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

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Abstract

The methanol adsorption-oxidation over V_2O_5 (transients) was studied by mass spectrometry (ME) of the desorption molecules produced over the catalyst by reactive interaction, at 40, 100 and 150ºC of temperatures. After that, temperature programmed desorption (TPD) was performed and the products were analyzed by ME.

From the transients study was concluded that methanol molecules remove some of the water molecules adsorbed onto the V_2O_5 and the products detected were formaldehyde, methanol and water.

The only products detected by TPD consisted of different amounts of water, formaldehyde, CO and, at low temperature, methanol. For those temperatures, V_2O_5 show only redox properties because neither condensation products nor CO_2 were detected.

Introduction

Some authors as Ai[1], Anderson[2], Louis et al, [3] and Allison et al.[4], have found that terminal oxygens (V=O) take part in hydrocarbon oxidation, and some others as Deo et al. [5] and Weber[6] have suggested that bridge oxygens are also involved in oxidation reactions.

Busca[7] has studied adsorption of methanol, formaldehyde, and formic acid on V_2O_5 and on V_2O_5 /SiO_2 , and found methanol adsorbed as metoxi on both catalysts, while formaldehyde is weakly adsorbed at low temperature. In turn, Badlani et al. [8] studied a large number of oxides by chemisorption, to find anisotropic adsorption onto V_2O_5 a 100ºC with a low number of active sites, approximately 0,7 μmol/m^2. Results encountered at 300ºC for methanol oxidation where that the TOF_{redox} (turn–over frequency) reaches about 90% of the TOF_{acid}, with a zero value for $TOF_{basic.}$

Adsorption/oxidation of methanol over pure V_2O_5 was experimentally studied by mass spectrometry and chromatography by Sambeth et al, [9,12] and Briand et al, [10] and,

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trhough DRIFT, by Sambeth et al. [11]. Major products found were formaldehyde, CO_2 and CO. As minor products, methyl formiate and methylal were observed, along with an unstable intermediate detected only by mass spectroscopy, hemimethylal (CH_3CH_2OH). Those authors have proposed a well founded reaction mechanism for methanol oxidation based on a experimental and theoretical study.

Ranea et al [13] have identified the adsorption sites of water molecules on V_2O_5 by TPD and theoretical study.

In this work, the objective is to deepen the knowledge of the methanol - V_2O_5 system by studying adsorption – oxidation transients and subsequent thermal programmed desorption of the adsorbed species.

Experimental Part.

The equipment consists of a U-tube Pyrex glass reactor. In the bottom part of a widening of one of its branches, glass wool is placed, with the sample onto it. A thermocouple is located in a cleft close to the sample.

The reactor inlet is connected by stainless steel heated pipeline to the gas feed system through which He circulates, allowing vaporizable liquids to be injected via a heated septum or alternatively, gases by a gas sample valve with a variable volume loop.

Immediately after the reactor outlet, the sampling system of the mass spectrometer was placed, and part of desorbed substances is assigned to it, since the system is brought from atmospheric pressure to 10^{-5} bar without mass discrimination.

This is achieved by bringing pressure from atmospheric value to 1 mbar through a capillary (laminar flow) and, from this pressure to the final value through a plate of properly sinterized material (molecular flow).

After sampling with the mass spectrometer, flow continues up to thermal conductivity detector (catarometric cell) to be then purged.

An electric furnace heats the reactor and control of temperature is carried through electronic devise, which the proper heating ramp is obtained for the reactor/furnace system being used.

Monitoring of catarometric cell in real time carried out by a data acquisition program, which also allows programming of the acquisition conditions of the analogic signal.

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A computer through a high-speed analogical/digital data acquisition module, which stores experimental parameters, takes these signals from the mass spectrometer.

The previous data are read in by another program, designed at CINDECA to generate an ASCII file containing the masses, acquisition time, temperature, the catarometric cell response, and the intensity maxima of the different masses. Then, by using a commercial program, these files were read in to obtain the intensity variation of the different masses as a function of temperature or time depending on the specific study being executed.

The study of the transients is carried out by the admission of various methanol pulses (0.5 μl), after each of which the system is left to reach equilibrium and were conducted at temperatures of 40, 100 and 150°C. Further TPD was carried out at a heating rate of 10ºC/min from that temperature up to 500°C in He current.

In both instances, composition of desorbed products were monitored by ME.

Vanadium Pentoxide was prepared by precipitation from a vanadile chloride solution by neutralization with ammonium hydroxide in an ice-water bath under stirring. Then dried at 100°C and calcined in air at 550°C. Before each study the sample was calcined *in situ* under oxygen current at 500°C for 1 h.

