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# In situ DRIFTS study of the adsorption–oxidation of $CH_3OH$ on $V_2O_5$

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**Abstract**

The oxidation of $CH_3OH$ on $V_2O_5$ has been studied from room temperature to 250°C. The reaction products were analyzed by on-line gas chromatography (GC) and the adsorbed species were characterized by "in situ" diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS). Both isothermal and non-isothermal experiments were carried out in order to identify adsorbed species in the oxidation of $CH_3OH$ on $V_2O_5$ catalysts. The interaction of $CH_3OH$ with the$V_2O_5$ surface results in the formation of methoxy groups and V–OH species as stated by DRIFTS. The infrared spectra suggest that more than one catalytic site are involved in the adsorption process. The formation of V–OH and the resulting reduction of the vanadia catalyst leading to $V^{4+}$=O and $V^{3+}$ groups is inferred from DRIFTS data and X-ray diffraction patterns of the used catalysts showing the presence of reduced oxide phases. As the reaction proceeds, the adsorbed methoxy species are oxidized to $H_2CO$, formate species, partial oxidation products, CO and $CO_2$. © 2000 Elsevier Science B.V. All rights reserved.

*Keywords:* $V_2O_5$; Methanol; DRIFTS; Oxidation; Adsorption

## 1. Introduction

Several authors have suggested that two or three kinds of methoxy species are formed on the surface of oxides after methanol adsorption. Boreskov et al. [1] have found using thermal desorption (TD) and infrared (IR) spectroscopy data that methanol adsorption on $MoO_3$ results in two weakly chemisorbed methanol intermediates and that both chemisorbed species participate in the formation of $H_2CO$. Moreover, Li et al. [2] have studied $CH_3OH$ adsorption on $CeO_2$ detecting three kinds of methoxy species adsorbed on the oxide surface. These authors also reported that $CH_3OH$ can be oxidized to formate

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species by surface oxygen of $CeO_2$. On Cu(110), two methoxy states are formed upon $CH_3OH$ adsorption at room temperature [3]. These authors suggested that the stability of methoxy groups is due to the presence of chemisorbed oxygen, a low initial oxygen coverage favors the least stable methoxy state, whereas high initial oxygen coverage favors the more stable one. The same behavior is observed upon adsorption of *n*-alcohols on $V_2O_5.nH_2O$ [4]: formation of alcoxide species interacting with the former V=O bonds.

Sambeth et al. [5], on studying the adsorption–oxidation of $CH_3OH$ on $V_2O_5$, showed that the Hall constant ($R_H$) of the solid decreases as a function of time upon methanol adsorption. This result implies electron transfer from methanol to the solid resulting in its partial reduction, with an increase in the number of carriers (electrons). At low temperatures, the formation of condensation products is favored being $H_2O$ (g) and $CO_2$ (g) production favored on increasing the reaction temperature.

The role of gaseous oxygen has been studied by several authors. Miyamato et al. [6] and Centeno et al. [7] showed that $O_2$ present in the reaction mixture reoxidizes the surface. Recently, Sokolovskii et al. [8] studied the adsorption of oxygen {$O_2 \rightarrow 2O$ (adsorbed)} on $V_2O_5/SiO_2$; their results indicate that O (adsorbed) lifetime is long enough to participate in the catalytic reaction leading to the primary formation of partial oxidation products.

There are three processes that can be envisaged for the desorption of adsorbed alcohol species in the presence of oxygen: (i) molecular desorption, (ii) evolution of oxidized chemical species produced by catalytic reaction and (iii) combustion products produced by interaction of the adsorbed layer with oxygen to produce CO, $CO_2$ and $H_2O$.

Fourier transform infrared spectroscopy (FT-IR) is ideal to identify functional groups, reactive sites, adsorbed species and intermediates on the surface of catalysts under reaction conditions. Diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS) allows to obtain the IR spectrum of samples in their original form being more sensitive to surface species than transmission IR. Moreover, its capability of controlling the environmental conditions has converted it into a powerful tool in surface chemistry [9,10]. As this technique allows to continuously monitor the surface state (oxidation/reduction of the catalysts) and the adsorbed species, we study in the present work by "in situ" DRIFTS the adsorption–oxidation mechanism of $CH_3OH$ on $V_2O_5$ and by on-line gas chromatography (GC) the oxidation products. From here, we propose a reaction model for the methanol oxidation on $V_2O_5$.

