

Fine analysis of by-products of the selective oxidation of isobutane into methacrolein and methacrylic acid over Mo–V–P catalyst

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Received 24 January 2006; accepted 4 July 2006

Available online 18 September 2006

Abstract

The nature of the products of the selective oxidation of isobutane into methacrolein and methacrylic acid over a Mo–V–P Keggin-type-structure catalyst was investigated at 593 K. Gas chromatography/mass spectrometry and ¹H and ¹³C NMR were complementary analytical methods to identify by-products. The quantification was realised by ¹H NMR and gas chromatography. Aromatic and linear carbon backbone products detected suggested that an isomerization occurred during the oxidation of isobutane. A better knowledge of the nature of the acid site on which isomerization occurs might design a powerful catalyst.

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Keywords: Oxidation; Isobutane; Methacrolein; Methacrylic acid; Keggin; Skeletal isomerization

1. Introduction

The use of methyl methacrylate has almost doubled in the last two decades and the trend will go on in the future. This monomer is mainly used for the production of polymethyl methacrylate (PMMA) and other polymer dispersions in paintings and coats [1].

Many processes have been developed for producing methacrylic acid, a precursor of methyl methacrylate. The most two significant processes are the acetone cyanhydrine process (ACH) and the two-step oxidation of isobutylene developed by different Japanese companies [2] (Japan Methacryl monomer, Mitsubishi Rayon, Kyodo Monomer).

Yet, several economical and ecological disadvantages are reported. In the first process hydrogen cyanide and acetone cyanhydrine are used and a large amount of ammonium sulfate waste are produced. In the second process, the cost of isobutylene as raw materials is very important.

The one-step oxidation of isobutane into methacrylic acid and methacrolein is an interesting alternative as isobutane is an abundant product in refinery or from natural gas and the expected low-cost of installation due to a one-step reaction.

A lot of papers [3,5–14] and patents [15–23] deal with the development of catalysts based on Keggin-type heteropolycompounds. Currently, with the most effective catalysts, high selectivities of methacrolein and methacrylic acid are obtained (>70%) but with low isobutane conversion [3]. A good formulation was developed by Schindler et al. [4]: Mo₁₂V_{0.5}P_{1.5}As_{0.4}Cu_{0.3}Cs_{1.4}O_x. The conversion rate of isobutane and the sum of the selectivities of methacrolein and methacrylic acid were respectively 21.8% and 55.7%.

Little is known regarding the nature of the products of the selective oxidation of isobutane on Keggin type heteropolycompounds based catalysts. Quite often, in the literature [3,5–14], the detected products by gas chromatography are only: isobutene, CO, CO₂, methacrolein, methacrylic acid and acetic acid. Busca et al. [5] also observed acrylic acid, isobutyric acid, acetone and maleic anhydride. Acrolein and acrylic acid were noticed by Paul et al. [9,10]. Mizuno et al. [7] confirmed the presence of acetone. Deng et al. [12] showed the production of acrylic acid.

In patents [15–28], isobutylene, carbon oxides, acetone, maleic anhydride, isobutyraldehyde, acetic, propionic, acrylic and isobutyric acids were detected.

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In this paper, two complementary analytical methods which are GC–MS and ^1H and ^{13}C NMR, are used to identify the unknown by-products which were then quantified by GC and ^1H NMR. This new approach is very useful to understand the possible mechanistic pathways of the oxidation of isobutane.

2. Experimental

2.1. Preparation of the catalyst

The catalyst was prepared according to the following recipe.

In a solution prepared by dissolving $\text{H}_4\text{PMo}_{11}\text{VO}_{40}$ (76.3% of purity, NIC) in deionised water, CuCl (97% of purity, Fluka), was added. The black solution was noted solution A.

A solution B of cesium nitrate was added dropwise in the solution A: the colour of the solution C obtained was initially brown, turned green and finally yellow.

A solution D was prepared by dissolving pyridine (100%, Acros) in deionised water. This solution was added dropwise in the solution C and the mixture was maintained at 353 K during 90 min.

Then, the water and the pyridine were removed at 800 mbar and 360 K.

The catalyst was dried at 393 K during 12 h.

The compound was crushed and the size of the particles was between 80 and 250 μm .

Finally, the catalyst was calcined under nitrogen at 723 K during 3 h.

