Methanol adsorption–oxidation over V_2O_5—a mass spectrometry study

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Abstract

The methanol 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 desorption (TPD) tests were conducted to analyze the products again by MS.

Conclusions drawn from study were that methanol molecules replace some of the water molecules adsorbed onto the V_2O_5, interact with those exhibiting higher adsorption energy and may suggest that methanol is linked to the solid through water molecules.

By TPD, only the following products were identified: different amounts of water, formaldehyde, CO and, at low temperature, methanol. For those temperatures, V_2O_5 shows only redox properties since neither condensation products nor CO_2 were encountered.
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1. Introduction

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

Busca [7] has studied the adsorption of methanol, formaldehyde, and formic acid on V_2O_5 and V_2O_5/SiO_2, and found adsorbed methanol in methoxy form on both catalysts, and a weak formaldehyde adsorption at low temperatures. In turn, Badlani and Wachs [8] studied a large number of oxides by chemisorption, to find anisotropic adsorption onto V_2O_5 at 100 °C with a low number of active sites, approximately 0.7 μmol/m^2.

Wachs et al. [9] studied methanol oxidation at 300 °C onto V_2O_5 and indicated 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. [10,13] and Briand et al. [11] and through DRIFT, by Sambeth et al. [12]. Major products

found were formaldehyde, CO_2 and CO. As minor products, methyl formate and methylal were observed, along with hemimethylal (CH_3CH_2OH), an unstable intermediate detected only by mass spectroscopy. Those authors have proposed a well-founded reaction mechanism for methanol oxidation based on the experimental and theoretical study.

In turn, Ranea et al. [14] have identified the adsorption sites of water molecules on V_2O_5 by TPD accompanied by a theoretical study.

In this work, the objective is to deepen knowledge of the methanol–water precipitated V_2O_5 system by studying adsorption–oxidation transients and subsequent temperature programmed desorption of the adsorbed species, especially water–methanol interaction over V_2O_5 surface.

2. Experimental

TPD or transients measurements from V_2O_5 surface were carried out in an ultra-high vacuum surface analysis reactor (base pressure ∼1.33×10^{-5} Pa). Two detectors were used: catarometric 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

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hydroxide in an ice-water bath under stirring. It was then dried at $100\,°C$, calcined in air at $500\,°C$ during 90 h and finally grinded. The V_2O_5 obtained is a non-stoichiometric compound with orthorhombic unit cells, its surface area being $2.7\,m^2/g$.

Prior to methanol adsorption in each run, the surface of the V_2O_5 sample ($\sim 0.4\,m^2$) was treated with oxygen under the following conditions: $P_{O_2} = 101\,325\,Pa$, $T = 500\,°C$, $t = 60\,min$.

Transients were studied by supplying various methanol pulses ($0.5\,\mu l$). After each, the system was left to reach equilibrium, the procedure being conducted at 40, 100 and $150\,°C$. In TPD, V_2O_5 temperature was increased linearly with time from the operating temperature up to $500\,°C$, using a heating rate of $10\,°C/min$, in He flow.

3. 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) and M75 (methylal).

Fig. 1 (transients at $40\,°C$) shows the intensity of the masses corresponding to only water, and methanol as a function of time, which are the products detected at that temperature. The first pulse is observed to produce a pronounced peak of the water mass, the subsequent peaks being considerably less intense, indicating that part of the adsorbed water is displaced by methanol.

In the transients carried out at 100 and $150\,°C$, the intensity of mass 18 increases very slowly during methanol pulses. With regard to methanol behavior in all temperatures, its intensity increases to become constant. Formaldehyde is

produced only in the test conducted at $150\,°C$. No signals representing dimethyl ether, methylal, CO, etc., were observed.

Products 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 for increasing test temperatures.

After the adsorption–oxidation process, the TPD of the adsorbed methanol was studied. In this regard, Figs. 2 and 3 ($40\,°C$) show that mass 18 generates two wide bands with maximum values at 116 and $238\,°C$, the first with less intensity than the second.