## 2. Experimental

Vanadium pentoxide was prepared by dissolving 6.13 g of $NH_4VO_3$ in 965 $cm^3$ of 8.0 M HCl (Merck P.A.) that was further neutralized to pH = 5 using a concentrated solution of $NH_3$ in water (Merck P.A.). The precipitated solid was filtered off, thoroughly washed with water to eliminate the $NH_4Cl$ formed during neutralization, dried at 120°C for 12 h and calcined at 500°C for 24 h. Thermal treatments were performed in either quartz or platinum containers to avoid bronze formation [11].

X-ray diffraction patterns of both fresh and used $V_2O_5$ were obtained in the $\theta/2\theta$ mode between 5° and 60°. A Phillips PW 1390 instrument (CuK$\alpha$ radiation and Ni filter) operated at 40 kV and 20 mA was utilized. Electron microscopy analysis was performed in a Phillips SEM 505 electron microscope.

DRIFTS spectra were obtained in a Nicolet 510P infrared spectrometer with a KBr optics and a deuterated triglycine sulfate (DTGS) detector. An environmental DRIFTS chamber, equipped with ZnSe windows (Spectra-Tech 0030-101), allowing in situ treatments up to 500°C and 1 atm was coupled to the spectrometer. The sample was placed inside the chamber without packing or dilution [10]. The spectra are obtained by co-adding 200 scans collected at 4 $cm^{-1}$ resolution after referencing the interferogram to that of an aluminum mirror. The spectra are presented in Kubelka–Munk mode without any further manipulation.

Prior to reaction, the catalyst was activated for 1 h in pure $O_2$ at 500°C to eliminate organic contamination, $N_2$ was then admitted in the reaction chamber at the same temperature and the sample kept in this condition for 1 h to remove excess oxygen. This treatment was performed for both isothermal and non-isothermal DRIFTS experiments.

In the isothermal experiment, the catalyst was cooled down to 150°C in $N_2$ flow and a reference spectrum collected before admitting into the DRIFTS cell the reaction mixture. In this experiment, spectra are taken as a function of time on stream. Methanol saturated synthetic air was obtained by flowing 30 ml $min^{-1}$ of synthetic air (Sociedad Española del Oxigeno, SEO, 99.99%) through methanol (Merck P.A.) at room temperature.

In the non-isothermal experiment, the catalyst was cooled down to room temperature under $N_2$ flow after the activation process. Then, the reaction temperature was ramped at $5°C \cdot min^{-1}$ up to in the presence of the reactive stream. The spectra are then collected while ramping the temperature. Due to acquisition delay, the temperature accuracy is $\pm 10°C$.

Catalytic tests were carried out in a U-shaped borosilicate glass reactor working in integral conditions and equipped with a gas chromatograph (Shimadzu GC 8A). Porapak T (for the analysis of $CO_2$, methanol and catalytic products) and a 5A zeolites (for the analysis of CO) were used for the analysis of the reaction products. The catalyst (300 mg, 0.4 $cm^3$ catalytic bed) was, as in the DRIFTS experiments, activated at 500°C in air and further cooled down to the reaction temperature prior to admitting the reaction mixture in the reactor. For avoiding any interference, the carrier gas was dehydrated using a molecular sieve (zeolite 4A). Temperatures of reaction were varied at random between 100°C and 250°C, the reaction products were analyzed after 2 h in stream and the reactor outflow was analyzed after 2 h in isothermal reaction conditions. For the kinetic study, the catalyst was heated to 150°C and the reactive flow was introduced in the reactor, analyzing the reactor outflow as a function of the time on stream.