2.2. Characterization techniques for the catalyst

Chemical analyses for Mo, P, V, Cs and N were made by atomic emission. FT-IR spectrum was recorded in the wave number range 400–4000 cm^{-1} on a Perkin-Elmer spectrophotometer using KBr pellets. The X-ray patterns were obtained at room temperature on a Siemens D5000 diffractometer using $\text{Cu K}\alpha$ radiation. A refinement program developed at the LCPS (Laboratoire de Cristallographie et Physico-chimie du Solide) was used to determine the value of lattice parameters. The BET surface and the BJH porous volume were determined using a Gemini 2360.

2.3. Reaction conditions

A tubular isothermal fixed bed reactor was used to determine the catalytic activity. To ensure a uniform heating, the stainless steel tube reactor was in a molten salt bath, in which a nitrogen flow was bubbling.

The selective oxidation of isobutane is highly exothermic. To avoid the formation of hot spots, the catalyst was mixed with the same volume of carborundum particles of similar size. Moreover, three beds of carborundum particles sized respectively 0.250, 0.484 and 1.680 mm were laid on each side of the catalyst bed.

The reaction feed is composed by 12.3% of isobutane (0.316 NL/h), 6.4% of oxygen (0.164 NL/h), 75.5% of helium containing 1% of krypton (1.938 NL/h) and 5.8% of water

(0.149 NL/h). The gas reactants and the water were fed respectively by a set of Brooks mass flow controllers and a Gilson HPLC pump.

The reaction pressure and temperature were 1 bar and 593 K.

The contact time was defined as the ratio of the catalyst volume (2 mL) and the feed flow at the NTP conditions. It was fixed at 2.8 s.

A blank test was done in the same conditions by substituting the 2 mL of the catalyst by 2 mL of carborundum (0.250 mm). Only traces of CO_x were detected, which were the products of some gaseous phase reactions.

2.4. Analysis of the reaction products

The catalyst was activated during one night at 593 K under helium flow fixed at 1.80 NL/h. Then, the stationary regime was obtained after 2 h under the reaction conditions.

2.4.1. Gas reactants and products

Gaseous compounds at the inlet and the outlet of the reactor were analysed by an on-line TCD gas chromatograph operating with two parallel columns: a 10 m long-molecular sieve 5 A for the detection of oxygen, krypton and carbon monoxide, and an apolar 10 m long-Silicaplot for the detection of isobutane, carbon dioxide, isobutene and other potential alkanes or alkenes.

The columns and detector temperatures were respectively at 353 and 483 K.

Krypton was used as an internal standard.

2.4.2. Organic compounds

After 2 h on stabilization stream, the polar organic compounds were trapped in water during 2 h and analysed by a FID gas chromatograph equipped with a polar 30 m long-EC 1000 (Alltech) column. A split/splitless injector at 423 K with a division ratio of 1/5 was used. The detector temperature was 513 K.

The temperature program of the column was as follows: 40 °C (2 min), a ramp of 10 °C/min until 240 °C, 240 °C (1 min).

Valeric acid was used as an internal standard with manual injections.

These first analyses were used to determine the selectivities and the conversion of each reactant and product after 4 h. Carbon and oxygen balances were calculated and were above 99%.

Acidity of the trapped solution was evaluated from acid–base titration using sodium hydroxide as the titrant and phenolphthalein as the coloured indicator.

The results were compared with the total acidity obtained from the chromatographic data.

2.4.3. Determination of by-products

In order to characterize the by-products obtained during the reaction, a concentrated sample was obtained by trapping organic products in deuterium oxide during 3 h after 4 h on stream. This sample was then analysed by NMR and GC–MS.

2.4.4. Sample

A special flask of 5 mL was used to trap the organic compounds in 3 mL of deuterium oxide. The solution was frozen

between each analysis to avoid consecutive reactions of aldolisation and condensation.

2.4.5. GC–MS

Gas chromatography coupled with mass spectrometry was used to characterize some products not detected before. The apparatus is a Thermofinnigan PolarisQ mass spectrometer. It is composed by an electron impact source (70 eV) and an ion trap mass analyser.

The chromatographic conditions are the same as previously, except that the column diameter is not 0.5 mm but 0.25 mm, more adapted for GC–MS.

The Xcalibur software is used to identify the products.

2.4.6. NMR

^1H and ^{13}C NMR spectra were recorded on Bruker AC300 spectrometer (300 MHz) at 25 °C. This spectrometer is equipped with a Bruker software Topspin.

