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The role of promoters in the oxidehydrogenation of ethane over structurally stable Keggin-type heteropolyoxomolybdates

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Abstract

Potassium salts of 12-molybdophosphoric acid (Keggin-type heteropolycompounds) were tested as catalysts for the oxidehydrogenation of ethane. The catalyst composition comprised at least one atom of antimony per Keggin formula, which induced a considerable structural stability in the primary structure of the heteropolycompound. The base composition was doped with variable amounts of cerium, chromium and iron ions. Each ion showed a peculiar effect in enhancing the catalytic performance: cerium and chromium mainly affected the catalytic activity, so counteracting the deactivating effect induced by antimony addition, while iron improved the selectivity. A further improvement of the selectivity was achieved by adding a slight excess of phosphorus in the composition, and by partial replacement of molybdenum with tungsten. All catalysts showed an initial unstable catalytic performance; the attainment of a stable performance was also a function of the composition. The best catalytic composition was finally obtained, corresponding to $K_2P_{1.2}Mo_{10}W_1Sb_1Fe_1Cr_{0.5}Ce_{0.75}O_n$; the catalyst exhibited a stable catalytic performance for 100 h at least; the spent compound was characterized by an XRD pattern exhibiting only the features of the cubic heteropolycompound.

Keywords: Promoters; Oxidehydrogenation of ethane; Keggin-type heteropolyoxomolybdates

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1. Introduction

Keggin-type heteropolyoxometalates have been finding increasing applications in recent years as catalysts for both heterogeneous and homogeneous acid-type and oxidation reactions [1–4]. They possess unique features of reactivity, such as very strong intrinsic acidity as well as oxidizing properties; both features can be suitably tuned by modification of the compounds composition, i.e. by variation of the cationic composition, as well as by substitution of either molybdenum or tungsten in peripheral positions in the anion with other transition metals, such as vanadium.

In previous works we reported the surprising effect of structural stabilization induced by the addition of at least one atom of antimony per Keggin unit in ammonium/potassium salts of the 12-molybdophosphoric acid [5,6]. It was shown that the incipient structural decomposition of these salts, usually occurring at around 400°C, was increased by 80–100°C by the presence of antimony. This gave us the possibility to employ these systems for reactions which

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usually need high temperatures to be carried out; in fact, it is well known that the most limiting restriction to the possibility of employing these materials as catalysts for heterogeneous gas-phase reactions lies in the instability of the Keggin structure, which can decompose in the reaction environment, with corresponding worsening of its performance. Therefore, the antimony-doped compounds were tested as catalysts for the oxidehydrogenation of ethane. This reaction has been the object of several investigations over the last years [7–10], due to the interest in the development of a process for the synthesis of ethylene which might compete with the capital-intensive steam cracking of ethane; the main interest lies in the possibility of integrating a process which produces ethylene with high selectivity (without the presence of other olefins, as occurs in the case of paraffin steam cracking) with a process which converts the olefin in the presence of molecular oxygen (for instance, with an ethylene oxychlorination plant). The pure dehydrogenation of ethane suffers from thermodynamic constraints, and would require too high temperatures to reach acceptable conversions; the addition of molecular oxygen (oxidehydrogenation) overcomes this limit.

In previous works [5,6] we found that a drawback of antimony addition is a decrease in the catalytic activity, likely due to a stabilisation of the reduced state of molybdenum (Mo^{5+}), which could not act as readily as a redox-type centre as in the absence of antimony. For this reason, it was necessary to add small amounts of metal ions (iron, chromium and cerium) in order to obtain catalysts which were characterised by thermal structural stability, constant catalytic behaviour for at least 100 h, and by acceptable activity in ethane oxidehydrogenation and selective in the formation of ethylene. As shown in Table 1, the best composition of the catalyst was found to be $K_3PMo_{11}Sb_1Fe_1Cr_{0.5}Ce_{0.25}O_n$. The best selectivity to ethylene (in the range 70 to 80%, with CO and CO_2 as the by-products) was obtained with an oxygen-to-hydrocarbon ratio close to the stoichiometric one, with feedstock composition being at the fuel-lean side of the flammability bell. It was hypothesized that cerium and chromium were able to counteract the inhibiting effect of antimony, the presence of which favoured a reduction of Mo^{6+} to Mo^{5+} and hindered the oxidising power of molybdenum active sites in the Keggin unit. The Keggin-type structure of the heteropolycompound was necessary in order to achieve a good catalytic performance; in fact, the destruction of the structure by thermal treatment led to a fall in activity. It can be therefore assumed that the peculiar properties of the polyoxometalates, coupled to the redox properties of the dopant metals added, are necessary in order to obtain the ethane activation and its selective conversion to ethylene.

Table 1
Catalytic performance of the $K_3PMo_{12}O_{40}$ and of the same compound after addition of different metal ions. Data were collected after 3 h time-on-stream [5,6]

Catalyst composition	Ethane conversion (%)	Ethylene selectivity (%)
$K_3PMo_{12}O_{40}$	3.8	40
$K_3PMo_{11}Sb_1O_n$	2.5	44
$K_3PMo_{11}Sb_1Fe_1O_n$	2.3	83
$K_3PMo_{11}Sb_1Fe_1Ce_{0.25}O_n$	3.2	62
$K_3PMo_{11}Sb_1Fe_1Ce_{0.25}Cr_{0.5}O_n$	5.9	60

The aim of the present work is to study the reactivity of these antimony-stabilized transition metals-doped Keggin-type polyoxometalates under fuel-rich conditions, in order to maximize both productivity and selectivity to ethylene. The formulation of the catalyst has been fine-tuned in order to guarantee the best catalytic performance in terms of structural stability, stable catalytic performance with time-on-stream, activity and selectivity.

2. Experimental

The preparation of the samples was done according to the following procedure: an aqueous solution of calculated amounts of $K(SbO)C_2H_4O_6 \cdot 5H_2O$, $(NH_4)_6Mo_7O_{24} \cdot 4H_2O$, KNO_3 (when K-to-Sb ratios higher than 1 had to be obtained), $SbCl_3$ (when ratios lower than 1 had to be obtained), $H_3[P(W_3O_{10})_4] \cdot 22H_2O$ (for samples containing W) and $(NH_4)H_2PO_4$ was prepared by dissolving the salts in a minimum volume of water, with stirring and heating up to 80°C. HNO_3 was then added dropwise to the solution obtained. During the addition of the acid, the colour of the solution progressively changed from pale green to blue, green and yellow; at the same time, a precipitate was obtained. The addition of the acid was stopped when a stable yellow colour of the slurry was obtained. The amount of molybdenum used was proportionally decreased as the amount of antimony was increased. For samples containing other metal ions as dopants, a solution was prepared which contained the following salts: $Fe(NO_3)_3 \cdot 9H_2O$, $Cr(NO_3)_3 \cdot 9H_2O$, $Ce(NO_3)_3 \cdot 6H_2O$. This solution was added dropwise to the first solution, before HNO_3 addition.