## 3. Results

The results of the catalytic tests as a function of the reaction temperature are shown in Table 1. Methanol conversion increases on increasing the reaction temperature up to 200°C. At this temperature, total conversion is achieved. The selectivities of the partial oxidation products (formaldehyde, hemimethylal ($CH_3OCH_2OH$), methylal {$(CH_3O)_2CH_2$} and methyl formate) pass through a maximum at 150°C and then decrease, the same behavior being observed for the reaction yield. The selectivity towards CO shows a complex pattern. It is important at lower temperatures and decreases at 150°C remaining constant from this temperature. The CO reaction yield is, however, approximately constant over the range of studied temperatures. $CO_2$ selectivity and reaction yield increase continuously with temperature, particularly above 150°C. These results show that combustion reactions of methanol and/or products, with gaseous or lattice oxygen, become important at high temperatures (> 150°C). On the basis of these results, we have chosen the temperature at which the $H_2CO$ yield is maximum for studying the possible modification of conversion and selectivity as a function of time on stream. The results are given in Table 2. At such temperature, methanol conversion and $CO_2$ selectivity and yield increase with time on reaction. The selectivity towards all other products, except CO, decreases with reaction time. However, the reaction yield for all of them shows a maximum

Table 1
Conversion and selectivites of the methanol oxidation reaction over $V_2O_5$, as function of the reaction temperature

| Temperature (°C) | Conversion (%) | Selectivity (%) | | | | | |
|---|---|---|---|---|---|---|---|
| | | $H_2CO$ | $CH_3OCH_2OH$ | $(CH_3O)_2CH_2$ | $HCOOCH_3$ | CO | $CO_2$ |
| 100 | 19 | 73 | – | 1 | – | 19 | 6.5 |
| 120 | 31 | 70 | 0.9 | 0.8 | 1.8 | 19.5 | 7 |
| 150 | 80 | 74 | 0.8 | 1 | 4.2 | 5.5 | 13.3 |
| 200 | 100 | 41 | – | – | – | 7.3 | 51.7 |
| 250 | 100 | 16.5 | – | – | – | 6.5 | 77 |

Table 2
Conversion and selectivites of the methanol oxidation reaction over $V_2O_5$, as function of the time on reaction at 150°C

| Tiempo (h) | Conversion (%) | Selectivity (%) | | | | | |
|---|---|---|---|---|---|---|---|
| | | $H_2CO$ | $CH_3OCH_2OH$ | $(CH_3O)_2CH_2$ | $HCOOCH_3$ | CO | $CO_2$ |
| 1.5 | 17.5 | 64.0 | 5.3 | 1.3 | 5.7 | 4.6 | 19.0 |
| 5 | 48.6 | 72.0 | 0.9 | 1.0 | 4.5 | 5.0 | 14.0 |
| 12 | 65.0 | 42.0 | – | 0.2 | 4.0 | 6.8 | 47.0 |
| 20 | 89.5 | 22.0 | – | – | 2.8 | 6.2 | 69.0 |
| 30 | 96.1 | 12.0 | – | – | – | 4.3 | 83.7 |
| 48 | 99.6 | – | – | – | – | 3.0 | 97.0 |

at time that depends on the oxidation degree of carbon in the final product. The maximum yield for $H_2CO$, $CH_3OCH_2OH$ and $(CH_3O)_2CH_2$ occurs at 5 h, for $HCOOCH_3$ and CO at around 20 h and for $CO_2$ at 48 h.

