Catalysis Letters 39 (1996) 275–279

Ethene oxidation over supported heteropoly acids

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Received 23 August 1995; accepted 23 February 1996

Heteropoly acids of composition $H_{3+x}PMo_{12-x}V_xO_{40}$ supported on silica and γ-alumina catalysed the ethene oxidation with high selectivity to acetic acid. Acidic properties of the catalytic system, heteropoly anion structure and surface area affect the oxidation reaction.

Keywords: heterogeneous catalysis; heteropoly acids; ethene oxidation; acetic acid

1. Introduction

Heteropoly acids with Keggin structure have been successfully employed as catalysts for a variety of processes. The presence of very strong acidic protons makes them active for reactions proceeding via a carbonium ion mechanism [1–3]. On the other hand, the transition metals present in the Keggin structure allow their use as catalysts for oxidation reactions [3–7]. Red-ox properties of heteropoly compounds with Keggin structure depend both on polyanion elements [1,3,8] and countercations [4,5]. 12-heteropoly compounds with Mo as the main polyatom (which can be partly exchanged with V) are usually employed as catalysts for oxidation reactions. Vanadium-substituted unsupported and supported heteropoly acids were found to be very active for catalytic oxidation of acrolein and methacrolein to the appropriate acids [9,10]. The oxidation of acetaldehyde to acetic acid has been reported to occur over HPMo and its caesium salt with high selectivity [11,12]. The olefin oxidation over heteropoly acids was investigated by Ai [13,14], who has found high conversion of 1-butene and butadiene with maleic anhydride and furan as the main products. According to this author ethene, propylene and benzene were scarcely oxidised over HPMo and its salts. On the other hand, ethene oxidation to acetaldehyde over the $Pd/HPMoV/SiO_2$ system under heterogeneous conditions, at temperatures below 373 K, has been recently reported [15]. At temperatures higher than 373 K, ethene was oxidised to acetic acid, but unfortunately, deep oxidation towards CO and CO_2 was predominant if palladium was present in the catalytic system.

This work is focused on direct oxidation of ethene to acetic acid on supported and unsupported $H_{3+x}PMo_{12-x}V_xO_{40}$. The correlation between acidic properties, heteropoly anion structure and oxidation activity and selectivity has been examined.

2. Experimental

Catalysts: The $H_{3+x}PMo_{12-x}V_xO_{40}$ ($x = 0, 1, 2, 3$) heteropoly acids were prepared according to literature data [16] and they were used as unsupported catalysts after calcination at 573 K for 2 h. The silica support was a commercial product calcined at 873 K for 6 h. γ-alumina was prepared by hydrolysis of aluminium isopropoxide according to the procedure described in ref. [17] with subsequent calcination at 873 K for 6 h. The surface areas of the supports were 237 and 208 m^2/g, respectively. The supported catalysts with HPA loading of 9–50 wt% were prepared by incipient wetness technique, then dried at 373 K and eventually calcined at 573 K for 2 h.

Catalytic measurements: Ethene oxidation was carried out at 503 and 573 K using a continuous flow reactor working under atmospheric pressure. The feed (ethene, air and steam with volume ratio 1 : 20 : 4) was introduced into the catalyst bed with apparent residence time, $W/F = 60$ mg min/ml ($W =$ weight of catalyst, in mg.; $F =$ flow rate of reagents, in ml/min).

Acidity of the samples was estimated from their activity for dehydration of 2-propanol (at 448 K) and for disproportionation of toluene (at 573 K). The test reactions were carried out in a pulse micro reactor connected to the GC.

IR spectra were recorded (KBr pellets) using a Perkin-Elmer model 180 spectrophotometer. The ethene and pyridine adsorption was studied using an IR vacuum cell. The catalysts were prepared as self-supported wafers and placed into a vacuum cell provided with NaCl windows. The sample was heated at 573°C in the presence of oxygen for 1 h, then cooled down to room temperature (RT) and evacuated at RT. IR spectra were recorded at RT. Ethene was introduced into the vacuum cell at RT (50 Torr) and heated at 423 K for 1 h. Spectra were recorded either without evacuation of ethene or after short (15 min) evacuation at room temperature. Pyridine was introduced into the sample in the vacuum cell at room temperature and evacuated at 423 K for 1 h. The spectra of adsorbed pyridine were recorded at RT. Ethene was introduced into the sample after adsorption of pyridine in the same way as into the neat catalyst. After 1 h heating at 423 K the IR spectra were recorded.