The slurry obtained was dried overnight at 120°C, and the solid was then calcined at increasing temperature (two hours at each intermediate temperature): 180, 200, 220, 320 and 370°C. The final temperature of calcination was either 450, or 500 or 550°C, and was maintained for 24 h.

Powder XRD data were obtained with a Philips PW 1050/81 diffractometer, controlled by a PW1710 unit using Ni-filtered Cu K_α radiation.

The catalytic tests were carried out in a stainless-steel laboratory flow reactor, at atmospheric pressure. The products were analyzed by gas chromatography. Ethane and ethylene were analyzed with a Carbosieve D column, with the oven temperature maintained at 100°C, and a FID. CO and CO_2 were analyzed by means of a Carbosieve S column with the oven temperature programmed from 40 to 220°C, and a TCD. No other products were detected.

3. Results

3.1. The improvement of the catalytic performance through the variation of metal dopants content

3.1.1. The effect of cerium and chromium

Fig. 1 reports the values of ethylene concentration at the reactor outlet and of selectivity on a catalyst with composition $K_3P_1Mo_{11}Sb_1Fe_1Cr_{0.5}Ce_{1.5}O_n$, when the concentrations of the reactants in the feedstock (ethane and oxygen) were progressively increased, while maintaining the hydrocarbon-to-oxygen ratio constant at 2.0 (the stoichiometric value for the conversion of ethane to ethylene). The productivity to ethylene was almost proportional to the reactants concentration; this allowed us to exclude a saturation of the active centres; in addition, the selectivity was constant. These data indicate that the best operative conditions that guarantee the highest productivity to ethylene (without penalizing the selectivity) are at fuel-rich conditions.

Since a modification of the gas phase composition can greatly affect the redox level of the catalyst surface, the effect of cerium and

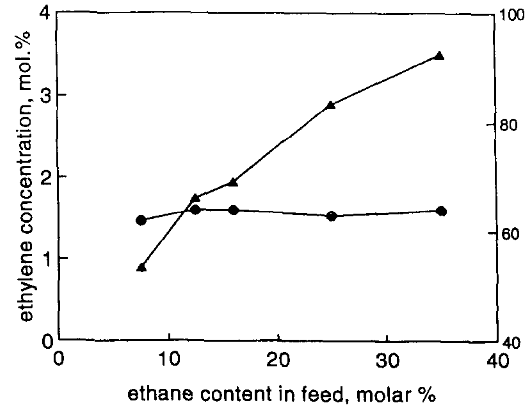

Fig. 1. Ethylene concentration at the reactor outlet (△) and selectivity to ethylene (○) as functions of the ethane content in feedstock. Catalyst $K_3P_1Mo_{11}Sb_1Fe_1Cr_{0.5}Ce_{1.5}O_n$. Reaction conditions: T 550°C, residence time 12 s, ethane/oxygen molar ratio 2.0.

chromium contents in the catalyst on the catalytic behaviour has been studied under fuel-rich conditions; a series of samples were prepared which contained increasing amounts of cerium, from 0 to 1.5 atom per Keggin unit (KU), and a fixed amount of iron and chromium, 1.0 Fe atom/KU and 0.5 Cr atom/KU (which were found to be the optimal amounts for low ethane concentration, i.e. fuel-lean conditions); the formal composition of the compounds was therefore $K_3PMo_{11}Sb_1Fe_1Cr_{0.5}Ce_xO_n$. On each sample data were collected after 20 h time-on-stream; for some samples, those containing less than 0.5 atom of Ce per KU, it was not possible to reach a fully stable catalytic performance within this period; for samples containing an amount of Ce higher than 0.5 and lower than 1.0 atom/KU, after an initial rapid decrease of activity and selectivity the performance was more stable, even though a slow deactivation was yet present. The samples containing more than 1.0 atom of Ce exhibited the most stable catalytic performance.

For each composition results were acquired by varying the residence time; Fig. 2 compares the ethane conversion as a function of the residence time for the various catalysts, under relatively stable catalytic performance. Fig. 3 gives the corresponding selectivities to ethylene at the various levels of ethane conversion. For all catalysts the conversion increased when the residence time was increased; the progressive increase in the cerium content led to a corresponding increase in the activity in the range 0 to 0.75 cerium atom/KU; above 0.75 cerium atoms, the activity decreased. The selectivity trend was similar for all catalysts; it decreased due to the preferred formation of carbon oxides. Therefore, it seems that under such conditions the main contribution to the decrease of the selectivity is a consecutive reaction of combustion with the ethylene formed. The CO-to-CO_2 ratio increased on increasing the ethane conversion, from approximately 2 to 4; this suggests that the parallel reaction of ethane oxidation leads to both CO and CO_2, while the consecutive reaction of ethylene combustion mainly leads to CO. However, the observed effect might also be due a variation in oxygen concentration; tests made by feeding ethylene can help in clarifying the reaction network; these tests will be described in a following section.

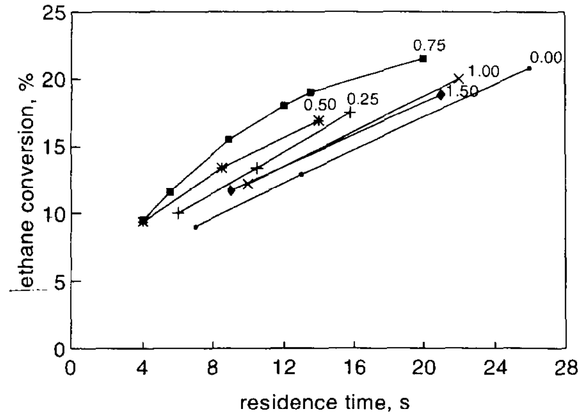

Fig. 2. Ethane conversion as a function of residence time. Catalysts: $K_3P_1Mo_{11}Sb_1Fe_1Cr_{0.5}Ce_xO_n$. Reaction conditions: T 550°C, feedstock composition: 25 mol% ethane, 12 mol% oxygen, rest helium. Numbers indicate the value of x in $K_3P_1Mo_{11}Sb_1Fe_1Cr_{0.5}Ce_xO_n$.

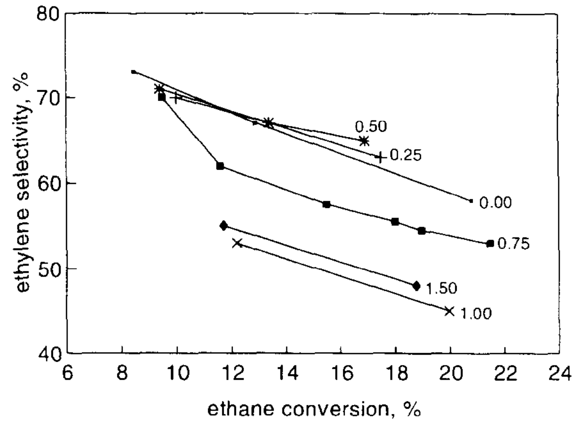

Fig. 3. Selectivity to ethylene as a function of residence time. Catalysts, symbols and reaction conditions as in Fig. 2. Numbers indicate the value of x in $K_3P_1Mo_{11}Sb_1Fe_1Cr_{0.5}Ce_xO_n$.