Formaldehyde desorption produces a peak at $192\,°C$, whereas CO does so at $212\,°C$. Methanol, in turn, exhibits two peaks, one at $100\,°C$ and another, of smaller area, at $179\,°C$; this may suggest that methanol adsorbs at $40\,°C$ on two different sites, i.e., both as molecular methanol and as methoxy group [8,15], respectively.

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 superficial reaction of the OH generated in the formation reaction of formaldehyde and CO.

In the TPD done at $100\,°C$ (Fig. 4) mass 18 shows only a very wide maximum at $245\,°C$, whereas formaldehyde presents a peak at $196\,°C$, and CO at $212\,°C$. The band exhibited by methanol at $165\,°C$ is small and can be assigned to recombination of the methoxy adsorbed species.

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

Signals representing dimethyl ether, methylal, CO_2, etc., were not observed at any temperature. At 100 and $150\,°C$,
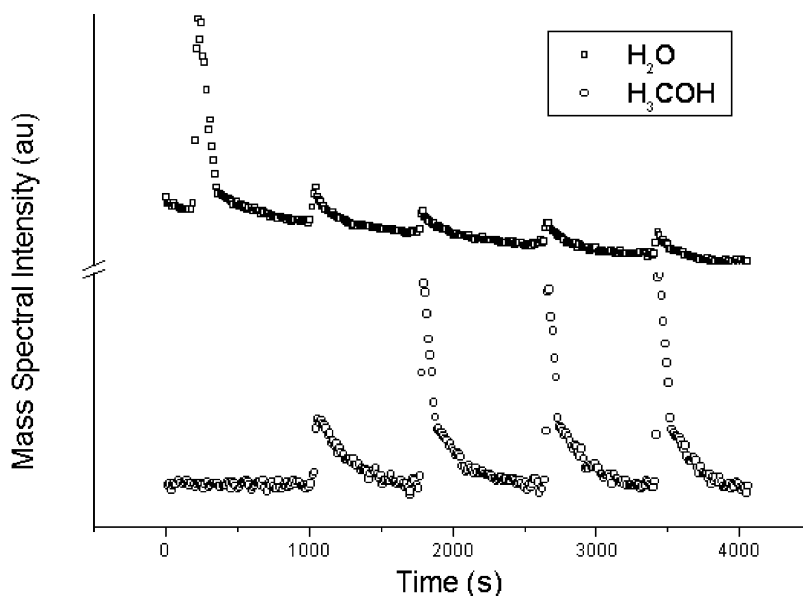

Fig. 1. Desorption spectra of methanol pulses over V_2O_5 for mass intensities of H_2O, H_2CO and H_3COH. Experimental temperature: $40\,°C$.
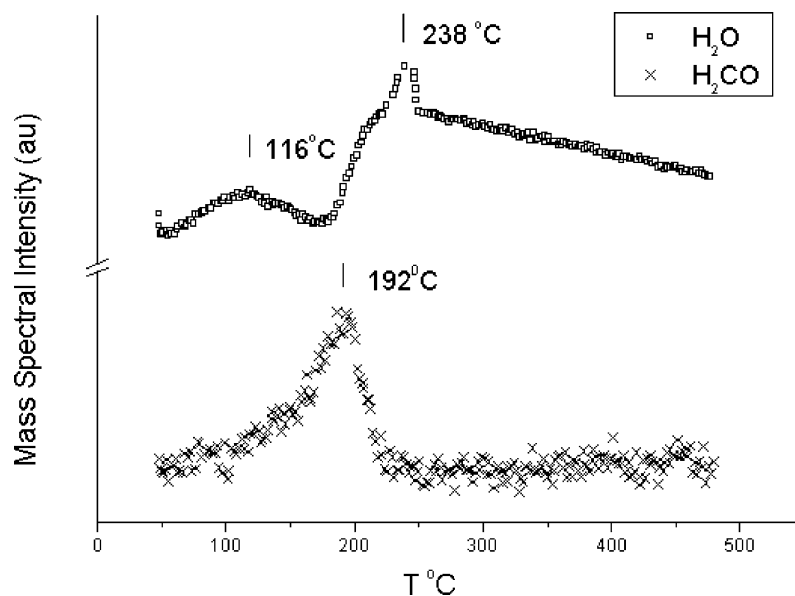
Fig. 2. TPD spectra of methanol on V_2O_5 for H_2O and H_2CO mass intensities. Experimental temperature: 40 °C.

mass 18 shows only a band corresponding to superficial reaction of the OH generated in the formation reaction of formaldehyde and CO.

