

## NOTE

# Oscillatory Behavior during Methanol Oxidation on Mo–Ca–O/SiO<sub>2</sub> Catalyst

We have recently reported on the observation of an oscillatory behavior during mild methanol oxidation on a silica-supported molybdenum catalyst (1). This unusual behavior in mild oxidation on oxide catalysts is nevertheless well known for CO total oxidation on platinum or palladium catalysts (2–5). The oscillatory behavior appears as a periodic or nonperiodic (chaotic) variation in the reaction rate and selectivities, although the external conditions of the reaction (oven reactor temperature, flow rate, and feed composition) are constant. This phenomenon was extensively studied for total oxidation reactions occurring on metallic catalysts (5) and comparatively, only a few number of examples of mild oxidation reaction on oxide catalysts are reported in the literature (6–9). Nevertheless, the diversity of the catalytic reactions showing an oscillatory behavior suggests that this phenomena is rather common in the complex system formed by catalyst, products, and reactants.

We report here on the study of an oscillatory behavior observed during methanol oxidation on a calcium molybdate catalyst supported on silica.

The Mo–Ca–O/SiO<sub>2</sub> catalyst (SiO<sub>2</sub> XOA 400, Rhône-Poulenc) was prepared by two consecutive incipient wetness–calcination procedures as described in Ref. (1). The concentration of the impregnation solution was adjusted in order to obtain a catalyst containing 10 wt% of molybdenum, with a Ca/Mo atomic ratio of 1. Only CaMoO<sub>4</sub> was visible by Raman spectroscopy (10).

A reference catalyst without Ca, but with the same Mo content (10 wt%), was prepared by the same method, the first step being only a wetting of the silica support by pure water.

The catalysts were treated, *in situ*, for 2 h at 450°C under a pure oxygen flow before each measurement.

The catalytic methanol oxidation reaction was performed in a conventional fixed-bed flow reactor which was 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 gases exiting to the reactor, allowing us to monitor the composition of the gases exiting the reactor. Additionally, it was possible to analyze the reaction products by an on-line chromatographic system.

The variations of the catalytic bed temperature were monitored by a thermocouple (chromel–alumel) whose junctions were located inside the catalytic bed and outside the reactor but close to the wall, in order to record directly the temperature difference ( $\Delta T$ ) between the reactor furnace and the catalyst.

The reactant feed mixture was prepared by using mass flow controllers (Brooks 5850) for oxygen and diluent 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<sub>3</sub>OH/O<sub>2</sub>/He, 8.4/15.6/76.0 (mol%). A second line for the reactant feed containing the deuterated methanol (Aldrich, CD<sub>3</sub>OD, D > 99.8 atom%), identical to the first line, allows us to perform an isotopic transient experiment by commuting a four-port valve.

*In situ* infrared experiments were performed in an *in situ* dynamic infrared cell installed on a NICOLET 5SX interferometer sample compartment. A complete description of the cell was given elsewhere (11). This system allows us to record infrared spectra of adsorbed species, in temperature, during the catalytic reaction.

At reaction temperatures close to 250°C we have observed a periodic increase in the intensity of ionic currents corresponding to the reaction products, especially for methyl formate ( $m/e = 60$ ) and CO<sub>2</sub> ( $m/e = 44$ ), whereas oxygen, characterized by  $m/e = 16$  (methanol contributes also to the  $m/e = 32$  ion), presented an opposite trend (Fig. 1). The oscillatory behavior was observed in the temperature range 230–270°C. The influence of the reaction temperature, the feed composition, the catalyst weight, and the total flow rate on the periodicity of the oscillation are presented in Table 1. The period increases slightly with the catalyst weight, whereas it decreases when the oxygen partial pressure and the reaction temperature increase, the latter parameter being predominant. This behavior shows that the oscillation period depends only on the parameters which influence directly the reaction rate, suggesting that the reaction mechanism could be at the origin of the oscillatory behavior.

