Heteropoly compounds as precursors of catalysts for oxydehydrogenation of ethane

K. Nowińska, A. Wącław, M. Sopa, and M. Klak

Faculty of Chemistry, A. Mickiewicz University, Grunwaldzka 6, 60-780 Poznań, Poland

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Lacunary tungstophosphoric heteropoly compounds of Keggin structure modified with excess of manganese ions and subsequently calcined at 430–500 °C show high activity and selectivity in oxydehydrogenation of ethane. Steady state ethane conversion is about 25% and selectivity towards ethene 60%. The active catalytic system being a result of reaction between a lacunary heteropoly compound and excess of manganese (II) cations does not show the Keggin structure anymore.

1. Introduction

Catalytic oxidation of light paraffins for the purpose of formation olefins or oxygen-containing organic compounds such as alcohols, aldehydes or acids is a process of potential commercial importance with respect to utilisation of alkanes. However, light paraffins show very low reactivity and they require a high temperature for their activation, whereas the partial oxidation products are much more reactive and may be easily oxidised to CO_2 under the reaction conditions. Mixed oxides [1,2] and also modified heteropoly compounds (HPC) of Keggin structure containing molybdenum or tungsten as terminal atoms [3–5] have been considered as catalysts for ethane, propane and *i*-butane oxidation. Ethylene is a very important reagent for many industrial processes. It is produced mainly by means of the endothermic, high-temperature pyrolysis of propane. This energy-consuming technology could be replaced by the catalytic oxydehydrogenation of ethane. However, the selectivity of the catalysts is rather low and carbon oxides are usually the main products. We have recently found that lacunary heteropoly compounds modified with manganese ions show high selectivity for propane oxydehydrogenation. We have also proved that excessive manganese ions influence significantly the activity of the modified samples. The aim of the following study was to gain a better understanding of the effect of excessive manganese ions on the possible transformation of lacunary heteropoly compounds.

2. Experimental

Lacunary heteropoly compounds were synthesised by means of alkalisation of an aqueous solution of 12-tungstophosphoric acid with 0.5 M aqueous solution of $KHCO_3$ up to a pH value of 2–5.2 in order to remove one terminal tungsten atom from the Keggin unit. Subsequently, Mn^{2+} ions were introduced into octahedral lacuna and into cationic position. For more details see [5]. The samples were characterised by means of thermogravimetric measurements (DTA, DTG), XRD patterns and FTIR and Raman spectroscopies.

The mixed oxide-like systems containing tungsten, phosphorus, manganese and potassium were prepared *via* an aqueous slurry comprising the ions of interest (H_3PO_4, $MnCl_2{\cdot}4H_2O$) and Na_2WO_4 in related amounts. The slurry was heated at 90 °C for 4 h, which was followed by water evaporation at about 100 °C. The paste was dried at 130 °C overnight and subsequently calcined at 400 or 500 °C for 6 h.

The samples were characterised by means of FTIR and Raman spectroscopies and also by XRD patterns.

All the samples were tested for ethane oxidation reaction. Ethane was oxidised at 400 and 430 °C in a continuous flow reactor at $\mathrm{WHSV} = 0.22$ or $0.12\,\mathrm{g/(g\,h)}$, using 0.5 g of catalyst (grain of 0.5–1.0 mm) and the following feed composition: $\mathrm{air : ethane} = 25:1$.

3. Results and discussion

It was reported earlier [5] that over-stoichiometric manganese ions introduced into lacunary heteropoly compounds influenced significantly the oxidative activity of modified HPC. It was also suggested that a thermal treatment in the range of 460–480 °C resulted in a reaction of lacunary heteropoly compounds with over-stoichiometric Mn^{2+} ions to form the oxide-like system. One could believe that the newly formed system may be responsible for the activity in the oxydehydrogenation reaction.

