Transient isotopic study of methanol oxidation on unsupported V$_2$O$_5$
Mechanism of methylal formation

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Abstract

The mechanism of methylal formation by methanol oxidation on unsupported V$_2$O$_5$ catalyst has been investigated in transient isotopic experiments, performing an exchange between CH$_3$OH and CD$_3$OD. Adsorbed methoxy groups and hemimethylal (CH$_3$OCH$_2$OH) have been identified as intermediate species, the hemimethylal being formed by reaction between an activated methanol species ($^\bullet$CH$_2$OH) and the surface methoxy groups. The methylal is then obtained by a dehydration reaction between hemimethylal and a methanol molecule or a surface methoxy group. We can also propose that the methyl formate formation (HCOOCH$_3$) could occur by hemimethylal oxidative dehydrogenation, the hemimethylal (CH$_3$OCH$_2$OH) appearing then as the key intermediate in the methanol oxidation to methylal and methyl formate. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Methanol oxidation; V$_2$O$_5$; Mechanism; Methylal; Hemimethylal; Transient isotopic experiments; Deuterated methanol

1. Introduction

The catalytic oxidation of methanol is a convenient structure-sensitive reaction, widely used to characterize the oxide surfaces in terms of acido-basicity and redox properties [1]. In mild reaction conditions, four main products are formed, namely dimethyl ether (CH$_3$OCH$_3$:DME), formaldehyde (CH$_2$O:F), methyl formate (HCOOCH$_3$:MF) and methylal (CH$_3$OCH$_2$OCH$_3$:ML).

Dimethylether is characteristic of an acidic behaviour, whereas formaldehyde, methyl formate and methylal are produced by at least one redox step. Selectivities are depending on the nature of the catalyst, but also on the methanol conversion and on the reaction temperature.

Generally speaking, a low reaction temperature (180°C) favours the formation of intermediate products between formaldehyde and carbon oxides (MF and ML), whereas at high temperature (300°C), only formaldehyde and carbon oxides are formed [1,2]. For a given temperature, the influence of the methanol conversion is more complex, the yields of formation of the different redox products passing

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through a maximum for different conversions [3,4]. By increasing the contact time, maximum yields for ML, F, MF are observed on unsupported V_2O_5 or MoO_3 at a conversion of 20–30%, 70–80%, 80–90%, respectively [4,5]. Carbon oxides are the main products for a conversion close to 100%. On highly dispersed molybdenum oxide supported on silica [6,7], methyl formate is selectively formed (90%) at low conversion, at a temperature as high as 280°C, suggesting the possibility of different reaction pathways depending on the nature of the catalyst [1].

The methanol mild oxidation mechanism has been investigated by several authors by kinetic or spectroscopic methods, but the nature of the reaction intermediates has never been unambiguously identified and is still controversial [8–16]. Nevertheless, the knowledge of the mechanism of the reaction is needed to improve the understanding of the methanol catalytic oxidation and to develop its use as a sensitive and accurate tool in oxide surface characterization.

Pure kinetic methods, based on the analysis of the reaction rates and on the nature of the reaction products, allow only to fit an hypothetical model with experimental data, the better the fit, the more likely the model will describe correctly the true reaction mechanism. However, even for a perfect fit, the mechanism deduced from these experiments remains always speculative. In some cases, spectroscopic techniques such as Raman or FT-IR of adsorbed molecules [8] allow to detect species which are present during the reaction course, but the problem is to determine whether these species are reactive or not. The transient kinetic isotopic techniques, are a good alternative to pure kinetic methods since by changing one of the reactants by its homologue containing at least one isotopically labelled atom, it is possible to obtain accurate informations about the nature of the surface reaction intermediates and/or, in some favourable cases, their residence time and amount on the catalyst surface [17]. Moreover, the kinetic isotopic effect recorded at the steady-state can bring additional informations about the rate determining step of the reaction [18,19].

In this work, we have investigated the mechanism of methanol oxidation on unsupported V_2O_5. We have particularly followed the mechanism of methy-

lal formation by performing transient experiment, exchanging in the reactant feed, CH_3OH to CD_3OD and reversely.

2. Experimental

2.1. Catalysts preparation

Unsupported V_2O_5 was prepared according to the work of Klissurski et al. [20] by decomposition of vanadyl oxalate ($H_2V_2O_2(C_2O_4)_3$). Vanadyl oxalate was prepared by direct dissolution of commercial V_2O_5 (BET surface area less than $2\,m^2/g$) previously calcined at 600°C, in an aqueous solution of oxalic acid (0.24 mol/l). The quantity of V_2O_5 was adjusted (10.9 g/l) according to the stoichiometry of the following reaction:

$$V_2O_5 + 4H_2C_2O_4$$
$$\rightarrow H_2V_2O_2(C_2O_4)_3 + 3H_2O + 2CO_2$$
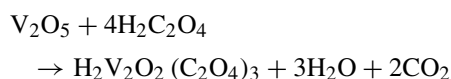
After evaporation of the water and drying, the resulting blue crystallized solid (vanadyl oxalate) was calcined for 3 h, under air at 350°C. We have checked by X-ray diffraction that the clear brown powder obtained after calcination was the V_2O_5 crystallized phase. The BET surface area was measured as $36\,m^2\,g^{-1}$ [20].

2.2. Apparatus

The catalytic methanol oxidation reaction was performed in a conventional fixed-bed flow reactor connected to a mass spectrometer (Anagaz 200, Delsi-Nermag) through a heated stainless steel capillary tube (1.5 m length; internal diameter 0.35 mm) sampling continuously a small part of the exiting reactor flow. This apparatus (see Fig. 1) allows to analyze the flow composition at a maximum frequency of one spectra (1–100 uma range) per second. Additionally, it was possible to analyze the reaction products by an on-line gas chromatographic system [21].