Fig. 1 shows the DRIFTS spectra obtained "in situ" during the reaction at 150°C as a function of the reaction time. In order to have a better observation of the changes produced in the catalyst IR spectra, Fig. 2 shows the successive difference spectra. The spectrum of the catalyst after the activation process and before reaction (Fig. 1, trace A), presents no bands due to hydroxyl groups in the 4000–3000 $cm^{-1}$ region and the structure of the V=O overtones bands (two bands at 1971 and 2020 $cm^{-1}$) is characteristic of crystalline $V_2O_5$ [7,12,13]. Once the methanol is introduced in the DRIFTS cell, several bands characteristic of adsorbed methoxy groups appear. Those bands in the 3030–2800 $cm^{-1}$ region and the three observed at 1055, 1030 and 1005 $cm^{-1}$ are due to $\nu(CH_3)$ and $\nu$(C–O) of adsorbed methoxy species, respectively [2,14,15]. The groups of bands between 3700 and 3600 $cm^{-1}$ are assigned to $\nu$(OH) of V–OH groups resulting from RO–H dissociation on the catalysts surface. Some other weak bands attributed to $\delta(CH_3)$ (1473 and 1454 $cm^{-1}$), $CH_2$ of $H_2CO$ species (1278 $cm^{-1}$ [16]) and formate species (1670–1500 and 1350–1300 $cm^{-1}$) are also observed. Besides this, a band at 2078 $cm^{-1}$ appears. Schraml-Marth and Baiker

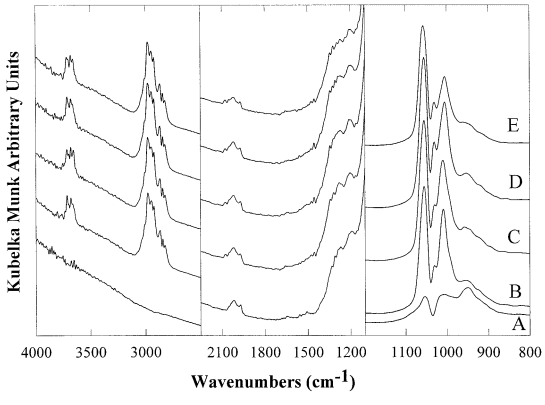



Fig. 1. In situ DRIFTS spectra of the adsorption–oxidation of $CH_3OH$ on $V_2O_5$ at 150°C, as a function of time on reaction. (A) Before reaction, (B) 1 h, (C) 2 h, (D) 3 h and (E) 4 h.

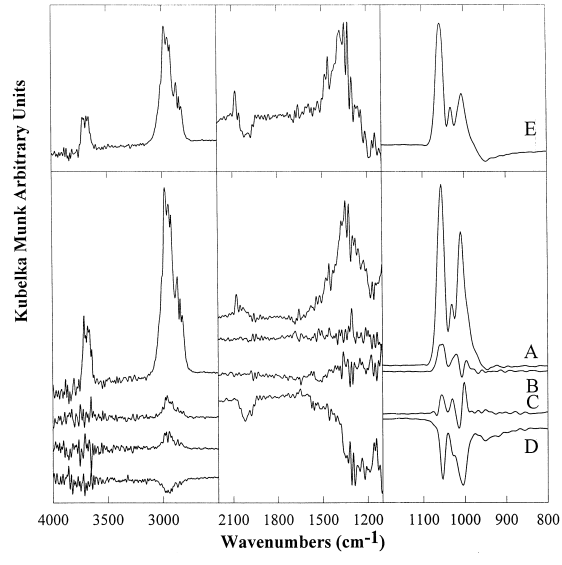



Fig. 2. Succesive difference DRIFTS spectra of the adsorption–oxidation of $CH_3OH$ on $V_2O_5$ at 150°C, as a function of time on reaction. (A) 1-h initial, (B) 2–1 h, (C) 3–2 h, (D) 4–3 h and (E) 4-h initial.

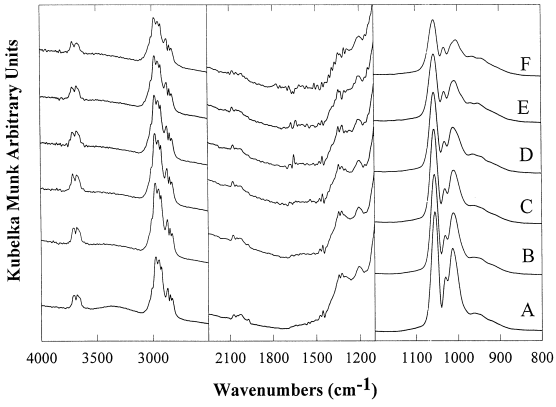



Fig. 3. In situ DRIFTS spectra of the adsorption–oxidation of $CH_3OH$ on $V_2O_5$ as a function of temperature. (A) 35°C, (B) 62°C, (C) 91°C, (D) 123°C, (E) 155°C and (F) 184°C.

