Catalysis Letters 1 (1988) 35–40

HETEROPOLYSALT-SUPPORTED HETEROPOLYACIDS AS A NEW CLASS OF ACID-BASE AND REDOX CATALYSTS

K. BRÜCKMAN, J. HABER, E. LALIK and E.M. SERWICKA *

Institute of Catalysis and Surface Chemistry, Polish Academy of Sciences, 30-249 Kraków, ul. Niezapominajek 1, Poland

Received: 21 December 1987

Heteropolyacid catalysts of composition $H_{3+n}PV_nMo_{12-n}O_{40}$ ($n = 0,1,2,3$) when supported on $K_3PMo_{12}O_{40}$ desplay new types of acid-base and redox properties and have enhanced thermal stability.

1. Introduction

Catalysts based on heteropolyacids with the Keggin structure have been successfully tested in a great variety of chemical processes, the undoubtful achievement on the industrial scale being the selective oxidation of unsaturated aldehydes [1]. A major drawback of these catalysts is their relatively low thermal stability resulting in a more or less rapid degradation of the Keggin unit under catalytic conditions, accompanied by a parallel fall in the catalytic performance. Goodenough et al. [2–4] in a recent extensive study of acrolein oxidation over the $K_xH_{3-x}PMo_{12}O_{40}$ ($0 \leqslant x \leqslant 3$) system found that the best catalytic performance could be obtained for $x = 2.5$. They postulated that at this composition the catalyst consisted of the $H_3PMo_{12}O_{40}$ acid phase stabilized in the form of an epitaxial, isostructural layer at the surface of the $K_3PMo_{12}O_{40}$ particles. The latter, in contrast to the acid phase, is a water insoluble compound, thermally stable up to 1000 K, crystallizing in a cubic lattice.

An interesting question of far-reaching implications may be asked as to whether it is a general phenomenon that hetero-polyacids with the Keggin structure may be supported on the appropriate heteropolysalts becoming thus stabilized in the anhydrous form which otherwise decomposes in the conditions of the catalytic reaction. Heteropolyacids derived from $H_3PMo_{12}O_{40}$ by substitution of one to three molybdenum atoms by vanadium seemed, in view of their similarity with the parent acid [5], particularly promising objects. Furthermore, the literature data indicate the advantageous properties of such compounds in the

---

* Author to whom the correspondence should be addressed.

selective oxidation processes, as well as in the C-C bond formation on methanol conversion [6–8]. For this reason the research into their thermal stability and stabilization effects is of great potential significance. Since all water insoluble salts of these acids with the alkaline cations (K^+, Cs^+, Rb^+, NH_4^+,) are isomorphous with $K_3PMo_{12}O_{40}$, this compound was chosen to serve as a support for each member of the studied series of acids.

2. Experimental

The $H_{3+n}PV_nMo_{12-n}O_{40} \cdot xH_2O$ ($n = 0, 1, 2, 3$) heteropolyacids were obtained according to the method of Tsigdinos and Hallada [9] and are further denoted H_3, H_4, H_5, H_6. The $K_3PMo_{12}O_{40}$ support, abbreviated further K_3, was prepared by the method described by Tsigdinos [10]. Its BET surface area was 160 m^2/g. Catalysts corresponding formally to 1 monolayer coverage with the acid component, denoted hereafter H_3/K_3, H_4/K_3, H_5/K_3, H_6/K_3, were prepared by impregnation of the support with the desired quantity of aqueous solution of the respective acid, followed by evaporation to dryness. All catalysts, pure and supported, were subjected to the calcining treatment at 623 K for 3 hours. The BET surface area of the pure calcined acids was 1–3 m^2/g, of the supported samples 5–8 m^2/g, and of the support 70 m^2/g. In order to check on the acid-base and redox properties of the catalysts dehydration of isopropanol at 403 K and selective oxidation of acrolein at 623 K were tested with the pulse reactor technique and analysed by gas chromatography as reported previously [11]. The resistivity to thermal shocks was examined for samples subjected for 1 hr to an additional heat treatment at 673 K. X-ray diffractions were obtained with the DRON 2 diffractometer, using the CuKα radiation. IR transmission spectra were recorded with the SPECORD M-80 spectrometer.