Having taken into account the above, two series of catalysts containing the same concentration of related

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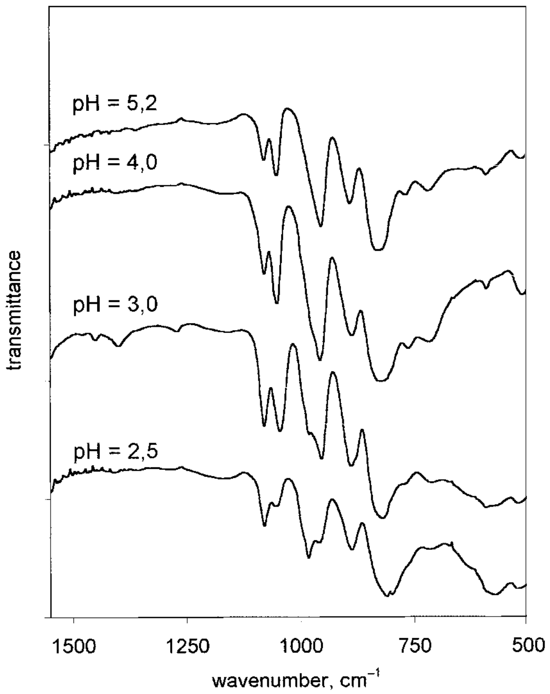

Figure 1. FTIR spectra of the manganese-modified lacunary heteropoly compounds (HPW) synthesised by alkalisation at different pH.

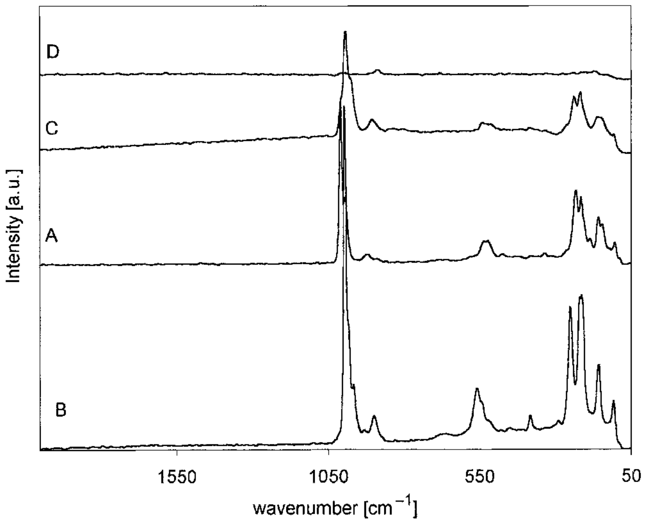

Figure 2. Raman spectra of HPW of regular structure (spectrum A), and manganese-modified lacunary HPW synthesised at pH = 5.2 (spectrum B) and pH = 3.0 (spectrum C); D—sample synthesised at pH = 3.0 and calcined at 400 °C.

oxides (MnO, P_2O_5, WO_3) were prepared. The first one, based on heteropoly compounds, was prepared by modifying tungstophosphoric lacunary heteropoly compounds ($PW_{11}O_{39}^{-7}$) with manganese ions, as was already described earlier [5]. The second one was synthesised by mixing related amounts of H_3PO_4, $MnCl_2 \cdot 4H_2O$ and Na_2WO_4 in an aqueous solution at about 90 °C for 4 h with subsequent drying at 70–100 °C and calcination at 400 or 500 °C.

As-synthesised samples prepared by the modification of lacunary heteropoly anions of Keggin structure (pH of partial degradation in the range 2.5–5.2) and modified with manganese ions show the proper lacunary structure, which was confirmed by FTIR (figure 1) and Raman (figure 2) spectra. FTIR spectra of lacunary heteropoly compounds synthesised in the range of pH 2.5–5.2 showed splitting of the band of P–O bond (figure 1), which indicated lower symmetry of the central atom environment resulting from one terminal atom removal. The Raman bands of lacunary heteropoly anions showed a characteristic shift of the main band towards the higher frequencies [6,7], relating to the band of HPW of regular structure (figure 2, lines B and C). The intensity of Raman bands of lacunary HPW was lower for the sample synthesised at low pH (figure 2, line C), and they almost disappeared after thermal treatment at 400 °C (figure 2, line D).

