Enhancement of catalytic activity of the ammonium/potassium salt of 12-molybdophosphoric acid by iron ion addition for the oxidation of isobutane to methacrylic acid

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The oxidation of isobutane to methacrolein and methacrylic acid was carried out over potassium/ammonium salts of 12-molybdophosphoric acid (Keggin-type heteropoly compounds), with overall selectivity to the desired products higher than 50%. The addition of iron to the catalyst composition led to a substantial enhancement of the catalytic activity, with an increase in the yield to the desired products, even though the selectivity decreased. The catalysts all have a secondary cubic structure, and are stable in the reaction environment. No trace of structural decomposition was found in spent catalysts. It was found that the addition of iron led to a substantial increase in the catalyst acidity and it is proposed that the Lewis acidity might play a role in the activation of the paraffin.

Keywords: heteropoly compounds; isobutane oxidation; methacrylic acid; methacrolein; iron

1. Introduction

Today, more than 90% of the methyl methacrylate on the market is produced via the acetone cyanohydrin process. This route, however, as a result of increasing production costs and of the environmental impact will be of little or no interest in the future. Indeed, environmental laws have forbidden the shipment of HCN and have required manufacturers to build on-site plants for the synthesis of cyanhydric acid from methane and ammonia. Moreover, recovery of sulphuric acid via thermal decomposition of ammonium sulphate (a co-product of the acetone cyanhydrin process) is another drawback of this process [1].

In recent years, different methods based on C3 and C4 processes have been proposed for the production of methyl methacrylate to be employed in place of the actual process [1]. The route from isobutane (using catalytic oxidation) is especially attractive because of the low cost of the raw material, the simplicity of a one-step process and the very low environmental impact.

A few studies have been published in patents [2–5], and recently one work devoted to the oxidation of isobutane over transition-metals-modified heteropoly compounds has been published [6]. Much of the patent literature concerns the production of methacrolein and methacrylic acid in the gas phase by oxidation of isobutane, with selectivity higher than 50%, using Keggin-type heteropoly compounds as heterogeneous catalysts containing phosphorus as the central element and molybdenum as the peripheral atom, modified by additions of vanadium and copper, and stabilized through the addition of cesium.

It has recently been shown that mixed potassium/ammonium salts of 12-molybdophosphoric acid, thermally stable up to 400°C, are active in the oxidehydrogenation of isobutyric acid to methacrylic acid [7]. The salt in the potassium form was stable up to 500°C, but its activity was considerably lower than that of mixed ammonium/potassium salts. The importance of the secondary cubic structure in guaranteeing stable catalytic performance was also pointed out.

In the present study, attention was focused on the formation of methacrylic acid and methacrolein from isobutane with heteropoly compounds with the composition $K_1(NH_4)_2PMoO_{12}$, which had been modified by the addition of iron. The effects of catalyst composition on the structural behaviour, surface acidity and catalytic activity were studied.

2. Experimental

The method for the synthesis of the catalysts has been described in previous studies [7,8]. The desired amounts of $(NH_4)_3Mo_7O_{24}$, H_3PO_4, KNO_3 were dissolved in water, and then 10 ml of HNO_3 was poured into the solution in order to precipitate a yellow compound which is the mixed salt of ammonium and potassium. A solution of $Fe(NO_3)_3$ was added drop by drop into the resulting slurry, which was then dried at 90°C for 8 h, 120°C for 12 h, 140°C for 12 h and 170°C for 12 h. The solid obtained was slowly heated for 6 h to the final calcination temperature, which was maintained for 6 h. The salts $K_1(NH_4)_{2-y}PMo_{12}O_{40} + Fe_x$ where $x = 0–1.5$ and y is the amount of NH_4^+ ions replaced by iron cations, were prepared. Hereinafter these salts will be referred to in the abbreviated form as K_1Fe_x.

Fourier-transform infrared (FT-IR) spectra were recorded with a Perkin-Elmer 1750 instrument. Spectra in the skeletal vibration region for heteropoly compounds (400–2000 cm^{-1}) were recorded using the KBr disc technique and calibrated amounts (0.3%) of heteropoly compound. Spectra for the characterization of the surface acidity were recorded using the self-supporting disc technique. The samples were pretreated by evacuation at 300°C under vacuum for 1 h in order to remove crystallization and coordination water.