Selectivities, reaction rate, and conversion have been measured at the lowest and highest parts of the oscillation cycle. The conversion varies from 3.5% at the lowest part to 60% at the upper part of the oscillation cycle, whereas the

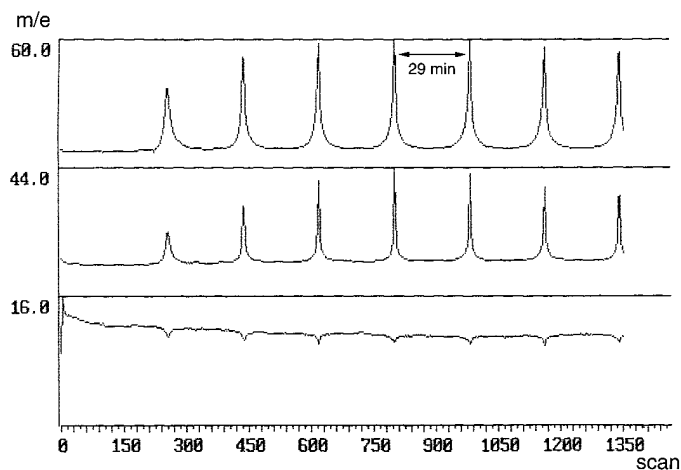


FIG. 1. Variation in function of the number of scans (1 scan = 9.6 s) of the ionic currents for  $m/e = 60$  ( $\text{HCOOCH}_3$ ),  $m/e = 44$  ( $\text{CO}_2$ ), and  $m/e = 16$  ( $\text{O}_2$ ).  $T_R = 250^\circ\text{C}$ ;  $\text{CH}_3\text{OH}/\text{O}_2/\text{Ar} = 8.4/15.3/76.3$  (mol%); 50 mg of catalyst.

methyl formate selectivity increases simultaneously from 23 to 75%. The results are gathered in Table 2 where we have added, for comparison, the results obtained with the  $\text{Mo}/\text{SiO}_2$  reference catalyst ( $\text{Mo} = 10$  wt%).

The temperature of the catalyst was continuously monitored during the reaction. It appears that the catalyst bed temperature increases with the reaction rate when an oscillation occurs (Fig. 2). Nevertheless, it seems that the reaction rate begins to increase before the temperature. The value of the maximum of the difference between the tem-

TABLE 1

Variation of the Oscillation Period (in Minutes) as a Function of the Reaction Conditions

(a)  $P_{\text{CH}_3\text{OH}} = 64$  Torr;  $\text{CH}_3\text{OH}/\text{O}_2/\text{Ar} = 8.4/15.6/76.0$  (mol %); Total Flow Rate ( $Q_T$ ) = 29.5  $\text{cm}^3/\text{min}$

Reaction temperature ( $^\circ\text{C}$ )	Catalyst weight (mg)				
	39	50	60	84	147
230	61	68	66	—	68
240	40	44	46	51	—
250	24	29	30	35	28
260	14	15	17	19	19
270	3	3	9	9	—

(b)  $P_{\text{CH}_3\text{OH}} = 64$  Torr; Catalyst Weight = 147 mg; Reaction Temperature = 260 $^\circ\text{C}$

$P_{\text{O}_2}$ (Torr)	$Q_T$ ( $\text{cm}^3/\text{min}$ )	$\text{O}_2/\text{CH}_3\text{OH}$	Period (min)
161	21.3	2.5	16
116	19.7	1.8	19
116	29.5	1.8	19
63	27	1.0	26

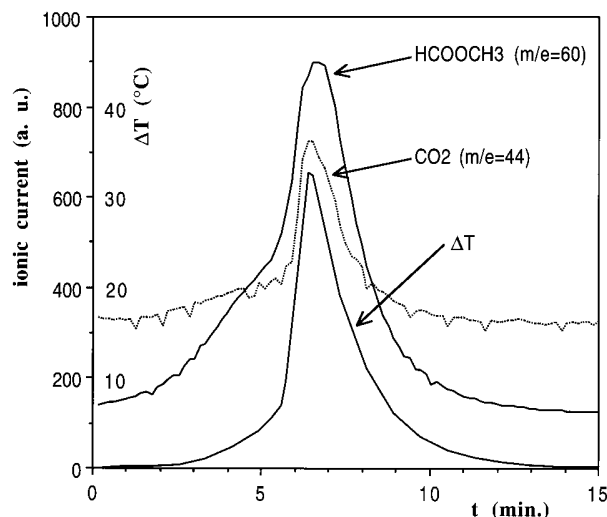


FIG. 2. Temperature and ionic currents profile during an oscillation.  $T_R = 250^\circ\text{C}$ ;  $\text{CH}_3\text{OH}/\text{O}_2/\text{Ar} = 8.4/15.3/76.3$  (mol%); 147 mg of catalyst.

perature furnace and the temperature of the catalyst ( $\Delta T$ ) varies as a function of the catalyst weight and the reaction temperature as shown in Table 3. The variation of the catalyst bed temperature means that a transfer limitation phenomenon, likely due to the exothermicity of the reaction ( $\Delta H_{\text{HCOOCH}_3} = -210$  kJ/mol;  $\Delta H_{\text{CO}_2} = -675.9$  kJ/mol), occurs during the oscillation cycle.