Results and discussion

The following masses were assigned to the different substances, M18(H_2O), M28(CO), M30(formaldehyde), M31(methanol), M44(CO_2), M46(dimethyl-ether) y M75(methylal).

Fig. 1 (transients at 40ºC) shows the intensity of the masses corresponding to water, and methanol as a function of time, which are the only products detected at that temperature.

The first pulse is observed to produce a pronounced peak of the mass corresponding to water, the subsequent peaks being of considerably less intensity. Methanol mass increases with the first peaks to become then constant, indicating that part of the adsorbed water is displaced by methanol.

In transients carried out at 100 and 150ºC, the intensity of mass 18 increases very slowly during methanol pulses.

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With regard to methanol behavior, its intensity increases for all temperatures to become constant subsequently. Formaldehyde is produced only in the test conducted at 150ºC

Fig N 1

No signals representing dimethyl ether, methylal, CO, etc, were observed.

Productos resulting from the adsorption-oxidation of methanol were also measured with a catarometric cell, and the times required to reach equilibrium after each pulse were observed to decrease as tests are being carried out at higher temperatures.

After the adsorption-oxidation process, the TPD of the adsorbed methanol was studied and Fig. 2 and 3 (40ºC) show mass 18 generating two wide bands with maxima at 116 and 238ºC, the first with less intensity than the second. Formaldehyde produces a peak at 192ºC, CO does so at 212ºC, whereas methanol exhibits two peaks, one at 100ºC and another, smaller, at 179ºC. This may suggest that methanol adsorbs at 40ºC on two well different sites, possibly as molecular methanol and methoxy [8, 14].

With respect to mass 18, the first band is assigned to the remaining water, and the second wide band, which starts at 180°C, to the water produced from the OH generated in the formation reaction of formaldehyde and CO.

Fig 2 and fig. 3.

In the TPD carried out at 100ºC (Fig. Nº 4) mass 18 shows only a very wide maximum at 245ºC, whereas formaldehyde presents a peak at 196ºC, and CO, at 212ºC. The band exhibited by methanol at 165ºC is small.

The second band of the methanol desorption in the test to 40ºC (179ºC) and the unique

In the test to 100ºC (165ºC) can be assigned to recombination of the metoxy adsorbed species.

Fig. 4

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At 150ºC (Fig. 5) a wide band representing water is observed with a maximum at 261ºC, along with a formaldehyde peak at 210ºC, and another for CO at 229ºC. No signal was observed for methanol.

Fig. 5

Signals representing dimethyl ether, methylal, CO_2, etc, were not observed at any temperature.

At 100 and 150°C, mass 18 shows only a band corresponding to formation of formaldehyde and CO.

In TPD experiments carried out at 40, 100 and 150ºC, the signal corresponding to water shifts towards higher temperatures showing a similar behavior as the peaks representing the other products detected.

Methanol molecular adsorption at low temperatures takes place in strong interaction with the water molecules of the solid [13]. Although methanol removes some of the water molecules belonging to the catalyst, it still interacts with the remaining (band exhibited at 116°C in the TPD for the experiment at 40ºC), and are desorbed at a slightly lower temperature (100ºC). On the other hand, in the tests conducted at 100°C, the first band representing water did not appear, and the methanol desorption is carried out at a much higher temperature (165ºC) being in the order of the second peak in the test at 40ºC (179ºC).

The fact that methanol is desorbed at a lower temperature than water may suggest that methanol is linked to the solid through water molecules, since, in the absence of water, no molecular methanol adsorption takes place.

Concerning the methoxy formed at all the adsorption temperatures studied, its decomposition is carried out in two, well defined steps, possibly because the previous adsorption occurs on different type of sites. The first step consists of formaldehyde desorption at temperatures of 192 and 196 (almost the same) for the tests at 40 and 100ºC and, for the remaining test, at 210ºC.The second step is the desorption of CO (conducted at a temperature

30°C higher) at 212ºC for the first tests and 229ºC for the test at 150ºC.

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For the test at the maximum temperature, where methanol is adsorbed only as methoxy, the decomposition temperature is observed to coincide to that proposed in the literature [8].

Conclusions

On adsorbing at 40°C, methanol displaced part of the water molecules previously adsorbed onto V_2O_5.

In the transients measurement study, the only substances detected were formaldehyde, methanol and water.

The methanol – V_2O_5 interaction is slow for the test to 40ºC and increases with temperature.