The selectivity trend was the same for samples in the range 0 to 0.50 Ce atoms, while it was slightly lower with 0.75 cerium atoms (mainly due to an increase in the contribution of the consecutive reaction), and remarkably lower with 1.0 and 1.5 Ce atom/KU.

Therefore, the effect of cerium is two-fold: on one hand, in order to achieve a stable enough catalytic performance, it is necessary to have at least 0.75 Ce atom/KU; on the other hand, the best improvement from the activity point of view is for cerium contents in the 0.5–0.75 atom/KU range, and from the selectivity point of view in the 0 to 0.5 Ce atom range. The best compromise is achieved with a Ce content of 0.75 atom/KU.

These data indicate that small amounts of cerium favour the rate of alkane activation, probably enhancing the rate of Mo^{5+} reoxidation (which is depressed by antimony addition) without remarkably affecting the selectivity to ethylene; higher amounts than 1.0 Ce atom/KU negatively affect the activity, likely because they excessively stabilize the high-valent state of molybdenum, and also are responsible for an increase in the oxidative degradation of the formed ethylene.

Catalysts containing various amounts of chromium were prepared, which contained an amount of cerium corresponding to 0.75 atom/KU. The effect of the chromium addition is summarized in Fig. 4, which reports the ethane conversion and the corresponding selectivity to ethylene at fixed reaction conditions: temperature 550°C, residence time 12 s, ethane 25%, oxygen 12% in the feed. The effect of chromium was comparable to that observed for cerium, suggesting that the two metals perform a similar action; the activity showed a maximum with the chromium content, while the selectivity was approximately constant for the lowest chromium content (up to 0.5 atom/KU), thereafter decreasing more markedly. The best results were obtained for 0.5 atom/KU.

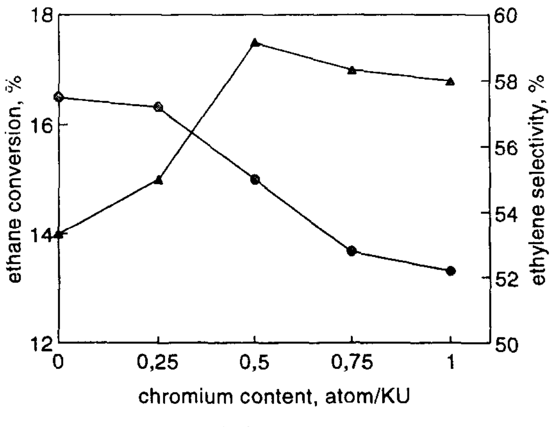

Fig. 4. Ethane conversion (△) and selectivity to ethylene (O) as functions of the chromium content in $K_3P_1Mo_{11}Sb_1Fe_1Cr_xCe_{0.75}O_n$. Residence time 12 s, other conditions as in Fig. 2.

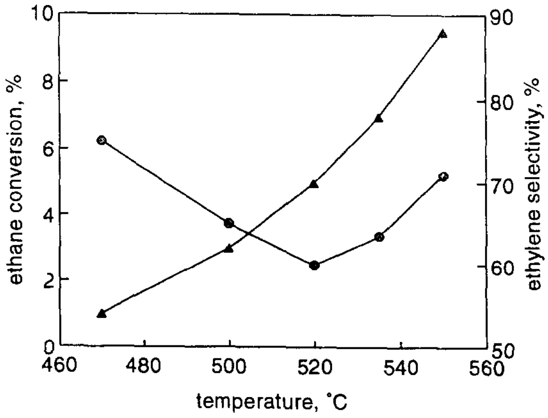

Fig. 5. Ethane conversion (△) and selectivity to ethylene (O) as functions of the reaction temperature. Catalyst $K_3P_1Mo_{11}Sb_1Fe_1Cr_{0.5}Ce_{0.75}O_n$. Reaction conditions: residence time 4 s, feedstock composition: 25 mol% ethane, 12 mol% oxygen.

The effect of the reaction temperature on the catalyst with the composition $K_3P_1Mo_{11}Sb_1Fe_1Cr_{0.5}Ce_{0.75}O_n$ is illustrated in Fig. 5. The selectivity slightly decreased in the 470–520°C range, and then increased again; temperatures higher than 550°C could not be employed, because the catalyst slowly decomposed, with a corresponding worsening of catalytic performance. The trend of selectivity with temperature is in favour of a change of mechanism at temperatures higher than 500°C, in agreement with literature indications [8,9]. Highest temperatures can favour the occurrence of more selective, heterogeneously-initiated homogeneous reactions of oxygen-assisted decomposition of radical intermediate species to ethylene. At lower temperatures, instead, the mechanism is likely to be completely heterogeneous

Since a completely heterogeneous mechanism would be in principle preferable, the effect of other catalysts components has been studied, in order to increase the catalytic activity and allow the operation to be carried out at lower temperatures.

3.1.2. The effect of potassium and antimony

In previous works [5,6], we reported that one way to improve the thermal structural stability of these heteropolycompounds is to add antimony to the catalyst composition. In fact, the potassium/ammonium salts of the 12-molybdophosphoric acid show incipient decomposition of the primary structure at between 400–420°C [11]; the same occurs for the ammonium salts, while the potassium salts are stable up to 480–500°C. For all salts, the addition of antimony remarkably increased the thermal stability; the most stable compound was the antimony-doped potassium salt, with 1.0 Sb atom/KU, which remained structurally intact in air up to 600°C. However, the most stable compounds were found to be characterized by the lowest catalytic activity; the addition of 1 atom of antimony per KU remarkably decreased the catalytic activity, and this was attributed to a stabilization of the reduced molybdenum state, induced by the presence of antimony.

The effect induced by the presence of potassium and of antimony has been studied also in the metal modified compound $K_xPMo_{11}Sb_yFe_1Ce_{0.75}Cr_{0.5}O_n$, in order to check whether it were possible to further increase the catalytic activity by lowering the potassium and antimony contents, without penalising the structural stability. Samples were prepared with the formal composition $K_xPMo_{11}Sb_1Fe_1Ce_{0.75}Cr_{0.5}O_n$, with a potassium amount varying from 0 to 3 atom/KU. The results on the catalytic activity are summarized in Fig. 6, at the following reaction conditions: temperature 470°C, residence time 9.4 s, ethane 35%, oxygen 16%. In all cases a relatively stable catalytic performance allowed us to acquire reproducible results.

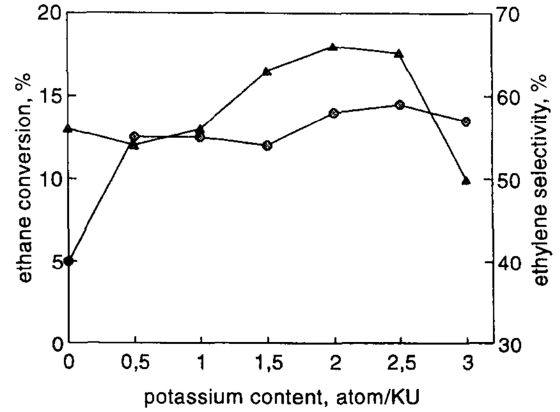

Fig. 6. Ethane conversion (△) and selectivity to ethylene (O) as functions of the potassium content in $K_xP_1Mo_{11}Sb_1Fe_1Cr_{0.5}Ce_{0.75}O_n$. Reaction conditions: T 470°C, residence time 9.4 s, feedstock composition: ethane 35 mol%, oxygen 16 mol%, rest helium.