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 samples were supported in a sample holder with a depth of 1 mm.

The oxidation of isobutane was carried out in a continuous flow reactor at atmospheric pressure. The fixed-bed stainless steel tube reactor was 400 mm long and had an inner diameter of 11.5 mm. It was mounted vertically and immersed in a cylindrical electric furnace.

Unless otherwise indicated, the standard feed composition was the following: isobutane 26%, oxygen 13%, water 12%, and the remainder helium; 3 ml (about 3 g) of catalyst were diluted with 3 ml of steatite. The catalyst used was granulated into particles ranging from 0.3–0.6 mm in size. The total flow rate was 50 ml/min, with a residence time of 3.6 s. The reactor outlet was kept at 250°C in order to prevent product condensation and methacrylic acid polymerization.

All reaction products were analysed by gas chromatography. A 70 cm column of 10% SP-1200 + 1% H_3PO_4 on Chromosorb WAW connected to a FID detector was used to separate isobutane, methacrolein, isobutyric acid, acetic acid and methacrylic acid. The oven temperature was programmed to rise from 40 to 100°C at a rate of 16°C/min. The isobutane–isobutylene separation was carried out using a 5 m column of 23% SP-1700 on Chromosorb PAW connected to a FID detector. The analysis of carbon oxides and oxygen was carried out using two columns connected to a TCD detector in isothermal conditions at 45°C. For the analysis of CO_2, a 4 m column of Poropack QS was used and a 2 m column of Carbosieve 2S was used for CO and oxygen.

Mass balances were calculated on an oxygen account basis for the products and were usually in the range 90–110%.

3. Results

3.1. CHARACTERIZATION OF THE CATALYSTS

The X-ray diffraction patterns (fig. 1) and infrared spectra of the samples with and without iron in the structure and calcined at 350°C were practically the same. The infrared spectra of all the samples containing different amounts of iron and calcined at 350°C did not exhibit significant differences in the range of 600–1100 cm^{-1}. The bands characteristic of the Keggin unit were observed and can be assigned according to the literature [9,10] as follows: the asymmetric stretch of the central atoms–oxygen bond (ν_{as}(P–O) at 1063 cm^{-1}), the asymmetric stretch of peripheral atoms–terminal oxygen atom bond (ν_{as}(Mo=O) at 962 cm^{-1}) and the

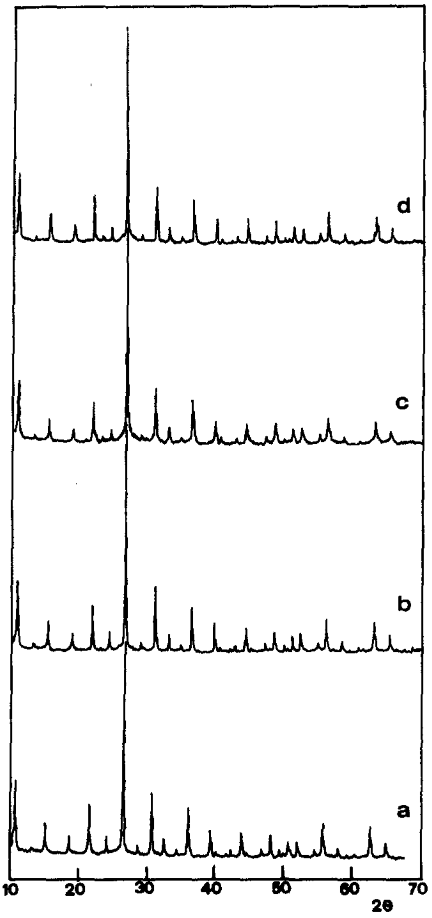


Fig. 1. XRD patterns of the K_1Fe_x samples after calcination at 350°C. (a) $x = 0$; (b) $x = 0.5$; (c) $x = 1.0$; (d) $x = 1.5$.

Mo–O–Mo stretches of the inter- and intra-octahedral bridges (ν_{as}(Mo–O–Mo)$_{inter}$ at 867 cm^{-1} and ν_{as}(Mo–O–Mo)$_{intra}$ at 788 cm^{-1}). In addition to the bands associated with the Keggin anion, two sharp bands at 1624 and 1412 cm^{-1} attributed to the bending vibration of lattice water and a vibration of the ammonium ion respectively were observed for each sample. The intensity of the band relative to ammonium decreased as the amount of iron increased, but still could be seen even for the highest iron content.