3. Results and discussion

Solid lines in fig. 1 (a) and (b) show the behaviour of pure and supported acids calcined in a standard way in the isopropanol dehydration, i.e. in reaction sensitive to the presence of acid centres at the surface of the catalyst. The series of pure acids show the maximum of propene yield for the H_4 sample, whereas the acidity of the supported catalysts measured by the yield of propene does not vary with the number of vanadium atoms. The additional heat treatment results in the lowering of the activity of pure acids (Fig. 1(a)–dashed line), the fall being quite dramatical for H_5 and H_6. The latter effect is in agreement with the TGA/DTA data for our samples. Their thermal stability, as measured by the temperature at which the exothermic peak accompanying the final destruction of the Keggin unit appears [5], is following: H_3-707 K, H_4-715 K, H_5-685 K, and H_6-669 K. Quite

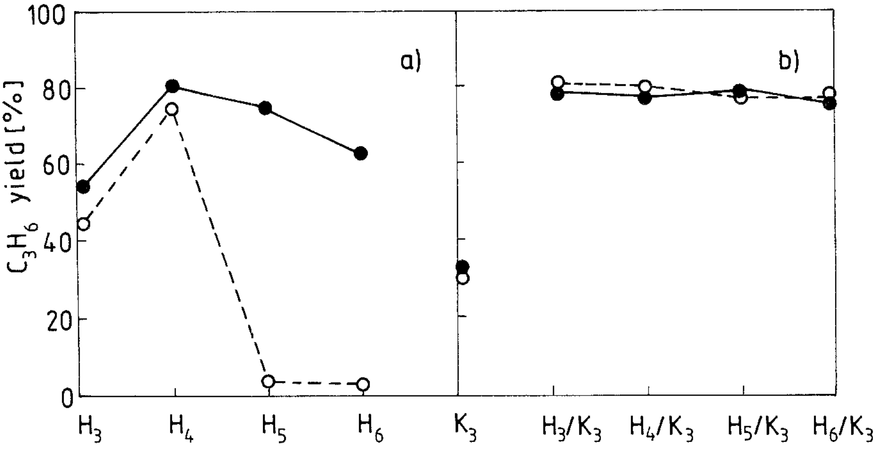

Fig. 1. Yield of propene in the catalytic dehydration of isopropanol: (a) pure acids, (b) pure support and acids supported on K_3; ●-catalysts after standard treatment at 623 K, ○-catalysts overheated at 673 K.

different behaviour display the supported acids. Dashed line in fig. 1 (b) shows that overheating had no effect on their activity which remained at the same level as before the additional thermal treatment.

Results of acrolein oxidation to acrylic acid over standard and overheated samples are equally spectacular, as shown in fig. 2. The maximum yield of acrylic acid on pure heteropolyacids is observed for the H_4 sample, although all vanadium containing catalysts perform better than the unsubstituted compounds (fig. 2 (a)–solid line). Overheating results in a drop of the acrylic acid yield, again particularly drastic for the H_5 and H_6 samples, (fig. 2 (a)–dashed line). The yield

