

# 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 of higher adsorption energies as methanol.

The following products were identified by TPSR at low temperatures ( $< \sim 150$  °C) variable amounts of water, isopropanol, propylene and acetone and, at  $\sim 200$ – $300$  °C. water, CO,  $CO_2$ , isopropyl ether. Isopropanol oxidation to acetone only use oxygen from  $V_2O_5$ . In turn, CO and  $CO_2$  desorptions are related with incomplete isopropanol oxidation to acetone, which is limited by the proportion of oxygen available in the solid. Formation of CO and  $CO_2$  occurs at the expense of atmospheric oxygen (He impurity). For such temperatures,  $V_2O_5$  shows acid and minima redox properties.

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## 1. Introduction

Some authors working about  $V_2O_5$  as Ai [1], Andersson [2], Louis et al. [3] and Allison and Goddard [4] have found that the terminal oxygen ( $V=O$ ) participates in hydrocarbon oxidation, while others as Deo and Wachs [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 concerted mechanism of adjacent acid and basic surface sites to give acetone [8,9].

The same authors, studying the isopropanol reaction over  $TiO_2$ , have found that ether formation is minimized in the presence of oxygen.

Kulkarni and Wachs [10] have studied isopropanol oxidation over several pure metal oxide catalysts, among them  $V_2O_5$ , and

observed catalyst activity in the range of 135–190 °C, where significant quantities of isopropyl ether are produced along with propylene.

The same authors measured the  $TOF_{redox}$  (turnover frequency) to be  $0.018\text{ s}^{-1}$ , whereas, the  $TOF_{acid}$  resulted much higher,  $18\text{ s}^{-1}$ .

Hussein and Gates [11] have studied the reaction of isopropanol over  $Y_2O_3$  and proposed the formation of two isopropoxide species, one bridge-bonded to two cations, yield propylene, while the terminal isopropoxide species, bond to a single cation, give acetone.

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

In this work, the objective is to deepen the knowledge of the isopropanol-precipitated  $V_2O_5$  system by studying the adsorption–oxidation transients and subsequent temperature programmed surface reactions (TPSR) of the adsorbed species. Special attention will be paid to water–isopropanol interaction over  $V_2O_5$  surface in comparison with water–methanol, and to the origin of precursors of  $CO_x$  formation.

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## 2. Experimental

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

Two detectors were used: a catarometric cell (Shimadzu GC-8A), employed as real time detector and a mass quadrupole spectrometer Balzers. QMG 112A, to monitor the composition of desorbed products.

Vanadium pentoxide was prepared by precipitation from a vanadyl chloride solution after neutralization with ammonium hydroxide in stirred ice-water bath. Then, the material was dried at  $100^\circ\text{C}$ , calcined in air at  $500^\circ\text{C}$  during 90 h and finally ground.

The  $V_2O_5$  obtained here is a non-stoichiometric compound with orthorhombic unit cells with a surface area of  $2.7\text{ m}^2/\text{g}$ .

In each run, before isopropanol adsorption, the  $V_2O_5$  sample surface ( $\sim 0.4\text{ m}^2$ ) was treated with oxygen under the following conditions  $PO_2 = 101,325\text{ Pa}$ ,  $T = 500^\circ\text{C}$ ,  $t = 60\text{ min}$ .

The transients were studied by supplying various isopropanol or acetone pulses ( $0.7\ \mu\text{l}$ ). After each, the system was left to reach equilibrium. This type of procedure was conducted at 40, 100 and  $150^\circ\text{C}$  for isopropanol and at  $40^\circ\text{C}$  for acetone.

Ultra high purity He (99.999%) was used as carrier gas. In TPSR, the temperature of  $V_2O_5$  was increased linearly with time, starting at the transient temperature ( $40, 100$  or  $150^\circ\text{C}$ ) up to  $500^\circ\text{C}$ . The heating rate used was  $10^\circ\text{C}/\text{min}$ .

## 3. Results

The following mass-to-charge ratios were assigned to identify the substances,  $M/e = 18$  ( $\text{H}_2\text{O}$ ),  $M/e = 28$  (CO),  $M/e = 41$  (propylene),  $M/e = 43$  and  $M/e = 58$  (acetone),  $M/e = 44$  ( $\text{CO}_2$ ),  $M/e = 45$  (isopropanol) and  $M/e = 43, M/e = 45$  and  $M/e = 87$  (isopropyl ether).