[12] have observed in the DRIFTS spectra of reduced vanadia/titania catalysts a V=O overtone band at ca. 2060 $cm^{-1}$ assigned to $V^{4+}$=O groups. This overtone band occurs at higher wave numbers than those of oxidized vanadia catalysts. The observation of this band points to a reduction of the vanadium atoms. This is consistent with the work of Pak et al. [17], which demonstrates that methoxy formation involves the reduction of $V^{5+}$ to $V^{4+}$. No bands due to C=O groups, at about 1700 $cm^{-1}$, are detected at this temperature.

As can be seen in Fig. 2, changes described above are produced mainly in the first hour of reaction. Between 2 and 3 h, only a weak adsorption of methanol as methoxy groups is observed. However, after reacting the system for 4 h, a decrease in the intensity of the bands due to the $V^{5+}$=O at 1971 and 2020 $cm^{-1}$ as well as of the bands ascribed to adsorbed methoxy groups is observed (Fig. 2, curve D). This result indicates that after 4 h in stream, the coverage of methoxy groups decreases and that the catalyst surface has been reduced since the intensity of the bands corresponding to $V^{5+}$=O groups decreases. The presence of $V^{3+}$ species is assumed since it has no V=O groups. Besides these $V^{3+}$ surface cations, the presence of $V^{4+}$=O groups is clear since the intensity of the band at 2078 $cm^{-1}$ remains unchanged. Fig. 2, curve E clearly demonstrates that after 4 h in stream, the intensity of the band at 2078 $cm^{-1}$ is higher than in the activated catalyst, while the intensity of the bands at 1971 and 2020 $cm^{-1}$ is considerably smaller.

The $CH_3OH/O_2$ reaction on vanadia catalysts has been studied as a function of temperature by in situ DRIFTS. Fig. 3 shows the IR spectra of the adsorbed species. For enhancing weak features, the spectra are ratioed to that obtained in the presence of the reaction stream at 35°C. These spectra are shown in Fig. 4. From RT to 150°C, every spectrum presents the same absorption bands described above for the isothermal reaction at 150°C. However, we must remark that the intensity of the methoxy bands pass through a maximum at around 60°C; this phenomenon is similar to that reported by Burchman and Wachs [18] for supported $V_2O_5$. Besides this, weak bands due to molecular $H_2O$ at about 3400 ($\nu$(OH)) and 1630 $cm^{-1}$ ($\delta(H_2O)$) are observed. The formation of $H_2O$ could be consequence of the condensation of two hydroxyl groups, such as Centeno et al [7] and Jehng et al. [19] have proposed, resulting in a reduction of the oxidation state of the solid [6,20].

On raising the temperature above 150°C, very weak bands in the 1650–1500 and 1350–1300 $cm^{-1}$ regions appear; these bands are assigned to formate species. At higher temperatures (> 200°C), bands of very low intensity due to C=O (1772, 1745 and 1713 $cm^{-1}$) and C–H species (2803 and 2760 $cm^{-1}$) were found. Busca et al. [21] have found similar

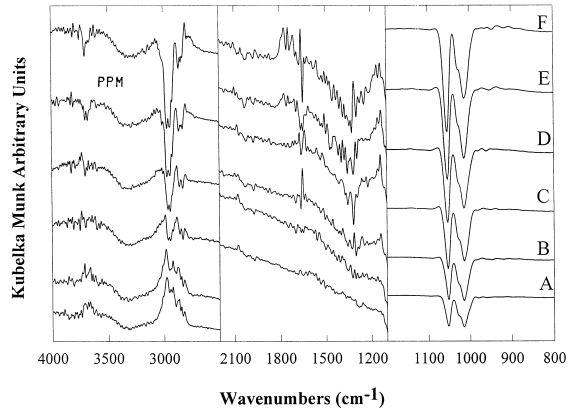



Fig. 4. Difference DRIFTS spectra of the adsorption–oxidation of $CH_3OH$ on $V_2O_5$ as a function of temperature. (A) 62–35°C, (B) 91–35°C, (C) 123–35°C, (D) 155–35°C, (E) 184–35°C and (F) 200–35°C.