The reactant feed mixture was prepared by using mass flow controllers (Brooks 5850) for oxygen and diluting gas (He or Ar) and a saturator–condenser system for methanol (Aldrich, HPLC grade, purity > 99.9%), in order to ensure a typical composition of $CH_3OH/O_2/Ar = 8.4/15.6/76.0$ (mol%). A second
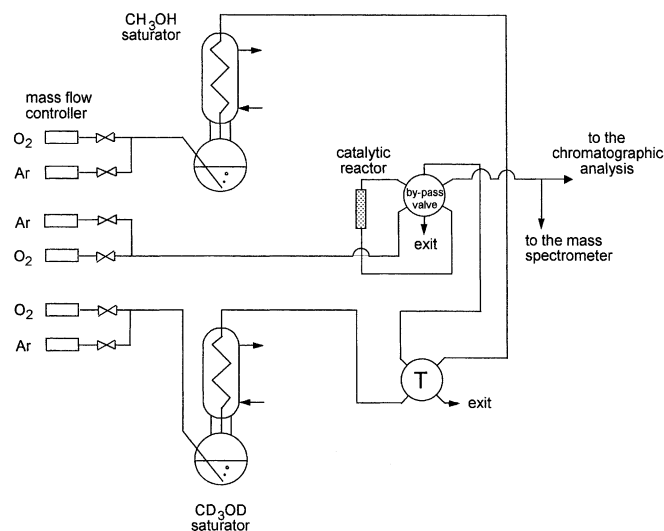
Fig. 1. Apparatus scheme.

line for the reactant feed containing the deuterated methanol (Aldrich, CD_3OD, $D > 99.8$ at.%), identical to the first one, allows to perform isotopic transient experiment by commuting a four ports valve [21].

2.3. Principle of the transient isotopic experiments

A CH_3OH to CD_3OD transition (called $H \rightarrow D$ transition) or CD_3OD to CH_3OH transition (called $D \rightarrow H$ transition) can be performed by rotating the four ports valve T (see Fig. 1). The methanol/O_2/Ar flow is then abruptly replaced by an identical flow (same flow rate and composition) but containing the corresponding deuterated or hydrogenated methanol.

In a $H \rightarrow D$ transition, CH_3OH is rapidly changed by CD_3OD in the gas phase surrounding the catalyst, whereas on the catalyst surface, adsorbed methanol and intermediate species are still present. Thus, during a time depending on the reaction rates and on the amount of adsorbed intermediate species, deuterated and hydrogenated material are in presence, leading to the formation of hydrogenated-deuterated products by consumption of the hydrogenated intermediate species which are replaced by the deuterated ones. The nature, and the localization of the deuterium atoms in the transitory products, are very useful informations to determine the nature and the composition of these intermediate species.

After the hydrogenated species were replaced by the deuterated ones, no more deuterated-hydrogenated products were observed.

2.4. Products identification by mass spectrometry

In the mass spectrometer, methylal $CH_3OCH_2OCH_3$ ($m/e = 76$) is mainly detected as the $CH_3OCH^+OCH_3$ ion ($m/e = 75$) after the loss of one hydrogen atom from the central carbon [22]. Moreover, a fragmentation occurs in the ionization chamber, leading to the formation of $(CH_3OCH_2)^+$ ion ($m/e = 45$), corresponding to the loss of one methoxyl group [22,23]. When methylal is deuterated, the same ionization and fragmentation effects occur. Thus, the methylal will be detected in the 75–82 and 45–50 m/e range, depending on the amount of deuterium atoms present in the molecule. Methyl formate $HCOOCH_3$ and hemimethylal CH_3OCH_2OH can also be formed by the reaction [1,10–12]. Methyl formate is detected as $HCOOCH_3^+$ ion ($m/e = 60$). We can then expect to detect the deuterated species in the 61–64 m/e range.

The ionization of hemimethylal occurs in a similar way than the methylal one, so that the main ion observed is CH_3OCH^+OH ($m/e = 61$) [10–12]. The deuterated hemimethylal are expected to be observed in the 62–66 m/e range.

Table 1
Catalytic behavior of V_2O_5 in methanol (CH_3OH and CD_3OD) oxidation[a,b]

Selectivities (%)

	CH_3OH				CD_3OD					
DME	3.8	5.2	4.9	4.4	10.1	10.8	13.3	13.6	14.1	11.7
F	44.8	51.9	59.0	63.4	13.4	20.2	28.8	33.3	42.9	39.4
MF	3.1	5.7	11.2	15.9	0.6	1.7	4.1	6.9	21.1	26.6
ML	48.2	37.1	23.7	14.4	75.8	67.3	53.4	45.7	20.6	20.7
CO_x	0.1	0.1	1.2	1.9	0.1	0.0	0.4	0.5	1.3	1.5
Overall reaction rate (mmol/h/g)	6.18	5.84	5.28	5.10	2.21	1.83	1.59	1.49	1.46	1.64
Conversion[c] (%)	14.8	18.5	25.1	32.3	8.4	11.6	15.0	17.7	27.8	31.1

[a] T: 185°C; CH_3OH or $CD_3OD/O_2/He = 8.4/15.6/76$ mol%; $m_{cata} = 281$ mg.

[b] DME: dimethyl ether; F: formaldehyde; MF: methyl formate; ML: methylal; CO_x: carbon oxides.

[c] The various conversions are obtained by varying the total flow rate.

3. Results

3.1. Preliminary experiments

Before any isotopic transient experiment, a preliminary kinetic study has been performed, by using CH_3OH or CD_3OD, to determine the catalytic behavior of our V_2O_5 sample in steady-state conditions. The results, expressed relatively to the methanol consumption, are presented in Table 1. As expected from previous studies, the selectivities varies with both the methanol conversion and the nature of the methanol used (CH_3OH or CD_3OD). According to our experiments, the selectivities in formol and methyl formate formation increase with the methanol conversion, at the expense of the methylal one. As expected, a strong kinetic isotopic effect (KIE) was observed, excepted for the dimethyl ether formation. The values of the ratio of the reaction rates (R_H/R_D) presented in Table 2 at isoconversion of the methanol (15, 20, 25 and 30%)

Table 2
Kinetic isotopic effects calculated at isoconversion of the methanol[a]

Conversion (%)	15	20	25	30
$R_{total (CH_3OH)}/R_{total (CD_3OD)}$	3.9	3.9	3.6	3.3
R_{CH_2O}/R_{CD_2O}	6.1	5.7	5.0	5.0
$R_{(CH_3O)_2CH_2}/R_{(CD_3O)_2CD_2}$	3.4	3.3	3.4	2.7
$R_{CH_3OCH_3}/R_{CD_3OCD_3}$	1.2	1.5	1.2	1.2

[a] T: 185°C; CH_3OH or $CD_3OD/O_2/He = 8.4/15.6/76$ mol%.

were calculated from reaction rate values estimated by interpolation of the experimental ones.

