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Abstract: The isopropanol adsorption-oxidation over V₂O₅ (transient study) was monitored by mass spectrometry (MS) of desorbed molecules produced over the catalyst by reactive interaction at 40, 100 and 150°C. Then, Temperature Programmed Surface Reaction (TPSR) tests were conducted to analyse the products again by MS. The acetone adsorption - oxidation was also studied at 40°C by the same techniques. It was concluded that isopropanol molecules replace some of the water molecules adsorbed onto the V₂O₅ but do not interact with molecules with higher adsorption energies as methanol.

The following products were identified by TPSR: various amounts of water, isopropanol, propylene and acetone at low temperature (< ~ 150°C) and water, CO, CO₂, isopropyl ether at higher temperature (~ 200 - 300° C). Isopropanol oxidation to acetone only use oxygen from V₂O₅. Desorption of CO and CO₂ is related with incomplete isopropanol oxidation to acetone, which is limited by the proportion of oxygen available in the solid. Formation of CO and CO₂ occurs at the expense of atmospheric oxygen (He impurity). For such temperatures, V₂O₅ shows acid and minima redox properties.

Cover Letter

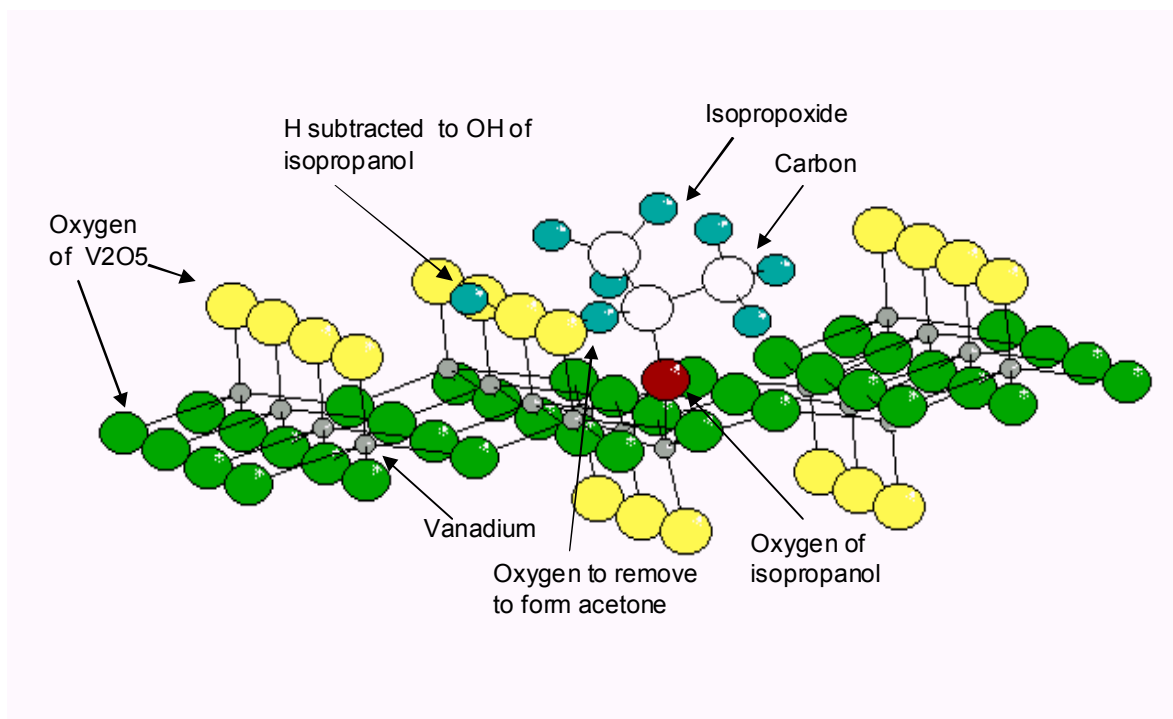
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Title: ISOPROPANOL ADSORPTION–OXIDATION OVER V_2O_5 - A MASS SPECTROMETRY STUDY.

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Summary:

The isopropanol and acetone adsorption-oxidation over V_2O_5 were studied by transients and Temperature Programmed Surface Reaction (TPSR) tests

It was concluded that isopropanol molecules replace some of the water molecules adsorbed but do not interact with molecules with higher adsorption energies as methanol.

Isopropanol oxidation to acetone only uses oxygen from V_2O_5 . Desorption of CO and CO_2 is related with incomplete isopropanol oxidation to acetone.

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ISOPROPANOL ADSORPTION–OXIDATION OVER V_2O_5 - A MASS SPECTROMETRY STUDY.

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Abstract

The isopropanol adsorption-oxidation over V_2O_5 (transient study) was monitored by mass spectrometry (MS) of desorbed molecules produced over the catalyst by reactive interaction at 40, 100 and 150°C. Then, Temperature Programmed Surface Reaction (TPSR) tests were conducted to analyse the products again by MS. The acetone adsorption – oxidation was also studied at 40°C by the same techniques. It was concluded that isopropanol molecules replace some of the water molecules adsorbed onto the V_2O_5 but do not interact with molecules with higher adsorption energies as methanol.

The following products were identified by TPSR: various amounts of water, isopropanol, propylene and acetone at low temperature (< ~ 150°C) and water, CO, CO₂ isopropyl ether at higher temperature (~ 200 – 300° C). Isopropanol oxidation to acetone only use oxygen from V_2O_5 . Desorption of CO and CO₂ is related with incomplete isopropanol oxidation to acetone, which is limited by the proportion of oxygen available in the solid. Formation of CO and CO₂ occurs at the expense of atmospheric oxygen (He impurity). For such temperatures, V_2O_5 shows acid and minima redox properties.