Table 1 show interferences between different compounds having the same  $M/e$  ratio and high relative intensities, so identification became difficult. On the other hand, detection of ratios with low relative intensities, even in the absence of interference was more difficult; however, the latter were used whenever possible.

## 4. Isopropanol adsorption–oxidation over $V_2O_5$

Fig. 1 (transients at  $40^\circ\text{C}$ ) shows the intensity of the masses corresponding to water and excess of reactant, isopropanol, the two products detected at that temperature as a function of time (pulses).

Table 1  
Percentage relative intensities of the fragment ions of compounds, which are in the system and experience interferences

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

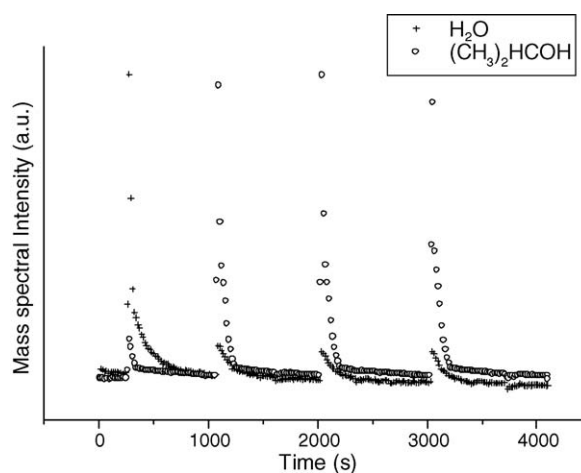


Fig. 1. Desorption spectra of isopropanol pulses over  $V_2O_5$  for mass intensities of  $\text{H}_2\text{O}$  and  $(\text{CH}_3)_2\text{CHOH}$ . Experimental temperature:  $40^\circ\text{C}$ .

In the figure mentioned above, the first isopropanol peak (pulse) is of less intensity than the succeeding ones. Therefore, most isopropanol is adsorbed during the first pulse.

The water mass also produces a pronounced first peak, being the subsequent peaks considerably less intense. This, in turn, means that part of the water adsorbed on  $V_2O_5$  is displaced by isopropanol adsorption.

Concerning the transients carried out at  $100^\circ\text{C}$ , the same behavior was observed for isopropanol but with rather less intensity because acetone and propylene production was scarce.

The experiment carried out at  $150^\circ\text{C}$  shows no isopropanol signal, a small amount of acetone and a higher quantity of propylene. No signals representing to CO,  $\text{CO}_2$  and isopropyl ether were observed.

Products resulting from the adsorption–oxidation of isopropanol were also measured with a catarometric cell, and the practical 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, in Fig. 2, for adsorption at  $40^\circ\text{C}$ , the water mass exhibits two bands with maxima at 88 and  $238^\circ\text{C}$ , the first with more intensity than the second, and, in addition, several shoulders.

Both CO and  $\text{CO}_2$  produce two bands each, at 218 and  $306^\circ\text{C}$  being the CO bands more intense than those for  $\text{CO}_2$ . In turn, among the CO bands, the first is more intense than the second, while the intensities of the two  $\text{CO}_2$  bands were similar.

The isopropanol oxidation to CO and  $\text{CO}_2$  occurred at the expense of atmosphere oxygen (He impurity). In Fig. 3, oxygen is observed to decrease for increasing CO and  $\text{CO}_2$  bands (the last is not shown but the ratio of CO to  $\text{CO}_2$  can be observed in Fig. 2).