3. Results

3.1. Characterization of the catalyst

The catalyst composition is $\text{Cs}_3\text{HCu}_{0.12}\text{Pyridine}_{0.6}\text{PMo}_{11}\text{VO}_x$ according to the chemical analysis. The FT-IR spectrum shows four characteristic bands of the molybdophosphate Keggin structure at 1062, 962, 868 and 784 cm^{-1} assigned to ν as(P–O), ν as (Mo–O terminated), ν as (Mo–O–Mo) of the same trimetallic group and ν as (Mo–O–Mo) between two different trimetallic group [29]. The absence of shoulders on the first band suggested that the V^{5+} atoms were in an extraframework position noted VO_x . This elimination of the vanadium is associated with the production of phosphate species, according to the literature [11,30,31].

The X-ray diffraction pattern corresponds to the cubic lattice of $\text{Cs}_3\text{PMo}_{12}\text{O}_{40}$. The lattice parameter refinement indicates a value of 11.817 Å.

The BET surface and the BJH pore volume are respectively 15.6 m^2/g and 0.046 cm^3/g , which are very low for a heteropolyanion: sintering may have occurred during the calcination at 723 K.

3.2. Catalytic behaviour

Isobutane and oxygen conversions were respectively 1.7 and 10.2%.

Table 1 indicates the selectivities after 4 h of reaction.

The main products excepted CO_x are methacrolein, methacrylic acid, acetic acid and isobutylene as usually claimed in the literature. To our knowledge, it is the first time in the literature that the selectivities of propene, propanaldehyde and acetaldehyde are determined in the oxidation of isobutane.

The low conversion of isobutane is advantageous for determining the reaction intermediates because it is more likely to detect the primary products.

However, the number of moles of condensed acid products measured by an acid–base titration is a little different from the

Table 1

Selectivities of the products of the oxidation of isobutane catalysed by $\text{Cs}_3\text{HCu}_{0.12}\text{Pyridine}_{0.6}\text{PMo}_{11}\text{VO}_x$ at 593 K

Product	Selectivity (%)
Propene	1.6
Isobutylene	5.3
Carbon monoxide	17.5
Carbon dioxide	25.7
Acetaldehyde	0.9
Propionaldehyde	0.01
Acetone	2.1
Acrolein	0.6
Methacrolein	25.4
Acetic acid	5.5
Propionic acid	0.3
Isobutyric acid	0.07
Acrylic acid	1.2
Methacrylic acid	14.1

number of moles of acids calculated on the basis of the chromatographic data: the former is evaluated to 0.20 and the latter to 0.22 mmol. Yet, the 0.02 mmol of difference is more important than the accepted deviation.

Other unknown peaks appeared in the chromatogram of the solution and they may be associated with some acid compound.

3.3. GC–MS

Table 2 reports the products identified by GC–MS in addition to those already quantified. The retention time and the ratio m/z of the main ionic fragments are noted.

The difference observed between the acidity evaluated by the acid–base titration and the chromatographic data could be explained by the production in small amount of formic acid, 2-furoic acid, benzoic acid and *p*-toluic acid.

The detection of the couple aldehyde–carboxylic acid suggests that the formation of the carboxylic acid form is produced through aldehyde oxidation.

In order to confirm the identification of these products and to detect other by-products, ^1H and ^{13}C NMR spectra were recorded.

Table 2

Identification of products by GC–MS and their mass spectrometry characteristics

Product	Retention time (min)	m/z main fragments
Methanol	0.93	29, 31, 33
Methylvinylketone	1.22	24, 43, 55, 71, 86
Methylpropylketone	1.49	43, 71, 86
Formic acid	8.81	44, 45, 46
4-Cyclopentene-1,3-dione	9.80	42, 50, 68, 96
<i>p</i> -Cresol	9.67	39, 50, 53, 109, 110
Benzaldehyde	9.95	50, 76, 92, 103
<i>p</i> -Tolualdehyde	10.45	39, 40, 69, 91, 119
Citraconic anhydride	11.26	39, 40, 69, 87
2,3-Dimethylmaleic anhydride	11.96	39, 40, 68, 96
Phenol	14.39	39, 50, 66, 94, 95
2-Furoic acid	16.25	39, 95, 112, 113
Benzoic acid	18.20	50, 51, 77, 105, 122, 123
<i>p</i> -Toluic acid	19.05	39, 46, 63, 91, 119, 136