Introduction

Some authors working about V_2O_5 as Ai [1], Anderson [2], Louis et al. [3] and Allison et al. [4] have found that terminal oxygen (V=O) participates in hydrocarbon oxidation, while others as Deo et al. [5] and Weber [6] suggested that bridge oxygen is also involved in oxidation reactions.

Isopropanol decomposition has long been considered as a chemical probe reaction for surface acid-base properties [7].

Isopropanol experiences dehydration to give propylene on acid surface sites and dehydrogenation via a concerted mechanism of adjacent acid and basic surface sites to give acetone[8, 9]

The same authors studied the isopropanol reaction over TiO₂ have found that formation of ether is minimized in the presence of oxygen.

Kulkarni et al. [10] have studied isopropanol oxidation over several pure metal oxide catalysts among them V_2O_5 and indicated that this is active in the 135- 190°C temperature range, where significant quantities of isopropyl ether along with propylene are produced.

The same authors measured the TOF_{redox} (turnover frequency) to be 0.018 [s^{-1}] and the TOF_{acid} , which results in high value of 18 [s^{-1}].

Hussein et al. [11] studied the reaction of isopropanol over Y_2O_3 and proposed formation of isopropoxide species which are bridge bonded to metal atoms (yield propylene) and the terminal isopropoxide species give acetone.

In turn, Ranea et al [12] have identified the adsorption sites of water molecules on V_2O_5 by TPSR accompanied by a theoretical study.

In this work, the objective is to deepen knowledge of the isopropanol - precipitated V_2O_5 system by studying adsorption – oxidation transients and subsequent Temperature Programmed Surface Reactions of the adsorbed species. In special, attention will be paid to water – isopropanol interaction over a V_2O_5 surface in comparison with water-methanol interaction and about of the precursors of CO and CO_2 formation.

Experimental Part.

TPSR and transient measurements of V_2O_5 surface were carried out in an ultra-high vacuum surface analysis reactor (base pressure $\sim 1.33 \cdot 10^{-5}$ Pa)[13].

Two detectors were used: catalytic cell (shimadzu GC-8A), employed as real time detector and mass quadrupole spectrometer Balzers. QMG 112A, with which the composition of desorbed products was monitored.

Vanadium pentoxide was prepared by precipitation from a vanadyl chloride solution by neutralization with ammonium hydroxide in an ice-water bath under stirring. It was then dried at 100°C, calcined in air at 500°C during 90h and finally grinded.

The V_2O_5 obtained is a non-stoichiometric compound with orthorhombic unit cells, its surface area being 2.7 m^2/g .

In each run, before isopropanol adsorption, the V_2O_5 sample surface ($\sim 0.4 m^2$) was treated with oxygen under the following conditions $P_{O_2} = 101325$ Pa, $T = 500^\circ C$, $t = 60$ min.

The transients were studied by supplying various isopropanol or acetone pulses (0.7 μl). After each, the system was left to reach equilibrium, being the procedure conducted at 40, 100 and 150°C for isopropanol and only at 40°C for acetone.

Ultra high purity He (99.999%) was used as carrier gas. In TPSR, V_2O_5 temperature was increased linearly with time from the transient temperature (40, 100 or 150°C) up to 500°C, using a heating rate of 10°C/min.

Results

The following mass-to-charge ratios were assigned for identifying to different substances, $M/e=18$ (H_2O), $M/e=28$ (CO), $M/e=41$ (propylene), $M/e=43$ and $M/e=58$ (acetone), $M/e=44$ (CO_2), $M/e=45$ (isopropanol) and $M/e=43$, $M/e=45$ and $M/e=87$ (isopropyl ether).

Table N 1

Table N 1 show interferences between different compounds with equal M/e ratio and high relative intensities, making them difficult to identify them. In case, ratios with low relative intensities, even in the absence of interference, detection is more difficult; however, the latter were used whenever possible.

Isopropanol adsorption – oxidation over V_2O_5 .

Fig. 1 (transients at 40°C) shows the intensity of the masses corresponding to water and excess of reactant (isopropanol) which are the two products detected at that temperature as a function of time (pulses).

In that figure, the first isopropanol peak (pulse) can be observed to be of less intensity than subsequent peaks indicating during the first pulse most of isopropanol is adsorbed.

The water mass can also be observed to produce a pronounced first peak, with subsequent peaks being of considerably less intensity, indicating that part of the adsorbed water on V_2O_5 is displaced by isopropanol adsorption.

In the transients carried out at 100°C, the same behavior is observed for isopropanol but with rather less intensity because they show scarce acetone and propylene production.

The experiment carried out at 150°C shows no isopropanol signal, a small amount of acetone and higher quantity of propylene. No signals representing to CO , CO_2 and isopropyl ether were observed.

Products resulting from the adsorption-oxidation of isopropanol were also measured with a catarametric cell, and the times required to reach equilibrium after each pulse were observed to decrease for increasing test temperatures.

After the adsorption-oxidation process, the TPSR of the adsorbed isopropanol was studied. In this regard, Fig. 2, for adsorption at 40°C, shows that the mass of water generates two bands with maxima at 88 and 238°C, the first with more intensity than the second, and several shoulders.