TPD of species remaining after the transients study on V_2O_5 allowed different amounts of water, CO and, at low temperatures, methanol to be detected.

Methanol adsorption at 40ºC proceeds on two types of site with desorption temperatures of 100 and 179ºC, being the amount desorbed from the higher temperature site very small.

The second band of the methanol desorption in the test to 40ºC (179ºC) and the unique

In the test to 100ºC (165ºC) can be assigned to recombination of the metoxy adsorbed species.

Molecular methanol adsorption at low temperatures occurs because of a strong interaction with the water molecules present in the solid. The fact that methanol desorbs al lower temperature than water suggests that methanol may be linked to the solid trough water molecules.

Where methanol adsorbs only as methoxy, decomposition temperature is observed to coincide with the literature value [8].

At these worked temperatures, the only sites shown by V_2O_5 possess redox properties, since no condensation products (acidic sites) nor CO_2 (basic sites) were detected.

Referencias

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[1] Ai,. M.; J.Catal. 77, 279, 1982

[2] Andersson, A.; J. Solid State Chem. 42, 279, 1982.

[3] Louis, C., Tatibouët, J. y Che, M;. J.Catal. 109, 354, 1988

[4] Allison, J. y Goddard, W.; J. Catal. 92, 127, 1985.

[5] Deo, G. Y Wachs, I.; J. Catal. 129. 307, 1991.

[6] Weber, R.; J. Phys.Chem. 98, 2999, 1994.

[7] Busca, G.; J. Mol. Catal. 50, 241, 1989.

[8] Badlani, M. y Wachs, I.; Catal. Lett. 75, 3-4, 137, 2001

[9] Sambeth, J., Gambaro, L., Thomas, H.; Adsorp. Sci. Technol. 12, 171, 1995.

[10] Briand, L., Gambaro, L. y Thomas, H.; Latin Am. App. Res. 25, 63, 1995.

[11] Sambeth, J., Centeno, M., Paúl, A., Briand, L., Thomas, H. Y Odriozola J.; J. Mol. Catal.

A, 161, 89, 2000.

[12] J. Sambeth, A. Juan, L. Gambaro and H. Thomas. XV Simposio Iberoamericano de Catalisis. Cordoba. Argentina. Septiembre 1996. Vol. 2 1037

[13] V. A. Ranea, J. L. Vicente, E. E. Mola, P. Arnal, H. Thomas and L. Gambaro. Surf. Sci.,

463 115 (2000).

[14] L. J. Burcham, L. E. Briand and I. E. Wachs. Langmuir 17, 6175 (2001)

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Captions

Fig. 1. Mass intensity of H_2O, H_2CO and H_3COH vs. methanol pulses at 40ºC.

Fig. 2. TPD for H_2O and H_2CO in the test carried out at 40ºC.

Fig. 3. TPD for CO and H_3COH in the test conducted at 40ºC.

Fig. 4. TPD for H_2O, CO, H_2CO and H_3COH in the test at 100ºC.

Fig. 5. TPD for H_2O, CO and H_2CO in the test performed at 150ºC.