3.2. Transient isotopic experiments

3.2.1. H → D transition

The profile of the ionic currents of the ions detected in the methylal m/e domains (75–82 and 45–50) are presented in Figs. 2 and 3, respectively, for a transient
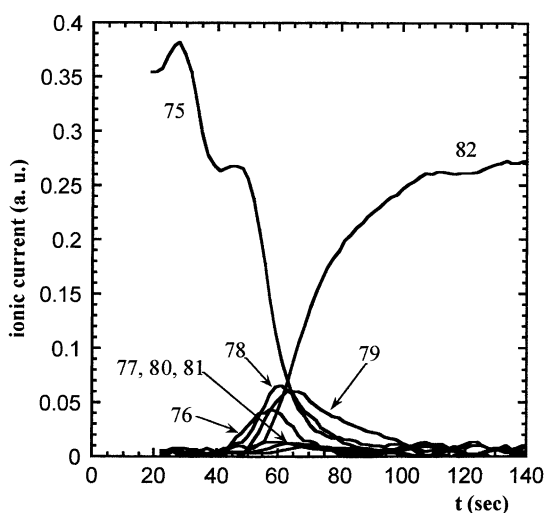

Fig. 2. H → D transition. Ionic current profiles of the methylal characteristic ions, $T = 185$°C; (CH_3OH or CD_3OD)/$O_2He = 8.4/15.6/76$ mol%, main ions: $m/e = 75$: $CH_3OCH_2OCH_3$; $m/e = 76$: $CH_3OCD_2OCH_3$; $m/e = 78$: $CD_3OCH_2OCH_3$; $m/e = 79$: $CD_3OCD_2OCH_3$; $m/e = 82$: $CD_3OCD_2OCD_3$, minor ions: $m/e = 77$, 80 and 81: unassigned ions.
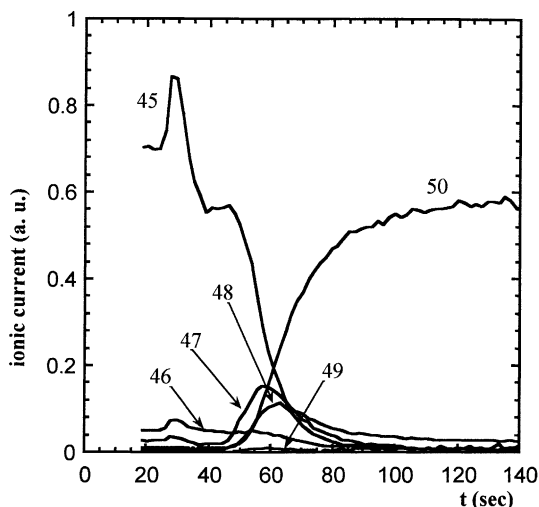
Fig. 3. H $\rightarrow$ D transition. Ionic current profiles of the methylal fragments characteristic ions, $T = 185°C$; (CH$_3$OH or CD$_3$OD)/O$_2$He = 8.4/15.6/76 mol%, $m/e = 45$: CH$_3$OCH$_2^+$; $m/e = 46$: 1 D fragment and CH$_3$OCH$_3^+$ (dimethyl ether); $m/e = 47$: 2 D fragment identified as CH$_3$OCD$_2^+$; $m/e = 48$: 3 D fragment identified as CD$_3$OCH$_2^+$; $m/e = 49$: unassigned 4 D fragment; $m/e = 50$: CD$_3$OCD$_2^+$.

experiment corresponding to the exchange of CH$_3$OH by CD$_3$OD.

As expected, we observed, in function of time, the disappearance of the deuterium-free methylal and the appearance of the fully deuterated one, detected by ions at $m/e = 75$ and 45, and at $m/e = 82$ and 50, respectively. The formation of partially deuterated methylal is evidenced by the transitory presence of ions at $m/e = 76$, 78 and 79, together with fragments at $m/e = 47$ and 48. The fragmentation of the methylals in the mass spectrometer leads to the appearance of ions in the m/e range 45–50, corresponding to the CH$_3$OCH$_2^+$ ion and its homologues variously substituted by deuterium. As shown in the Fig. 3, the almost total absence of the ions CH$_2$DOCH$_2^+$ ($m/e = 46$) and CHD$_2$OCD$_2^+$ ($m/e = 49$) shows that the H–D scrambling on the methyl group is only of minor importance, as already observed for supported catalysts [21,24]. The profile variation of $m/e = 46$ ion is assignable to the presence of dimethyl ether (CH$_3$OCH$_3$; $m/e = 46$) in the reaction products.

Table 3
Key table to identify the various methylals expected to be formed in the transient experiments by assuming no hydrogen–deuterium scrambling

Detected ions (m/e)		Methylal formula
75	45	CH$_3$OCH$_2$OCH$_3$
76	47	CH$_3$OCD$_2$OCH$_3$
78	45, 48	CD$_3$OCH$_2$OCH$_3$
79	47, 50	CD$_3$OCD$_2$OCH$_3$
81	48	CD$_3$OCH$_2$OCD$_3$
82	50	CD$_3$OCD$_2$OCD$_3$

Assuming the absence of hydrogen–deuterium scrambling in C–H bonds, the Table 3 gives a key to identify the different methylals.