XRD patterns recorded for lacunary heteropoly compounds synthesised at different pH and modified with manganese ions are shown in figures 3 and 4. The samples prepared at low pH and dried at 100 °C indicated patterns originating both from lacunary heteropoly anion and from the regular Keggin structure (figure 3). Calcination at 400 °C resulted in decrease in the intensity of XRD patterns, whereas the treatment at higher temperatures (500 and 650 °C) led to the appearance of new patterns, which indicated formation of a new phase.

XRD reflectance of the samples synthesised at pH = 5.2 and dried at 100 °C showed rather low intensity except for the main peak characteristic of lacunary structure (2 theta 9.2) (figure 4). Calcination at 400 °C and 500 °C resulted in rebuilding of the regular HPW structure. The subsequent thermal treatment at 650 °C led to the appearance of new reflectance indicating the presence of a new phase.

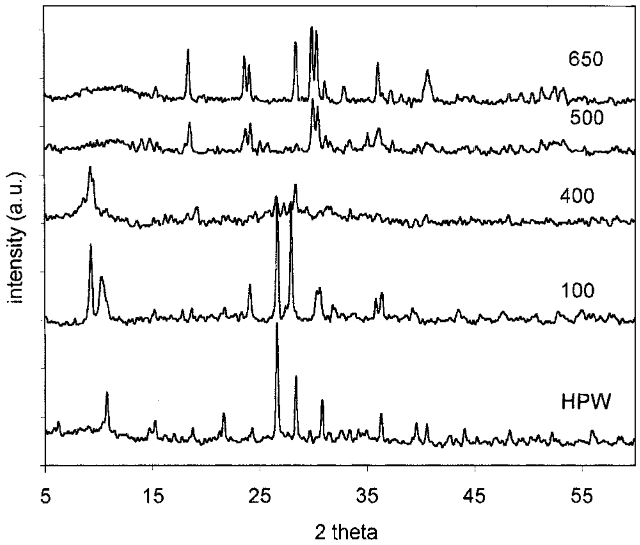

Figure 3. XRD patterns of HPW and manganese-modified lacunary HPW synthesised at pH = 3.0 and calcined at different temperatures.

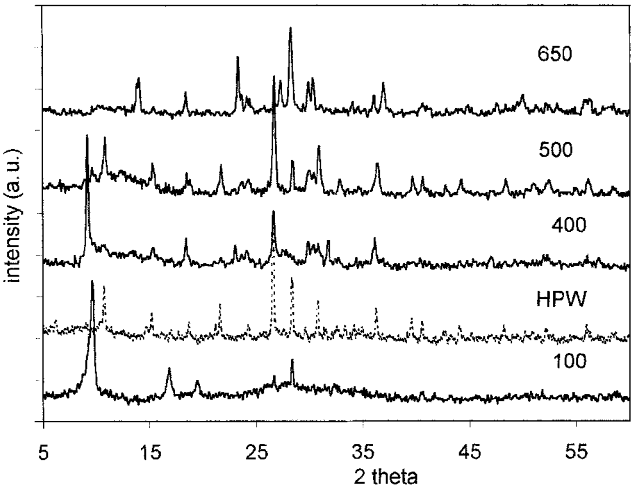

Figure 4. XRD patterns of manganese-modified lacunary HPW synthesised at pH = 5.2 and calcined at different temperatures.

The new reflectance, which appeared in XRD patterns recorded after high temperature treatment of manganese modified heteropoly compounds (figures 3 and 4), can be attributed neither to manganese [8,9] nor to tungsten [10,11] oxides.