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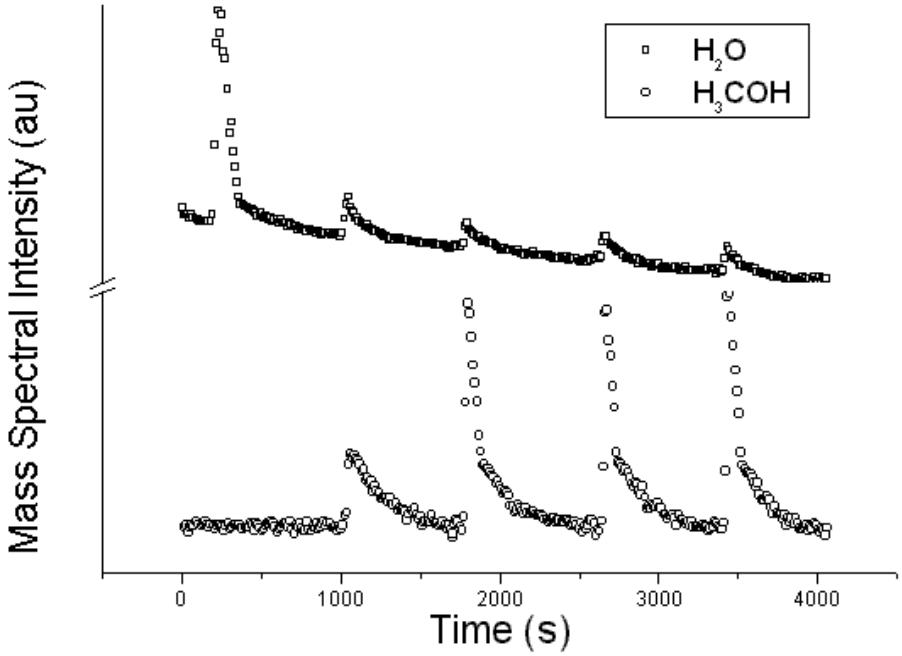
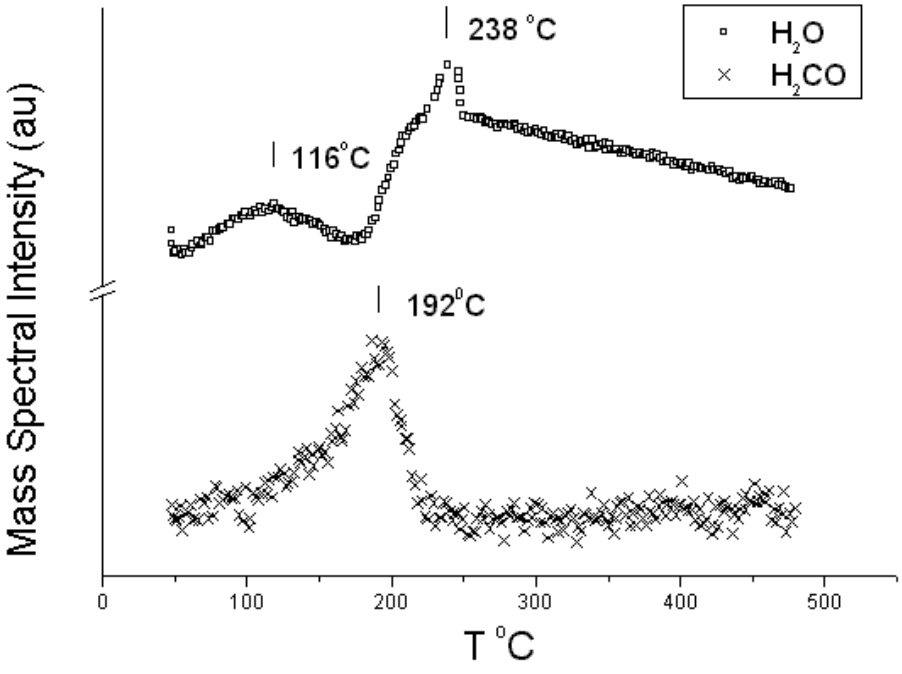


Figure 1



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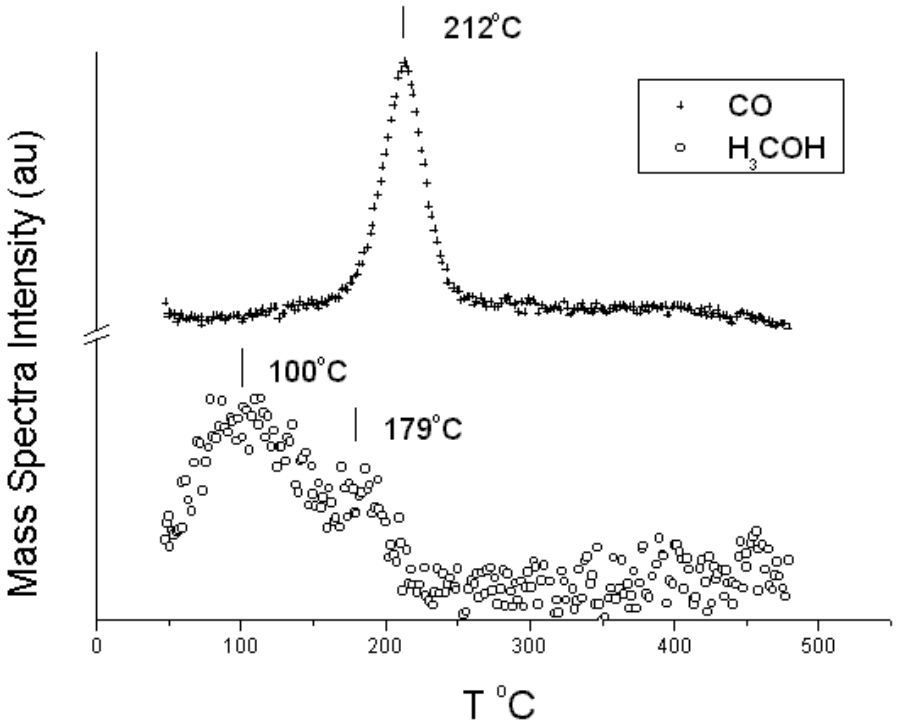