To study the role of heat transfer on the oscillatory behavior, we have performed some additional experiments by using a 2 wt%  $\text{Mo Ca-Mo-O}/\text{SiO}_2$  catalyst ( $\text{Ca}/\text{Mo} = 1$ ) prepared identically to the 10 wt%  $\text{Mo}$  catalyst, and by diluting the 10 wt%  $\text{Mo Ca-Mo-O}/\text{SiO}_2$  catalyst ( $\text{Ca}/\text{Mo} = 1$ ) with an equal weight of silica support. An oscillatory behavior was observed for all of these experiments with, however, some differences from the undiluted  $\text{Ca-Mo-O}/\text{SiO}_2$  (10 wt%  $\text{Mo}$ ) catalyst:

(i) A slight increase in the period was observed for the 2 wt%  $\text{Mo}$  catalyst (21 min instead of 19 min for the 10 wt%  $\text{Mo}$  catalyst;  $T^\circ = 260^\circ\text{C}$ ; catalyst, 84 mg;  $\text{CH}_3\text{OH}/\text{O}_2/\text{Ar}$ , 8.4/16.2/75.4 mol%).

(ii) An increase in the width of the temperature or methyl formate peak profile of the oscillation cycle (about two times higher for the diluted catalyst; see Table 4).

(iii) An increase in the estimated methyl formate amount formed during the high activity part of the oscillation cycle (Table 4), measured by integrating, as a function of time, the methyl formate signal ( $m/e = 60$ ) of the mass spectrometer above the value corresponding to the low catalytic activity part of the oscillation cycle.

Isotopic transient experiments were performed by a fast exchange of the reactant feed containing  $\text{CH}_3\text{OH}$  with that containing deuterated methanol ( $\text{CD}_3\text{OD}$ ), or by the reverse operation, the composition of the reactant feeds and

TABLE 2

Selectivities and Formation Rates Measured at the Highest (Maximum) and Lowest (Minimum) Position of the Oscillation Cycle ( $T = 260^\circ\text{C}$ ;  $m_{\text{catalyst}} = 147$  mg;  $\text{CH}_3\text{OH}/\text{O}_2/\text{Ar} = 8.4/21.1/70.5$  (mol%))

	$\text{HCOOCH}_3$	$\text{CH}_2\text{O}$	$(\text{CH}_3\text{O})_2\text{CH}_2$	$\text{CO}_2$	$\text{CO}$	$\text{CH}_3\text{OCH}_3$
Maximum (conversion = 60%)						
Selectivity (%)	75	6	3	5	11	0.2
Formation rate (mmol/h/g)	14.0	1.2	0.6	1.0	2.0	0.04
Minimum (conversion = 3.5%)						
Selectivity (%)	23	43	27	4	$\epsilon$	3
Formation rate (mmol/h/g)	0.3	0.5	0.3	0.05	$\epsilon$	0.03
$\text{Mo}/\text{SiO}_2^a$ (conversion = 2%)						
Selectivity (%)	65	21	10	3	$\epsilon$	1
Formation rate (mmol/h/g)	5.6	1.8	0.8	0.3	$\epsilon$	0.1

<sup>a</sup>  $\text{Mo}/\text{SiO}_2$ :  $\text{Mo} = 10$  wt%;  $m_{\text{catalyst}} = 10$  mg.

the total flow rates being maintained constant. The mass spectrometer was used to follow the transitory formation of deuterated–hydrogenated products in addition to the replacement–disappearance of methanol. These changes were performed at different places of the oscillation cycle, but the qualitative results were quite identical. The main results are the transitory formation of a mixed deuterated–hydrogenated methyl formate, which is characterized by an  $m/e$  of 63 for  $\text{CH}_3\text{OH}$  to  $\text{CD}_3\text{OD}$  exchange and 61 for  $\text{CD}_3\text{OD}$  to  $\text{CH}_3\text{OH}$  exchange (Fig. 3). These products were identified as  $\text{HCOOCD}_3$  and  $\text{DCOOCH}_3$  for  $m/e = 63$  and 61, respectively. The transitory formation of these products strongly suggests that the methyl formate is formed by the reaction of gaseous methanol on an adsorbed formate intermediate species. Whatever the moment at which the transient experiment exchanging  $\text{CH}_3\text{OH}$  by  $\text{CD}_3\text{OD}$  was started, an oscillation was immediately triggered, whereas no effect occurs when  $\text{CD}_3\text{OD}$  is replaced by  $\text{CH}_3\text{OH}$ . The oscillation after the transient  $\text{CD}_3\text{OD} \rightarrow \text{CH}_3\text{OH}$  starts after about one period delay. During this oscillation, an important formation of  $\text{DCOOCH}_3$  is observed ( $m/e = 61$ ), indicating that deuterated materials are still present on the catalyst surface several minutes after the methanol was changed.