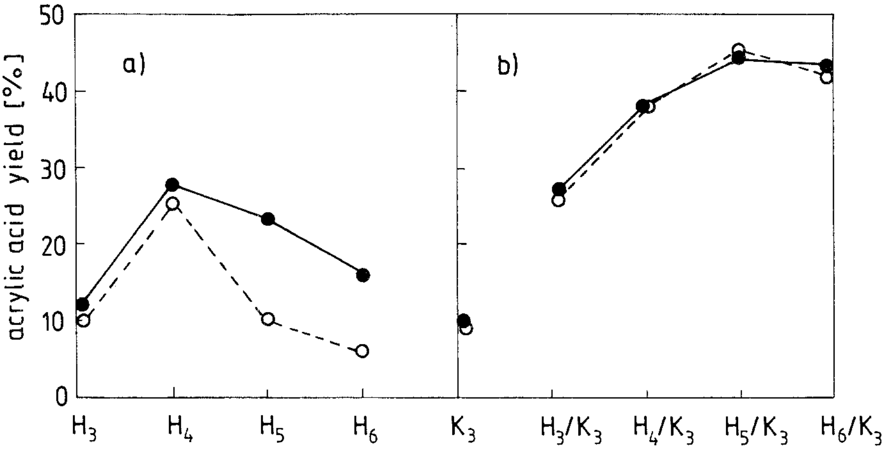

Fig. 2. Yield of acrylic acid in the catalytic oxidation of acrolein: (a) pure acids, (b) pure support and acids supported on K_3; ●-catalysts after standard treatment at 623 K, ○-catalysts overheated at 673 K.

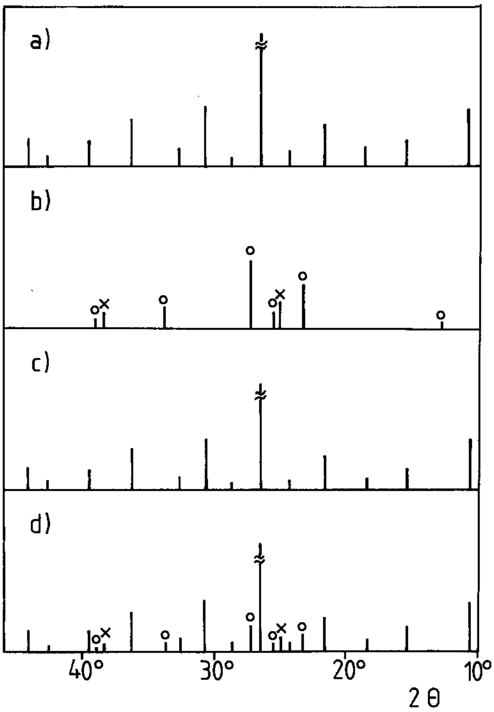

Fig. 3. X-ray diffraction spectra of: (a) K_3 after standard treatment at 623 K, (b) H_5 overheated at 673 K, (c) H_5/K_3 overheated at 673 K, (d) mechanical mixture of H_5 overheated at 673 K and K_3 in ratio as for H_5/K_3.

of acrylic acid over the supported acids shows different dependence on the vanadium content (fig. 2 (b)–solid line). Here the best performance is obtained for the catalysts with the highest vanadium content. Overheating does not in the least affect the catalytic performance of the supported samples.

The presented data clearly indicate the stabilization of the acid phase at the surface of the $K_3PMo_{12}O_{40}$ for all tested heteropolyacids. The effect is most pronounced for the least thermally stable members of the series. The X-ray and IR data confirm the stabilizing effect of the support on the heteropolyacid structure. Figure 3 shows as example the X-ray diffractions of (a) pure support K_3, (b) overheated H_5, (c) overheated H_5/K_3 and (d) mechanical mixture of K_3 and overheated H_5 in ratio as in H_5/K_3. Pure support gives the typical powder spectrum of the $K_3PMo_{12}O_{40}$ cubic lattice. Overheated H_5 shows peaks due to MoO_3 and some other, yet unidentified, product of the decomposition of the Keggin unit (anhydrous, undecomposed H_5 is practically amorphous to X-ray). The overheated supported H_5 shows only the pattern characteristic for the cubic lattice of the support, in agreement with the idea of formation of the epitaxial, isostructural layer of the acid on the top of the $K_3PMo_{12}O_{40}$ particles. Finally,