We can then assign the presence of the ions at $m/e = 76$ and 47, 78 and 48, and 79 and 47 to CH$_3$OCD$_2$OCH$_3$, CD$_3$OCH$_2$OCH$_3$ and CD$_3$OCD$_2$OCH$_3$, respectively.

In addition, we have also observed the transitory formation of the partially deuterated methanol CD$_3$OH and CH$_3$OD (ions at $m/e = 35$ and 33) due to the fast OH–OD exchange occurring between the deuterated methanol and the surface hydroxyl groups and between deuterated and hydrogenated methanol molecules (Fig. 4):
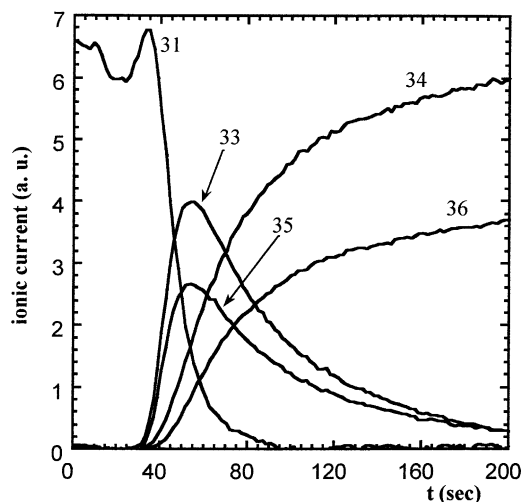

Fig. 4. OH–OD exchange occuring during a H $\rightarrow$ D transition, $T = 185°C$; (CH$_3$OH or CD$_3$OD)/O$_2$He = 8.4/15.6/76 mol% $m/e = 31$: CH$_3$OH (as CH$_2$OH$^+$); $m/e = 33$: CH$_3$OD and CD$_3$OH (as CD$_2$OH$^+$); $m/e = 34$: CD$_3$OD (as CD$_2$OD$^+$); $m/e = 35$: CD$_3$OH; $m/e = 36$: CD$_3$OD.
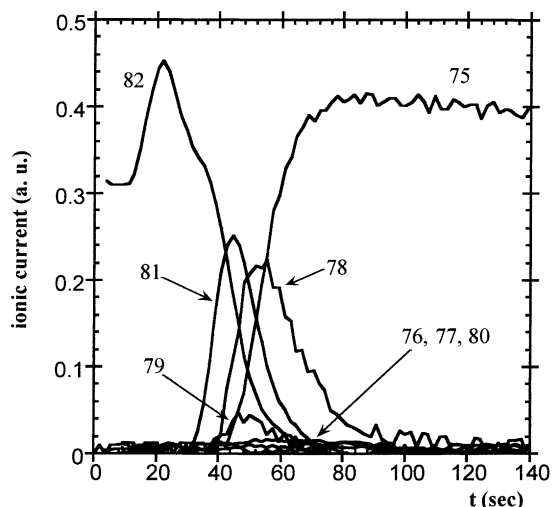
Fig. 5. D → H transition. Ionic current profiles of the methylal characteristic ions, $T = 185°C$; (CH_3OH or CD_3OD)/$O_2He = 8.4/15.6/76\,mol\%$, main ions: $m/e = 75$: $CH_3OCH_2OCH_3$; $m/e = 78$: $CD_3OCH_2OCH_3$; $m/e = 79$: $CD_3OCD_2OCH_3$; $m/e = 81$: $CD_3OCH_2OCD_3$; $m/e = 82$: $CD_3OCD_2OCD_3$, minor ions: $m/e = 76$, 77 and 80: unassigned ions.
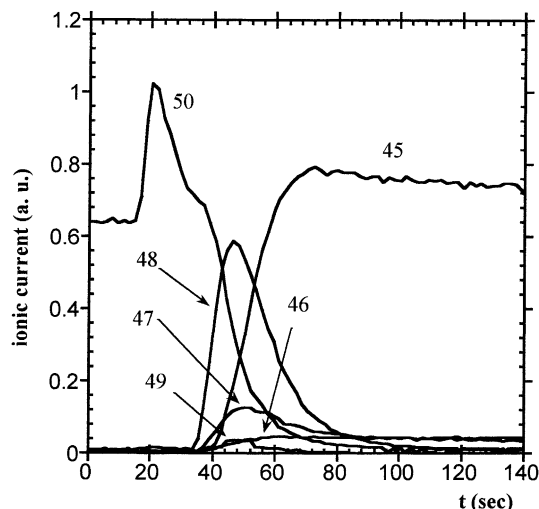
Fig. 6. D → H transition. Ionic current profiles of the characteristic methylal ions fragments, $T = 185°C$; (CH_3OH or CD_3OD)/$O_2He = 8.4/15.6/76\,mol\%$, $m/e = 45$: $CH_3OCH_2^+$; $m/e = 46$: 1 D fragment and $CH_3OCH_3^+$ (dimethyl ether); $m/e = 47$: 2 D fragment identified as $CH_3OCD_2^+$; $m/e = 48$: 3 D fragment identified as $CD_3OCH_2^+$; $m/e = 49$: unassigned 4 D fragment; $m/e = 50$: $CD_3OCD_2^+$.

$$CD_3OD + \overset{OH}{\underset{|}{|}} \rightleftharpoons CD_3OH + \overset{OD}{\underset{|}{|}}$$

$$CD_3OD + CH_3OH \rightleftharpoons CD_3OH + CH_3OD$$
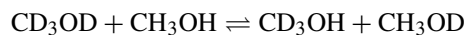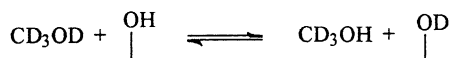
3.2.2. D → H transition

By CD_3OD to CH_3OH exchange, we have observed the same behavior than for the CH_3OH to CD_3OD exchange. The D → H transition is also characterized by the transitory formation of partially deuterated methanol and methylal. The partially deuterated methylals are revealed by ions at $m/e = 78$, 79 and 81

and by the fragments at $m/e = 47$ and 48 (Figs. 5 and 6). As previously shown and according to the Table 3, the presence of ions at $m/e = 78$ and 48, 79 and 47, and 81 and 48 can be assigned to $CD_3OCH_2OCH_3$, $CD_3OCD_2OCH_3$ and $CD_3OCH_2OCD_3$, respectively.