Figures N° 1 and 2

Both CO and CO₂ produce two bands each, at 218 y 306°C being the CO bands more intense than those for CO₂; in turn, among the CO bands the first is more intense than the second, while the two CO₂ bands exhibit similar intensities.

The isopropanol oxidation to CO and CO₂ occurs at the expense of atmosphere oxygen (He impurity), In fig. 3, oxygen is observed to decrease for increasing CO and CO₂ (the last is not shown but relation between CO y CO₂ it can see in fig 2) bands.

In figure 4, several desorptions at various temperatures are observed in the same experiment, isopropanol at 97°C; acetone at 146°C; propylene at 158°C and a small band of isopropyl ether at 297°C. the presence of last compound can be verified in fig. 5 with the mass/charge 87, because although its intensity is very low (15% of the maximum (mass 45)), this mass is not interfered by other compounds present in the system and the ratio was large enough to be used.

Figures N° 3 and 4

The TPSR conducted over sample with isopropanol adsorbed at 100°C, shows in Fig. 6 two water bands at 173 y 239°C, the first less intense and two bands for both CO and CO₂, with maxima at 222 y 310°C, with the same relationships between them as that for 40°C.

Figures N° 5 and 6.

In the same experiment, figure 7 show the bands corresponding to propylene at 155°C, acetone at 159°C and isopropyl ether at 302°C. No signal for isopropanol was detected.

At 150°C, Fig. 8 shows a wide band representing water between 250 and 350°C approximately; concerning CO and CO₂, the low temperature bands present in the

previous test almost disappeared. The temperature the unique band exhibit a maximum at 316°C.

Figures N° 7 and 8

Figure 9 presents one small band at 278°C for masses 43 and 45, which can be assigned to isopropyl ether.

In Fig 10 can be observed bands of water desorption are observed, with and without previous isopropanol adsorption. In the first case, water adsorbed on V_2O_5 is desorbed in a band with maximum at 88°C, the other shoulders and bands being produced various oxidation or dehydration processes. In the second case, water desorbs in a broad band where the maximal include the range of 77-88° C [13].

Figures N° 9 and 10

Acetone adsorption – oxidation over V_2O_5

In the transient study at 40 °C, acetone, on adsorption, also displaces part of the adsorbed water molecules, being the rest of H_2O molecules desorbed as such in the TPSR test by the isopropanol adsorption-oxidation at 40°C.

In same TPSR test, acetone, is desorbed as such, at 113 °C, whereas isopropyl ether does so at 303°C. This temperature coincides with the desorption temperature of the latter compound in the TPSR experiment of isopropanol (Fig. 11). On the other hand, no propylene was obtained.

Fig. 12, shows both CO and CO_2 desorption bands at temperatures 194, 212 °C and at 310 C

Figures N° 11 y 12

Discussion

In the transient study of isopropanol and acetone adsorption, the detected substances were isopropanol, acetone, propylene, and water.

In the transient study carried out at 40°C, isopropanol replaces some of the water molecules with lower adsorption energy on V_2O_5 (fig 1) but does not interact with other water molecules of higher adsorption energy.

The displaced water corresponds with the first part ($\approx 77^\circ\text{C}$) of the desorbed water band in the TPSR experiment carried out without previous isopropanol adsorption. This (first part of the band) is not observed in the experiment with isopropanol adsorption Fig. 10.

The water molecules remaining bound to the solid were not displaced by isopropanol (transients) and are desorbed in the TPSR tests at the same temperature as that for the adsorption tests with and without previous isopropanol adsorption at 88°C (Fig 10).

Therefore, isopropanol does not interact with the water molecules adsorbed with higher energy on V_2O_5 , possibly because of stereo hindrance.

In contrast, methanol interacts with them and shifts the temperature of water desorption toward higher values [14].

With increase of temperature in the transients studies, the V_2O_5 becomes more reactive.

In the tests (transient) carried out at 100 and 150°C , acetone production is similarly scarce. In contrast, for the same experiments, propylene production increased with temperature and with the decrease of unreacted isopropanol.

The transient experiments carried out at all temperatures did not consume atmospheric oxygen (helium impurity)

With regard to the TPSR study, the amount of CO was decreased and that for CO_2 increased for increasing temperature.

Desorption temperatures for CO and CO_2 increased only a few degrees when experimental temperature was increased (Fig. 2, 6 and 8).

At all temperatures of TPSR experiments, isopropyl ether was obtained in small amounts, regardless of temperature. In the experiments carried out at 40 and 100°C , that desorption occurs at about 300°C , and at 280°C in the high temperature test (fig 4,5,7 y 9)

The reactant in excess (isopropanol) is only detected in the 40°C experiment and disappears at high temperatures. The acetone and propylene are produced in the TPSR conducted at 40 and 100°C and were not detected at high temperature. Acetone decreases for increasing temperatures unlike propylene, which remains unchanged.

Isopropanol adsorption takes place, at 40°C in the form of molecular or isopropoxide species. The former is desorbed as such, at 98°C and the second, some of them are adsorbed on redox sites and others on acidic sites.

The firsts (on redox sites), leading to acetone at intermediate temperature ($\approx 150^\circ\text{C}$) followed by the production of CO, CO_2 and isopropyl ether at high temperature, 200 - 300°C .

Acetone oxidation proceeds at the expense of the oxygen of the solid, without use of atmospheric oxygen (helium impurity) Fig.10, and therefore is limited by the amount of oxygen the solid can provide, leaving species on the surface, possibility isopropoxide, that can be subsequently oxidized.