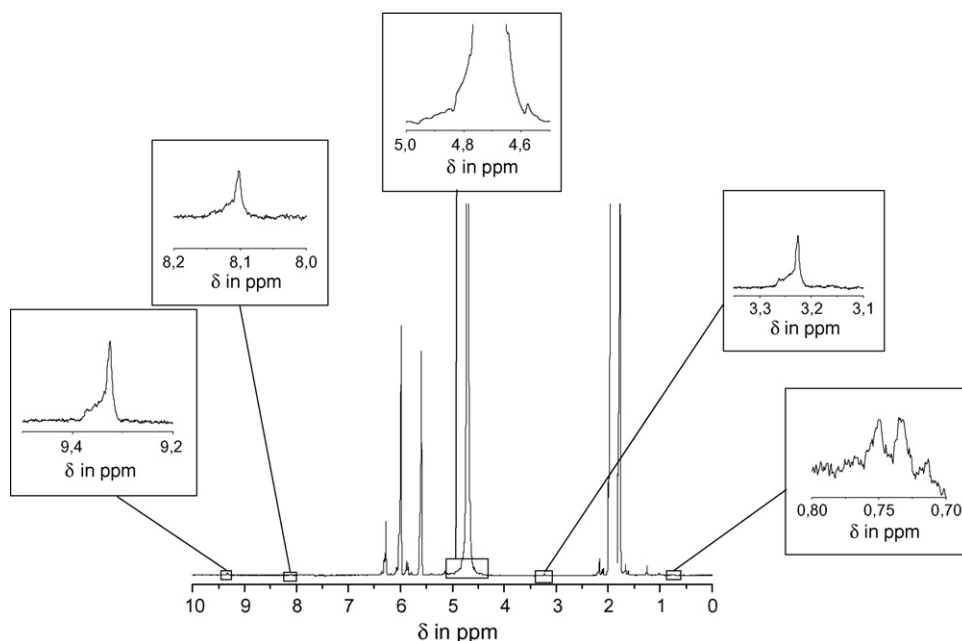


Fig. 1. ^1H NMR spectrum of the organic products dissolved in deuterium oxide between 4 and 7 h of reaction.

3.4. ^1H NMR

The ^1H NMR was used to identify potential other products not eluted on the EC 1000 column and to confirm or not the species detected by GC–MS.

The ^1H NMR spectra (Fig. 1) could be divided into four main different domains:

- Methyl proton in α position of a carbonyl group (1.6–2.2 ppm),
- Ethylenic proton in α position of a carbonyl group (5.5–6.4 ppm),
- Benzenic proton and ethylenic proton engaged in a cycle (6.5–7.4 ppm),
- Aldehydic proton (9.2–9.4 ppm).

The labile protons are in the region of the protons of the water. Table 3 lists the ^1H chemical shift assignments for the products observed in this study.

Other peaks appeared with a weak intensity between 2.2 and 2.4 ppm and between 6.4 and 7.5 ppm and were associated with the products detected in GC–MS. Nevertheless, it was not possible to assign each peak to each product, but the shape of the spectrum was in agreement with the GC–MS results.

3.5. ^{13}C NMR

The ^{13}C NMR is not a sensitive method and the carbon natural abundance is only 1.1%. Yet, the chemical shifts region is bigger than those of the ^1H NMR spectra. Thus, it is more efficient to determine different environment of the carbon.

This method is complementary to the ^1H NMR.

Table 3
Products detected by ^1H NMR and their characteristics

Product	Chemical shift (ppm)
Acetone	CH_3 , s, 2.118
Acrolein	H gem of $\text{C}=\text{O}$, dd, 6.30, 6.35, under the 6.27 ppm main peak; H aldehydic, s, 9.33
Methacrolein	CH_3 , s, 1.77; H in <i>cis</i> position for $\text{C}=\text{O}$, s, 6.02; H in <i>trans</i> position for $\text{C}=\text{O}$, s, 5.59; H aldehydic, s, 9.32
Acetic acid	CH_3 , s, 2.09
Acrylic acid	H in <i>trans</i> position for $\text{C}=\text{O}$, dd, 5.78, 5.85, 5.88, 5.92; H in <i>cis</i> position for $\text{C}=\text{O}$, dd, 6.07, 6.18 and under 5.98 ppm main peak; H gem of $\text{C}=\text{O}$, dd, 6.30, 6.35, under the 6.27 ppm main peak
Methacrylic acid	CH_3 , s, 1.77; H in <i>cis</i> position for $\text{C}=\text{O}$, s, 6.02; H in <i>trans</i> position for $\text{C}=\text{O}$, s, 5.59
Methanol	CH_2 , s, 3.26
Formic acid	CH, s, 8.10
Methanediol	CH_2 , s, 4.57
Isobutanol	CH_3 , d, 0.73; H gem of OH, s, 3.27; CH, s, not observed
Maleic acid	CH, s, 6.28