In Fig. 4, several desorptions at various temperatures are observed in the same experiment, isopropanol at  $97^\circ\text{C}$ , acetone at  $146^\circ\text{C}$ , propylene at  $158^\circ\text{C}$  and a small band of isopropyl ether at  $297^\circ\text{C}$ . The presence of the last compound can be verified in Fig. 5 with a mass/charge ratio of 87. Although its intensity is very low (15% of the maximum (mass 45)), this

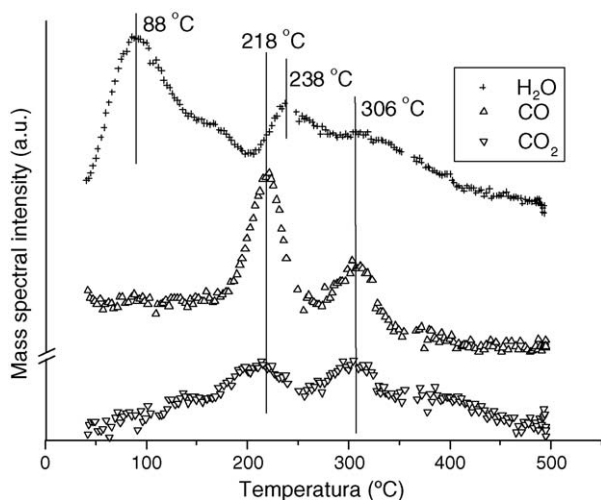


Fig. 2. TPSR spectra of isopropanol on  $V_2O_5$  for  $H_2O$ ,  $CO$  and  $CO_2$  mass intensities. Experimental temperature:  $40^\circ C$ .

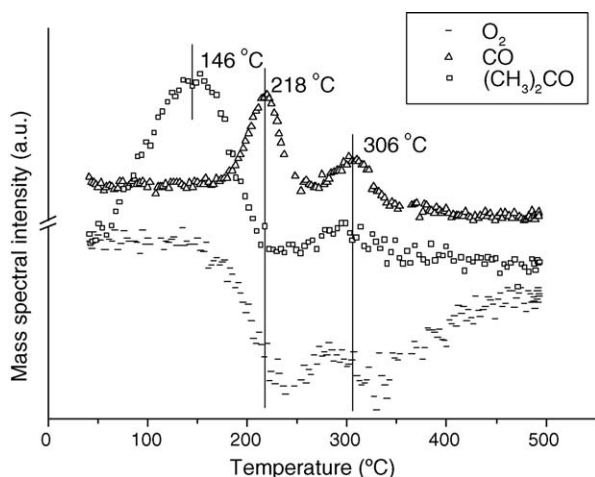


Fig. 3. TPSR spectra of isopropanol on  $V_2O_5$  for  $CO_2$ ,  $(CH_3)_2CO$  and  $O_2$  mass intensities. Experimental temperature:  $40^\circ C$ .

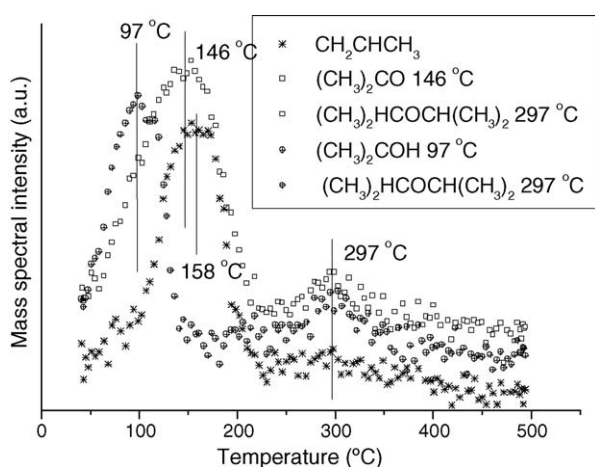


Fig. 4. TPSR spectra of isopropanol onto  $V_2O_5$  for mass intensities corresponding to  $CH_2CHCH_3$ ,  $(CH_3)_2CO$ ,  $(CH_3)_2CHOH$  and  $(CH_3)_2HCOCH(CH_3)_2$ . Experimental temperature:  $40^\circ C$ .

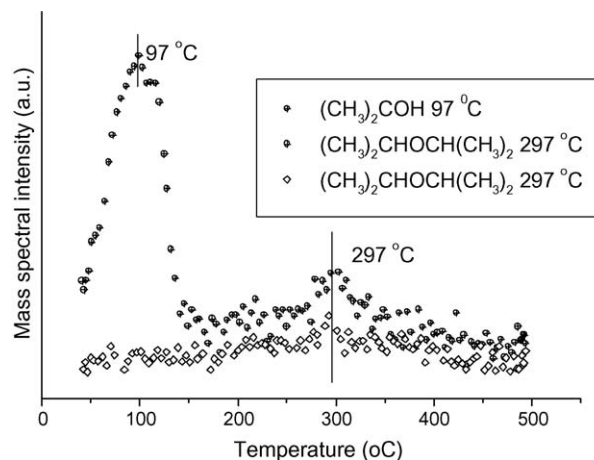


Fig. 5. TPSR spectra of isopropanol over  $V_2O_5$ , for mass intensities of  $(CH_3)_2HCOCH(CH_3)_2$  and  $(CH_3)_2CHOH$ . Experimental temperature:  $40^\circ C$ .

mass is not interfered by those from other compounds present in the system and the ratio was large enough to be used.