As expected, the three partially deuterated methylals transitory formed by the D → H transition can be deduced from the formula of those obtained by the H → D transition, by replacing H by D and D by H (see Table 4), showing that the mechanism of methylal formation does not change by using deuterated methanol instead of CH_3OH.

Table 4
Partially deuterated methylal, transitory observed during the H → D and D → H exchanges

H → D			D → H		
Formula	Ion	m/e	Formula	Ion	m/e
$CH_3OCD_2OCH_3$	$CH_3OCD^+OCH_3$	76	$CD_3OCH_2OCD_3$	$CD_3OCH^+OCD_3$	81
$CD_3OCH_2OCH_3$	$CD_3OCH^+OCH_3$	78	$CH_3OCD_2OCD_3$	$CH_3OCD^+OCD_3$	79
$CD_3OCD_2OCH_3$	$CD_3OCD^+OCH_3$	79	$CH_3OCH_2OCD_3$	$CH_3OCH^+OCD_3$	78

4. Discussion

The catalytic oxidation of methanol has been widely studied on supported or unsupported oxide catalysts, but only a few number of these studies propose a detailed mechanism for the methylal or methyl formate formation. Depending on the authors, the surface intermediate species involved in the methylal or methyl formate formation are quite different. Nevertheless, almost all of the mechanisms proposed, include as the first step of the reaction, the formation of a surface methoxy group, further oxidatively dehydrogenated into an adsorbed formaldehyde species [13,15,16,25,26] or a dioxomethylene species [8,14]. On these intermediates, the reaction of one molecule of methanol leads to the formation of a hemimethylal species, bonded to the surface ($CH_3OCH_2O–S$) by the oxygen belonging to the previous formaldehyde species [10–12,15,16], or simply adsorbed on the catalyst surface ($CH_3OCH_2OH_{ads}$). This latter product (hemimethylal) was unambiguously detected in the gas phase by Sambeth et al. [10–12] at $m/e = 61$, corresponding to the CH_3OCH^+OH ion. The methylal formation occurs then by the reaction of an other methanol molecule on the bonded or adsorbed hemimethylal. The methyl formate formation is assumed to be formed by oxidative dehydrogenation of the hemimethylal species [27], or by reaction of a methanol molecule on an adsorbed formate which is formed by disproportionation between two dioxomethylene species leading to the formation of a formate and a methoxy group [8,14]. This overall mechanism can be summarized as given in Fig. 7.

In terms of methanol exchange during an isotopic transient experiment, we can thus expect the formation of partly deuterated methylal or methyl formate compounds. According to this mechanism and if we consider the CH_3OH to CD_3OD exchange (H → D transition), we should expect the formation of the partly deuterated methylal $CH_3OCH_2OCD_3$ and $CD_3OCH_2OCD_3$, characterized by ions at $m/e = 78$, 48, 45 and 81, 48, respectively. We can also expect the formation of the partly deuterated methyl formate CD_3OCHO at $m/e = 63$, and the possible presence of partly deuterated hemimethylal (CD_3OCH_2OD and CD_3OCH_2OH) as ions at $m/e = 65$ and 64, this latter products resulting from the reaction of CD_3OH (due to the fast OH–OD exchange occurring between CD_3OD and the OH surface hydroxyl groups) with the expected surface intermediate.

Experimentally, we observe (see Table 4) the formation of the partly deuterated methylal at $m/e = 79, 78$
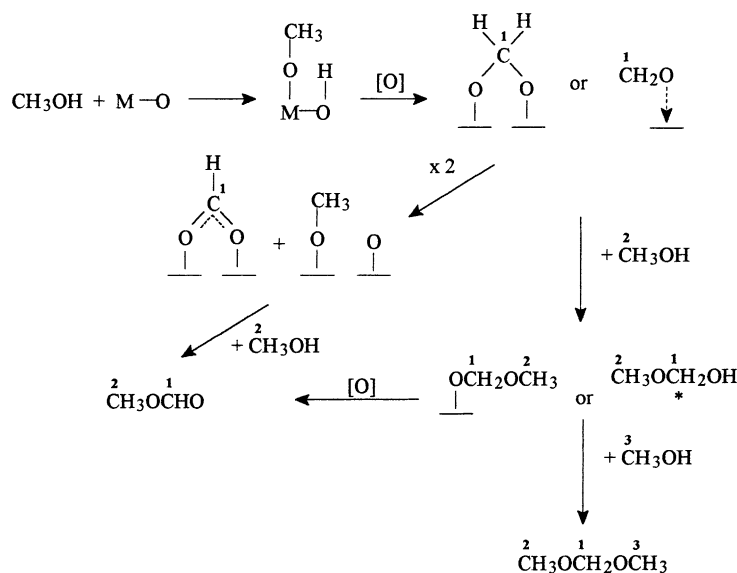

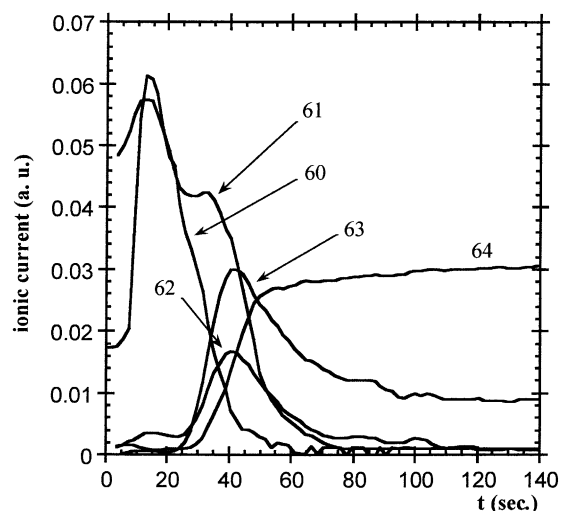Fig. 7. Mechanism of the methylal formation according to the [7,9–11,13–15].