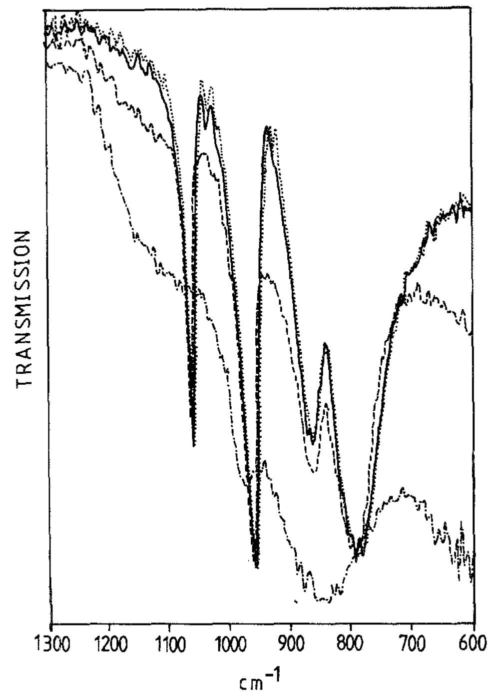

Fig. 4. IR spectra of: ——— K_3 after standard treatment at 623 K, –·–·– H_5 overheated at 673 K, ····· H_5/K_3 overheated at 673 K, – – – mechanical mixture of H_5 overheated at 673 K and K_3 in ratio as for H_5/K_3.

the mixture of the support and overheated H_5 in the quantitative ratio corresponding to that of the supported H_5/K_3 sample shows both peaks characteristic for the $K_3PMo_{12}O_{40}$ phase and those found in the decomposed H_5. IR spectra corresponding to the X-ray diagrams are shown in fig. 4. Also here it is evident that the H_5 phase becomes stabilized against overheating when impregnated on the K_3 support. The IR spectrum of the overheated H_5/K_3 catalyst does not differ from that of the support and is typical of the undestroyed Keggin anions. On the other hand the mechanical mixture of the overheated H_5 and K_3 shows, besides the peaks characteristic for the latter, also the features of a decomposed H_5, as can be seen by comparison with the spectrum of the pure, overheated H_5 where the characteristic Keggin unit pattern is practically annihilated.

Our results prove clearly that intimate contacts between the heteropolyacid of the $H_{3+n}PV_nMo_{12-n}O_{40}$ series and the $K_3PMo_{12}O_{40}$ support created during the preparation of impregnated samples produces a new quality of the supported acid layer, which becomes resistant against treatment at elevated temperatures. The catalytic tests further indicate that the interaction with the support leads not only to the strengthening of the heteropolyacid structure, but also to the pronounced modification of its acid-base and redox properties.

References

[1] R. Pearce and W. Patterson, in: *Catalysis and Chemical Processes* (Leonard Hill, 1981) p. 279.

[2] J.B. Black, N.J. Clayden, P.L. Gai, J.D. Scott, E.M. Serwicka and J.B. Goodenough, J. Catal. 106 (1987) 1.

[3] J.B. Black, J.D. Scott, E.M. Serwicka and J.B. Goodenough, J. Catal. 106 (1987) 16.

[4] E.M. Serwicka, J.B. Black and J.B. Goodenough, J. Catal. 106 (1987) 23.

[5] H.-G. Jerschkewitz, E. Alsdorf, H. Fichtner, W. Hanke, K. Jancke and G. Ohlmann, Z. Anorg. Allg. Chem. 526 (1985) 73.

[6] M. Misono, in: *The Chemistry and Uses of Molybdenum*, eds. H.F. Barry and P.C.H. Mitchell (Ann Arbor, Michigan, 1982) pp. 289–295.

[7] M. Akimoto, H. Ikeda, A. Okabe and E. Echigoya, J. Catal. 89 (1984) 196.

[8] J.B. McMonagle and J.B. Moffat, J. Catal. 91 (1985) 132.

[9] G.A. Tsigdinos and C.J. Hallada, Inorg. Chem. 7 (1968) 137.

[10] G.A. Tsigdinos, Ind. Eng. Chem. Res. Dev. 13 (1974) 267.

[11] K. Brückman, J. Haber and T. Wiltowski, J. Catal. 106 (1987) 188.