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Ethane to acetic acid oxidation over supported heteropoly acids

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Abstract

Molybdo(vanado)phosphoric heteropoly acids of Keggin structure supported on oxide supports (SiO_2, TiO_2, Al_2O_3) were used as catalysts for ethane to acetic acid oxidation in the range of reaction temperature from 250 to 400 °C. Vanadium atoms introduced into Keggin structure enhanced oxidative activity of catalytic system, while vanadyl groups exchanged into cationic position diminished ethane conversion. Nature of support (acidic or base centres on the surface) influenced both ethane conversion and distribution of products. Ethane oxidation over silica- and titania-supported $HPMoV_x$ was due to the presence of regular or defected Keggin structure while low catalytic performance on alumina-supported samples was attributed to mixed Mo–V–P oxides formed as a result of $HPMoV_x$ decomposition. Presence of water vapours in the reaction mixture was indispensable both for catalysts surface modification and for acetic acid desorption.

Keywords: Ethane oxidation; Heteropoly acids; FT-IR spectroscopy; Acetic acid production

1. Introduction

Light paraffins oxidation attracts the attention of both many research groups and chemical industry as they are available and relatively cheap reagents [1]. The selective oxidation occurring with oxygen insertion into alkane molecules may result in the production of alcohols, aldehydes or carboxylic acids [2], while the oxidative dehydrogenation may be a source of olefins [3]. However, considering the very low reactivity of alkanes, especially of short-chain hydrocarbons, the very severe conditions (high temperature) have to be employed for reagents activation. In a consequence, the reaction of total oxidation leading to the thermodynamically most stable products (CO_2 and H_2O) predominates. Many different catalysts such as mixed transition metal oxides [4,5], irreducible metal oxides [6] and also supported noble metals [7] were tested as catalysts for selective oxidation of light paraffins. Among the potential catalysts also heteropoly compounds were considered as promising catalysts for this reaction [8–11]. Heteropoly acids of formula $H_{(3+x)}PMo_{(12-x)}V_xO_{40}$ (abbr. $HPMoV_x$) showing the unique catalytic features due to their bifunctional nature (strong acidic protons and transition metal ions) and feasibility of different modifications were applied as an active catalysts both for acidic and oxidative reactions. Unsupported heteropoly compounds (acids and caesium salts) containing molybdenum and vanadium atoms in anion structure have been used as catalysts for hydrocarbons oxidation in the range of temperature from 300 to 425 °C [8–11]. Oxygen bearing compounds (aldehydes and acids) were formed as a result of propane and i-butan oxidation in the presence of unsupported caesium salt of $HPMoV_x$ modified additionally with transition metal cations. Ethane oxidation resulted only in ethene (product of oxydehydrogenation reaction) and carbon oxides. No acetaldehyde and acetic acid was reported among the products [9]. In the earlier report by Moffat [12] it was presented that using silica-supported HPMo, at temperature as high as 540 °C, ethane was transformed not only to ethene and CO_x but also to oxygen-bearing product (acetaldehyde). However, acetic acid was not observed and despite of high temperature, ethane conversion did not exceed 3%.

Industrial production of acetic acid is dominated by methanol carbonylation process. However, direct ethane to acetic acid oxidation would be an attractive alternative route

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considering the low cost of ethane feedstock and high investment expenditure for methanol carbonylation. Energetic and economic analysis of direct ethane to acetic oxidation process has been performed recently [13] and it was suggested that further increase in selectivity towards acetic acid is necessary to make this method competitive to methanol carbonylation.

Considering the above, a number of contributions searching for new catalytic systems active in ethane to acetic acid oxidation has been developed. Oshikara et al. [14] have used heteropolymolybdate of Anderson structure modified with vanadium, gallium or iron ions as catalysts for ethane to acetic acid oxidation, however, the yield of acetic acid did not exceed 0.3%. Linke et al. [15,16] have studied mixed oxide catalyst modified with traces of palladium and they have evidenced two-step mechanism of oxidation involving ethane oxydehydrogenation to ethene and subsequent Wacker oxidation to acetic acid. Ruth et al., using oxide multiphase (Mo–Nb–O) catalyst achieved the best acetic acid yield (about 2%) at 240 °C, under pressure of 2 MPa and with contact time 79 s [5]. Higher yields of acetic acid were reported only in patent literature [17].