Fig. 8. H $\rightarrow$ D transition. Ionic current profiles of the ions observed in the $m/e = 60$–64 range (methyl formate and hemimethylal domain), $T = 200°C$; (CH$_3$OH or CD$_3$OD)/O$_2$He $= 8.4/15.6/76$ mol%, $m/e = 60$: HCOOCH$_3$ (intensity divided by 10 on the figure); $m/e = 61$: DCOOCH$_3$ and CH$_3$OCH$_2$OH (as CH$_3$OCHOH$^+$); $m/e = 62$: CH$_3$OCD$_2$OH (as CH$_3$OCDOH$^+$) and CH$_3$OCH$_2$OD (as CH$_3$OCHOD$^+$); $m/e = 63$: CH$_3$OCD$_2$OD (as CH$_3$OCDOD$^+$) and HCOOCD$_3$; $m/e = 64$: DCOOCD$_3$.

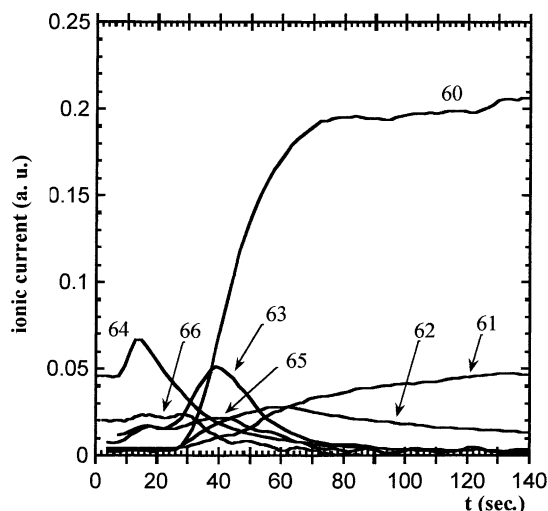Fig. 9. D $\rightarrow$ H transition. Ionic current profiles of the ions observed in the $m/e = 60$–66 range (methyl formate and hemimethylal domain). $T = 200°C$; (CH$_3$OH or CD$_3$OD)/O$_2$He $= 8.4/15.6/76$ mol%, $m/e = 60$: HCOOCH$_3$; $m/e = 61$: DCOOCH$_3$ and CH$_3$OCH$_2$OH (as CH$_3$OCHOH$^+$); $m/e = 62$: CH$_3$OCD$_2$OH (as CH$_3$OCDOH$^+$) and CH$_3$OCH$_2$OD (as CH$_3$OCHOD$^+$); $m/e = 63$: CH$_3$OCD$_2$OD (as CH$_3$OCDOD$^+$) and HCOOCD$_3$; $m/e = 64$: DCOOCD$_3$; $m/e = 65$: CD$_3$OCD$_2$OH (as CD$_3$OCDOH$^+$) and CD$_3$OCH$_2$OD (as CD$_3$OCHOD$^+$); $m/e = 66$: CD$_3$OCD$_2$OD (as CD$_3$OCDOD$^+$).

and 76, which have been assigned to CH$_3$OCD$_2$OCD$_3$, CH$_3$OCH$_2$OCD$_3$ and CH$_3$OCD$_2$OCH$_3$, respectively. Moreover, in the region $m/e = 60$ to 64 corresponding to the partially deuterated methyl formates and hemimethylals, we only observe unambiguously (Fig. 8) the transitory formation of products characterized by ions at $m/e = 62$ and 63 which can be assigned to CH$_3$OCH$_2$OD, CH$_3$OCD$_2$OH ($m/e = 62$) and CH$_3$OCD$_2$OD ($m/e = 63$). The $m/e = 61$ ion current profile seems to result to the contribution of both a decreasing and a transitory product formation during the transient experiment, which can be assignable to the disappearance of CH$_3$OCH$_2$OH, and the transitory formation of CH$_3$OCDO.

For the reverse methanol exchange (CD$_3$OD to CH$_3$OH), the same difference exists between expected and observed deuterated products (expected: CD$_3$OCD$_2$OCH$_3$, ions at $m/e = 79$, 50 and 47; CH$_3$OCD$_2$OCH$_3$, ions at $m/e = 76$ and 47; observed: CD$_3$OCH$_2$OCD$_3$, ions at $m/e = 81$ and 48; CD$_3$OCD$_2$OCH$_3$, ions at $m/e = 79$, 50 and 47;

CD$_3$OCH$_2$OCH$_3$, ions at $m/e = 78$, 48 and 45). In the $m/e = 60$ to 66 region, the formation of transitory products (Fig. 9) is evidenced by the observation of ions at $m/e = 62$, 63 and 65. The almost total absence of a transitory ion at $m/e = 61$, means that the partially deuterated methyl formate CH$_3$OCDO is not extensively formed during this transient experiment, as it could be expected from the mechanism presented in the Fig. 7. All these differences between this mechanism and the experimental observations show that it is unable to describe correctly our experiments.

We should then reinvestigate the possible nature of the intermediate species.

In a H $\rightarrow$ D transition (Fig. 2), the ionic currents of the $m/e = 76$ and $m/e = 78$ ions, pass through a maximum which appears before the maximum of the $m/e = 79$ ion. We can thus deduce that the partly deuterated methylal CH$_3$OCD$_2$OCH$_3$ ($m/e = 76$) and CD$_3$OCH$_2$OCH$_3$ ($m/e = 78$) are fastly formed by the reaction of the deuterated methanol on the surface intermediates species, whereas the methylal
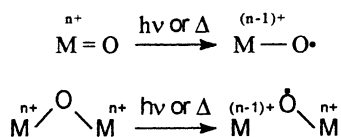
$CD_3OCD_2OCH_3$ ($m/e = 79$) results from surface transformation of the deuterated methanol.

The formation of $CD_3OCH_2OCH_3$ could be easily explained by the reaction of CD_3OD on a deuterium-free hemimethylal species. The formation of hemimethylal as reaction intermediate was already proposed by Sambeth et al. [10–12] and evidenced in our experiments by the decay of the $m/e = 61$ ionic current (CH_3OCH^+OH) immediately after the methanol exchange (Fig. 8).