The data show that the least active compound is the one containing the highest amount of potassium; the best results were obtained for the sample containing 2.0 K atom/KU. The selectivity was practically unaffected by the amount of potassium; the least selective was the catalyst without potassium. After reaction, the samples containing less than 2.0 K atom/KU were partly decomposed; this may explain the lower catalytic activity of these samples. Therefore, structural stability at the conditions employed is guaranteed only when at least 2 K atom/KU are present, besides 1 Sb atom/KU.

The effect of modification of the antimony content in the catalyst containing 2 K atom/KU is summarized in Fig. 7. Samples possessing the highest activity (for instance, the one containing 1 Sb atom/KU) were characterized by the lowest selectivity; however, the effect on selectivity was much less marked than the one upon activity, and consequently the highest yields are obtained on the most active compounds. Concerning the structural stability, samples with less than 1.0 Sb atom/KU were partly decomposed after reaction, so justifying their lower activity. Samples with at least 1 Sb atom/KU were instead structurally intact; higher amounts of antimony, though inducing an exceptional

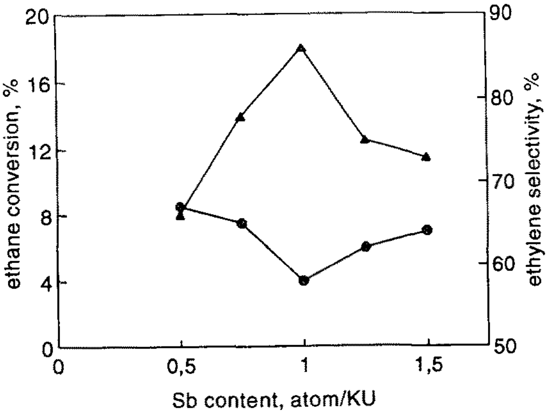

Fig. 7. Ethane conversion (△) and selectivity to ethylene (○) as functions of antimony content in $K_2P_1Mo_{12-x}Sb_xFe_1Cr_{0.5}Ce_{0.75}O_n$. Reaction conditions as in Fig. 6.

structural stability, were detrimental because they led to a fall in the activity.

The data clearly indicate that when severe operative conditions are employed, such as temperatures close to 500°C and high hydrocarbon concentrations, the catalytic performance is greatly affected by the structural stability; the salts containing 2 K atom/KU and 1 Sb atom/KU at least are the most active mainly because they do not structurally decompose under such conditions; higher amounts of potassium and of antimony lead to a decrease in activity.

On the basis of the data here reported, it can be concluded that a catalyst formulation which combines structural stability and good activity and selectivity has the following formal composition: $K_2PMo_{11}Sb_1Fe_1Cr_{0.5}Ce_{0.75}O_n$; this catalyst can be used without structural decomposition up to 480–490°C at high hydrocarbon concentration. The sample containing 3 K atom/KU can be employed at even higher temperatures (up to 550°C) without decomposition, but its lower activity leads at such conditions to ethylene yields comparable to those obtained at 470°C with the sample containing 2 K atom/KU; in addition, at temperatures higher than 550°C the reaction mechanism is likely to be homogeneous in part.

3.1.3. The effect of phosphorus

Samples were prepared which contained a slight excesses of phosphorus with respect to the stoichiometric amount necessary for the development of the Keggin structure, in order to check whether the surface acidity could play a role in the reaction mechanism, enhancing the catalytic performance. It is known that in some oxidation reactions catalyzed by phosphorus-containing mixed oxides, such as in the case of the oxidation of *n*-butane to maleic anhydride [12], amounts of phosphorus higher than the stoichiometric requirement can greatly affect the catalytic behaviour, due to a modification of the surface acidic properties.

Fig. 8 summarizes the results obtained; the addition of phosphorus in excess does not practically affect the activity, but the selectivity is improved. A hypothesis can be formulated that an increased surface acidity favours the desorption of the basic ethylene, so limiting the unselective consecutive reactions of combustion. In order to confirm this effect, tests were done by feeding ethylene and oxygen with the following conditions: 4% ethylene in air, temperature 470°C, over the two catalysts with composition $K_2P_1Mo_{11}Sb_1Fe_1Cr_{0.5}Ce_{0.75}O_n$ and $K_2P_{1.2}Mo_{11}Sb_1Fe_1Cr_{0.5}Ce_{0.75}O_n$. The catalyst containing the stoichiometric amount of phos-

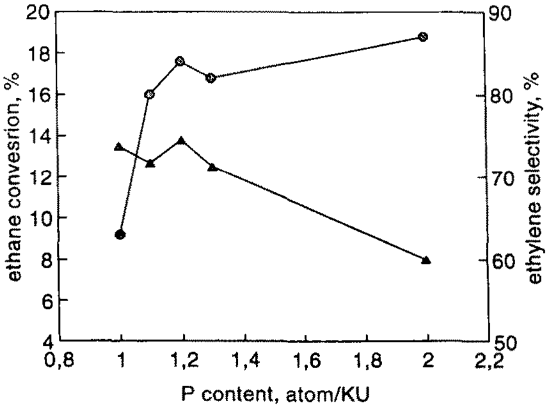

Fig. 8. Ethane conversion (△) and selectivity to ethylene (○) as functions of the phosphorus content in $K_2P_xMo_{11}Sb_1Fe_1Cr_{0.5}Ce_{0.75}O_n$. Reaction conditions: T 470°C, residence time 7 s, feedstock composition: ethane 35 mol%, oxygen 16 mol%.

phorus gave an ethylene conversion of 24% to CO_x, with a CO/CO_2 ratio equal to 4. The catalyst containing the excess phosphorus showed a similar conversion (26%); this indicates that the excess phosphorus does not affect the consecutive rate of ethylene overoxidation, but rather affects the relative importance of the two parallel reactions of ethane oxidation to ethylene and CO_x.

Another indication arising from these results is that the direct combustion of ethane gives both CO and CO_2, while that of ethylene gives mainly CO; in fact under the same conditions and with the stoichiometric composition, the oxidation of ethane gives a higher relative amount of CO_2, with a CO/CO_2 ratio in the range 1.5–2. These data therefore confirm the indications arisen from tests made by varying the residence time (see comments on Fig. 3).

The composition with a slight excess of phosphorus turned out to be superior, and has been employed for further study.

3.1.4. The effect of tungsten

Another method for affecting the redox properties of the Keggin anion is to change the primary composition by addition of metals that are known to substitute for molybdenum in peripheral positions in the anion, such as tungsten and vanadium. Samples were prepared by substitution of a fraction of molybdenum in the anion with increasing amounts of tungsten. Fig. 9 summarizes the results obtained, giving the ethane conversion and the selectivity to ethylene for the various compounds. Addition of tungsten caused a progressive considerable increase in initial activity (after 2 h time-on-stream) up to 1.0 W atom/KU, and a corresponding decrease in selectivity; the resulting yield was increased. This difference in activity was much less important under more stable catalytic conditions (after 15 h time-on-stream).