As the solid recovers the oxygen lost at higher temperature between 200 and 300°C, it leads to more oxidized products (CO and CO₂) fig 3.

The isopropoxide species that is adsorbed onto acidic sites leads, by dehydration to propylene production, which is not limited as acetone.

Acetone and propylene are obtained In the experiment at 150°C during the transient study rather than in TPSR, owing to the similar production temperature of both compounds.

The acetone adsorption – oxidation in the TPSR experiment lead to the same CO and CO₂ distribution and to the same temperatures than those of the TPSR experiment with isopropanol. This indicates that the species remaining onto the solid after acetone and propylene desorption are the same.

Given that adsorption – oxidation of acetone in the TPSR experiment does not produce propylene and considering the preceding paragraphs, propylene desorption is not found to leave adsorbed species. This also indicates that adsorption sites of precursors of acetone and propylene are different

The CO and CO₂ compounds are produced at two different temperatures, each of which are maintained similar in isopropanol or acetone adsorption oxidation experiments. In addition, in all experiments the intensities ratio of each species keep constant, suggesting two oxidation processes. The first can be associated with sites where oxygen from belonging to the isopropoxide species are linked to acidic sites which, together with neighbour basic sites, produce oxidation of the carbonyl species of isopropoxide to CO_x, i.e, the isopropoxide species experiences a rupture process at temperatures near 200°C, leaving methyl species linked onto the surface, which are subsequently oxidized to CO_x , at temperatures close to 300°C.

With regard to desorption of isopropyl ether, it is possibly formed on the surface (C-O-C bond) by rupture of the linkage between isopropoxide oxygen and the V⁺⁵ ; isopropyl ether then remains on the solid surface by the methyl groups and, therefore, is not oxidized at the carbonyl oxidation temperature but desorbed at the oxidation temperature of methyl groups to CO_x at 300°C.

Conclusions

In the transient study of isopropanol and acetone adsorption, the detected substances were isopropanol, acetone, propylene, and water

In the transient study carried out at 40°C isopropanol does not interact with the water molecules adsorbed with higher energy on V_2O_5 , possibly because of stereo hindrance. In contrast, methanol interacts with them and shifts the temperature of water desorption toward higher values.

With increase of temperature in the transients studies, the V_2O_5 becomes more reactive.

In TPSR of species remaining after the transient study on V_2O_5 , it detect different amounts of water, CO, CO_2 , acetone, propylene, isopropyl ether and at low temperature, isopropanol.

Isopropanol adsorption takes place, at 40°C in the form of molecular or isopropoxide species. The former is desorbed as such, at 98°C and the second, some of them are adsorbed on redox sites and others on acidic sites.

The first (on redox sites) leading to acetone at intermediate temperature ($\approx 150^\circ\text{C}$) followed by the production of CO, CO_2 and isopropyl ether at high temperature, 200-300°C.

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As the solid recovers the oxygen lost at higher temperature between 200 and 300°C, it leads to more oxidized products (CO and CO_2).

The isopropoxide species that is adsorbed onto acidic sites leads, by dehydration to propylene production, which is not limited as acetone.

The study of isopropanol and acetone adsorption – oxidation in the TPSR experiment indicates that the species remaining onto the solid after acetone and propylene desorption are the same.

Given that adsorption – oxidation of acetone in the TPSR experiment does not produce propylene and considering the preceding paragraphs, propylene desorption is not found to leave adsorbed species. This also indicates that adsorption sites of precursors of acetone and propylene are different.

The mechanism proposed of obtaining of CO and CO_2 consist the two oxidation processes. The first can be associated with sites where oxygen from belonging to the isopropoxide species are linked to acidic sites which, together with neighbour basic sites,

produce oxidation of the carbonyl species of isopropoxide to CO_x, leaving methyl species linked onto the surface, which are subsequently oxidized to CO_x, at temperatures close to 300°C.

.At all temperatures of TPSR experiments, isopropyl ether was obtained in small amounts, regardless of temperature.

With regard to desorption of isopropyl ether, it is possibly formed on the surface (C-O-C bond) by rupture of the linkage between isopropoxide oxygen and the V⁺⁵; isopropyl ether then remains on the solid surface by the methyl groups and, therefore, is not oxidized at the carbonyl oxidation temperature but desorbed at the oxidation temperature of methyl groups to CO_x at 300°C, which coincide with less oxygen concentration in the system.

At those operating temperatures, the sites shown by V₂O₅, possess majority acid and minority redox properties.

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Captions

Fig. 1. Desorption spectra of isopropanol pulses over V_2O_5 for mass intensities of H_2O and $(CH_3)_2CHOH$. Experimental temperature: $40^\circ C$.

Fig. 2. TPSR spectra of isopropanol on V_2O_5 for H_2O , CO and CO_2 mass intensities. Experimental temperature: $40^\circ C$

Fig. 3. TPSR spectra of isopropanol on V_2O_5 for CO_2 , $(CH_3)_2CO$ and O_2 mass intensities. Experimental temperature: $40^\circ C$

Fig. 4. TPSR spectra of isopropanol onto V_2O_5 for mass intensities corresponding to CH_2CHCH_3 , $(CH_3)_2CO$, $(CH_3)_2CHOH$ and $(CH_3)_2HCOCH(CH_3)_2$. Experimental temperature: $40^\circ C$

Fig. 5. TPSR spectra of isopropanol over V_2O_5 , for mass intensities of $(CH_3)_2HCOCH(CH_3)_2$ and $(CH_3)_2CHOH$. Experimental temperature: $40^\circ C$.

