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Oxidative dehydrogenation of ethane to ethylene over antimony-containing Keggin-type heteropolyoxomolybdates

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Abstract

The addition of antimony ions to the potassium/ammonium salts of the 12-molybdophosphoric acid greatly enhanced the thermal structural stability of the Keggin-type heteropolyoxometalates. This unexpected property allowed to employ these materials as catalysts for the oxidative dehydrogenation of ethane to ethylene, a reaction which requires high temperatures. The doping of the compounds with other metal ions increased the activity and the selectivity to ethylene.

1. Introduction

Keggin-type heteropolycompounds find application as heterogeneous catalysts in different oxidation reactions [1]: methacrolein and acrolein oxidation to the corresponding acids, isobutyric acid oxydehydrogenation to methacrylic acid [2]; the reactivity of these compounds is affected by their composition and redox properties. These compounds have also been reported to be active in the selective oxidation of paraffins, such as n-butane and n-pentane conversion to maleic anhydride and to mixtures of phthalic and maleic anhydrides, respectively, as well as in the oxidation of isobutane to methacrolein and methacrylic acid [3]. The polyfunctional nature of these compounds (strong Brønsted and Lewis acidity oxidizing properties) make these systems potentially useful for the activation of saturated compounds.

The most important drawback of heteropolycompounds, which limits their application as heterogeneous catalysts, is the structural decomposition, which occurs in air at temperatures close to 350°C [1]. Higher thermal structural stability is achieved by supporting the compounds, or by exchanging protons with alkali metals. However, usually this worsens the catalytic performance.

With the aim of modifying the redox properties of Keggin-type heteropolyoxometalates, we prepared potassium/ammonium salts of the 12-molybdophosphoric acid doped by addition of antimony ions. It was surprisingly found that the prepared systems were characterized by an exceptional thermal stability, and decomposed at temperatures higher than 500–550°C. In view of their structural stability at high temperatures, the prepared compounds were tested as catalysts in the oxidative dehydrogenation of ethane, a reaction that requires temperatures higher than 400–450°C.

2. Results and discussion

The samples were prepared according to the procedure previously reported [2]. Antimony

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Table 1. Summary of the catalytic performance of antimony-modified heteropolycompounds

Catalyst composition	Cond.	T,°C	Res.time,s	C_2H_6 conv.,%	C_2H_4 sel., %
$K_3P_1Sb_1Mo_{11}O_n$	a	540	2.7	5.7	41
$K_3P_1Sb_1Mo_{11}Fe_1O_n$	a	540	2.7	6.2	83
$K_3P_1Sb_1Mo_{11}Fe_1Ce_{0.25}O_n$	a	540	2.7	9.6	65
$K_3P_1Sb_1Mo_{11}Fe_1Ce_{0.25}Cr_{0.5}O_n$	a	540	2.7	17.2	62
"	a	540	10	26.1	74
"	b	550	12	16.0	68
$K_3P_1Sb_1Mo_{11}Fe_1Ce_{0.5}Cr_{0.5}O_n$	b	550	12	17.0	68
$K_3P_1Sb_1Mo_{11}Fe_1Ce_{1.5}Cr_{0.5}O_n$	b	550	12	17.0	56
$K_1P_1Sb_1Mo_{11}Fe_1Ce_{0.75}Cr_{0.5}O_n$	b	470	10	12.4	54
$K_2P_1Sb_1Mo_{11}Fe_1Ce_{0.75}Cr_{0.5}O_n$	b	470	10	18.1	54
$K_3P_1Sb_1Mo_{11}Fe_1Ce_{0.75}Cr_{0.5}O_n$	b	550	13	19.3	57
"	b	550	2.7	5.6	90
$K_3P_1Sb_1Mo_{11}Fe_1Cr_{0.5}O_n$	b	550	13	12.7	71

salts were added before precipitation of the heteropolycompounds from the aqueous acid solution. Samples containing increasing amounts of antimony were prepared. It was found that when one atom of Sb^{5+} per Keggin unit was added, the structural stability of the compound was remarkably increased: the temperature of incipient structural decomposition of the ammonium salt increased from 420 to 480°C, and of the potassium salt from 480 to 580–600°C. Characterization of the samples indicated that antimony might replace ammonium in cationic position inside the secondary structure of the compounds.