Thermogravimetric measurements performed for the samples prepared at low pH showed two endothermic effects in the temperature range from 400 to 500 °C (figure 5, line A). The weaker endothermic effect appeared at 430–440 °C and the stronger one at 460–480 °C. The main loss of mass for all the samples was observed at about 100 °C (figure 5, line D—DTG curve for the sample prepared at pH = 3.0, line C—DTG curve for the sample prepared at pH = 5.2). The sample prepared at low pH showed additional loss of mass at the temperature of endothermic effects (figure 5, line D). The sample prepared at pH 5.2 showed an endothermic effect at about 570 °C (figure 5, line B), which could be attributed to the decomposition of the Keggin unit, usually observed at about 600 °C [12]. Additional experiments showed that samples synthesised at low pH (2.5, 3.0, 3.5 and 4.2) and modified with manganese were melted at about 480 °C. This suggested that the endothermic effect recorded at about 480 °C could be due to melting of the mixture of lacunary HPW and excess of manganese. However, neither manganese oxides nor lacunary HPW show melting up to 535 °C. Therefore, the observed melting of the mixture could indicate that the lacunary HPW system in the excess of manganese ions was transformed into a new phase at a temperature of about 480 °C. This was consistent with results of Raman spectra (figure 2) and also with XRD measurements (figures 3 and 4), which indicated decomposition of the Keggin structure and formation of a new phase as a result of thermal treatment at about 500 °C. Taking into consideration the above results, we could expect that a mixed oxide system could be responsible for the oxidative activity of lacunary HPW modified with over-stoichiometric amounts of manganese. Therefore, the samples containing P_2O_5, WO_3 and MnO in exactly the same ratios as in catalysts prepared by means of modification of lacunary HPW with manganese ions were synthesised and characterised by XRD patterns and FTIR spectra. XRD patterns and FTIR spectra recorded for samples calcined at 100, 400, 500 and 650 °C are presented in figures 6 and 7 respectively. The samples dried at 100 °C indicated XRD patterns, which can be partly attributed to the Mn_2O_3 phase (reflectance labelled as *) [8,9]. Calcination at 400 °C resulted in the disappearance of low-intensity peaks attributed to Mn_2O_3; however, the strongest one was still present

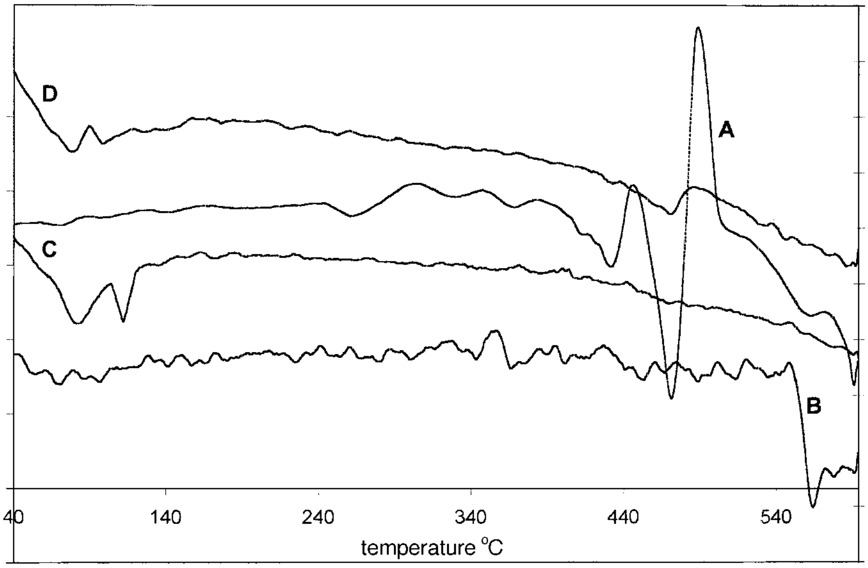

Figure 5. DTA and DTG effects of manganese-modified lacunary heteropoly compounds synthesised at pH = 3.0 (DTA—A, DTG—D) and pH = 5.2 (DTA—B, DTG—C).