Fig. 6. TPSR spectra of isopropanol on V_2O_5 . Mass intensities presented for H_2O , CO , CO_2 . Experimental temperature: $100^\circ C$

Fig. 7. TPSR spectra of isopropanol onto V_2O_5 . Mass intensities are shown for. CH_2CHCH_3 , $(CH_3)_2CO$ and $(CH_3)_2HCOCH(CH_3)_2$. Experimental temperature: $100^\circ C$.

Fig. 8. TPSR spectra of isopropanol on V_2O_5 for H_2O , CO and CO_2 mass intensities. Experimental temperature: $150^\circ C$

Fig. 9. TPSR spectra of isopropanol over V_2O_5 for mass intensity of $(CH_3)_2HCOCH(CH_3)_2$. Experimental temperature: $150^\circ C$.

Fig. 10. TPSR spectra of water and isopropanol over V_2O_5 , for mass intensities for H_2O without previously isopropanol adsorption and H_2O with previously isopropanol adsorption and $(CH_3)_2CHOH$. Experimental temperature: $40^\circ C$.

Fig. 11. TPSR spectra of acetone on V_2O_5 for $(CH_3)_2CO$ and $(CH_3)_2HCOCH(CH_3)_2$ mass intensities. Experimental temperature: $40^\circ C$.

Fig. 12 TPSR spectra of acetone on V_2O_5 . Mass intensities presented for CO and CO_2 .
Experimental temperature: 40°C.