TABLE 3

Variations of the  $\Delta T$  Values as a Function of the Reaction Temperature and the Catalyst Weight

Reaction temperature ( $^\circ\text{C}$ )	Catalyst weight (mg)			
	39	50	60	84
230	—	4	—	5
240	4	8.5	6	57
250	5	27	37	54
260	3	9.4	34	39
270	—	—	7	19

Since the infrared *in situ* apparatus is not equipped for continuous gas analysis, we have used the possibility of triggering an oscillation by changing  $\text{CH}_3\text{OH}$  to  $\text{CD}_3\text{OD}$  to be sure of observing an oscillation. The spectra recorded as a function of time after exchange of hydrogenated methanol ( $\text{CH}_3\text{OH}$ ) with deuterated methanol ( $\text{CD}_3\text{OD}$ ) are presented in Fig. 4. At  $250^\circ\text{C}$ , the methoxy groups are characterized (12) by two main bands in the CH stretching region at  $2860$  and  $2954$   $\text{cm}^{-1}$ , a shoulder being visible at  $2990$   $\text{cm}^{-1}$ . In addition, a weak band corresponding to the CH angle deformation ( $\delta\text{CH}_3$ ) appears at  $1460$   $\text{cm}^{-1}$ . These bands are characteristic of methoxy groups on silica (12–14). As soon as the reactant feed is changed, the IR bands corresponding to  $\text{Si}-\text{OCH}_3$  begin to decrease, whereas  $\text{Si}-\text{OCD}_3$  bands grow. Simultaneously, the exchange of OH surface groups ( $\nu \text{OH} = 3500\text{--}3770$   $\text{cm}^{-1}$ ) with surface OD groups ( $\nu \text{OD} = 2600\text{--}2780$   $\text{cm}^{-1}$ ) occurs. After about 15 min of contact with the reactant feed containing  $\text{CD}_3\text{OD}$ ,

TABLE 4

Effect of Catalyst ( $\text{Ca}-\text{Mo}-\text{O}/\text{SiO}_2$ ; 10 wt% Mo) Dilution by Pure Silica on the Oscillation Parameters ( $T = 260^\circ\text{C}$ ;  $\text{CH}_3\text{OH}/\text{O}_2/\text{Ar} = 8.4/19.3/70.5$  (mol %))

Catalyst	Period (min)	$\Delta T$ ( $^\circ\text{C}$ )	$t_{1/2}\Delta T^a$ (s)	$t_{1/2}^b$ (s)	Amount $\text{HCOOCH}_3^c$ (a.u.)
Undiluted 50 mg	14.4	34	30	42	33710
Diluted 50 mg catalyst + 50 mg $\text{SiO}_2$	15.4	27	52	66	58840

<sup>a</sup> Half-height width of the catalyst temperature oscillation peak.

<sup>b</sup> Half-height width of  $m/e = 60$  signal of the mass spectrometer oscillation peak.

<sup>c</sup> Estimated amount (arbitrary units) of  $\text{HCOOCH}_3$  formed during the high catalytic activity part (oscillation peak) of the oscillation cycle, obtained by integrating the  $m/e = 60$  signal.