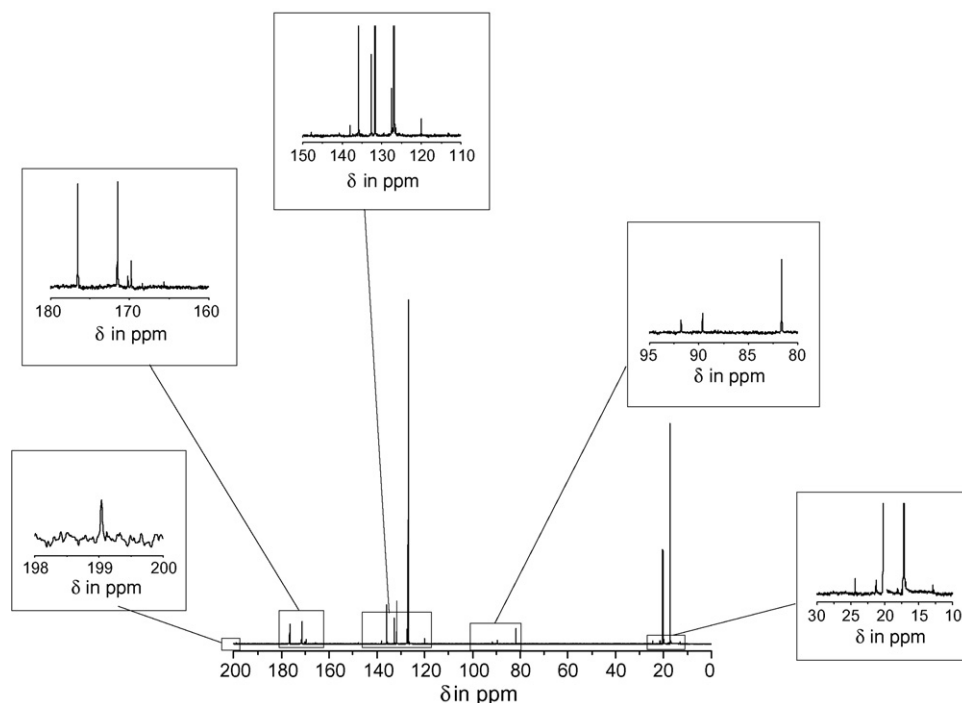


Fig. 2. ^{13}C NMR spectrum of the organic products dissolved in deuterium oxide between 4 and 7 h of reaction.

The ^{13}C NMR spectra (Fig. 2) could be divided into four main different regions:

- Methyl and methylene carbons (0–30 ppm),
- Carbon in α position of an oxygen (60–100 ppm),
- Ethylenic carbon (110–150 ppm),
- Carbonyl carbon (160–180 ppm).

The ^{13}C chemical shift assignments of the products are listed in Table 4.

The three peaks at 81, 89 and 92 ppm could be associated with formaldehyde derivatives (methanediol, polyoxomethylene and 1,3,3-trioxane).

The NMR and GC–MS are complementary methods to characterize by-products. Finally, these compounds were quantified by GC and ^1H NMR.

3.6. Quantification

Table 5 indicates the selectivities of each by-product. The four first products selectivities were evaluated thanks to ^1H NMR

Table 4
Products detected by ^{13}C and their characteristics

Product	Chemical shift (ppm)
Acetone	CH_3 , s, 21.30; $\text{C}=\text{O}$ not seen
Methacrolein	CH_3 , s, 17.26; CH , s, 132.63; CH , s, 147.74; $\text{C}=\text{O}$, s, 199.04
Methacrylic acid	CH_3 , s, 17.26; CH , s, 126.95; CH , s, 135.83; $\text{C}=\text{O}$, s, 171.52
Acetic acid	CH_3 , s, 20.27; $\text{C}=\text{O}$, s, 176.53

data, whereas the others' were determined thanks to chromatographic data.