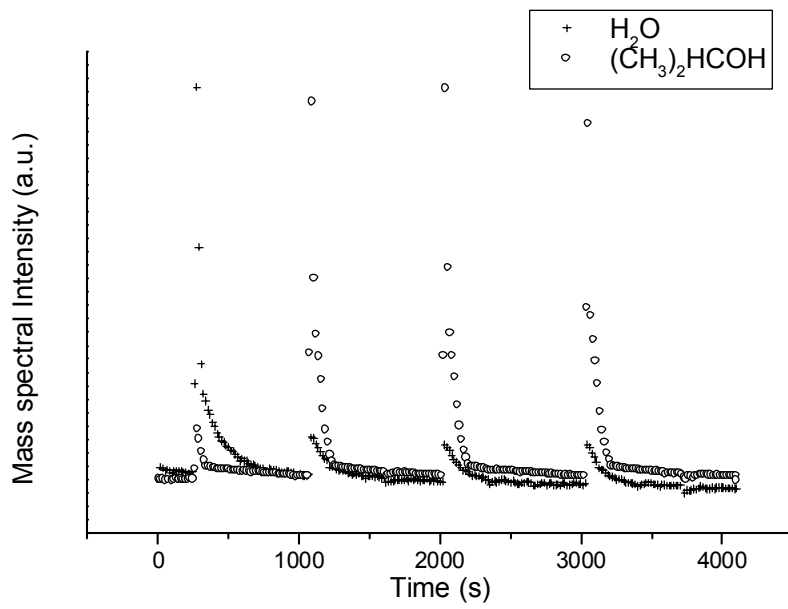


Figure N°1

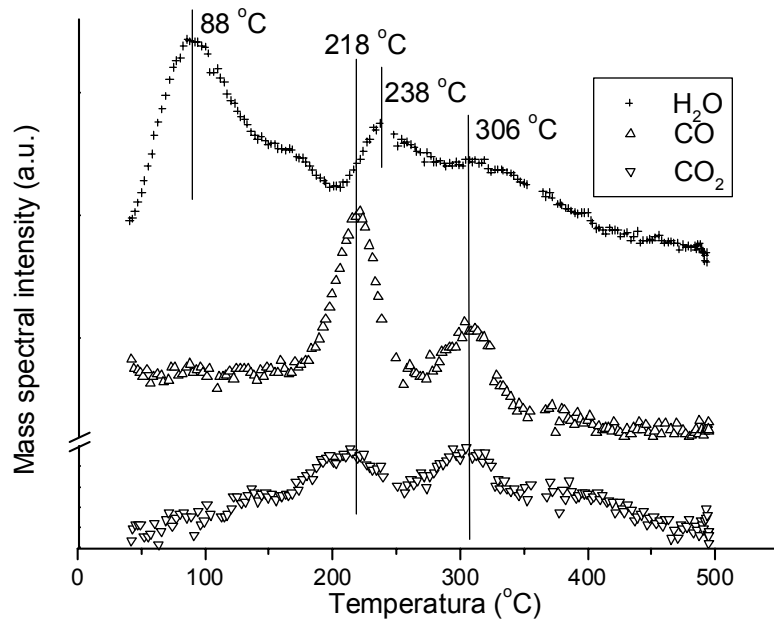


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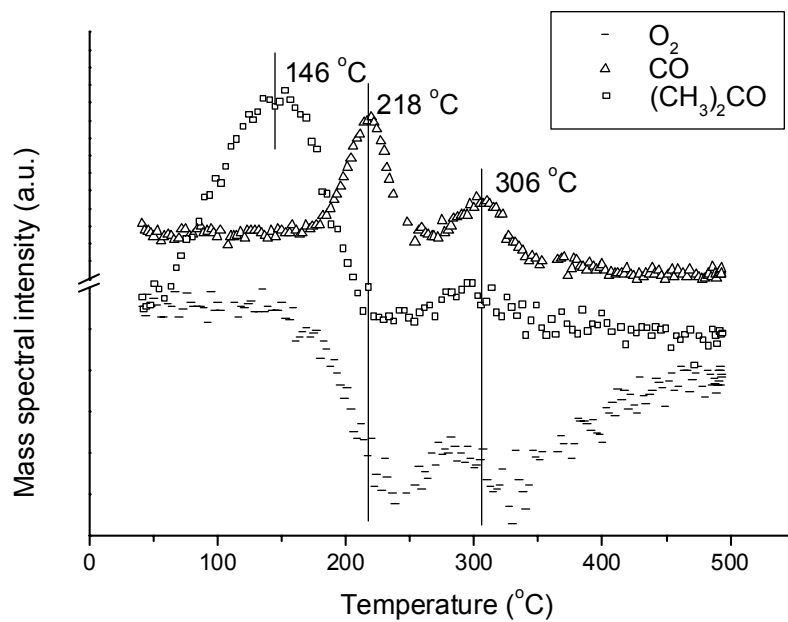


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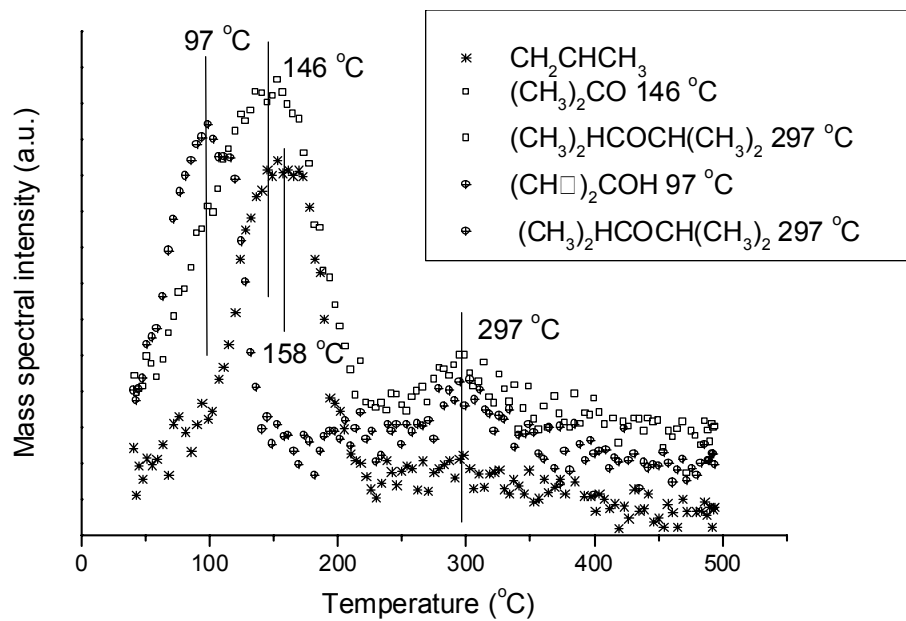


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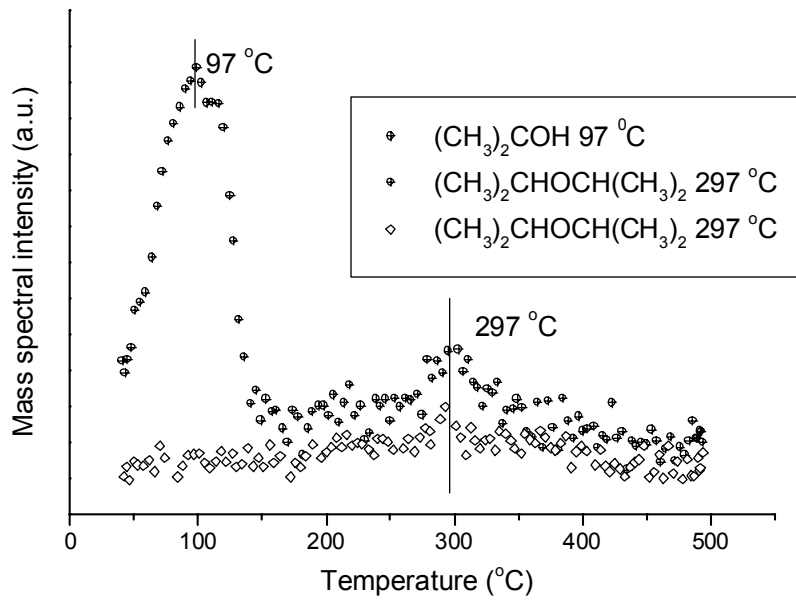


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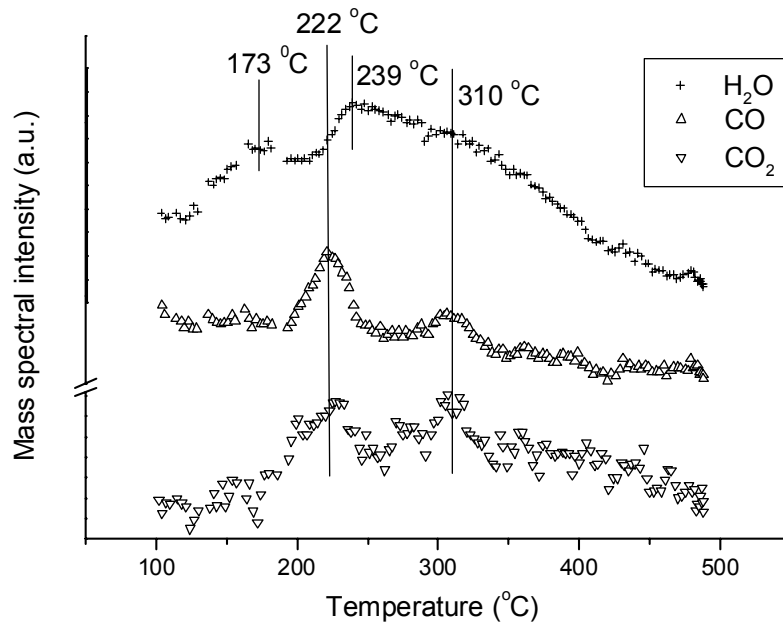