We can expect that $CH_3OCD_2OCH_3$ is formed by the same mechanism. This hypothesis implies that a partly deuterated hemimethylal species $CH_3OCD_2O(H$ or $D)$ is previously formed on the catalyst surface by reaction between a one carbon intermediate species and the deuterated methanol. It seems then reasonable to identify the one carbon species to a surface methoxy group or a strongly adsorbed form of methanol. On this species, the reaction of a deuterated methanol molecule leads to the formation of the hemimethylal species $CH_3OCD_2O(H$ or $D)$, the methyl group ($CH_3–$) arising from the one carbon surface species, whereas the methylene group ($–CD_2–$) comes from the reacting deuterated methanol molecule.

The nature of the catalytically active site on unsupported V_2O_5 is still controversial, terminal (V=O) [28,29] or bridged (V–O–V) [30–33] oxygen sites have been proposed for H abstraction from the methanol molecule. The V_2O_5 (0 1 0) plane, where both sites are present is generally considered as the more favourable plane for the methanol oxidation [28,29,31,34].

According to Sojka and Che [35], the methanol can be easily activated by an homolytic C–H bond breaking on a metal-oxo (M=O) group. The same activation mechanism can be expected to occur on a bridged oxygen. Under irradiation or by thermal activation, a one electron transfer can occur to the cation, leading to the formation of an oxygen radical species $O^•$ bonded to a partly reduced cation:
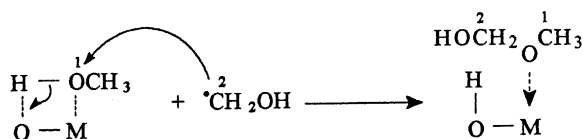
$$M \overset{n+}{=} O \xrightarrow{h\nu\ or\ \Delta} \overset{(n-1)+}{M} — O^•$$

$$\overset{n+}{M} \diagup \overset{O}{} \diagdown \overset{n+}{M} \xrightarrow{h\nu\ or\ \Delta} \overset{(n-1)+}{M} \overset{\overset{•}{O}}{} \diagdown \overset{n+}{M}$$

The reaction of the methanol on such a kind of

site, could lead to the formation of the highly reactive radical species $^•CH_2OH$ [35,36]:

$$\overset{(n-1)+}{M}-O^• + CH_3OH \rightarrow \overset{(n-1)+}{M}-OH + {}^•CH_2OH$$
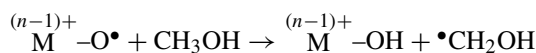
We can then propose that the $^•CH_2OH$ species react with a surface methoxy group or a strongly adsorbed methanol to form the hemimethylal species:

In the transient experiments, if for instance CH_3OH is rapidly changed for CD_3OD, the same mechanism can occur, CD_3OD (or CD_3OH due to the fast OH–OD exchange) is then activated by a C–D bond cleavage to form the radical species $^•CD_2OD$ or $^•CD_2OH$. The reaction of these intermediates with the non-deuterated surface species, leads to the formation of the partly deuterated adsorbed hemimethylal which can desorb as CH_3OCD_2OD (detected at $m/e = 63$) or CH_3OCD_2OH (detected at $m/e = 62$) (Fig. 8) or to be oxidatively dehydrogenated to form the methyl formate CH_3OCDO ($m/e = 61$). The methylal can then be formed by reaction of the hemimethylal intermediate with a surface methoxy group or with an adsorbed methanol. According to this mechanism, at the beginning of the transient, two kinds of deuterium-free species are present at the catalyst surface: methoxy groups and hemimethylal. The deuterated methanol which is just arriving in the gas phase can react on hemimethylal intermediate to form $CH_3OCH_2OCD_3$ (ion at $m/e = 78$), or to be activated as $^•CD_2OD$ (or $^•CD_2OH$), leading to the rapid formation of CH_3OCD_2OD (or CH_3OCD_2OH) and consequently $CH_3OCD_2OCH_3$ (ion at $m/e = 76$) by reaction with the surface methoxy groups. When the hydrogenated surface species are partly replaced by the deuterated ones, $CH_3OCD_2OCD_3$ (characterized by an ion at $m/e = 79$) can be formed by reaction of the partly deuterated hemimethylal ($CH_3OCD_2O(H,D)$) with a deuterated surface methoxy group or by reaction of the fully deuterated hemimethylal with a remaining non-deuterated surface methoxy group.

According to our proposed mechanism, we can expect a primary kinetic isotopic effect during the

steps involving a C–H or a O–H bond breaking. Since no KIE has been found by using CH_3OD instead of CH_3OH [18,19], we can infer that the main effect observed in our experiments comes from a C–H bond breaking which is consistent with the formation of the proposed $^\bullet CH_2OH$ intermediate, this reaction being rate determining. Moreover, if the surface density of the methoxy groups is controlled by the ratio between their formation and their consumption rates, the amount of methoxy groups on the surface must be higher for the reaction with CD_3OD since the $^\bullet CD_2O(D,H)$ intermediates which react with the methoxy groups are produced more slowly than $^\bullet CH_2OH$, due to the kinetic isotopic effect. In the transient experiments, the amount of transitory methylals $CH_3OCD_2OCH_3$ ($m/e = 76$), $CH_3OCD_2OCD_3$ ($m/e = 79$) and $CD_3OCH_2OCD_3$ ($m/e = 81$), $CH_3OCH_2OCD_3$ ($m/e = 78$), formed during a H–D or D–H exchange, respectively, appears as a rough measurement of the amount of methoxy groups present on the catalyst surface just before the transient. By comparing the surface of the peak drawn by the variation with time, during the transient experiment, of the ionic current of the ions 76 and

79 (H–D exchange) and 78 and 81 (D–H exchange), it appears that the amount of methoxy groups was much lower for the reaction with CH_3OH than with CD_3OD, as previously supposed.