The knowledge of these selectivities is very important to understand the different possible mechanistic pathways.

4. Discussion

The first interesting observation is the formation of linear-carbon-backbone oxidation products as maleic acid (hydrolysis of maleic anhydride) and methylvinylketone. The skeletal isomerization occurs during the oxidation of isobutane. It is worth mentioning that no traces of *n*-butane or butenes are detected in the isobutane bottle according to chromatography.

The formation of aromatic products such as *p*-cresol, phenol, benzaldehyde, *p*-tolualdehyde, benzoic and *p*-toluic acids might be the result of the oxidation of some aromatic compounds produced by Diels–Alder reaction.


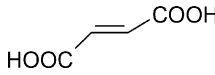
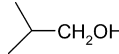
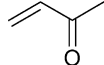
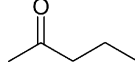
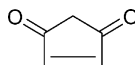
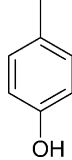
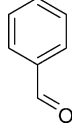
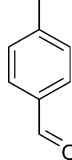
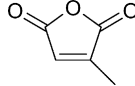
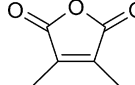
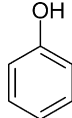
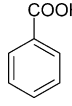
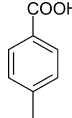
In gas phase, pericyclic reactions may occur between isobutene and propene which are observed in GC. Therefore, other alkenes such as ethylene and hypothetical butenes could react to produce also 2-pentene and 3-methyl-2-butene.

Oxidative dehydrogenation and Diels–Alder reactions could produce benzene, toluene and xylene. The oxidation of these compounds leads to the aromatic products identified in Table 5. In a patent [32], the authors also detected these aromatic products during the oxidation of isobutene on $\text{P}_{1.2}\text{Mo}_{11}\text{VCu}_{0.3}\text{Q}_x\text{K}_{1.5}$ where Q corresponds to choline.

Citraconic and 2,3-dimethylmaleic anhydrides are oxidation products of toluene and xylene.

The methylpropylketone, 2-furoic acid and cyclopentenedione are oxidation products of 2-pentene.

Table 5
 Selectivities of the by-products of the oxidation of isobutane catalysed by $Cs_3HCu_{0.12}Pyridine_{0.6}PMo_{11}VO_x$ at 593 K

Product	Formula	Selectivity (%)
Methanol ^a	CH_3OH	5×10^{-2}
Formic acid ^a		9×10^{-2}
Maleic acid ^a		2.6
Isobutanol ^a		4×10^{-2}
Methylvinylketone		2.4×10^{-3}
Methylpropylketone		1.7×10^{-4}
4-Cyclopentene-1,3-dione		1.1×10^{-2}
<i>p</i> -Cresol		3.2×10^{-4}
Benzaldehyde		3.4×10^{-3}
<i>p</i> -Tolualdehyde		8.6×10^{-4}
Citraconic anhydride		6.6×10^{-1}
2,3-Dimethylmaleic anhydride		1.6×10^{-1}
Phenol		5.5×10^{-3}
Benzoic acid		6×10^{-2}
<i>p</i> -Toluic acid		1.1×10^{-2}

^a Selectivity determined by ¹H NMR spectrum.