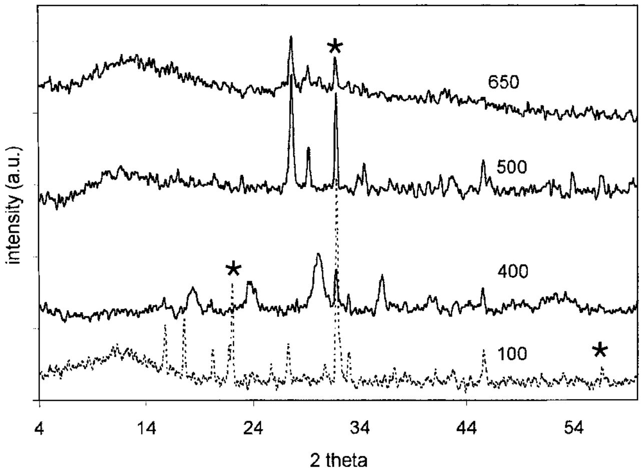

Figure 6. XRD patterns of the oxide-like catalysts calcined at 100, 400, 500 and 650 °C (symbol * indicates reflectance of Mn_2O_3).

even after calcination at 650 °C. Apart from this peak, several new peaks appeared, which can be attributed neither to manganese nor to tungsten oxides. The presence of a new reflectance indicated the formation of a new phase. The comparison of XRD patterns, recorded for the oxide-like system (figure 6) and for lacunary heteropoly compounds modified with manganese and subsequently calcined in the temperature range of 400–650 °C (figure 5), suggested that the thermal treatment of two different precursors resulted in the formation of different materials. Also FTIR spectra of two systems synthesised

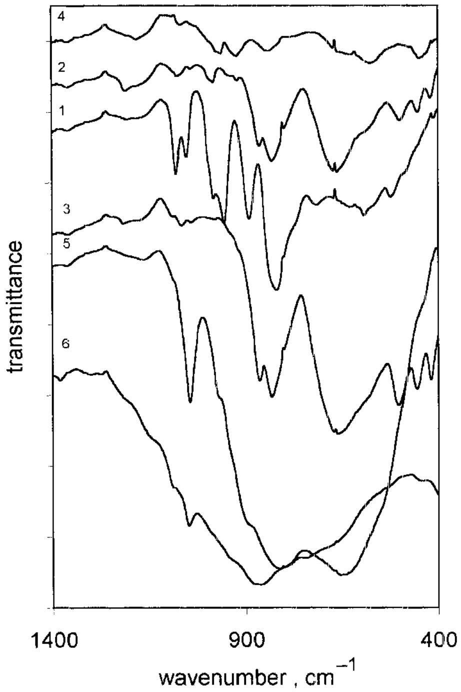

Figure 7. FTIR spectra of manganese-modified lacunary heteropoly compounds (pH = 3.5—1, 2, 3) and oxide-like samples (4, 5, 6) calcined at 100 °C (spectra 1 and 4), 400 °C (spectra 2 and 5) and 500 °C (spectra 3 and 6).