The XRD patterns for the K_1Fe_x salts were typical of the cubic structure without the presence of additional lines relative to other phases. For example, the XRD patterns for $K_1Fe_{1.5}$ calcined at increasing temperature are reported in fig. 2. The calcination at 400°C led to the appearance of diffraction lines of MoO_3. Indeed, calcination at temperatures higher than 350°C led to the decomposition of some of the compounds prepared, especially when the amount of iron added was higher

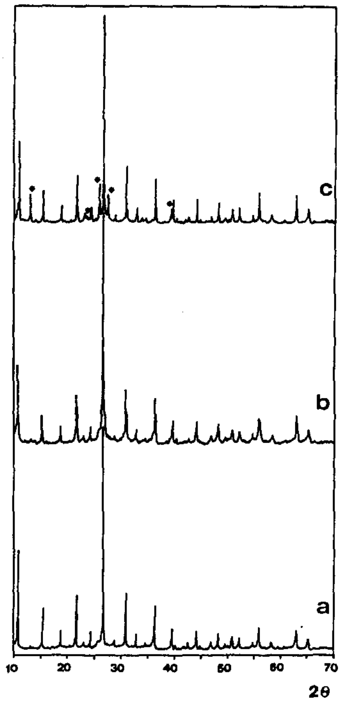


Fig. 2. XRD pattern of the $K_1Fe_{1.5}$ sample at increasing calcination temperatures; (a) 170°C, (b) 350°C, (c) 370°C. (*) MoO_3.

than $x = 0.5$. For this reason, the highest calcination temperature employed for all samples was 350°C.

3.2. EFFECT OF THE AMOUNT OF IRON

The catalytic oxidation of isobutane at 350°C over K_1Fe_x samples was investigated. Fig. 3 shows the variation in catalytic activity and yield of the products as a function of the amount of iron in the structure. All the data were collected after 17–20 h under stable catalytic conditions. All samples exhibited an initial catalytic behavior, which however became stable after approximately 10–15 h. The reaction products were methacrylic acid, methacrolein, isobutyric acid, acetic acid and carbon oxides.

The conversion increased gradually as the amount of iron increased. The increase is more marked between 0.5 and 1 iron atom per Keggin unit; the conversion of $K_1Fe_{1.5}$ is limited by the total conversion of oxygen. The yield of methacrolein is constant whereas the yield of methacrylic acid reaches a maximum for the sample with one atom per Keggin unit and then decreases for higher amounts of iron in the structure. The yield in higher oxidation products such as acetic acid and carbon oxides increases nearly linearly with the increasing amount of iron.

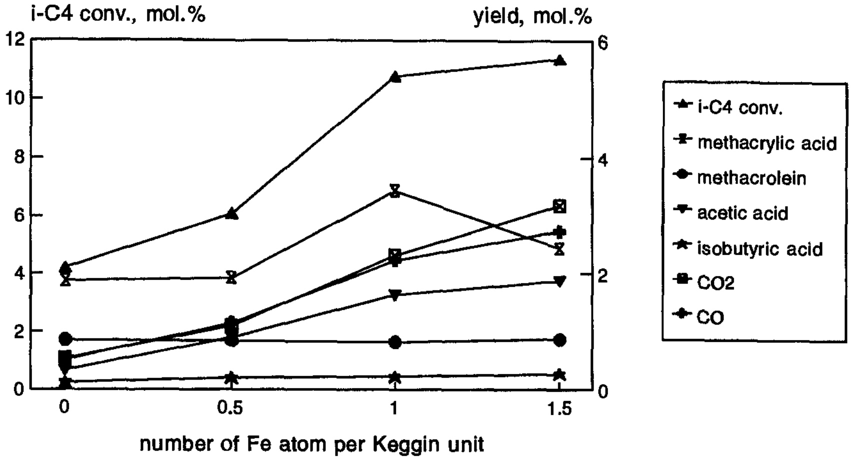


Fig. 3. Isobutane conversion and yield of the products as functions of the value of x in K_1Fe_x; conditions: temperature 350°C, residence time 3.6 s, isobutane 26%, oxygen 13% and water 12% (remainder helium).

