.

4. Discussion

Before attempting to interpret the TGA/DTA and Raman results it is important to discuss in more detail the microscopic structure of the supported catalysts. The BET surface area of the K_3 support is 160 m^2/g. Scanning electron microscope image [3] shows that the powder consists of round or hexagonal, apparently smooth grains, of ca. 0.5–1.0 μm diameter which corresponds to the morphological surface area of ca. 1 m^2/g. Analysis of the sample porosity from the argon adsorption isotherm shows that despite the apparent regular morphology the grains are very porous [13]. Pore size distribution for the K_3 support presented in fig. 5 indicates that it is the intragranular sorption in the area of meso and micropores that is responsible for the observed high values of specific surface. Assuming that on impregnation the micropores of radius below 20 Å are blocked with the first layer of the deposit, the effective surface of the support is reduced to roughly one third of the BET value. If also part of the mesopores with the radius less than 40 Å become blocked, the available surface of the support is further reduced down to ca. 15% of the initial value. This may easily happen in view of large dimensions of the Keggin anions ($\cong$ 11 Å) and explains the reduction of the specific surface area from 160 m^2/g for the pure support to 20–30 m^2/g after impregnation (see Materials). Therefore, one has to bear in mind that the formal coverage of one monolayer in fact corresponds to several layers of the acid deposit.

Thermogravimetric analysis shows clearly that the intimate interaction between the members of the $H_{3+n}PV_nMo_{12-n}O_{40}$ series and the $K_3PMo_{12}O_{40}$ support produces surface acid coats of enhanced thermal stability both in the range corresponding to the loss of water of crystallization and in the range of stability of the dehydrated acid materials. These conclusions can be drawn from the observed changes in the TGA profiles indicating enhanced resistivity of the surface acid deposits against dehydration associated with the release of crystalline water (fig. 4) and from the DTA results showing shifts towards higher temperatures of the exothermic peaks signifying final decomposition of the Keggin units (fig. 3). The phenomenon has a general character and is independent of the composition of the supported acid.

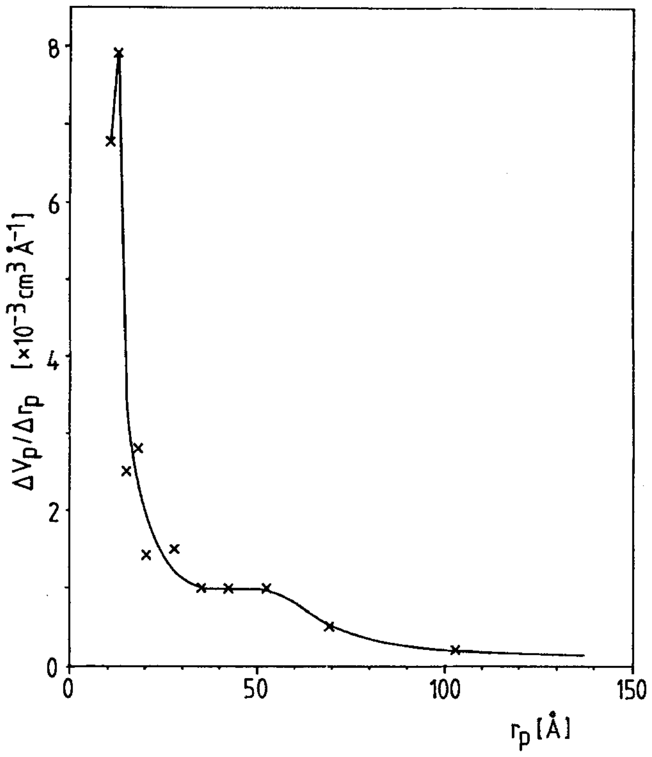

Fig. 5. Pore size distribution curve from argon adsorption at 77 K.

Analysis of the Raman spectra allows to get some insight into the structure of surface acid coats in the supported catalysts. The absence of the band at 1010–1012 cm^{-1} typical of the "anhydrous" acid phase and similarity with the spectra of acid hydrates and solutions indicates that a certain number of crystallization water molecules are present in the structure. On the other hand, the similarity of the bands in the 230–250 cm^{-1} region, sensitive to the cationic surrounding, to those found for the pure acids points to protons acting as counteractions and indicates that the surface layer consists of an acid phase rather than of the solid solution involving potassium cations.

Therefore, in agreement with earlier findings [1], we postulate that the stabilization effect is the consequence of formation of an epitaxial acid layer derived from the $H_{3+n}PV_nMo_{12-n}O_{40}.xH_2O$, isostructural with the cubic lattice of the $K_3PMo_{12}O_{40}$ support particles.
Electron microscope data [1] demonstrated that in the $H_3PMo_{12}O_{40}$ partially dehydrated through calcination a phase exists that is isostructural with the potassium salt of this acid and with the 12-tungstophosphoric acid hexahydrate described by Brown et al. [12]. In the latter case the authors established that the cationic positions in such a hydrate are occupied by $(H_5O_2)^+$ diaquahydrogen ions. They also pointed out that this structure is isomorphous with insoluble

cubic salts of various 12-heteropolyanions, and that, when necessary, can accommodate the extra protons expected from the stoichiometry of related heteropolyacids.

In view of this, we tentatively visualise the surface layers deposited on the potassium salt, partly at least, as hexahydrates of the respective acids. Although, on their own, such hexahydrates are unstable and difficult to obtain, the epitaxial relationship with the support provides suitable ground for their stabilization. Lack of the bands characteristic of the "anhydrous" phase in the calcined supported samples shows that the surface acid coat quickly restores the water content necessary to maintain the structure, whereas unsupported acids remain to some extent dehydrated and give rise to the maximum at 1010–1012 cm^{-1}.

5. Conclusions

Thin heteropolyacid coats deposited on the $K_3PMo_{12}O_{40}$ salt become thermally stabilized due to the epitaxial relationship with the support. The stabilized layers contain hydrated protons and in their part isomorphous with the support can be visualised as hexahydrates of the respective acids.

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