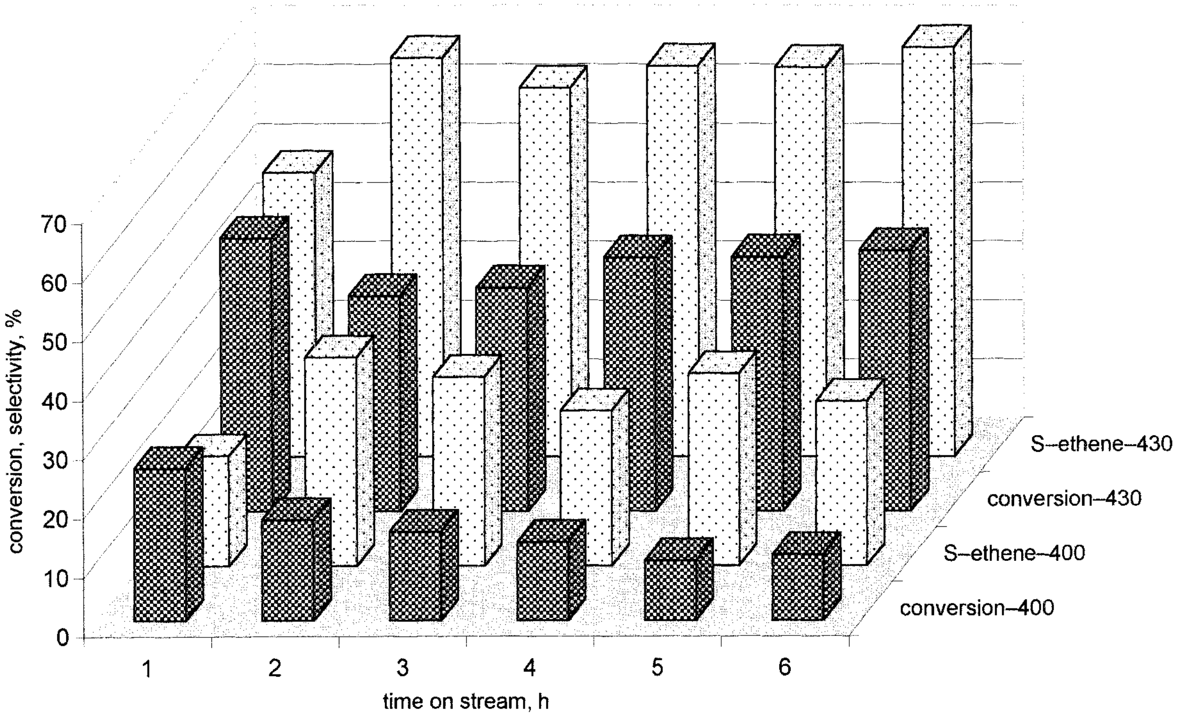

Figure 8. Ethane conversion and selectivity towards ethene over manganese-modified lacunary heteropoly compound calcined at 430 °C (pH of synthesis = 3.5; reaction temperature: 400 and 430 °C).

from different precursors and calcined in the temperature range from 100 to 500 °C (figure 7) indicated the formation of diverse substances.

All the samples prepared were tested for ethane oxidation reaction at 400 and 430 °C. The manganese-modified lacunary HPW prepared at low pH showed high ethane conversion and also high selectivity towards ethene (about 60%). Increase in the reaction temperature from 400 to 430 °C resulted in significant increase in ethane conversion and also in the selectivity towards ethene (figure 8). Some decrease in ethane conversion was observed during the first 2 h of the reaction. Prolongation of the reaction time up to 10 h affected the ethane conversion to a very small degree. Previous calcination of the samples based on the manganese-modified HPW (low pH of syntheses) at 500 °C resulted in a very stable, although slightly lower, oxidative activity (figure 9). The stoichiometric manganese salt of lacunary heteropoly acid ($Mn_{2,5}PW_{11}MnO_{39}$) prepared at pH = 5.2 showed very low activity for ethene oxidation (figure 10), as was similarly found for the propane oxidation process [5].

Mixed oxide-like catalysts showed very high initial ethane conversion and also very high selectivity to ethene (figure 11). Both ethane conversion and selectivity to ethene decreased with time on stream. However, even after 6 h on stream, ethane conversion was still higher than 20% and selectivity was about 50%. Selectivity to oxygenates remained stable while the selectivity to CO_2 increased with time on stream. Calcination of the mixed-oxide samples at 500 °C resulted in significant decrease in their oxidative activity and only traces of ethane conversion were recorded. This indicated that the high-temperature calcination of the mixed oxides affected their transformation into an inactive system. The transformation process of oxide-like catalysts towards an inactive system could proceed slowly during the oxidation reaction upon 430 °C and it could be responsible for the slow deactivation process.

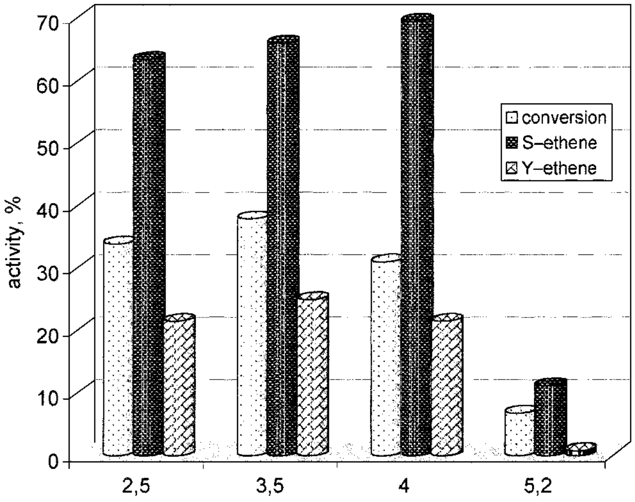

Figure 10. Comparison of the oxidative activity of manganese-modified lacunary HPW synthesised at different pH (ethane oxidation at 430 °C).