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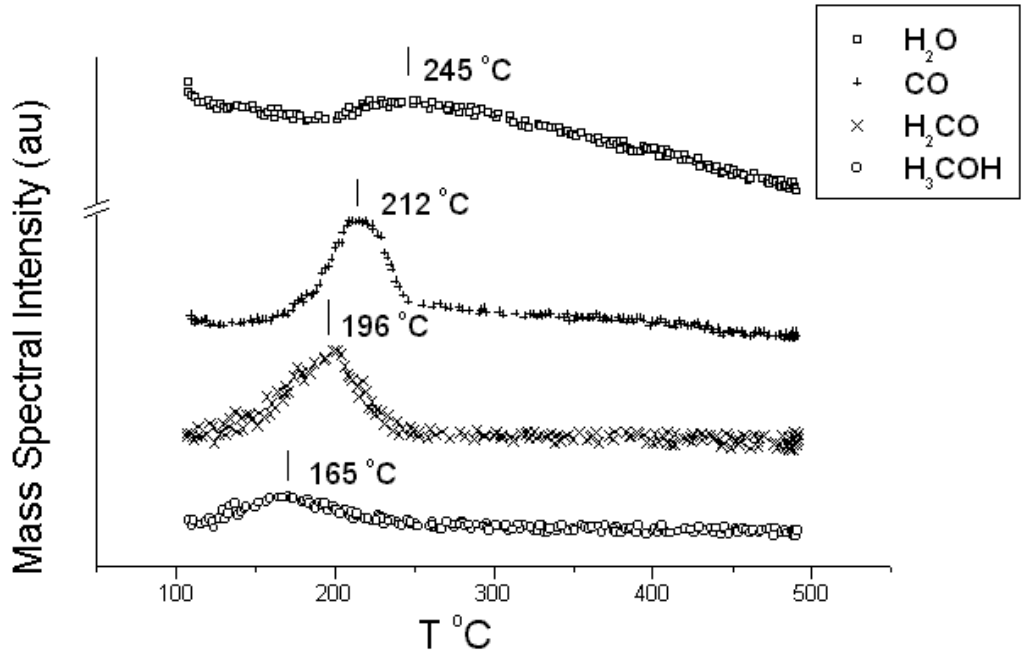

Figure 4

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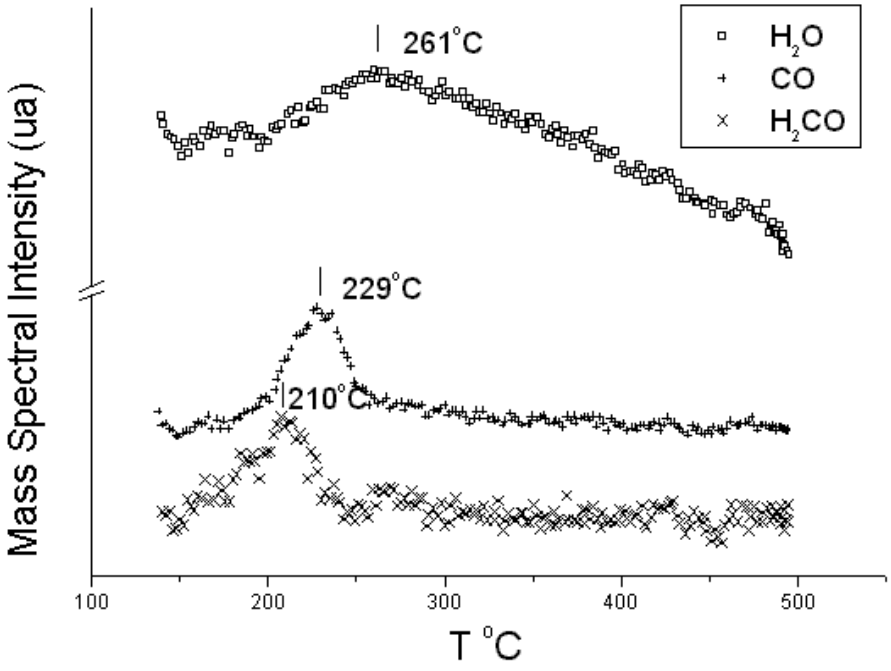

Figure 5

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