The TPSR conducted over sample with isopropanol adsorbed at  $100^\circ C$ , shows two water bands at  $173$  and  $239^\circ C$ , being the first less intense and two bands for both  $CO$  and  $CO_2$ , with maxima at  $222$  and  $310^\circ C$ , with the same ratios between them as observed for  $40^\circ C$ . This behavior is similar to that observed in Fig. 2.

In the same experiment, Fig. 6 shows the propylene bands at  $155^\circ C$ , acetone bands at  $159^\circ C$  and bands for isopropyl ether at  $302^\circ C$ . The isopropanol signal was not detected.

At  $150^\circ C$ , the TPSR shows a wide band representing water between about  $250$  and  $350^\circ C$ . With regard to  $CO$  and  $CO_2$ , the low temperature bands present in the previous test almost disappeared. The single band remaining exhibited a maximum at  $316^\circ C$ , in a behavior similar to that shown by Fig. 2. The TPSR also presents one small band at  $278^\circ C$  for masses  $43$  and  $45$ , which can be assigned to isopropyl ether.

In Fig. 7, water desorption bands are observed, with and without previous isopropanol adsorption. In the first situation,

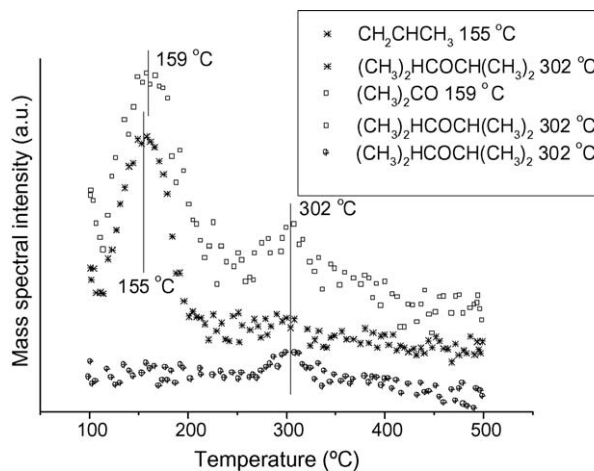


Fig. 6. TPSR spectra of isopropanol onto  $V_2O_5$ . Mass intensities are shown for  $CH_2CHCH_3$ ,  $(CH_3)_2CO$  and  $(CH_3)_2HCOCH(CH_3)_2$ . Experimental temperature:  $100^\circ C$ .

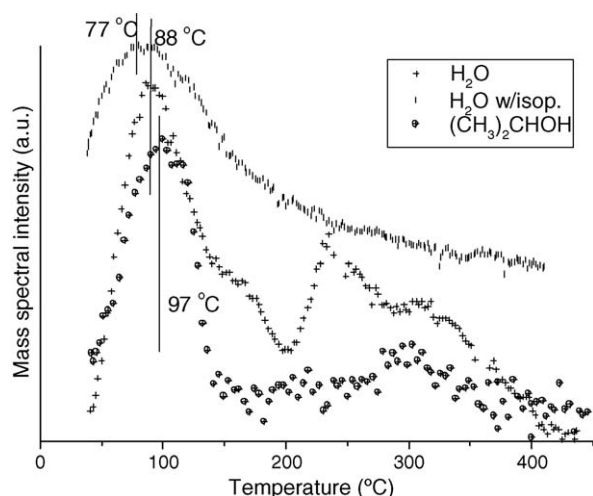


Fig. 7. TPSR spectra of water and isopropanol over  $V_2O_5$ , for mass intensities for  $H_2O$  without previously isopropanol adsorption and  $H_2O$  with previously isopropanol adsorption and  $(CH_3)_2CHOH$ . Experimental temperature:  $40^\circ C$ .

water adsorbed on  $V_2O_5$  is desorbed, which is represented by a band of maximum =  $88^\circ C$ . The other shoulders and bands being produced by various oxidation or dehydration processes. In the second condition, water desorbs while exhibiting a wide band showing a maximum around  $77$ – $88^\circ C$  [13].