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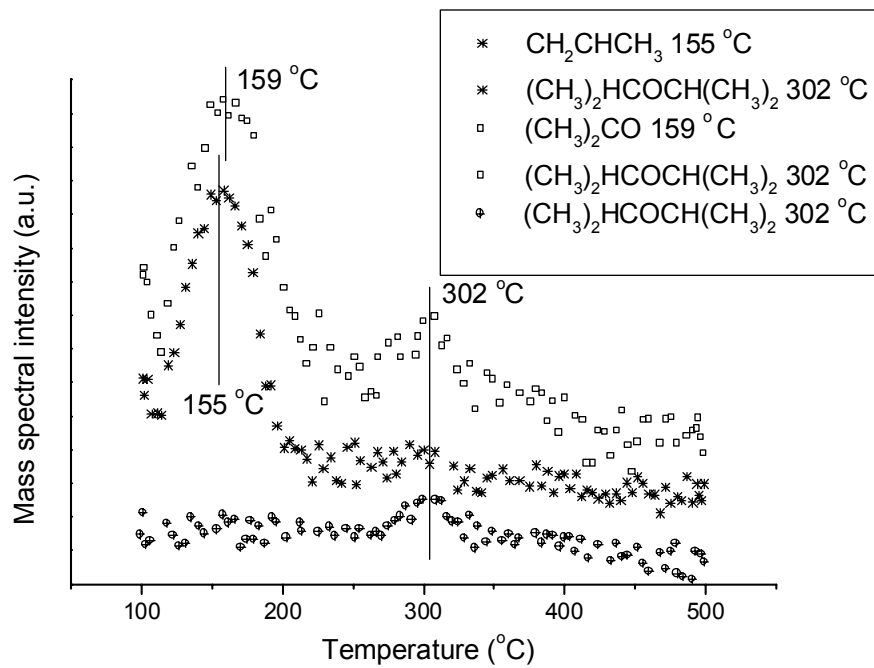


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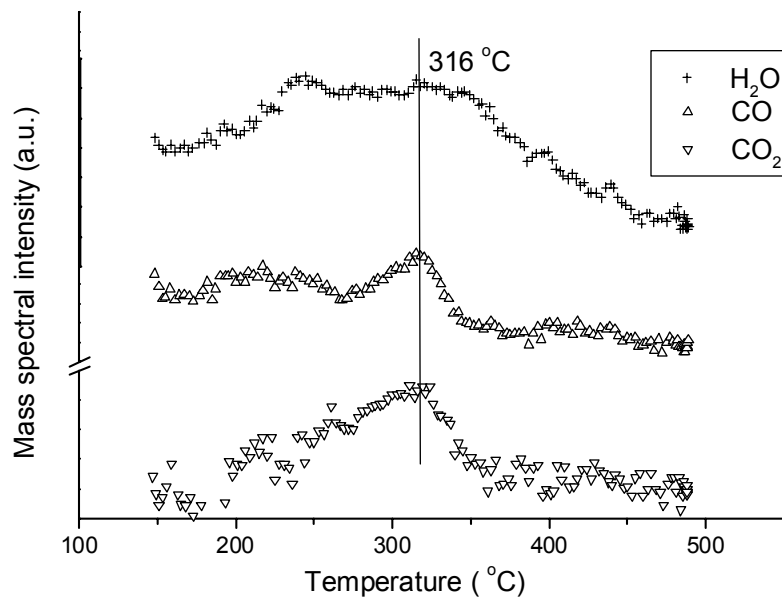


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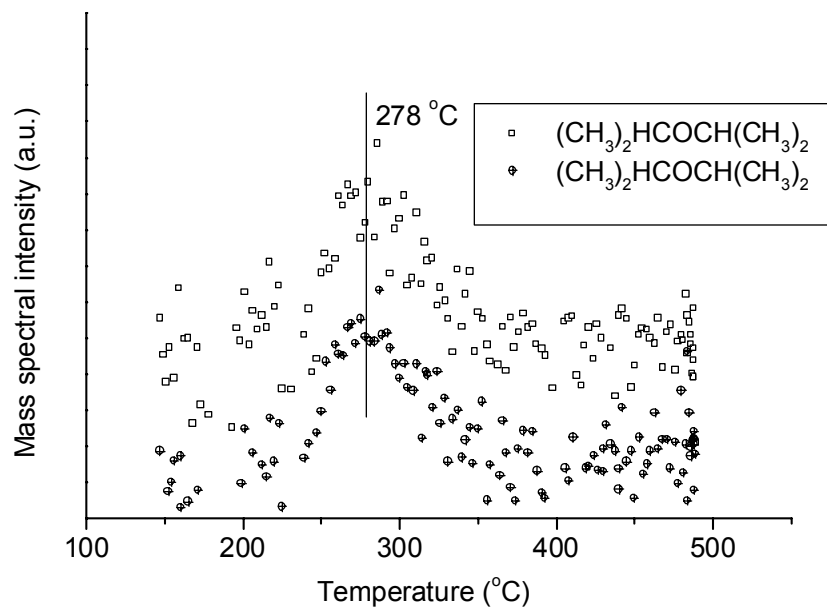