3. Results and discussion

Ethene oxidation was performed at 503 and 573 K over free and supported (silica or γ-alumina) $H_{3+x}PMo_{12-x}V_xO_{40}$ ($x = 0, 1, 2, 3$) heteropoly acids. Acetic acid and CO_2 were the main products of the oxidation reaction. However, acetaldehyde and traces of acetone and methyl acetate were also found among the products. The oxidative activity of catalysts depended on the composition of the heteropoly anions (fig. 1) and the HPA loading (fig. 2), and it was correlated with the acidity of the samples (figs. 1 and 2). The experiments were performed for 3 h unless the catalyst was deactivated earlier.

The modification of 12-molybdophosphoric acid with vanadium atoms leads to a noticeable increase in ethene conversion and affects also the product selectivity (fig. 1, curve 2). The oxidative activity of heteropoly acids is usually attributed to the facility of reduction and reoxidation of the heteropoly anions [4–6] and also to their acidic properties [13,14,18]. According to Misono [1,8], the reducibility of a series of $HPMoV_x$ compounds increases with the value of x. On the other hand, for vanadium-substituted $HPMoV_x$ the number of protons also increases with the value of x, which should affect the acidity of the samples. It is also known that olefins and other electron-donating (i.e. basic) compounds have a strong affinity to catalysts possessing acidic centres and, as a result, can be strongly activated [18]. The acidity of free and supported catalysts was estimated from their activity in the standard acidic test reaction of 2-propanol dehydration (fig. 3). The series of pure acids show the maximum of propene formation for the HPMo sample, whereas the acidity of silica-supported catalysts increased from HPMo/Si to $HPMoV_2$/Si. The pure acids have very small surface areas (6–2 m^2/g going down from HPMo to $HPMoV_3$) while the silica supported samples have surface areas of 180–160 m^2/g (depending on HPA loading). Considering the above, the trends in the acidity changes for pure and supported heteropoly acids suggest that dehydration of 2-propanol at 448 K occurs mainly on the outer catalyst surface, not in the bulk. This conclusion is in agreement with literature [19,20]. According to Izumi [19] and Ohitsuka [20], the reactions catalysed by HPA at temperatures higher than 423 K in the vapour phase, proceed principally on the outer surface and not in the pseudo-liquid phase. At the temperature of 423 K or higher, only little water can exist in the HPA bulk and the crystal structure becomes too rigid to accept reagent within. In our work, the dehydration of 2-propanol was carried out at 448 K over heteropoly acids calcined at 573 K and according to the reports quoted above [19,20] the reaction can involve mainly protons from the outer surface, not from the

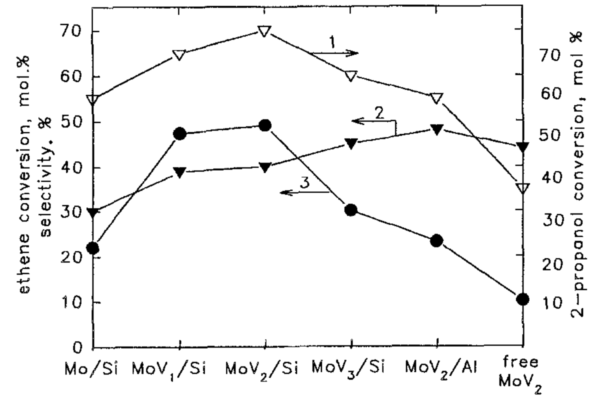

Fig. 1. Ethene oxidation and 2-propanol conversion over supported (30 wt%) $H_{3+x}PMo_{12-x}V_xO_{40}$ versus value of x; (1) total ethene conversion, (2) selectivity to acetic acid, (3) acidity of the samples expressed as an activity for 2-propanol dehydration.

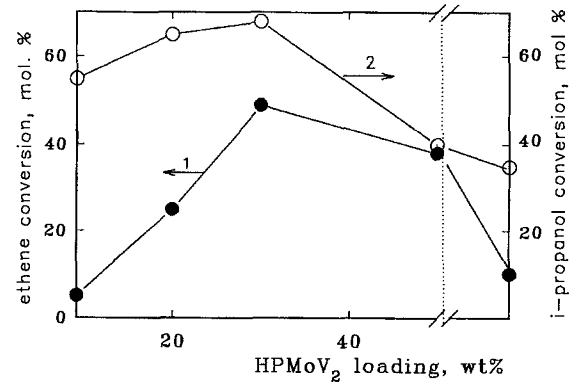

Fig. 2. Change of ethene conversion and $HPMoV_2$ acidity versus heteropoly acid loading on silica support; (1) ethene conversion (503 K); (2) 2-propanol conversion (448 K).