### 5. Acetone adsorption–oxidation over $V_2O_5$

In the transient study at  $40^\circ C$ , acetone adsorption also displaces part of the adsorbed water molecules, being the rest water molecules desorbed as such in the TPSR test by the isopropanol adsorption–oxidation at  $40^\circ C$ .

In the same TPSR test, acetone is desorbed as such at  $113^\circ C$ , whereas, isopropyl ether does so at  $303^\circ C$ . This temperature coincides with the desorption temperature of isopropyl ether in the TPSR experiment of isopropanol (Fig. 8). On the other hand, no propylene was obtained.

TPSR test also indicates that both  $CO$  and  $CO_2$  desorption bands at temperatures of  $194$ ,  $212$  and  $310^\circ C$ , are similar to those in Fig. 2.

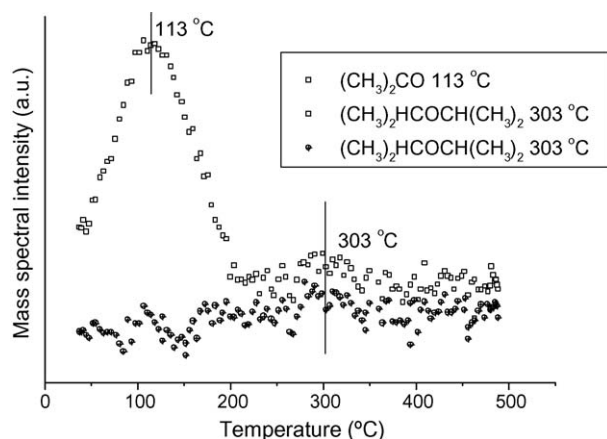


Fig. 8. TPSR spectra of acetone on  $V_2O_5$  for  $(CH_3)_2CO$  and  $(CH_3)_2HCOCH(CH_3)_2$  mass intensities. Experimental temperature:  $40^\circ C$ .

### 6. Discussion

Substances detected in the transient study of isopropanol and acetone adsorption, were isopropanol, acetone, propylene, and water. Concerning the transient study carried out at  $40^\circ C$ , isopropanol replaces some of the water molecules with lower adsorption energy on  $V_2O_5$  (Fig. 1) but does not interact with water molecules of higher adsorption energy.

The displaced water corresponds to the first part ( $\approx 77^\circ C$ ) of the desorbed water band in the TPSR experiment, conducted without previous isopropanol adsorption. This first part of the band is not observed in the experiment including isopropanol adsorption (Fig. 7).

The water molecules remaining bound to the solid were not displaced by isopropanol (transients). Instead, they are desorbed in the TPSR tests at the same temperature as that in the adsorption tests carried out with and without previous isopropanol adsorption at  $88^\circ C$  (Fig. 7). Therefore, isopropanol does not interact with the water molecules adsorbed with higher energy on  $V_2O_5$ , possibly because of steric hindrance.

In contrast, methanol does interact with them and shifts water desorption temperatures toward higher values [14]. On the other hand, by increasing the temperature in the transient studies, the  $V_2O_5$  becomes more reactive.

In the tests (transient) carried out at  $100$  and  $150^\circ C$ , acetone production is similarly scarce. In contrast, for the same experiments, propylene production increased with temperature and with the decrease of unreacted isopropanol. Transient experiments carried out at all temperatures did not consume atmospheric oxygen (helium impurity).

With regard to the TPSR study, increasing temperature produced a decrease in the amount of  $CO$  and an increase of  $CO_2$  concentration. Desorption temperatures for  $CO$  and  $CO_2$  increased only a few degrees when the experimental temperature was increased (Fig. 2).

In TPSR experiments, isopropyl ether was obtained in small amounts, regardless of temperature. On the experiments carried out at  $40$  and  $100^\circ C$ , the above-mentioned desorption occurs at about  $300^\circ C$ , and, for the high temperature test, at  $280^\circ C$  (Figs. 4–6).