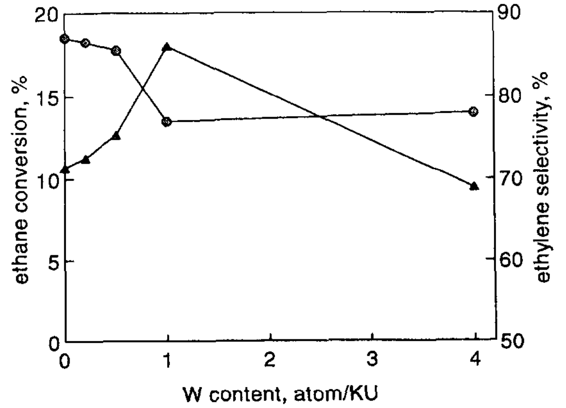

Fig. 9. Ethane conversion (△) and selectivity to ethylene (O) as functions of the tungsten content in $K_2P_{1.2}Mo_{11-x}W_xSb_1Fe_1Cr_{0.5}Ce_{0.75}O_n$. Reaction conditions: T 470°C, residence time 5.6 s, feedstock composition: ethane 35 mol%, oxygen 16 mol%, rest helium.

In conclusion, it can be considered that an optimized composition is the following: $K_2P_{1.2}Mo_{10}W_1Sb_1Fe_1Cr_{0.5}Ce_{0.75}O_n$.

3.2. Characterization of spent catalysts by XRD

Fig. 10 shows the XRD diffraction patterns of some samples employed for catalytic tests. Sample a is the $K_3PMo_{12}O_{40}$. compound after calcination at 500°C. It shows the typical pattern of the cubic structure, and no trace of structural decomposition. Sample b corresponds to the compound of composition $K_3PMo_{11}Sb_1Fe_1Cr_{0.5}Ce_{0.25}O_n$ after reaction, while sample c is the optimized compound with formula $K_2P_{1.2}Mo_{10}W_1Sb_1Fe_1Cr_{0.5}Ce_{0.75}O_n$ after calcination at 500°C, and sample d the same compound after 100 h time-on-stream (the maximum operative temperature having been 550°C). All doped samples exhibit the pattern typical of the cubic secondary structure. Reflections, attributable to molybdenum oxide, are also observed, but they are very weak, and indicate that the extent of structural decomposition is very low, confirming the structural stability of these compounds under reaction conditions.

3.3. The variation of catalytic performance with time-on-stream

Fig. 11 shows the ethane conversion and the selectivity to ethylene as functions of time-on-

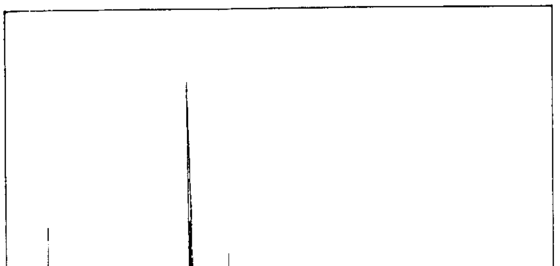

Fig. 10. X-ray diffraction patterns of $K_3PMo_{12}O_{40}$ calcined at 500°C(a), $K_3P_1Mo_{11}Sb_1Fe_1Cr_{0.5}Ce_{0.25}O_n$ spent after 50 h time-on-stream (b), $K_2P_{1.2}Mo_{10}W_1Sb_1Fe_1Cr_{0.5}Ce_{0.75}O_n$ calcined at 500°C (c) and spent after 100 h time-on-stream (d).

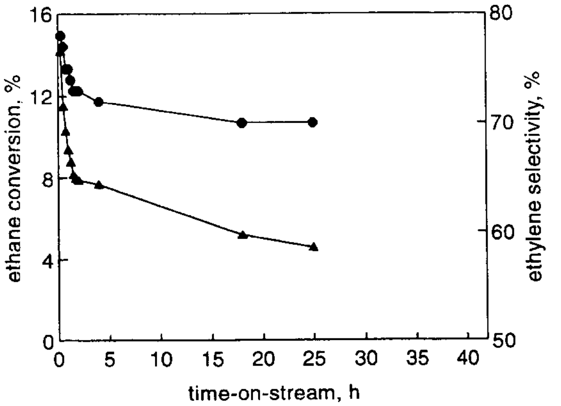

Fig. 11. Ethane conversion (△) and selectivity to ethylene (○) as functions of time-on-stream. Catalyst $K_3P_1Mo_{11}Sb_1Fe_1Cr_{0.5}Ce_{0.25}O_n$. Reaction conditions: T 550°C, residence time 4.0 s, feedstock composition: 25 mol% ethane, 12 mol% oxygen, rest helium.

stream under fuel-rich conditions for the catalyst which had been found to possess the best catalytic performance at fuel-lean conditions [5,6]: $K_3PMo_{11}Sb_1Fe_1Cr_{0.5}Ce_{0.25}O_n$. The following conditions were employed: ethane concentration 25%, oxygen concentration 12%, temperature 550°C, residence time 4.0 s. It is shown that the catalyst exhibits a rapid initial fall in activity and selectivity, occurring within the first hours of reaction, followed by a more gradual, progressive decrease; during the first 25 h of reaction the catalytic performance could not be stabilized at such conditions. The observed phenomenon was not due to the structural decomposition of the heteropolycompound, as demonstrated by the analysis of the spent catalyst. It is worth mentioning that under fuel-lean conditions (3% hydrocarbon) the catalyst indeed reached a stable catalytic performance within some hours [5]; since a variation in the gas composition likely modifies the oxidizing power of the gas phase itself, it can be assumed that the observed deactivation phenomenon is due to a modification in the redox surface properties of the catalyst. It is likely that an increase of hydrocarbon concentration progressively enhances the reduction level of the catalyst surface, thus decreasing the oxidizing capability of the catalyst. Therefore, it can be expected that the positive effect on the catalytic

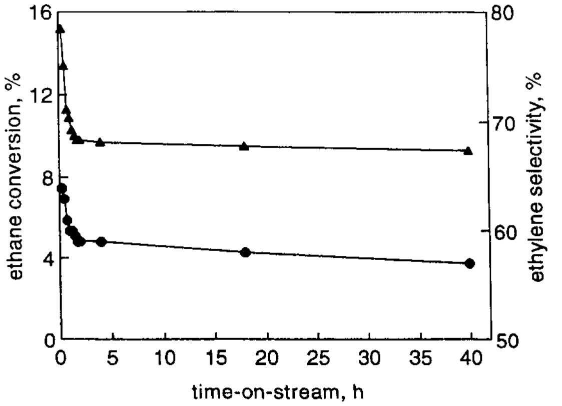

Fig. 12. Ethane conversion (△) and selectivity to ethylene (○) as functions of time-on-stream. Catalyst $K_3P_1Mo_{11}Sb_1Fe_1Cr_{0.5}Ce_{1.5}O_n$. Reaction conditions as in Fig. 11.

activity induced by the presence of higher cerium contents might also have a stabilizing effect on the variation of catalytic performance with time-on-stream. The behaviour of the sample containing 1.5 Ce atom/KU with the time-on-stream is shown in Fig. 12 (under the same experimental conditions as for Fig. 11); the same behaviour was exhibited by the samples containing at least 0.75 Ce atom/KU. It is shown that the catalyst, after the usual initial rapid decrease in activity, reached a more stable catalytic performance after approximately 20 h; the catalytic behaviour was not absolutely constant, but the variation was much lower than in the previous case.