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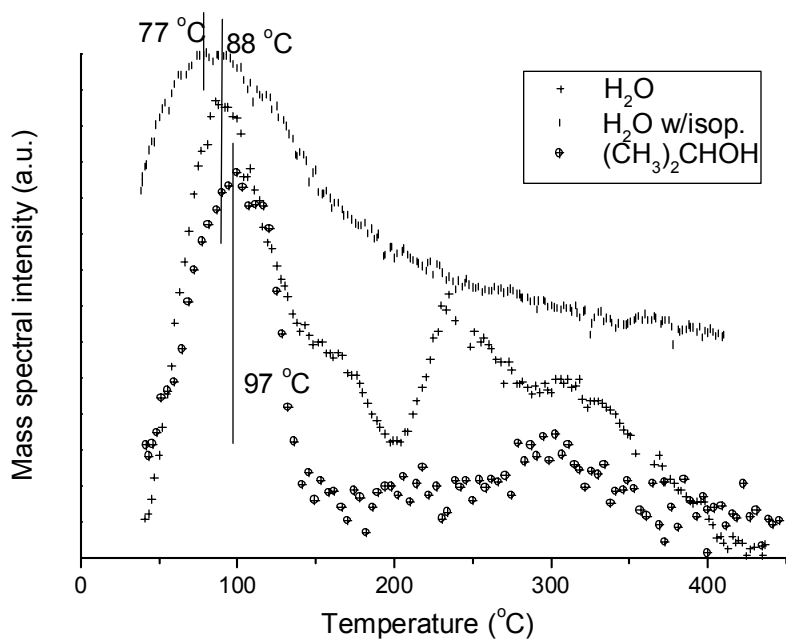


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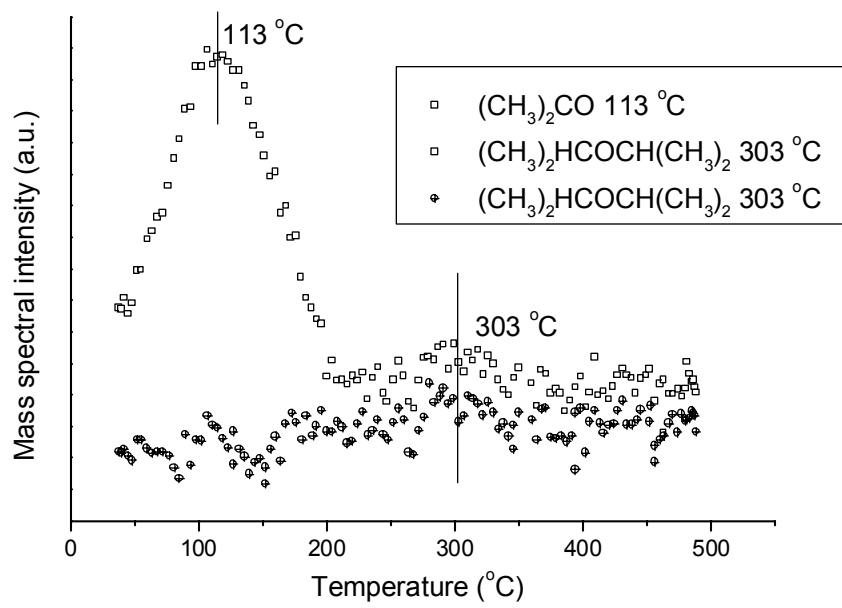


Figure N° 11

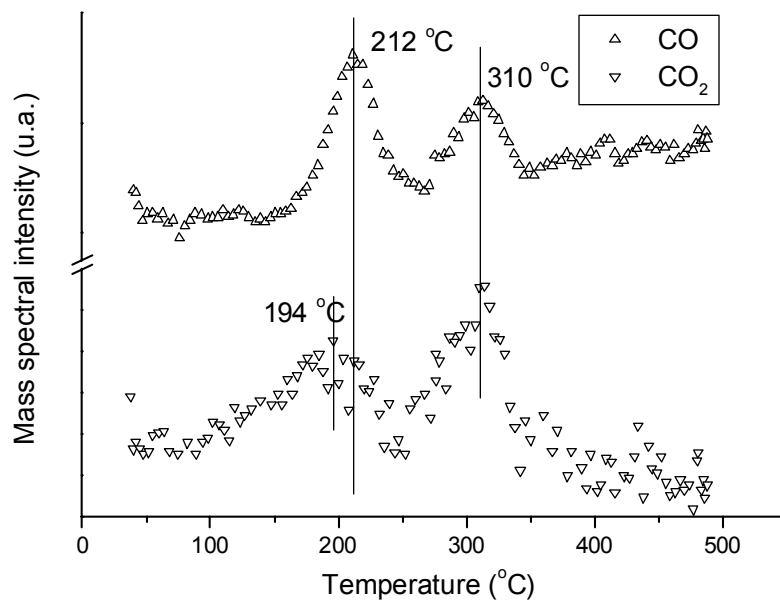


Figure N° 12

Table N 1. Relative intensities per cent of the fragment ions of compounds which are in the system and suffer interferences.

	M/e=43 (%)	M/e=45 (%)	M/e=58 (%)	M/e=87 (%)
Isopropanol	16	100		
Acetone	100		27	
Isopropyl ether	39	100		15