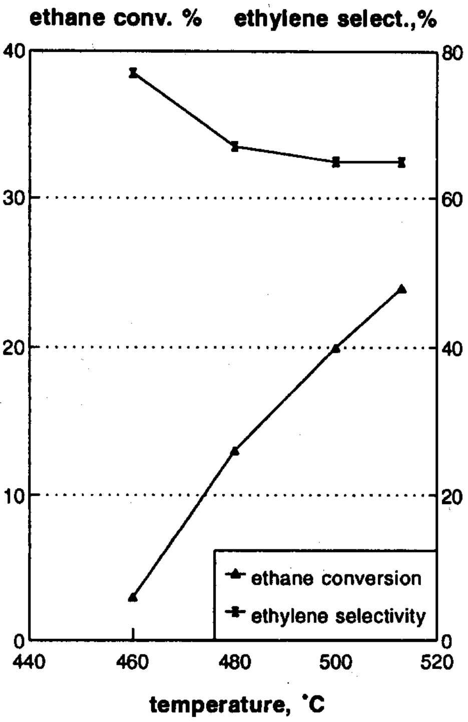

Fig. 1. Catalytic performance as a function of the reaction temperature. Residence time 7 s, ethane 3.6% and O_2 8% in the feed.

The prepared samples also exhibited good stability in the reaction environment, but poor activity. For this reason, variable amounts of different metal ions, such as iron, chromium and cerium, were also added to the compound composition in order to improve the activity and the selectivity to ethylene [4].

It is worth mentioning that: (i) all prepared heteropolycompounds exhibits the diffraction pattern typical of the *cubic* secondary structure; (ii) the potassium salts were structurally intact after reaction; ammonium and ammonium/potassium salts were partly decomposed when the temperature of reaction was higher than 450°C; (iii) a stable catalytic behavior was reached after 5–30 hours for the optimal catalytic compositions; (iv) the Keggin-type structure was fundamental in achieving a good catalytic performance; in fact, the decomposition of the compounds led to a fall of the activity; in addition, a catalyst which contained the same components but phosphorus, and therefore was not characterized by the Keggin structure, was not active in the ethane oxide hydrogenation under these conditions; (v) ethylene and CO_x (mainly CO_2) were the only products obtained; no formation of oxygenated compounds was observed.

Table 1 summarizes some of the catalytic results obtained; the data were collected under

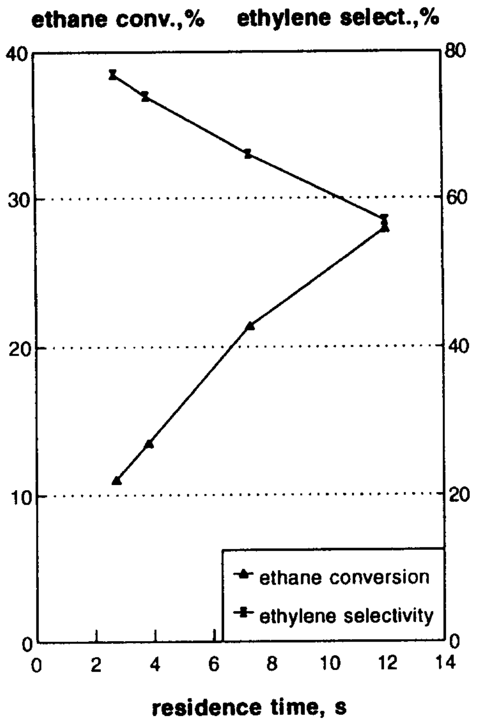

Fig. 2. Catalytic performance as a function of the residence time. Temperature 510°C, ethane 3.6%, O_2 10% in the feed.

stationary performance. The tests were done with the following conditions: (a) ethane 3%, oxygen 10%; (b) ethane 25 mol-%, oxygen 10%. The amount of catalyst employed was 3 g.

Catalysts which exhibited both a stable catalytic performance (an initial decrease in activity occurred, with a corresponding increase in selectivity, in the first 30 h time-on-stream, after which the performance was stable for 100 h at least) contained antimony as a structure stabilizer, iron as a dopant for selectivity, and chromium as a dopant for activity; the presence of cerium increased the activity, but its main effect was to enhance the stability of the catalytic performance with the time-on-stream.