Fig. 13 shows the catalytic performance as a function of the time-on-stream for the final catalyst composition developed (the $K_2P_{1.2}Mo_{10}W_1Sb_1Fe_1Cr_{0.5}Ce_{0.75}O_n$ compound). The experimental conditions were the following: 35% ethane in feed and 16% oxygen, at 5.\ 8 s residence time (4.0 s for the non-optimized composition) and temperature 470°C. With respect to catalysts whose behaviour is shown in Fig. 12, the activity is much improved (higher conversions are obtained at lower temperatures), and the selectivity also is remarkably enhanced.

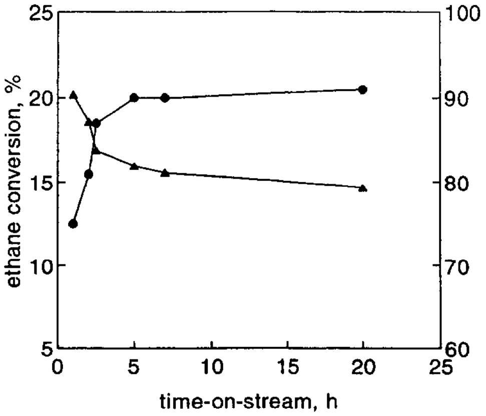

Fig. 13. Ethane conversion (△) and selectivity to ethylene (○) as functions of time-on-stream. Catalyst $K_2P_{1.2}Mo_{10}W_1Sb_1Fe_1Cr_{0.5}Ce_{0.75}O_n$. Reaction conditions: T 470°C, residence time 5.8 s, feedstock composition: 35 mol% ethane, 16 mol% oxygen, rest helium.

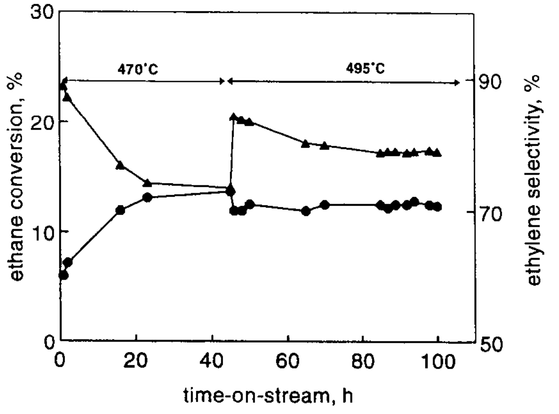

Fig. 14. Ethane conversion (△) and selectivity to ethylene (○) as functions of time-on-stream. Catalyst as in Fig. 13. Reaction conditions: T 470 and 495°C, residence time 10 s, feedstock composition: 80 mol% ethane, 20 mol% oxygen.

Tests have also been carried out at an even higher hydrocarbon-rich condition, as displayed in Fig. 14. The following conditions were employed: 80% ethane and 20% oxygen, residence time 10 s, temperature 470°C. Under such conditions the oxygen conversion is total at the very beginning of lifetime, and the ethylene concentration at the reactor outlet (as well as the productivity) is maximized. In this case, also, the catalyst showed an initial decrease in activity (with a lowering in oxygen conversion), but reached a stable catalytic performance with an ethylene selectivity of 74%. The temperature was further increased up to 495°C; after an equilibration stage, the catalytic behaviour stabilized; under these conditions, a selectivity to ethylene of 72% was reached, with 18% ethane conversion and 90% oxygen conversion. A further increase of the reaction temperature above 500°C led to a fall in activity and selectivity, due to a progressive destruction of the Keggin structure. Therefore, the temperature limit for the short-term operation of such catalyst is 500°C.

3.4. Catalytic tests under non-steady state conditions in the presence of HCl pulses

Tests were also done by feeding periodically one pulse of HCl in the reactor; the aim of these

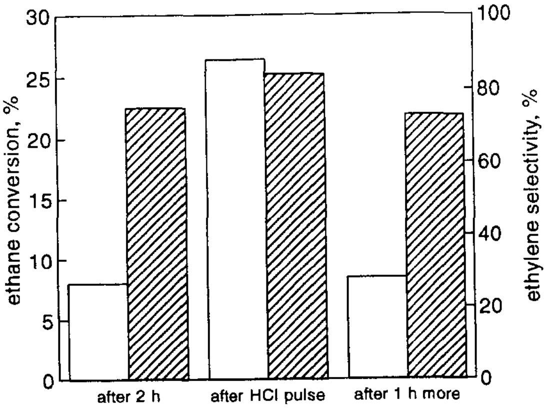

Fig. 15. Ethane conversion (left bar) and ethylene selectivity (right bar) on the catalyst $K_2P_{1.2}Mo_{10}W_1Sb_1Fe_1Cr_{0.5}Ce_{0.75}O_n$ before, immediately after and after 1 h more a pulse of gaseous HCl. Reaction conditions: T 470°C, residence time 3.5 s, feedstock composition 35 mol% ethane, 16 mol% oxygen, rest helium.

tests were to check whether such operation could lead to an enhancement of the catalytic performance, analogous to those reported in the literature to occur with basic oxides in the oxidative coupling of methane [13,14]. The results are summarized in Fig. 15, which compares the catalytic behaviour before and after the HCl pulse injection. It is shown that the acid addition yields an immediate huge improvement in the performance; however, the previous values of yield and selectivity are progressively recovered. Under such conditions the transitory yields obtained are exceptional, and would indicate the possibility of employing these catalyst together with a continuous feed of chlorine-containing compounds.

4. Discussion

4.1. The network of reaction, and the effect of the operative parameters

The reaction network consists of two parallel reactions of ethylene and CO_x formation, and of a consecutive reaction of ethylene overoxidation, with main formation of CO. In agreement, the direct oxidation of ethylene mainly yields CO, while in the oxidation of ethane, CO and CO_2 are formed in comparable amounts. While an isothermal increase in conversion leads to a remarkable decrease in selectivity, the effect of temperature on the selectivity is not so important; indeed, higher temperatures favour the formation of ethylene, likely due to an increase in the contribution of the selective homogeneous decomposition of desorbed ethyl radicals to ethylene [15,16]. However, higher temperatures (close to 550°C) can only be employed with catalysts which possess the highest structural stability, thus those that contain at least 3 K atom/KU; on the other hand, these exceptionally stable compounds are the least active. A decrease in the potassium content favours the activity but penalizes the structural stability. At 470°C the less stable catalysts (which however do not decompose at such conditions) yield ethylene with comparable activity and selectivity as do the most stable catalysts at 550°C.