Considering the ability of heteropoly compounds to activate alkanes at relatively low temperature (starting from 300 °C [10]) we have used 12-molybdo phosphoric acid modified with different number of vanadium atoms ($x = 0$–3) and supported on different oxide supports (γ-alumina, silica and titania) as catalysts for ethane to acetic acid oxidation. HPMoV$_x$/support systems showed relatively high acidity, which should additionally stimulate the advantageous conditions for acetic acid formation as it was suggested in the earlier report [18]. Acidity of supported system depended on oxide support nature [19], therefore, we have expected an influence of chemical surface feature of supports on oxidative activity of supported catalysts. Taking into account the possible release of vanadium atoms from the Keggin unit at temperature of oxidation reaction, the effect of vanadium atom localised in the Keggin structure or in vanadyl cationic position on oxidative activity of catalysts has also been investigated.

2. Experimental

Heteropoly acids (HPA) of Keggin structure ($H_{(3+x)}PMo_{(12-x)}V_xO_{40}$ (abbr. HPMoV$_x$)) were synthesised according to literature [20]. Correctness of synthesis was examined by FT-IR and ^{31}P NMR spectroscopy. ICP analysis was undertaken to estimate the number of vanadium introduced into heteropoly anions.

HPMoV$_x$ (x = 0, 1, 2, 3) were supported on SiO_2, Al_2O_3 and TiO_2 by incipient wetness method with following calcination at 350 °C for 2 h. Concentration of active phase in supported catalyst was in a range of 5–50 wt.%, which related to 0.3–4.6 mol% of HPMoV$_x$. SiO_2 was a commercial product of POCH, which was grounded and calcined at 500 °C. γ-Al_2O_3 and TiO_2 were synthesised by means of hydrolysis of respective i-propoxides with following washing, drying and calcination. Alumina was calcined at 600 °C for 6 h and titania was calcined at 400 °C for 10 h. From XRD measurements, it was concluded that alumina showed low crystallinity and could be described as γ-alumina, while titania showed the XRD patterns typical of anataz form. Catalytic test was performed under following conditions:

- 2 g of catalyst;
- atmospheric pressure;
- temperature of reaction: 250–400 °C;
- ethane:oxygen:water vapour:nitrogen = 2:1:1.8:4;
- WHSV = 0.35 g/g/h.

3. Results and discussion

Unsupported heteropoly compounds modified with small number of transition metal cations (HMPMoV$_x$) have been reported to catalyse propane, isobutane and ethane oxidation reactions [8–11]. The oxygen-bearing compounds were noted among the oxidation products. However, both alkanes conversion and selectivity towards oxygenates was the highest for i-butane oxidation and decreased subsequently for propane and ethane oxidation [9]. The use of caesium salt of HMPMoV$_x$ of much higher surface area than the free acids, resulted in the better oxidation performance thanks to better availability of active centres [9–11]. Considering the very low surface area of free heteropoly acids (1–6 m^2/g) the supporting of HPA on a high surface area carriers should also be advantageous.

Taking above into account, in the presented paper, heteropoly acids HPMoV$_x$ (x =0–3) were dispersed on oxide supports, such as SiO_2, Al_2O_3 and TiO_2 of surface area equal 250, 130 and 80 m^2/g, respectively, to make the active centres more available to reagents. HPMoV$_x$ was introduced on supports commonly with amount of 30 wt.% which related to the values expressed in mol% equal 1.4, 2 and 2.4 mol% for HPMoV$_x$ on SiO_2, TiO_2 and Al_2O_3, respectively (difference stem from different molecular weight of supports). Considering the area occupied by one KU (diameter of KU is about 1.2 nm; assuming the approximately circular shape of KU, an area occupied by one KU should be about 1.1 nm^2) one can calculate that this amount of HPMoV$_x$ could cover about 100 m^2. Taking into account the magnitude of surface area of the supports one can suppose that titania should be covered completely with the active phase, while silica and alumina only partly. However, it was demonstrated earlier [21] that accommodation of supported species does not occur equally on different crystallographic walls of support. Therefore part of surface may be covered with 2 or 3 layers of the active phase whereas some other part may be still uncovered. In a consequence an influence of oxide supports on alkane transformation on HPMoV$_x$ should be noted.