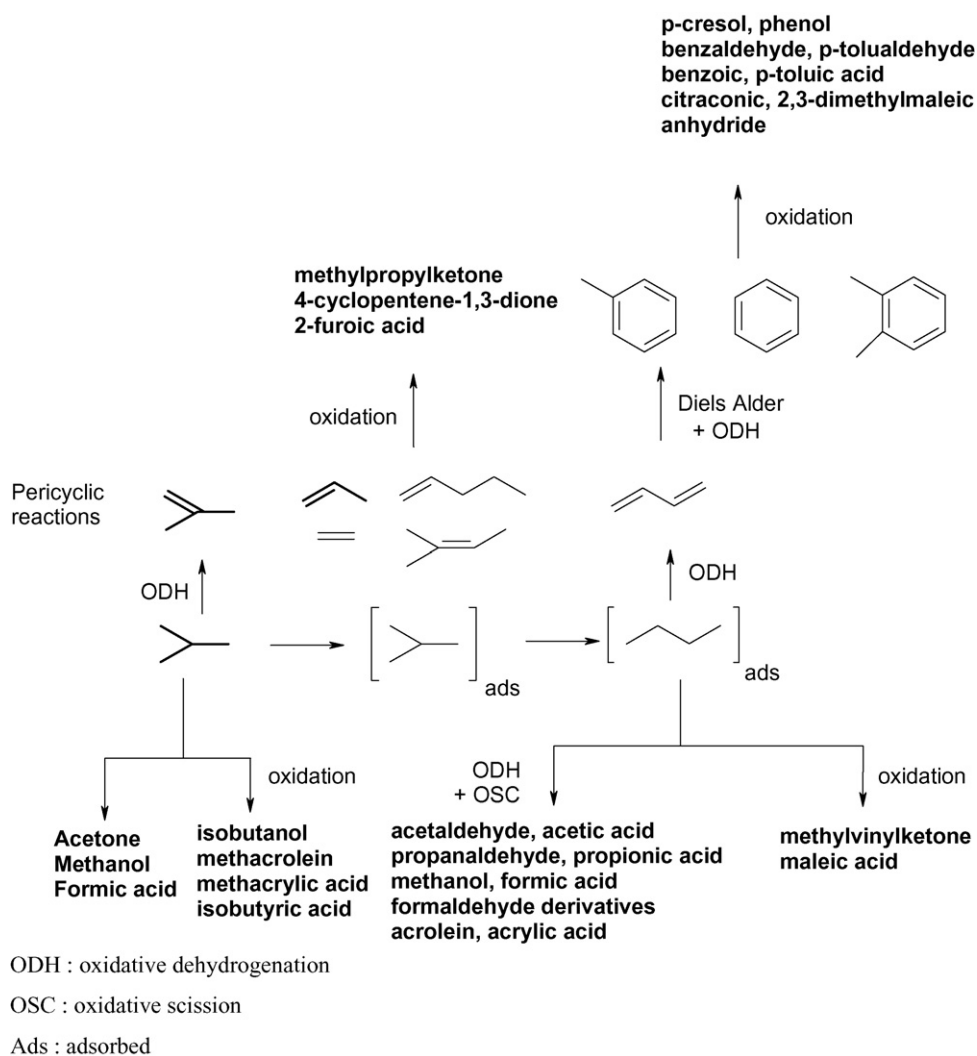


Fig. 3. Possible mechanistic pathway of the oxidation of isobutane.

Finally, methanol, formaldehyde derivatives and formic acid could be associated with oxidative scission of alkanes or alkenes. This assertion could be related to the formation of the major by-products shown in Table 2.

Acetaldehyde and acetic acid could be formed in part by direct oxidation of ethylene, also propanaldehyde and propionic acid could be produced by direct oxidation of propene.

Fig. 3 shows the different possible mechanistic pathways.

There are complex interactions between different physical and chemical phenomena: the adsorption/desorption of substrates, the intraparticle diffusion of alkenes to react in Diels–Alder reactions, the oxidative dehydrogenation to produce dienes, the oxidation and the skeletal isomerization linked to acidity properties of the catalyst.

The selectivity of maleic acid of 2.6% shows the skeletal isomerization is significant.

The selectivities of the aromatic compounds are around 10^{-3} – 10^{-2} %. This suggests that the desorption of alkenes and dienes is not kinetically favoured, in opposite to the oxidation.

5. Conclusion

GC–MS, ^1H and ^{13}C NMR are complementary analytical methods used to identify a large quantity of by-products never observed before in the literature.

^1H and ^{13}C NMR were used to confirm the nature of the products detected by GC–MS. Maleic acid, isobutanol and formaldehyde derivatives (methanediol, polyoxomethylene, 1,3,3-trioxane) are other compounds analysed by NMR and not identified by GC–MS due to the nature of the column.

This analytical method was very useful to highlight one specific phenomena which occurred during the oxidation of isobutane: the skeletal isomerization. Specific studies must be done to correlate carefully the type of isomerization and the nature of the acid site responsible for this phenomena: Lewis or Brønsted sites.

This new approach could be used to determine the reaction mechanism in alkane and alkene oxidation.

Acknowledgments

This work was financially support by Arkema. The authors are very grateful to D. André and G. Hamon for the preparation and characterization of the catalyst. They also thank L. Zaïr who performed preliminary results in analytical method with the help of the analytical division in the CRRA.

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