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

Isopropanol adsorption occurs at  $40^\circ C$  in the form of molecular and isopropoxide species. The former is desorbed as such, at  $98^\circ C$  and, while the latter shows variable behavior: some of the molecules are adsorbed on redox sites and others on acidic sites.

Those adsorbed on redox sites lead to acetone at intermediate temperature ( $\approx 150^\circ C$ ) followed by the production of  $CO$ ,  $CO_2$  and isopropyl ether at high temperature,  $200$ – $300^\circ C$ .

Acetone oxidation proceeds at the expense of the oxygen in the solid, without using atmospheric oxygen (helium impurity) (Fig. 7), and therefore is limited by the amount of oxygen the

solid can provide, leaving species on the surface, possibly isopropoxide, that can be subsequently oxidized.

As the solid recovers the oxygen lost at higher temperature (between 200 and 300 °C), oxidized products are produced (CO and CO<sub>2</sub>), Fig. 3.

The isopropoxide species 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, due to the similar production temperature of both compounds.

The acetone adsorption–oxidation in the TPSR experiment leads to the same CO and CO<sub>2</sub> distribution and to the same temperatures as those from 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 would not leave adsorbed species. This also indicates that adsorption sites of acetone and propylene precursors are different.

The CO and CO<sub>2</sub> compounds are produced at two different temperatures, each of which are maintained in isopropanol or acetone adsorption oxidation experiments. Besides, the intensities ratio of each species keeps constant in all experiments, suggesting two oxidation processes. The first may be associated with sites where oxygen belonging to isopropoxide species are linked to acidic sites. These, together with neighbour basic sites, oxidizes the carbonyl species of isopropoxide to CO<sub>x</sub>, i.e., the isopropoxide species undergoes rupture at temperatures near 200 °C, leaving methyl species onto the surface, which are then oxidized to CO<sub>x</sub>, at temperatures close to 300 °C.

With regard to desorption of isopropyl ether, it can be proposed the formation, on the surface, of (C–O–C bond) by rupture in the linkage between isopropoxide oxygen and the V<sup>5+</sup>. Isopropyl ether then remains linked to 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<sub>x</sub> at 300 °C.

## 7. Conclusions

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

At 40 °C, isopropanol did not interact with the strongly adsorbed water molecules, unlike methanol, which did interact.

The TPSR tests allowed us to detect variable amounts of water, CO, CO<sub>2</sub>, acetone, propylene, isopropyl ether and, at low temperature, isopropanol.

Isopropanol adsorbs at 40 °C as molecular species or in the isopropoxide form.

The former desorbs as such, while the latter adsorbs part in redox sites, and the rest in acidic sites. Molecules adsorbed in redox sites produce acetone; (~150 °C) and, subsequently, CO<sub>x</sub> and isopropyl ether (200–300 °C).

Acetone oxidation proceeds at the expense of the oxygen contained in the solid and, therefore, is a limited process, leaving adsorbed species in unoxidized state. As the solid recovers oxygen lost at higher temperature, such species are oxidized to CO<sub>x</sub>.

Isopropoxide species adsorbed onto acidic sites undergo dehydration, producing propylene, which is not limited by acetone.

The above means that the species remaining onto the solid after acetone desorption (acetone, on adsorption) and after propylene desorption (isopropanol, on adsorption) are the same.

Propylene desorption (isopropanol adsorption) does not leave adsorbed species. Thus, acetone and propylene adsorption sites should be different.

The oxidation mechanism proposed for the reaction leading to CO and CO<sub>2</sub> consists of two processes. The first can be associated to redox sites where the isopropoxide carbonyl species oxidize to CO<sub>x</sub> (~200 °C) leaving the methyl groups on the surface, which are subsequently oxidized to CO<sub>x</sub> (~300 °C).

In TPSR experiments, small amounts of isopropyl ether are obtained at all temperatures. Isopropyl ether is not oxidized to the carbonyl temperature, but desorbed at the oxidation temperature of methyl groups (~300 °C). In the temperature range investigated, V<sub>2</sub>O<sub>5</sub> presents predominantly acidic sites, though also redox sites.

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