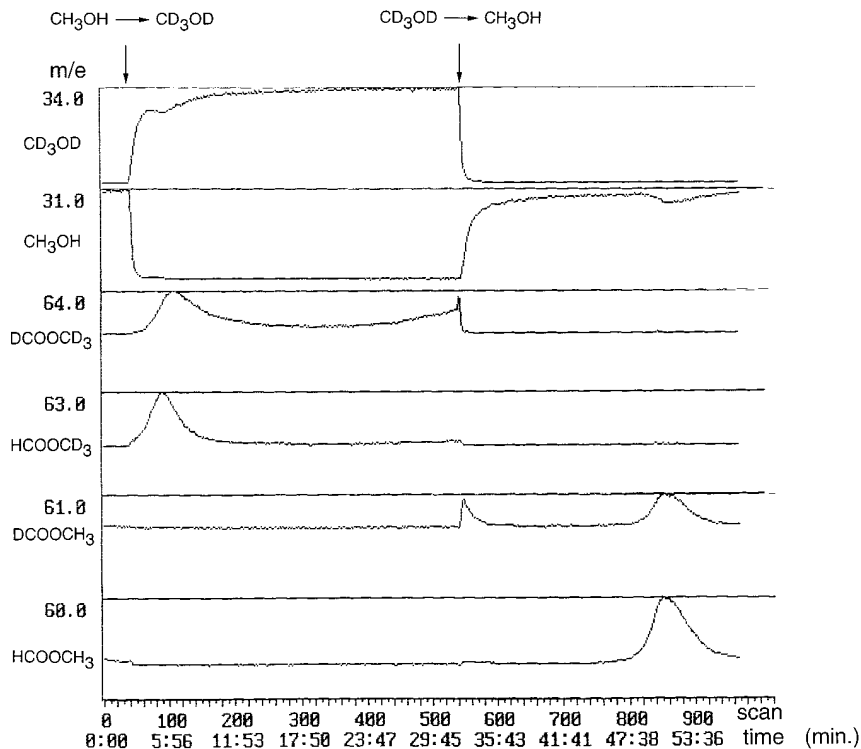


FIG. 3. Isotopic transient experiment: exchange  $\text{CH}_3\text{OH} \rightarrow \text{CD}_3\text{OD}$  and  $\text{CD}_3\text{OD} \rightarrow \text{CH}_3\text{OH}$ .  $T_R = 250^\circ\text{C}$ ;  $\text{CH}_3\text{OH}/\text{O}_2/\text{Ar} = 8.4/15.3/76.3$  (mol%); 50 mg of catalyst.

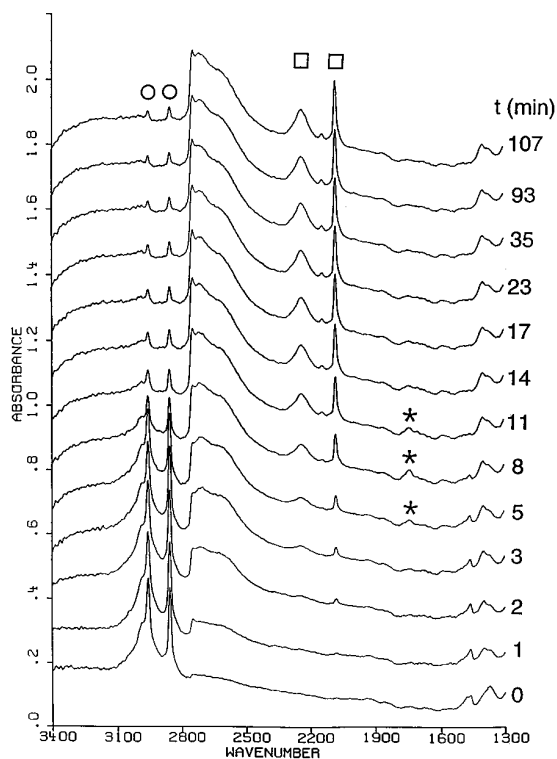


FIG. 4. IR *in situ* (difference spectra) as a function of time (min) after the exchange  $\text{CH}_3\text{OH} \rightarrow \text{CD}_3\text{OD}$ .  $T_R = 250^\circ\text{C}$ . O,  $\text{SiOCH}_3$ ; □,  $\text{SiOCD}_3$ ; \*,  $\text{SiOOCH}$ .

the IR spectra do not show important modifications and can be assigned to  $\text{Si-OCD}_3$  species, with trace amounts of  $\text{Si-OCH}_3$  which slowly decrease. The deuterated methoxy groups on silica are characterized (12) by three main bands at  $2080\text{ cm}^{-1}$  (intense and sharp),  $2145\text{ cm}^{-1}$  (weak), and  $2244\text{ cm}^{-1}$  (broad), assigned to CD stretching vibrations ( $\nu$  CD).

The main result, in addition to the decrease of  $\text{Si-OCH}_3$  and  $\text{Si-OH}$  bands and the increase of  $\text{Si-OCD}_3$  and  $\text{Si-OD}$  bands, is the transitory appearance of a small band in the  $1740\text{ cm}^{-1}$  region, assigned to a monodentate formate adsorbed on silica ( $\text{HCOO-Si}$ ) (13), whose maximum is observed about 10 min after the beginning of the methanol exchange. This band is clearly visible after subtraction of the spectrum of the catalyst alone (Fig. 4), its growth and decrease corresponding to an oscillation. No bands were observed that corresponded to mixed hydrogenated deuterated species on the catalyst surface ( $-\text{OCHD}_2$  or  $-\text{OCH}_2\text{D}$ ).