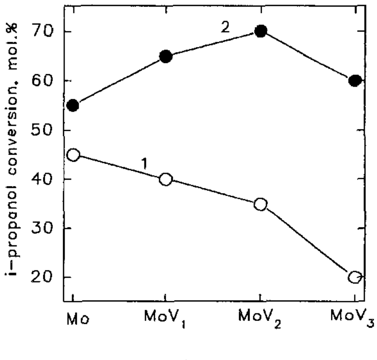

Fig. 3. Conversion of 2-propanol to propene over supported (2) and unsupported (1) $HPMoV_x$.

bulk. Heteropoly acids supported on silica in an amount close to the monolayer coverage (30 wt%) have almost all protons accessible for reagents (except the part that interacts with the support [21,22]). Therefore, the acidity of the supported samples, expressed as dehydration activity, increased with the value of x. On the other hand, the apolar ethene molecules can also be adsorbed only on the surface centres, not in the bulk [1,2,19]. Therefore, the correlation between acidity and ethene oxidation activity, observed in our paper (figs. 1 and 2) can be due to ethene activation on acidic centres.

Some decrease in the acidity of $HPMoV_3/Si$ can result from partial degradation of the acid during the calcination at 573 K. The IR spectra of this sample calcined at 573 K showed a lower intensity of the bands characteristic of the KU structure, indicating partial decomposition.

Neither free nor supported HPA containing Mo or Mo and V catalysed the toluene disproportionation at 573 K. This shows a lack of strong acidic centres on molybdenum and vanadium containing heteropoly acids, in agreement with reports by Serwicka et al. [23]. The toluene disproportionation reaction required strong acid sites [24,25] and it proceeded with a good yield over 12-tungstophosphoric and 12-tungstosilicic acids supported on silica and γ-alumina [26].

The ethene oxidation over different $HPMoV_x$ compounds supported on silica with loading of 30 wt% correlated with the acidity of the supported samples and it increased with the number of vanadium atoms introduced into the KU (fig. 1). The unsupported acids showed much lower activity for ethene oxidation than the supported ones and this activity decreased very fast (fig. 2).

The initial conversion of ethene over supported $HPMoV_x$ at 503 K was relatively high; however, the selectivity towards acetic acid was low and CO_2 was a predominant product. During the reaction, the ethene conversion decreased moderately but selectivity to acetic acid increased and remained relatively stable (fig. 4). If the experiment was extended to 8 h a continuous, slow decrease in ethene conversion was observed.

When ammonia was introduced into the catalyst working at 573 K, the oxidative activity fell down dramatically and it was only partially restored after 3 h of gas flow. This experiment confirms the influence of acidity on the ethene oxidation reaction. The importance of the presence of both acidic and basic sites for olefin oxidation over HPA was emphasised by Ai [13,14,18]. On the other hand, Misono et al. suggest [6] that rather low amounts of Brønsted acidic sites, besides the high oxidising ability, are profitable for acetic acid formation during the oxidation of acetaldehyde. In order to check the influence of acidic sites on ethene oxidation, the sodium salts of $HPMoV_1$ acid, with different amounts of sodium cations (1, 2, 3, 4), supported on silica, were tested for ethene oxidation (fig. 5). When all acidic protons were replaced by sodium cations no oxidation products were found over $Na_4PMo_{11}VO_{40}/SiO_2$ catalyst. This result follows our earlier finding concerning the importance of acidic sites. But, if protons were replaced by sodium only partially, the ethene conversion exceeded even the activity of the parent acid (fig. 5). The high oxidative activity of the sodium salt, notwithstanding its low acidity, is in agreement with Misono's conclusion [6]. Additionally, it is also known from the earlier reports [4,5,27], that sodium cations can affect the reduction and re-oxidation of heteropoly anions. Bondareva et al. [27] emphasised the much easier re-oxidation of potassium cation modified HPMo compared to pure acid. Therefore, the influence of sodium cations on the ethene oxidation can be attributed both to the distribution of acidic centres and the re-oxidation facility.

The IR spectra of fresh and working sodium salt (supported on silica) used for ethene oxidation (table 1) indicates that during the oxidation process the sodium salt undergoes the reduction in much less extent than the supported acid. This can probably result from slow reduction and fast re-oxidation of alkali salts as reported by Bondareva [27] and Akimoto [4,5].

When ethene was adsorbed on silica supported HPA at room temperature (in vacuum IR cell) no bands originating from chemisorbed species were found. After heat-

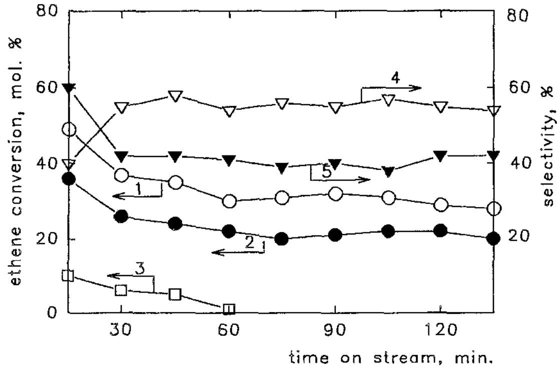

Fig. 4. Change in ethene conversion (curves 1, 2, 3) and selectivity to CH_3COOH (4) and to CO_2 (5) over $HPMoV_2/SiO_2$ (1, 2, 5), $HPMoV_2/Al$ (2) and free $HPMoV_2$ (3); reaction temperature 503 K.