3.3. DEPENDENCE ON RESIDENCE TIME

Fig. 4 shows the data obtained under standard conditions with different velocities of the feed flow for K_1Fe_0 (fig. 4a) and K_1Fe_1 (fig. 4b). With the increase in residence time, the conversion increases almost linearly. This allows the exclusion of film-diffusion as the rate determining step. For both samples, the selectivity to methacrolein decreases with increasing residence time. The selectivity to methacrylic acid decreases with increasing residence time for the catalyst with iron whereas for the catalyst without iron the selectivity is quite constant up to 3.6 s and tends to decrease with longer residence times. Among the by-products, the content of acetic acid, CO and CO_2 increases with increasing residence time for both samples.

3.4. SURFACE ACIDITY OF THE CATALYSTS

The introduction of iron into the structure of the heteropolyanion affects the surface acidity characteristics, studied by infrared spectroscopy using pyridine as the probe molecule. After preevacuation at 300°C for 1 h (fig. 5a), K_1Fe_0 was exposed to an excess of pyridine at 150°C for 20 min. The spectrum obtained after this treatment (fig. 5b) exhibits new bands associated with sorbed pyridine in the range of 1700–1400 cm^{-1}. The strong bands at 1636, 1608, 1538 and 1488 cm^{-1} are characteristic of protonated pyridine and the smaller band at 1582 cm^{-1} represents physically adsorbed pyridine [11]. When this sample was heated under vacuum up to 350°C for 20 min, the spectrum (fig. 5c) showed a significant attenuation of bands attributable to the pyridinium ion, and the disappearance of pyridine in the H-