The reverse transient experiment was performed by changing  $\text{CD}_3\text{OD}$  to  $\text{CH}_3\text{OH}$  after 110 min on stream under the reactant feed containing  $\text{CD}_3\text{OD}$ . After this time on stream, hydrogenated methoxy groups were almost completely exchanged with the deuterated methoxy groups as determined by the low intensity of residual bands at  $2860$  and  $2960\text{ cm}^{-1}$  (Fig. 5). As observed in the catalytic test experiments, this change does not trigger any oscillation. Only methoxy and hydroxy exchanges are visible by IR *in situ*.

A rough determination of the quantity of the carbonaceous species adsorbed on the catalyst surface can be done by recording the maximum reached by the temperature ( $\Delta T$ ) measured by our *in situ* thermocouple system, when these species are quickly oxidized in  $\text{CO}_2$ , by pure oxygen, at the temperature of the reaction. The measurements were performed at different given times of the oscillation cycle, after an Ar purge (30 s), in order to eliminate gaseous and slightly physisorbed methanol. We can then expect that the  $\Delta T$  values are roughly proportional to the quantity of carbonaceous species transformed into  $\text{CO}_2$ , as in thermal analysis experiments (DTA or DSC). The results are reported in Fig. 6, where we have also drawn an oscillation profile on which we have indicated the position of the carbonaceous species measurement (filled circle). The quantity of surface carbonaceous species quickly decreases when the oscillation starts, the replenishment of the surface species occurring slowly until another oscillation starts.

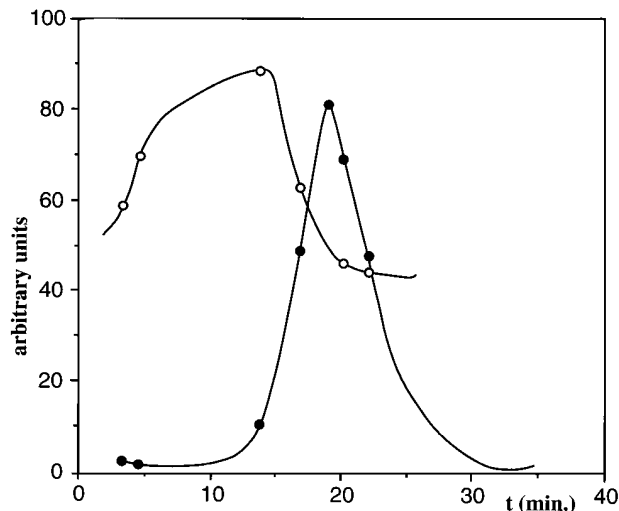


FIG. 6. Estimation by thermal analysis of the quantity of carbonaceous species at different positions of the oscillation cycle (O) and temperature profile during an oscillation (●).  $T_R = 250^\circ\text{C}$ ; 50 mg of catalyst.

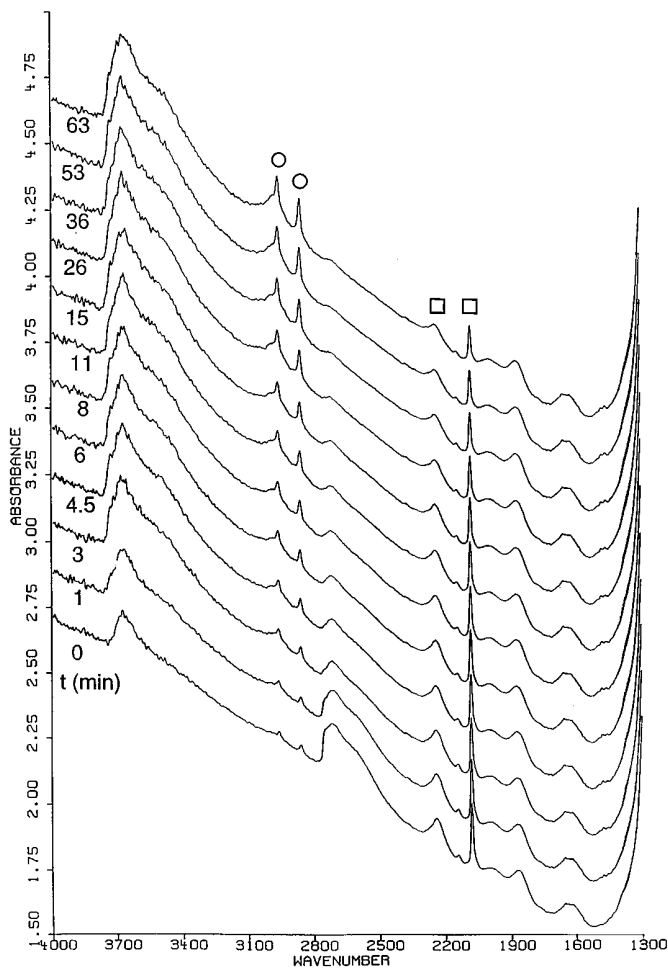
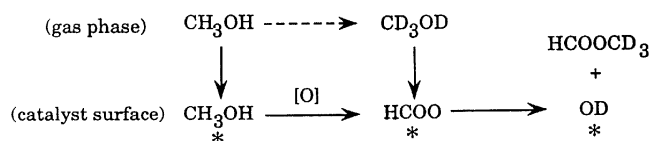