The productivity of ethylene is increased in the range 0 to 40% ethylene concentration, while the selectivity is maintained constant provided the oxygen-to-ethane ratio is maintained constant. This indicates that the inhibition of surface active centres does not occur up to high paraffin concentrations.

4.2. The effect of anion composition and of metal dopants on the catalytic properties

The data here reported indicate that the catalytic activity of the potassium salts of the 12-molybdophosphoric acid can be remarkably affected by varying the compound composition. The variation can be induced by modification of the anion composition in the primary Keggin structure, as well as by modifications in cationic composition, that is in the secondary structure of the compound. Tungsten is the only metal (besides vanadium) that can effectively substitute for molybdenum in the anion under our conditions of catalyst preparation; in fact, it is known that in order to replace molybdenum with other divalent or trivalent transition metals it is necessary to start from lacunary compounds; in addition, these compounds are structurally rather unstable, and are known to decompose at relatively low temperatures (200–300°C). All the other metals employed in the present work can either locate in the secondary framework of the compound or spread over the Keggin compound. Indeed, the overall cationic charge of the added metals is by far higher than the corresponding anionic charge of the Keggin anion; therefore, most metals are probably present in the form of finely dispersed oxides. In any case, it is worth mentioning that both the metal dopants and the Keggin structure are necessary in order to obtain a satisfactory catalytic performance; in fact, the structural decomposition of the optimized composition by calcination at high temperatures led to a very poor catalyst [5].

Concerning the position of antimony in the framework, Sb^{5+} possesses the same ionic size of Mo^{6+}, as well as a similar ionic charge, and might theoretically substitute for molybdenum in the primary structure; however, we were not able to find any indication in literature about this possibility.

The effect of the cationic composition on the catalytic performance in oxidation reactions has been widely studied in literature [17–20]. The nature and amount of alkaline and alkali earth metals greatly affect the activity and selectivity; this effect has been attributed either to a modification of the acidic properties, or to a variation of the redox properties of molybdenum. In the case of potassium salts of the 12-molybdophosphoric acid, it was found that for reactions carried out at relatively mild conditions (i.e. for the oxidehydrogenation of isobutyric acid to methacrylic acid) the potassium salts are less active than the ammonium salts, even though the latter are remarkably less stable than the former under the reaction environment [11].

Our results indicate that the effect of cerium is significant on both activity and on the variation of catalytic performance with time-on-stream. This is confirmed by literature data which indicate a significant effect of cerium on the redox properties of molybdenum, due to its high oxidizing power [18,19]. It is likely that cerium may counteract the reductive effect of antimony on molybdenum; indeed, antimony-containing spent catalysts without cerium were blue, indication of a significant extent of molybdenum reduction, while when cerium was added in at least 0.75 atom/KU the unloaded catalysts did not appear to be reduced. Chromium affects the activity in an analogous fashion. The effect of iron was found to be mainly an improvement of selectivity to ethylene; similarly, the excess of phosphorus significantly affected the selectivity to ethylene, favouring the reaction of ethylene formation with respect to the parallel one of ethane combustion, as confirmed by the tests made by feeding ethylene.

Finally, a significant effect on activity is induced by the presence of tungsten, when this substitutes for molybdenum. In the literature, there are not many comparisons between tungsten and molybdenum-containing Keggin compounds, even though indications exist that the redox properties of these compounds are greatly affected by the anion composition [1].

4.3. *The deactivation phenomena*

The variation in catalytic performance shown in Figs. 11–13 can be attributed to different phenomena.

(1) The first reason for catalyst deactivation may be the structural decomposition of the crystal make-up of the heteropolycompound. Our results indicate that the temperature of incipient decomposition is not only a function of the compound composition, but also of the gas phase composition. It has been shown that a compound structurally stable at reaction conditions up to 500°C can be obtained by salification of the polyoxoanion with potassium and by addition of antimony. As shown by XRD patterns of spent catalysts, in order to reach a sufficient structural stability it is necessary to have at least 2 potassium atoms and 1 antimony atom per Keggin unit.

(2) A second reason for catalyst deactivation may be the decrease in surface area. Before reaction, all compounds here reported possess specific surface areas falling in the range of 10 to 20 m^2/g (after calcination at 550°C for 4 h); after reaction at the same temperature the surface area is usually lower than 5–10 m^2/g. If the calcination is carried out at 470°C, the value of surface area is in the range 25 to 35 m^2/g, and after reaction at the same temperature is in the range 15 to 25 m^2/g. This decrease is not due to a structural decomposition, as it also occurred with samples which remained structurally intact in the reaction environment. Among the various metal promoters studied, no one was found to inhibit this phenomenon of surface area collapse.

The decrease in surface area could be due to the build up of heavy compounds on the catalyst surface. This hypothesis could be supported by the fact that a treatment in air of the catalyst effectively partially restored the activity which the catalyst exhibited at the very beginning of the catalytic tests. However, the treatment was not accompanied by a recovery of the initial surface area; therefore, the partial recover of catalytic activity must be due to other phenomena (i.e. a catalyst reoxidation), and the decrease in surface area must be due to factors other than the formation of heavy compounds.

Another hypothesis is that the decrease in surface area may occur as a consequence of a modification in the crystalline structure or morphology, such as an increase in the degree of crystallinity of the compound, or a variation in the cations distribution inside the secondary structure of the heteropolycompound. The XRD patterns of the spent catalysts seems to exclude a significant variation in the crystallinity of the catalysts with respect to samples before reaction. On the other hand, it is known that the surface area of heteropolycompounds is affected by the nature of cations which are located in the void space among the neighbouring Keggin anions [11,17–20]. A partial reduction of the molybdenum in the Keggin anion occurring during the first hours of reaction, with a variation in the global charge of the Keggin anion, must reasonably lead to a modification of the charge distribution, and of the amount of cations which are located in the heteropolycompounds secondary framework; the same has been found to occur in ammonium/potassium salts of the 12-molybdophosphoric acid, employed as catalysts for the oxidehydrogenation of isobutyric acid. It can be hypothesized that the observed rapid variation in catalytic performance reflects this change in the heteropolycompound structure, accompanied by a decrease in surface area.

(3) It is reported in the literature that in the reaction of methane oxidative coupling over basic oxides such as Li/Mg/O systems, the formation of surface hydroxycarbonates can lead to a surface poisoning of the catalyst [21]. The results obtained by feeding HCl pulses (displayed in Fig. 15) might be in favour of the formation of surface carbonates, which are readily decomposed in the presence of the acid pulse. Alternatively, the observed phenomenon can be explained by an improvement of the contribution of homogeneous decomposition of ethane to ethylene, induced by the presence of chlorine radicals. It is well documented in the literature that gas phase radical reactions can widely contribute to the formation of ethylene from ethane in the presence of molecular oxygen, above all when temperatures higher than 550°C are employed [8,9,15,16]; radical initiators, such as $Cl^{\cdot}$, greatly enhance the contribution of this phenomenon. This also occurs in the formation of C_2 products from methane by oxidative coupling: best yields have been reported when chlorine-containing compounds are fed to the reactor together with methane and oxygen [13,14].