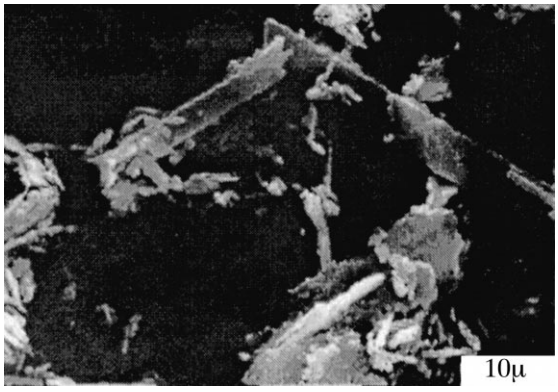



Fig. 5. SEM micrograph of fresh $V_2O_5$.

C=O bands on titania and iron oxide that they assigned to a perturbed molecular form of $H_2CO$, probably coordinated on Lewis acid sites.

The intensity of the $2\nu(V^{5+}{=}O)$ bands decreases with temperature, pointing to a reduction of the vanadium atoms during the reaction.

Figs. 5 and 6 show SEM micrographs of fresh and used $V_2O_5$ solid, respectively. The fresh catalyst exhibits the characteristic morphology of vanadium pentoxide appearing as plates and needles. In the used solid, small needles, as well as crystals with rounded edges and corners are detected; these being characteristic of a reduced vanadia phase.

A detailed analysis of the diffraction patterns of the fresh and used catalysts is shown in Table 3. As can be seen, only diffraction lines corresponding to $V_2O_5$ are observed for the fresh catalyst, whereas diffraction lines corresponding to $VO_2$(A), $VO_2$(B), $V_2O_4$ and $V_6O_{13}$ phases are observed for the used catalyst.

Table 3
X-ray diffraction analysis
$d$ = interplane distance, $I_{relative}$ = relative intensity to 3.20 A signal.

| $2\theta$ | $d$ (Å) | $I_{relative}$ (%) | Phase |
|---|---|---|---|
| *Fresh $V_2O_5$* | | | |
| 15.4 | 5.72 | 39 | $V_2O_5$ |
| 20.4 | 4.35 | 100 | $V_2O_5$ |
| 21.9 | 4.06 | 37 | $V_2O_5$ |
| 31.2 | 2.87 | 60 | $V_2O_5$ |
| 32.6 | 2.74 | 35 | $V_2O_5$ |
| 34.5 | 2.6 | 38 | $V_2O_5$ |
| 41.5 | 2.18 | 20 | $V_2O_5$ |
| 42.3 | 2.14 | 10 | $V_2O_5$ |
| 45.7 | 1.98 | 17 | $V_2O_5$ |
| 47.5 | 1.91 | 17 | $V_2O_5$ |
| 49.7 | 1.83 | 14 | $V_2O_5$ |
| 52.2 | 1.75 | 30 | $V_2O_5$ |
| 55.8 | 1.65 | 12 | $V_2O_5$ |
| 56.5 | 1.63 | 8 | $V_2O_5$ |
| 59.4 | 1.56 | 8 | $V_2O_5$ |
| *Used $V_2O_5$* | | | |
| 14.9 | 5.94 | 18.0 | $VO_2$(A) |
| 17.8 | 4.99 | 3.6 | $V_6O_{13}$, $VO_2$(B) |
| 25.4 | 3.5 | 6.3 | $V_6O_{13}$, $VO_2$(A), $VO_2$(B) |
| 26.9 | 3.31 | 14.0 | $V_6O_{13}$, $V_2O_4$ |
| 27.8 | 3.2 | 100.0 | $V_6O_{13}$, $V_2O_4$ |
| 33.4 | 2.68 | 6.8 | $V_2O_4$, $V_6O_{13}$, $VO_2$(A), $VO_2$(B) |
| 37.0 | 2.43 | 27.0 | $V_6O_{13}$, $V_2O_4$ |
| 38.4 | 2.34 | 2.7 | $V_6O_{13}$, $VO_2$(B) |
| 42.2 | 2.14 | 10.8 | $V_2O_4$ |
| 44.7 | 2.02 | 6.8 | $V_2O_4$, $VO_2$(B) |
| 45.6 | 1.99 | 11.3 | $V_6O_{13}$, $VO_2$(B), $VO_2$(A) |
| 49.5 | 1.84 | 2.5 | $V_6O_{13}$, $VO_2$(B), $V_2O_4$ |
| 53.0 | 1.73 | 4.0 | $V_2O_4$, $VO_2$(B) |
| 55.5 | 1.65 | 27.0 | $V_2O_4$, $V_6O_{13}$, $VO_2$(B), $VO_2$(A) |
| 57.6 | 1.60 | 15.3 | $V_2O_4$, $V_6O_{13}$, $VO_2$(A) |