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

At low temperatures, methanol replaces some of the water molecules with lower adsorption energy on V_2O_5 (Fig. 1), and interacts with those possessing higher adsorption energy [14]. This interaction increases desorption temperature of this molecules from ∼77 °C for V_2O_5 without previous methanol adsorption [14] to 116 °C with methanol adsorption. This water desorbs after methanol desorption (100 °C).

On the other hand, in the tests conducted at 100 °C, the first band representing water did not appear and methanol desorption is carried out at a much higher temperature (165 °C) being in the order of the second peak in the test at 40 °C (179 °C).

All the above may suggest that methanol is linked to the solid through water molecules since, in the absence of water, no molecular methanol adsorption takes place.
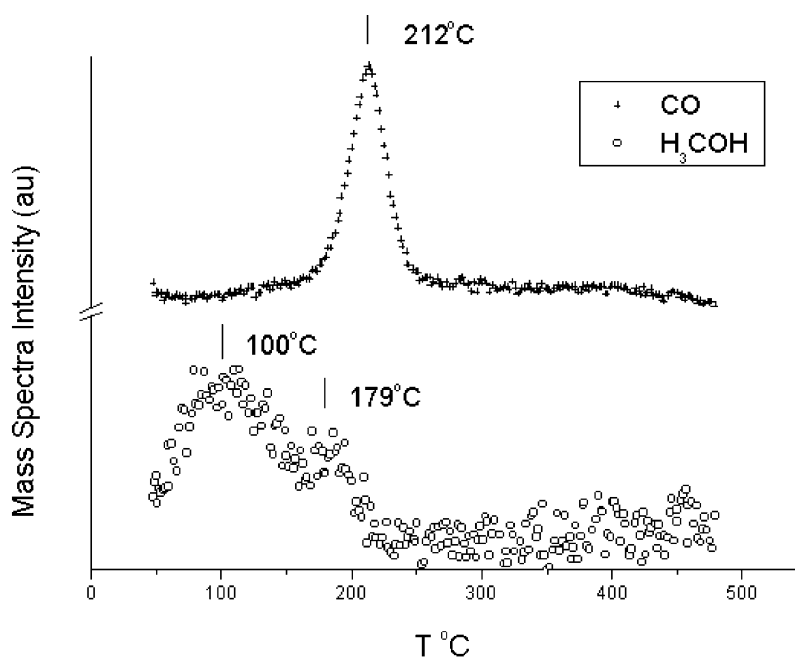

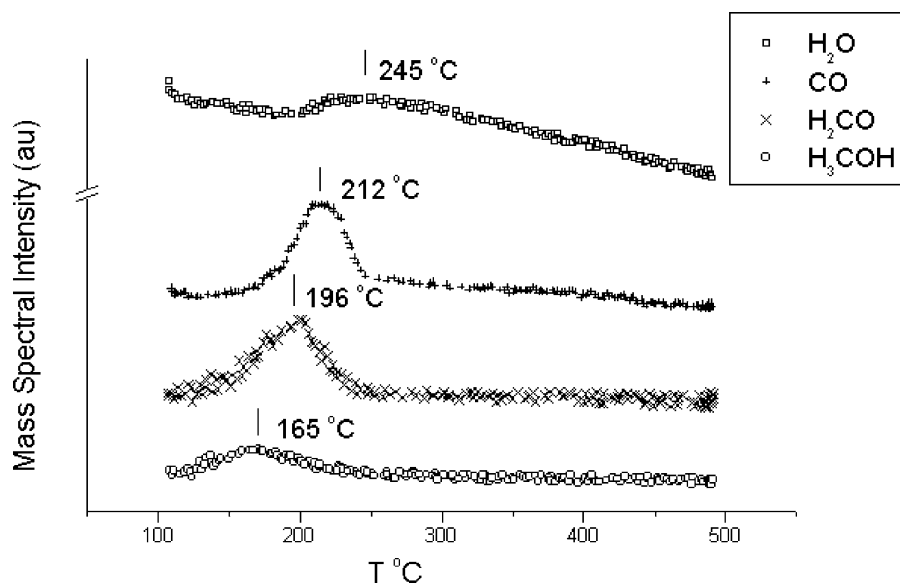Fig. 3. TPD spectra of methanol onto V_2O_5 for mass intensities corresponding to CO and H_3COH. Experimental temperature: 40 °C.