Figs. 1 to 4 report the effect of some operative parameters on the catalytic performance, for the catalyst with composition $K_3P_1Sb_1Mo_{11}Fe_1Ce_{0.25}Cr_{0.5}O_n$. The effect of temperature, shown in Fig. 1, is to decrease the selectivity to ethylene; this permits the exclusion of the presence of homogeneous effects, which are known to occur above 500–550°C, and which lead to a remarkable increase in the selectivity to ethylene. In fact, the desorption of ethyl radicals in the gas phase, preferred to the surface catalyzed oxidation of the intermediate when the temperature is raised above 500–550°C, leads to the occurrence of the selective homogeneous decomposition of the radical to ethylene. In our case, the results can be considered to be due only to surface effects.

The effect of residence time is displayed in Fig. 2. The selectivity to ethylene, when extrapolated to nihil conversion, is close to 100%. In other words, at very low conversion the only product is ethylene. However, on increasing the residence time the selectivity to ethylene is rapidly decreased. This shows the high specificity of the surface centers of the heteropolycompound in the formation of ethylene, and also suggests that the ethylene is quite unstable on these catalysts, and is easily decomposed to the carbon oxides (mainly

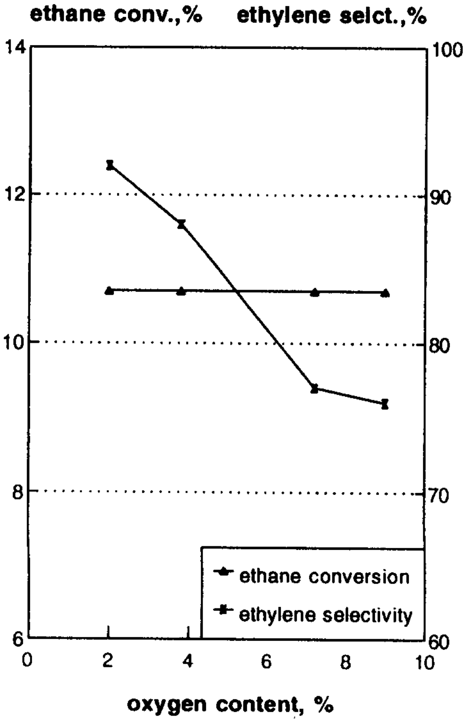

Fig. 3. Ethane conversion and yields as a function of the O_2 content in the feed. Temperature 510°C, residence time 2.7 s, ethane 3.6% in the feed.

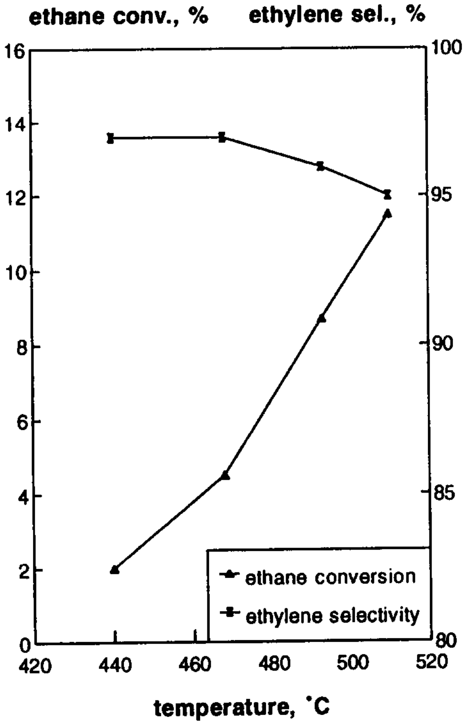

Fig. 4. Ethane conversion and yields as a function of the temperature. Residence time 2.7 s, ethane 3.6%, O_2 2% in the feed.

CO_2, with a CO_2-to-CO ratio close to 4. Fig. 3 shows the effect of the oxygen concentration in the feed. The selectivity to ethylene is decreased when the content of oxygen is increased. When the amount of oxygen is very low (2%, none the less in excess with respect to the stoichiometric amount for the complete conversion of ethane to ethylene) the selectivity to ethylene is higher than the 90%. The conversion of ethane is rather independent of the oxygen content; this might indicate that indeed the operating mechanism consists of a paraffin dehydrogenation, followed by an hydrogen oxidation. However, when the oxygen was completely cut-off, the activity was soon declined. Finally, Fig. 4 shows the effect of temperature when a low O_2 content is employed. The selectivity is very high up to 470°C, and then slightly decreases.

3. Acknowledgements

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4. References

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