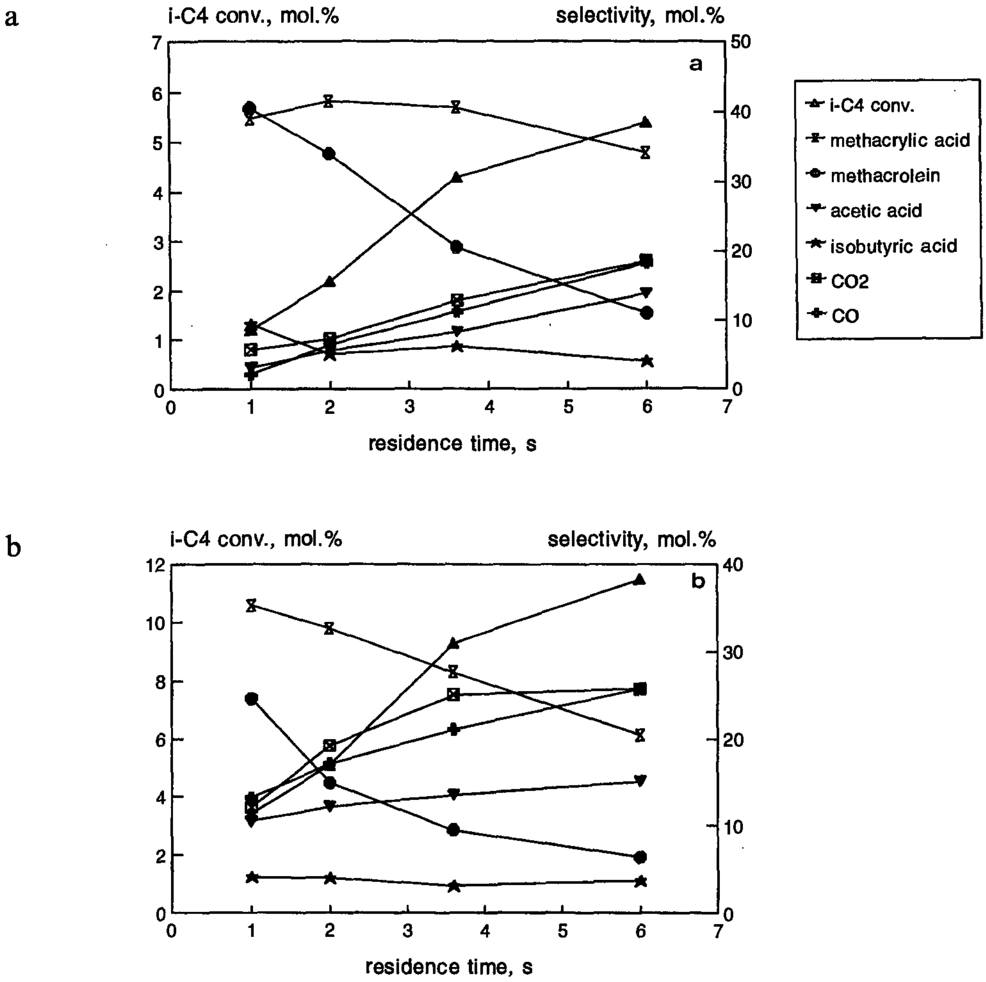


Fig. 4. Isobutane conversion and yield of the products as functions of the residence time; (a) catalyst K_1Fe_0; (b) catalyst $K_1Fe_{1.0}$; other conditions as in fig. 3.

bonded form. All the K_1Fe_x samples calcined at 350°C showed the bands of the pyridinium ion. It is possible to establish a relative scale of Brønsted acidity based on the peak area ratio A_{1538}/A_{1929}; the peak at 1929 cm^{-1} is attributed to an overtone of the ν(Mo=O) skeletal vibration. These results are reported in table 1. The A_{1538}/A_{1929} ratio increases when the amount of iron in the structure increases indicating an increase in the Brønsted acidity. After evacuation at 350°C the value of the ratio is quite similar for the samples of K_1Fe_0, $K_1Fe_{0.5}$ and K_1Fe_1, indicating approximately the same number of very strong Brønsted acid sites for all samples. For the sample with the highest iron content in the structure, the analogous number is nearly double that of the other samples.

In these spectra it is difficult to distinguish the appearance of the peak at around

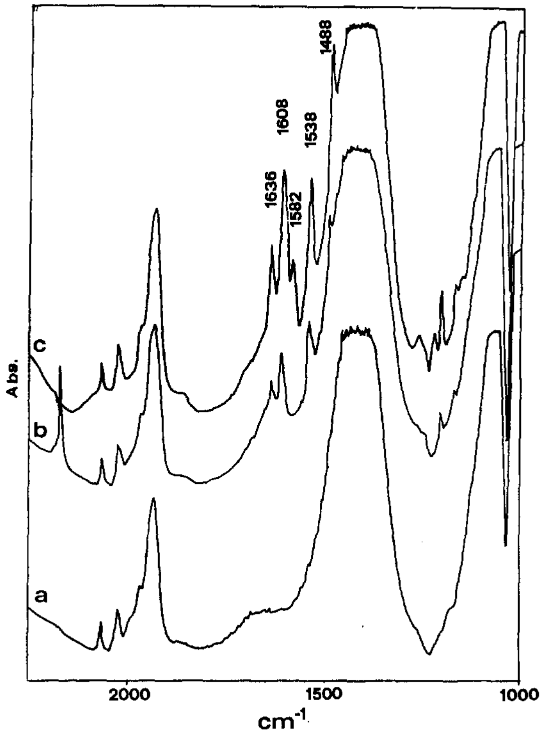


Fig. 5. FT-IR of the K_1Fe_0 sample after (a) evacuation at 300°C for 1 h, (b) adsorption of pyridine at 150°C for 20 min, (c) subsequent heating at 350°C under evacuation.

1450 cm^{-1} characteristic of coordinately (Lewis)-bound pyridine [11]. For this reason, the spectra reported in fig. 6 for the four samples were obtained by subtracting the spectrum of the dehydrated catalyst from the spectra obtained after pyridine adsorption. A new band characteristic of pyridine bound to Lewis sites appears at 1447 cm^{-1} for the samples of K_1Fe_1 and $K_1Fe_{1.5}$. The intensity of this band is greater for the sample with 1.5 atoms of iron per Keggin unit. This band disappears after evacuation at 350°C indicating that the Lewis acidity is medium strong.