During the H–D transition, the $^\bullet CD_2OD$ species formed at the beginning of the transient can react only with the OCH_3 methoxy groups to form the hemimethylal species $CH_3OCD_2O(D,H)$, which further react with an other OCH_3 group to form the methylal $CH_3OCD_2OCH_3$, identifiable by the ion 76. When the surface density of OCD_3 groups increases, the hemimethylal $CH_3OCH_2O(D,H)$ remaining on the surface and the $CH_3OCD_2O(D,H)$ newly formed can also react with these OCD_3 methoxy groups, leading to the formation of $CH_3OCH_2OCD_3$ ($m/e = 78$) and $CH_3OCD_2OCD_3$ ($m/e = 79$), respectively. Finally, the last OCH_3 groups are consumed by the $CD_3OCD_2O(D,H)$ species to form also $CH_3OCD_2OCD_3$ ($m/e = 79$). The position of the maximum of formation of the transitory methylals (see Fig. 2) can then be easily explained by the proposed mechanism and the surface density and the nature (OCH_3 or OCD_3) of the methoxy groups.
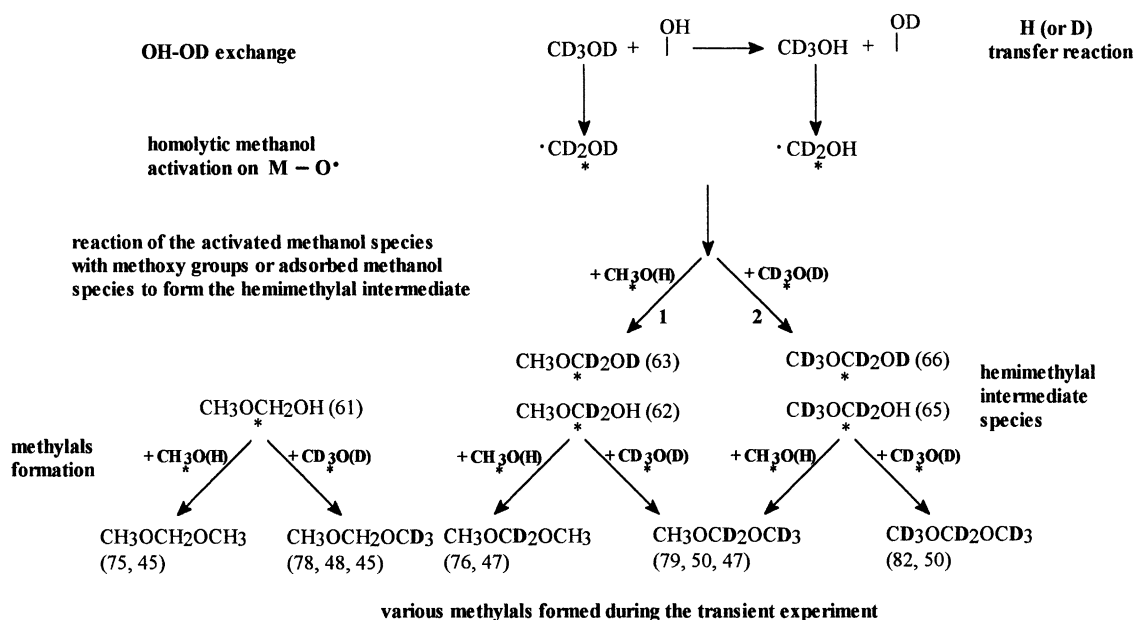

Fig. 10. Mechanism of the methylal formation deduced from our transient experiments.

During the D–H transient, the formation of the partly deuterated products can be explained by the same mechanism, but in this case the high surface density of the methoxy groups OCD_3 and the faster activation (KIE) of $CH_3O(H,D)$ to form the $^\bullet CH_2O(H,D)$ species, highly favor the rapid reaction of $^\bullet CH_2O(H,D)$ with the OCD_3 groups to form $CD_3OCH_2O(H,D)$ which further reacts with an other OCD_3 group to form $CD_3OCH_2OCD_3$ ($m/e = 81$), decreasing rapidly the methoxy groups surface density. As expected for the H–D transient, the remaining $CD_3OCD_2O(D,H)$ species can react with the new OCH_3 groups to form $CD_3OCD_2OCH_3$ ($m/e = 79$), as well as the $CD_3OCH_2O(H,D)$ which form $CD_3OCH_2OCH_3$ ($m/e = 78$). Simultaneously, the $CH_3OCH_2O(H,D)$ species formed from $CH_3O(H,D)$ and the OCH_3 methoxy groups react with the last OCD_3 groups to form also $CD_3OCH_2OCH_3$ ($m/e = 78$).

The low quantity of $CD_3OCD_2OCH_3$ ($m/e = 79$) formed during the D–H transient, which is of the same order of magnitude than the quantity of $CD_3OCH_2OCH_3$ ($m/e = 78$) formed in the H–D transient, means that the amount of hemimethylal species present on the catalyst surface is very low, whatever the nature of the methanol used.

The various products formed during the transient experiments can be then summarized by the mechanistic scheme presented in the Fig. 10.

5. Conclusion

The use of a transient isotopic method to investigate the methanol mild oxidation to methylal on unsupported V_2O_5 has allowed us to precise the reaction mechanism which can be summarized as follows:

1. The methanol reacts with the V_2O_5 surface to form methoxy groups or strongly adsorbed methanol species.
2. The methanol can also react with the V_2O_5 oxidation sites to form a $^\bullet CH_2OH$ species by an homolytic C–H bond breaking.
3. The $^\bullet CH_2OH$ species fastly reacts with the species formed in (1) (methoxy groups or strongly adsorbed methanol species) leading to the formation of hemimethylal (CH_3OCH_2OH) as an intermediate product.
4. The hemimethylal can either be oxidatively dehydrogenated to form the methyl formate (CH_3OCHO) or reacts with the (1) methoxy groups or with an adsorbed methanol species to form the methylal ($CH_3OCH_2OCH_3$).

The hemimethylal appears then as the key intermediate in the methanol oxidation to methylal and methyl formate.

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