Fig. 4. TPD spectra of methanol on V_2O_5. Mass intensities presented for H_2O, CO, H_2CO and H_3COH. Experimental temperature: 100 °C.
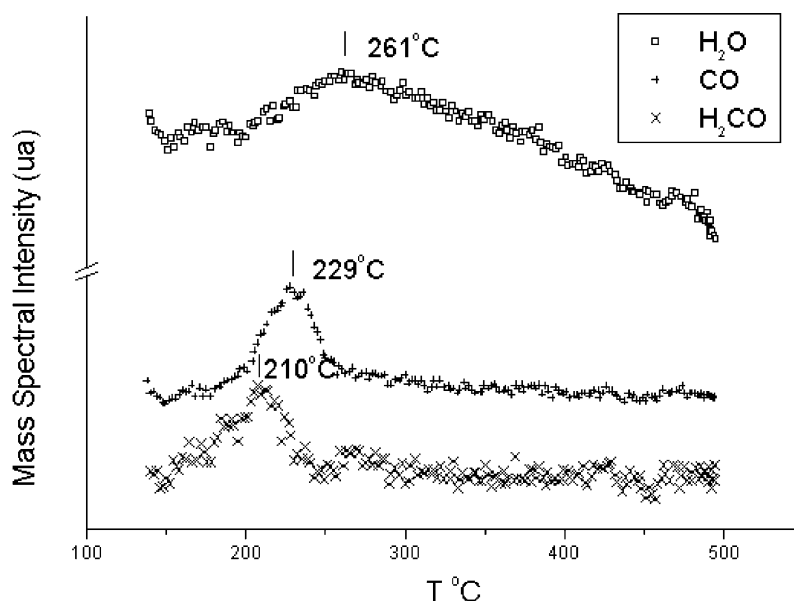

Fig. 5. TPD spectra of methanol onto V_2O_5. Mass intensities are shown for H_2O, CO and H_2CO. Experimental temperature: 150 °C.

Concerning the methoxy formed for all adsorption temperatures tested, its decomposition takes place in two well-defined molecular species, possibly because the previous adsorption occurs on different type of sites.

The first species consists of formaldehyde desorption at temperatures of 192 and 196 °C (almost the same) for the tests at 40 and 100 °C and, for the remaining test at 210 °C. The second species, the CO desorption takes place at above formaldehyde desorption temperature, i.e., at 212 and 229 °C for the tests at 100 and 150 °C.

For the test at the maximum temperature, where methanol is adsorbed only as methoxy, the decomposition temperature

coincides with the value proposed in the literature [8].

4. Conclusions

In the transient measurement study, the substances detected were only formaldehyde, methanol and water. The methanol–V_2O_5 interaction rate is slow for the test at 40 °C and increases with temperature.

TPD of species remaining after the transient study on V_2O_5 permits detection of different amounts of water, CO

and at low temperatures, methanol. Methanol adsorption at $40\,^\circ C$ proceeds on two types of sites with desorption temperatures of 100 and $179\,^\circ C$, being the amount desorbed from the higher temperature site very small.

In the test at $100\,^\circ C$, the band at $165\,^\circ C$ can be assigned to recombination of the methoxy adsorbed species. At low temperatures, the methanol replaces some of the water molecules, which have lower adsorption energy on V_2O_5, and interacts with those exhibiting higher adsorption energy.

This interaction makes desorption temperature to elevate from $\sim 77\,^\circ C$ for V_2O_5 without former adsorption of methanol to $116\,^\circ C$ with methanol adsorption. Water desorption occurs here after methanol desorption ($100\,^\circ C$).

It may suggest that methanol is linked to the solid through water molecules since, in the absence of water, no molecular methanol adsorption takes place. Where methanol is adsorbed only as methoxy, its decomposition temperature is observed to coincide with published values [8].

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

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