(4) A fourth reason for catalyst deactivation may be related to an excessive stabilization of a particular redox state for the molybdenum in the Keggin anion. It is likely that the catalyst undergoes a modification of its average redox level depending on the gas phase composition, exhibiting a corresponding variation in the cat-

alytic performance. However, once a stable redox level is reached, the catalyst should correspondingly exhibit a stable catalytic performance, in the absence of other deactivation phenomena. If this does not occur within acceptable periods of time-on-stream, it can be assumed that a slower but continuous variation of the oxidation state occurs, due to the inability of the molybdenum to reach a working redox state. For instance, it can be reasonably hypothesized that in the presence of high concentrations of hydrocarbon and with a particular catalyst composition, molybdenum is progressively reduced, and oxygen bulk diffusion (or incorporation of oxygen from the gas phase) are slower phenomena, which do not allow to reach a stable performance; correspondingly, the oxidizing power of the catalyst is progressively decreased. As mentioned above, the composition of the compound greatly affects this phenomenon; the addition of antimony favours the molybdenum reduction, so lowering the catalytic activity; it is necessary to add metals such as cerium, chromium and tungsten in order to recover the catalytic activity. Small amounts of these dopants can have a great effect on the redox properties of molybdenum, even though it cannot be excluded that they directly participate in the catalytic act.

The effect induced by the addition of the metal dopants on activity and selectivity also reflects in the behaviour of the catalytic performance with time-on-stream; if we look at the data in Figs. 13 and 14 we see that the selectivity to ethylene was increased with the time-on-stream, an opposite behaviour to that one in Figs. 11 and 12. A similar trend, with an increase in selectivity with time-on-stream, was observed for the catalyst with composition $K_2P_1Mo_{11}Sb_1Fe_1Cr_{0.5}Ce_{0.75}O_n$.

With respect to the latter catalyst, catalysts of Figs. 11 and 12 only possess an higher content of potassium; the amount of cerium (0.75 atom/KU) is intermediate between 0.25 and 1.5 (contained in catalysts of Figs. 11 and 12). The main effect obtained by decreasing the potassium content is the large increase in activity, which allows one to lower the operating temperature from 550°C to 470°C; on the other hand, it is impossible to use the catalyst with 2 potassium atom/KU at temperatures higher than 500°C, due to the occurrence of structural decomposition. It can be therefore assumed that the different behaviour with time-on-stream can be essentially due to the different temperature range employed, which might cause a change in the operating mechanism (see Fig. 5). Above 500°C it is currently believed that the contribution of surface-initiated homogeneous reactions to the formation of ethylene can be fundamental [16]. In particular, it has been reported that after activation of ethane on the catalyst surface with formation of an intermediate radical species, the latter can quickly desorb into the gas phase at high temperature, and be decomposed with high selectivity to ethylene. At lower temperatures, instead, either a different surface species is formed (an ethoxy species), or the adsorbed radical intermediate easily undergoes unselective oxidative attacks. In addition, the use of a high paraffin partial pressure (such as in our case) can favour the occurrence of gas-phase reactions.

In our case, it is likely that at high temperature a decrease of activity leads to a lower number of radical intermediate species, potential precursors of the oxygen-assisted homogeneous decomposition to ethylene, and that the contribution of the heterogeneous mechanism, mainly unselective at these conditions, causes a decrease of selectivity. At lower temperatures the mechanism is mainly completely heterogeneous, and variations in the surface redox properties are accompanied by a decrease in activity and a corresponding increase in selectivity, as usually occurs for heterogeneous redox-type mechanisms. Unfortunately, a direct demonstration of this hypothesis by an analysis of the variation of selectivity with time-on-stream at higher operative temperature with the optimized catalyst can not be given, because the catalyst decomposes.

A stable catalytic performance could be obtained after optimization of the chromium and cerium contents. The further refinement of potassium, phosphorus and tungsten contents allowed us to maximize activity and selectivity, and to lower the temperature of reaction and the residence time (from the initial conditions of 550°C and 12 s, to the final 470°C and less than 6 s), conditions at which the total conversion of the limiting reactant (oxygen) was obtained. More stable catalysts can be prepared, but they are less active and therefore have to operate at more severe conditions to achieve comparable conversions, thus at the proximity of the temperature of incipient structural decomposition.

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References

[1] M. Misono, Catal. Rev., Sci. Eng., 29 (1987) 269.
[2] Y. Ono, in J.M. Thomas and K.I. Zamaraev (Editors), Perspectives in Catalysis, Blackwell Scientific, London, 1992, p. 431.
[3] M.T. Pope, Heteropoly and Isopoly Oxometalates, Springer-Verlag, Berlin, 1983.
[4] I.V. Kozhevnikov and K.I. Matveev, Appl. Catal., 5 (1983) 135.
[5] S. Albonetti, F. Cavani, F. Trifirò and M. Koutyrev, Catal. Lett., 30 (1995) 253.
[6] F. Cavani, M. Koutyrev and F. Trifirò, Catal. Today, 24 (1995) 365.
[7] E. Morales and J.H. Lunsford, J. Catal., 118 (1989) 255.
[8] R. Burch and S.C. Tsang, Appl. Catal., 65 (1990) 259.
[9] E.M. Kennedy and N.W. Cant, Appl. Catal., 75 (1991) 321.
[10] S.T. Oyama and G.A. Somorjai, J. Phys. Chem., 94 (1990) 5022.
[11] S. Albonetti, F. Cavani, F. Trifirò, M. Gazzano, M. Koutyrev, F.C. Aissi, A. Aboukais and M. Guelton, J. Catal., 146 (1994) 491.
[12] G. Centi, F. Trifirò, J.R. Ebner and V.M. Franchetti, Chem. Rev., 88 (1988) 55.
[13] K. Otsuka, M. Hatano and T. Komatsu, in M.D. Bibby, C.D. Chang, R.F. Howe and S. Yurchak (Editors), Methane Conversion, Elsevier Science, Amsterdam, 1988, p. 383.
[14] R. Burch, G.D. Squire and S.C. Tsang, Catal. Today, 6 (1990) 503.
[15] A.F. Wagner, I.R. Slagle, D. Sarzynski and D. Gutman, J. Phys. Chem., (1990) 1853.
[16] F. Cavani and F. Trifirò, Catal. Today, 24 (1995) 307.
[17] M. Misono, N. Mizuno, K. Katamura, A. Kasai, Y. Konischi, K. sakata, T. Okuhara and Y. Oneda, Bull. Chem. Soc. Jpn., 55 (1982) 400.
[18] M. Akimoto, Y. Tsuchido, K. Sato and E. Echigoya, J. Catal., 72 (1981) 83.
[19] M. Akimoto, H. Ikeda, A. Okabe and E. Echigoya, J. Catal., 89 (1984) 196.
[20] G.B. McGarvey and J.B. Moffat, J. Catal., 132 (1991) 100.
[21] S.J. Korf, J.A. Roos, N.A. de Bruijn, J.G. van Ommen and J.H.R. Ross, Catal. Today, 2 (1988) 535.