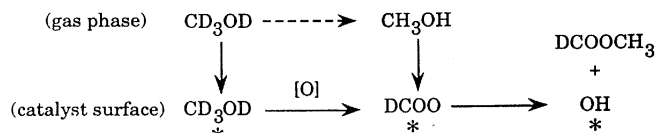
FIG. 5. IR *in situ* as a function of time (min) after the exchange  $\text{CD}_3\text{OD} \rightarrow \text{CH}_3\text{OH}$ .  $T_R = 250^\circ\text{C}$ . O,  $\text{SiOCH}_3$ ; □,  $\text{SiOCD}_3$ .

From transient experiments we can deduce that the methyl formate is formed by the reaction of gaseous methanol on an adsorbed surface formate ( $\text{HCOO}^-$ ) or formic acid ( $\text{HCOOH}$ ), as proposed for V-Ti-O catalysts (15, 16). During the transient experiment, the methanol was replaced faster by its isotopic homologue in the gas phase than on the surface where previously adsorbed forms of methanol are still present. These species can be oxidized, and they will desorb as formaldehyde or carbon oxides or react with gaseous methanol to form a deuterated-hydrogenated methyl formate. We can then propose the following mechanism for the methyl formate formation:

Exchange  $\text{CH}_3\text{OH} \rightarrow \text{CD}_3\text{OD}$



Exchange  $\text{CD}_3\text{OD} \rightarrow \text{CH}_3\text{OH}$



This reaction scheme is different to the mechanism proposed by Louis *et al.* (17) on the basis of kinetic considerations on a highly dispersed Mo/ $\text{SiO}_2$  catalyst, but both the nature of the active phase (highly dispersed Mo species or  $\text{CaMoO}_4$ ) and the molybdenum amount (less than 1 or 10%) which are different between Mo/ $\text{SiO}_2$  and our Mo-Ca-O/ $\text{SiO}_2$  catalyst could explain the discrepancies between the two proposed mechanisms. The mechanism of the oscillation appears to be more complicated, although the