Table 1
Band intensity ratios for the K_1Fe_x samples after adsorption and desorption of pyridine

Catalyst	A_{1538}/A_{1929}	
	after adsorption	after desorption
K_1Fe_0	0.48	0.32
$K_1Fe_{0.5}$	0.57	0.34
K_1Fe_1	1.17	0.37
$K_1Fe_{1.5}$	1.47	0.64

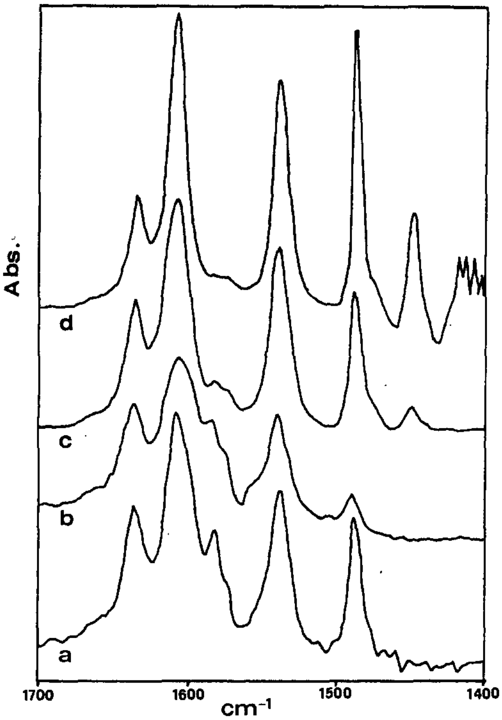


Fig. 6. Spectra of K_1Fe_x samples after adsorption of pyridine and subtraction of the spectrum relative to the catalyst before adsorption. (a) K_1Fe_0; (b) $K_1Fe_{0.5}$; (c) $K_1Fe_{1.0}$; (d) $K_1Fe_{1.5}$.

4. Discussion

The method of synthesis utilized in the present study is different from those usually employed in the literature of the preparation of heteropoly salts. The direct precipitation of the salts in an acidic medium leads to the formation of compounds having the cubic structure [7,8]. According to several authors this crystal symmetry accounts for an improved catalytic stability [7,12,13]. The XRD patterns obtained after calcination were essentially the same for all samples, and did not show the presence of any other phase associated with the iron. The compound obtained is crystalline and monophasic even when the amount of iron introduced during the preparation is greater than the amount of cation theoretically required to neutralise completely the $PMo_{12}O_{40}^{3-}$ anion. The spent catalysts have the same XRD patterns and infrared spectra as the fresh calcined catalysts; therefore neither the primary nor the secondary structure undergo modifications during the reaction.

Nevertheless, the surface area decreases markedly after reaction and the values are quite similar for all the catalysts (about 140 m^2/g for the fresh catalysts and about 8 m^2/g for the catalysts after reaction). We have observed that this phenomenon occurs at the beginning of the reaction; this can be associated with the unstable catalytic behavior which occurs in the first 10–15 h of reaction with a decrease of activity and an increase in selectivity, even though it cannot be excluded that a contribution to the observed phenomenon can derive from changes in the oxidation level of the molybdenum in the compound. In any case, it seems that the specific surface area is not a determining factor in the catalytic performance of these compounds.

After this initial unstable period, the activity and selectivity were stable all over the period of time which was necessary to evaluate the catalytic performance (usually, more than 100 h).

This study has shown that mixed heteropoly salts of ammonium and potassium doped with iron are effective catalysts for the production of methacrylic acid and methacrolein from isobutane. It is evident from the results obtained that the catalytic behavior depends on the amount of iron present. Iron could affect the redox properties of molybdenum in the Keggin unit and could also modify the acidity of the compound, thus affecting the interaction with the reactants. It is clear from fig. 3 that the higher iron content in the catalyst composition has a beneficial effect on the activity of the catalyst. Unfortunately, it has a negative effect on the selectivity since an increase in iron tends to privilege total oxidation. However, these antagonistic effects favour the partially oxidized products; indeed, the yield of methacrylic acid increases up to a composition of one iron ion per Keggin unit. On the contrary, the methacrolein yield remains almost unchanged in the range of compositions studied.