Fig. 6. SEM micrograph of used $V_2O_5$.

## 4. Discussion

DRIFTS study of the methanol/air reaction over $V_2O_5$ catalysts shows that methanol is adsorbed as methoxy groups in the catalyst surface. The number of methoxy bands suggests that the interaction adsorbent–adsorbate may be produced on more than one

surface sites in good agreement with literature [1,2,14,15,22,23]. A theoretical model of the interaction of methanol with the vanadia surface using extended Hückel methods have been reported by Sambeth et al. [24]. These authors found that $CH_3OH$ may adsorb on oxygen atoms mono- and tri-coordinated to vanadium atoms. The existence of more than one site having different basicity has been discussed on the basis of semiempirical and ab initio methods by Witko et al. [25].

The formation of methoxy groups implies the basic character of the surface oxygen atoms that hold H atoms. DRIFTS results show that a large number of OH groups are formed in this process at the same time that a reduction of surface vanadium atoms is produced ($V^{5+}$ to $V^{4+}$). Besides this, molecular water is also produced, probably as a result of hydroxyl condensation. The reduction of the catalyst during reaction is clearly seen in Table 3. Starting from an orthorhombic $V_2O_5$ structure, the catalyst under the reaction mixture is bulk-reduced having, once used, a complex mixture of crystalline structures that can be associated to $V_2O_4$, $VO_2$(A), $VO_2$(B) and $V_6O_{13}$ phases. The reduction of the $V^{5+}{=}O$ and the formation of $V^{4+}{=}O$ during the reaction is clearly demonstrated by the appearance of the $V^{4+}{=}O$ overtone band at 2078 $cm^{-1}$ and the disappearance of the $V^{5+}{=}O$ overtone bands at 1971 and 2020 $cm^{-1}$. It was also seen (Figs. 5 and 6) that exposure of the sample to the reaction atmosphere led to important morphological changes, the sample losing the characteristic morphology of vanadium pentoxide and presenting small needles and crystals with rounded edges and corners, typical of a reduced vanadia phase.

The formation of the surface hydroxyl groups results in a considerable weakening of the V–O bonds. If oxygen atoms resulting in hydroxyl groups are doubly coordinated oxygen atoms, the V–O–V bonds are considerably weakened and this bridging oxygen may be inserted in the adsorbed species [25]. Thus, it can be proposed, as in previous reports [26,27,28], that formaldehyde is produced from adsorbed methoxy groups. The formation of partial oxidation products, i.e. $HCOOCH_3$ (methylformate) and $(CH_3O)_2CH_2$ (methylal), would be produced by condensation of methoxy groups with formate species or formaldehyde. The formation of formate species might occur directly from methoxy groups or considering formaldehyde as intermediate [24].