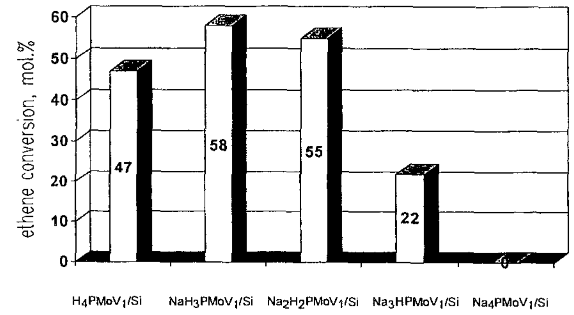

Fig. 5. Ethene oxidation over silica supported sodium salts of H_4PMoVO_{40} acid versus number of sodium cations in KU.

Table 1
Integrated intensities of $\nu_{960\,\mathrm{cm}^{-1}}$ and $\nu_{870\,\mathrm{cm}^{-1}}$ bands of fresh and working H_4PMoV_1/Si and $Na_2H_2PMoV_1$/Si catalysts

Catalysts	Integrated intensities (arb. units mg^{-1})	
	$\nu_{960\,\mathrm{cm}^{-1}}$	$\nu_{870\,\mathrm{cm}^{-1}}$
H_4PMoV_1/Si		
fresh	170	57
after ethene oxidation	168	20
$Na_2H_2PMoV_1$/Si		
fresh	133	59
after ethene oxidation	130	33

ing at 423 K for 1 h, the weak band at 1715 cm^{-1} with a shoulder at 1725 cm^{-1} (fig. 6) has appeared. These features can be due to ν(C=O) of carbonyl species formed on the catalyst surface as a result of ethene oxidation. Formation of acetaldehyde from ethene with further oxidation to acetates on metal oxide catalysts containing OH groups has been already reported [28–30]. Evacuation at RT reduced the intensity of these bands and an evacuation at the temperature of 353–373 K removed them completely. Pre-adsorption of pyridine followed by evacuation at 423 K eliminates the sites capable to adsorb ethene with following oxidation at higher temperature and we did not observe the bands at 1725 and 1715 cm^{-1} any more after further contact of the catalyst with ethene at 423 K. This suggests that the medium and weak acidic centres are involved in the ethene oxidation process. It is likely that acetaldehyde can be obtained from ethene by the reaction of the last one with acidic hydroxy groups ($H^+ \cdots O^-$ (KU)) and subsequent formation of intermediate ethoxy species, which are dehydrogenated to acetaldehyde very fast. Acetalde-hyde can be easily oxidised at the temperature of 423 K or higher with the formation of acetic acid. According to Ai [18], further oxidation of acidic compounds is rather difficult because they are activated slightly on the heteropoly acids surface which is poor in basic centres.

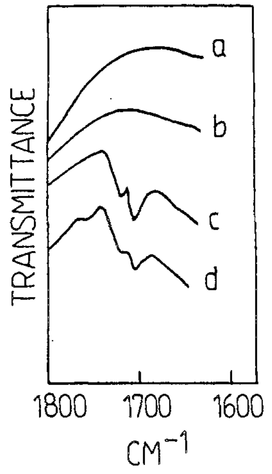

Fig. 6. IR spectra (vacuum cell) of ethene adsorbed on $HPMoV_2$/Si. (a) Adsorption at room temperature, no evacuation, (c) adsorption at 423, no evacuation, (d) sample (c) evacuated 15 min at room temperature, (b) sample after pyridine adsorption (evacuation at 423 K) followed by adsorption of ethene at 423 K without evacuation of the latter.

4. Conclusions

Silica and γ-alumina supported heteropoly acids containing Mo and V as polyatoms show high activity for ethene oxidation in contrast to unsupported ones. The modification of heteropoly anions by the partial replacement of molybdenum with vanadium atoms leads to a noticeable increase in ethene conversion. The acidity of the samples influences significantly the oxidative activity of heteropoly acids; however, there is no simple correlation between acidity and oxidation activity. The ethene adsorption occurs on weak acidic centres with the formation of adsorbed carbonyl species which are fast oxidised to acetic acid.

Acknowledgement

We thank the Polish Committee for Science Research (KBN) for financial support (Grant 3 T09A 168 08).

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