The catalytic behavior of the samples can be analyzed in terms of surface properties. A surprising characteristic of these samples, in which the overall positive charges due to the presence of potassium, ammonium and iron is largely higher than the negative charges of the Keggin anion, is the presence of Brønsted acidity. The acidity increases with increasing iron content, but the amount of very strong sites is quite similar for the samples of K_1Fe_0, $K_1Fe_{0.5}$ and K_1Fe_1. It was found that the acidity of the salts was affected considerably by the electronegativity (or acid–base property) of the cation as well as by the amount of the cation [14]. A fraction of the Brønsted acidity could arise from hydrolysis of the iron ion as occurs in zeolites [15,16]:

$$Fe^{3+} + H_2O \rightarrow FeOH^{2+} + H^+$$

$$Fe^{3+} + 2H_2O \rightarrow Fe(OH)_2^+ + 2H^+$$

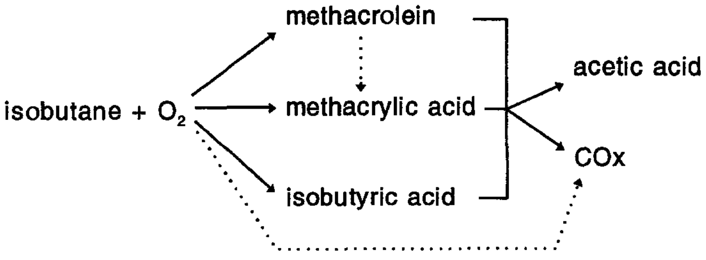
This could explain the increase in the medium-strong Brønsted acidity when the amount of iron is increased.

Iron partially replaces ammonium in the secondary framework of the heteropoly compound, as suggested by the decrease of the intensity of the IR band relative to the ammonium. The substitution, however, is not complete, as indicated by the fact that the IR absorption relative to the ammonium cation remains even at the highest iron content. The effective positive charge of iron, lower than 3+ due to its hydrolysis, can explain the overall charge balance, justifying the residual presence of ammonium as counterions in the secondary structure. On the other hand, the presence of finely dispersed iron oxide, undetected by XRD analysis, cannot be excluded.

The total acidity of the surface of the catalyst is very important in the reaction medium because acidity facilitates desorption of the products and avoids their total oxidation. Lewis sites can be attributed to the presence of an amorphous Fe_2O_3 dispersed on the surface of the heteropoly compound and could be very important in the first step of the reaction since this kind of acidity appears with the K_1Fe_1 sample and corresponds to a considerable increase in activity. In the oxidation of *n*-butane in maleic anhydride, it is known that the role of Lewis sites is to abstract two hydrogen atoms from the two CH_2 groups of *n*-butane via a concerted mechanism [17,18]. In the same way, for the ammoxidation of isobutane with mixed catalysts composed of Bi–Mo-based oxides and strong acidic Nb_2O_5, it is considered that the latter first extracts the hydrogen anion, H^-, from isobutane. The cation produced is transferred to the Bi–Mo-based oxide on which methacrylonitrile is formed by the ammoxidation of $CH_3C^+(CH_3)_2$ [19].

Fig. 4 shows that the selectivities to methacrylic acid and methacrolein decreased when the conversion increased. The selectivity of these products, extrapolated at a residence time as short as zero, is different from zero. This is in favour of a reaction network constituted of parallel reactions for the formation of isobutyric acid, methacrolein and methacrylic acid. These products undergo consecutive reactions to form acetic acid and carbon oxides. The parallel route of isobutane combustion appears to be of minor importance with respect to the selective routes to partially oxidized products. The reaction network deduced from the data is summarized in scheme 1.

The pathway leading to the formation of methacrolein is substantially unaltered by the addition of iron, while the route to the methacrylic acid is remarkably affected by the addition of iron (fig. 3). The acidic properties induced by iron, in terms of both Brønsted and Lewis acidity, affect the rate of methacrylic acid formation as well as the overall conversion of the isobutane, i.e. the activation of the reactant. It can be hypothesized that the modification of the acidic properties of the



Scheme 1. Reaction network of isobutane oxidation.

sites responsible for the formation of the methacrylic acid favours the rapid desorption of the latter, thus avoiding its overoxidation to carbon oxides.

Methacrylic acid and methacrolein may have a common reaction intermediate, obtained by activation of isobutane. This intermediate could be isobutene even though it has never been observed among the reaction products under normal reaction conditions. The absence of isobutene may be due to its quick transformation into the final products before any desorption from the catalyst surface can occur.

Acknowledgement

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