The reaction yield for partial oxidation products, in particular formaldehyde, is high. The fact that bands observed in the DRIFTS spectra assigned to formaldehyde and partial oxidation products are very weak may arise from either a low molar absorption coefficient for such species or to a fast desorption process once the partial oxidation products are formed. For reaction temperatures above 150°C or reaction times over 5 h, total oxidation of methanol to $CO_2$ is favored. DRIFTS data show that the $2\nu(V{=}O)$ bands in the 2100–1900 $cm^{-1}$ region strongly decrease after 4 h in reaction stream at 150°C. Moreover, the catalytic test shows that, from that time on reaction, a decrease in the selectivity of the reaction products and an intense increase in the $CO_2$ production occur. It is important to notice that the maximum rate of production for the different products occurs at times that correlate quite well with the average net formal charge of the oxidation product (Fig. 7). These observations are explained by oxidation reactions to $CO_2$, as Kittara

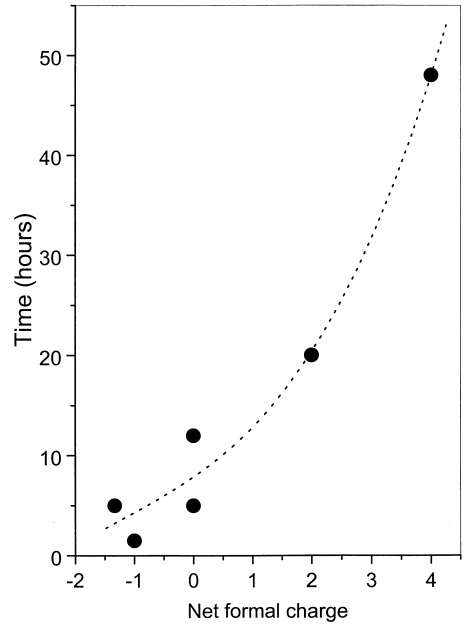
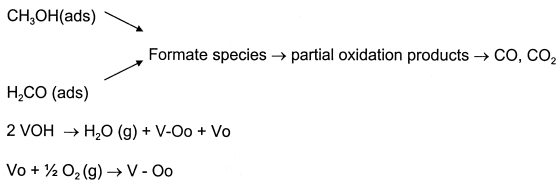



Fig. 7. Time on reaction at 150°C at which the reaction yield is maximum as a function of the average net formal charge of the oxidation product.

et al. described [4]. In our case, DRIFTS and catalytic data point to a reduction $V^{5+} \rightarrow V^{3+}$. The role of gaseous oxygen is to reoxidize the vanadium reduced in both the $CO_2$ production and methanol adsorption process. The sequence outlined in Fig. 7 might indicate that the oxidation state of the catalyst determines the selectivity towards partial oxidation products being oxidation of adsorbed molecules by lattice oxygen faster than catalyst reoxidation by gaseous oxygen.

Taking into account these observations, we can propose the following reaction model for the methanol/air reaction over $V_2O_5$ catalyst,

$$CH_3OH(g) + 2V(+5)\text{–}Oo + Vo$$
$$\rightarrow VOH + V(+4)\text{–}O + CH_3O\text{–}V$$
$$CH_3O\text{–}V + V\text{–}Oo \rightarrow H_2CO(g) + VOH + Vo$$
$$H_2CO(g) \leftrightarrow H_2CO(ads)$$




$$2VOH \rightarrow H_2O(g) + V\text{–}Oo + Vo$$
$$Vo + 1/2O_2(g) \rightarrow V\text{–}Oo$$

where Oo can be oxygen mono- or tri-coordinated to vanadium atoms, as proposed previously [24], and Vo is an oxygen vacancy.

## 5. Conclusions

From the "in situ" DRIFTS study of the $CH_3OH/O_2$ reaction on $V_2O_5$, some considerations about the reaction mechanism can be deduced:

(i) the interaction $CH_3OH\text{–}V_2O_5$ results in the formation of methoxy groups and OH species
(ii) the adsorption of $CH_3OH$ occurs on different surface sites
(iii) the formation of OH species has three effects, a high surface hydroxylation, $H_2O$ formation and reduction of $V_2O_5$
(iv) between 25°C and 150°C, the activity of the catalysts increases with temperature. Total oxidation reactions are important at temperatures higher than 150°C.

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