On the basis of the described results one can conclude that the modification of lacunary tungstophosphoric acid with excess of manganese (II) cations results in the

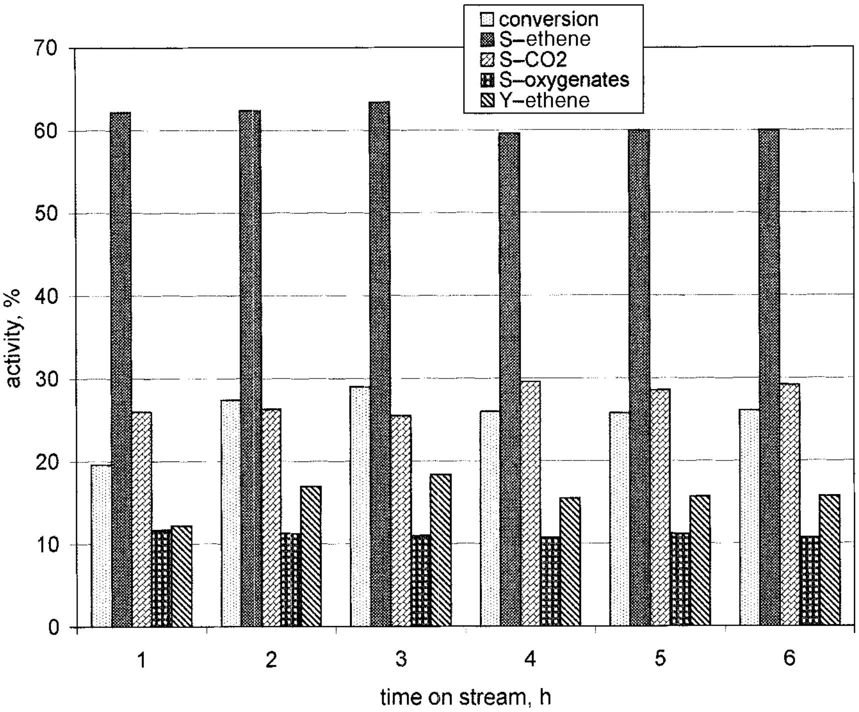

Figure 9. Ethane oxidation at 430 °C over manganese-modified lacunary HPW (pH = 3.5) calcined at 500 °C.

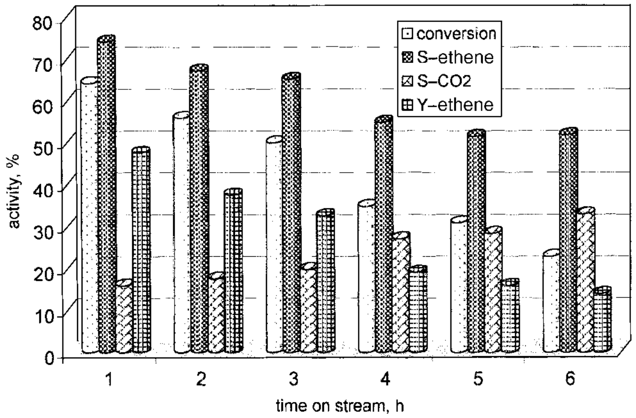

Figure 11. Ethane oxidation (430 °C) over mixed oxide-like catalysts calcined at 430 °C.

formation of a very active and selective catalyst for oxydehydrogenation of ethane. The active phase does not show the Keggin structure, but it also does not indicate features of a mixed-oxide system. It seems that the combination of Mn, W and P ions is very beneficial for the achievement of high selectivity in the ethane oxydehydrogenation process.

Acknowledgment

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