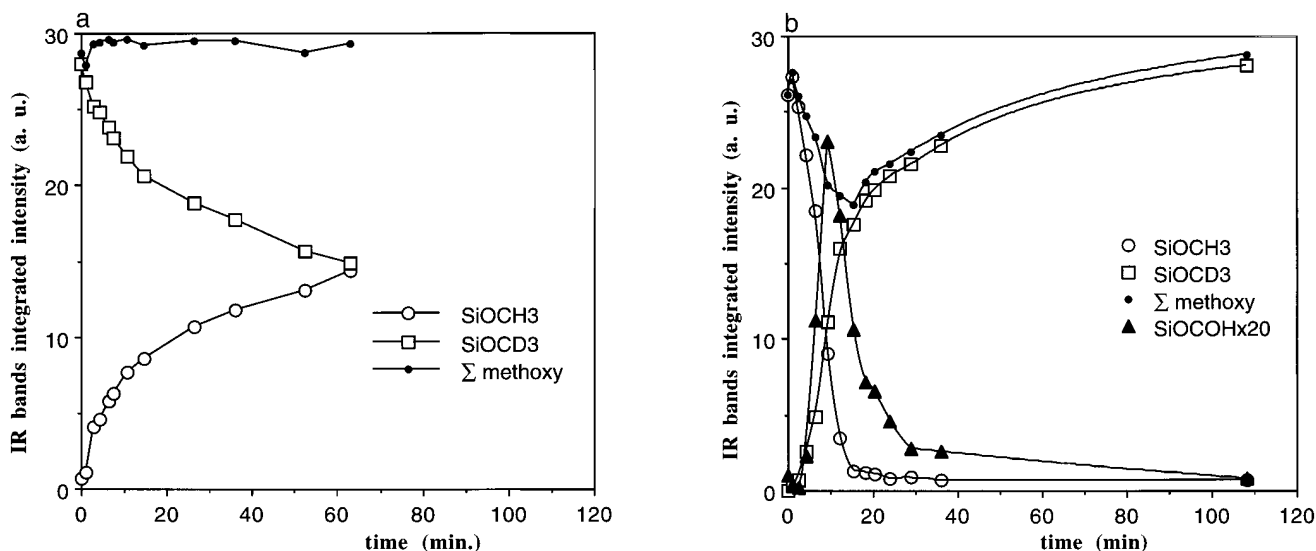


FIG. 7. (a) Variations of the amount of  $SiOCH_3$  ( $\circ$ );  $SiOCD_3$  ( $\square$ ), and the total amount of methoxy groups ( $\bullet$ ), as a function of time, after the exchange  $CD_3OD \rightarrow CH_3OH$  ( $T_R = 250^\circ C$ ). (b) Variations of the amount of  $SiOCH_3$  ( $\circ$ ),  $SiOCD_3$  ( $\square$ ),  $SiOCOHx20$  ( $\blacktriangle$ ), and the total amount of methoxy groups ( $\bullet$ ), as a function of time, after the exchange  $CH_3OH \rightarrow CD_3OD$  ( $T_R = 250^\circ C$ ).

methyl formate is also formed by direct reaction of gaseous methanol on a surface formate species.

Let us consider the quantitative results relative to methoxy groups ( $OCH_3$  and  $OCD_3$ ) in Figs. 4 and 5 obtained by integration of the  $\nu(CH_3)$  bands (between 3100 and 2780  $cm^{-1}$ ) and  $\nu(CD_3)$  bands (between 2320 and 2000  $cm^{-1}$ ) by assuming a  $I^\nu CH_3/I^\nu CD_3$  close to 2 (18), as verified. In Fig. 7a, it appears that the total amount of methoxy groups does not change when substituting  $CD_3OD$  with  $CH_3OH$ . However, the  $OCD_3 \rightarrow OCH_3$  exchange is slow, deuterated methoxy being still predominant even 1 h after the methanol exchange. This is in agreement with the transient isotopic experiments results which reveal the appearance of  $DCOOCH_3$  during the first oscillation after the  $CD_3OD \rightarrow CH_3OH$  exchange. Integration of the intensity of methoxy bands ( $OCH_3$  and  $OCD_3$ ) after  $CH_3OH \rightarrow CD_3OD$  alcohol exchange shows (Fig. 7b) that the total quantity of the surface methoxy groups rapidly decreases, simultaneously with the increase of the amount of the surface formate species, transitory detected by IR. This observation is in agreement with the results reported in Fig. 6 which shows that the quantity of carbonaceous species (mainly methoxy species) decreases during the oscillation.

Knowing from IR results that formate species on silica, formed by direct oxidation of silica surface methoxy groups, quickly react with gaseous methanol to form methyl formate, we can propose that the methyl formate observed during the oscillation paroxysm is formed by the reaction of the formate species (transitory observable by IR) with gaseous methanol. The simultaneous decrease of the amount of methoxy groups on silica strongly suggests that

these formate species were formed by the oxidation of the silica surface methoxy groups. This hypothesis is fully consistent with the difference in the rate of exchange of methoxy groups observed by IR during the transient experiments. When  $CD_3OD$  replaces  $CH_3OH$ , the amount of hydrogenated methoxy groups decreases abruptly 5 min after the exchange, while formate species begin to appear. Fifteen minutes after the exchange only less than 5% of the initial amount of methoxy groups are still present on the surface, but not all of the disappeared methoxy groups are replaced by deuterated methoxy groups, 35% of the methoxy groups being missing, as shown in Fig. 7b. By contrast, when  $CH_3OH$  replaces  $CD_3OD$ , more than 50% of the deuterated methoxy groups are still present 63 min after the exchange, the total amount of methoxy groups not showing any significant variation. This difference in the exchange rate is easily explained by the postulated mechanism of the oscillation. During the oscillation started by the exchange  $CH_3OH \rightarrow CD_3OD$ , the methoxy groups are rapidly oxidized into formate species which are quickly esterified by the gas phase methanol to form a methyl formate molecule and an hydroxy group on the silica surface, leading to a decrease in the total methoxy amount. For the reverse exchange ( $CD_3OD \rightarrow CH_3OH$ ), an oscillation is not started and the methoxy exchange occurs more slowly without changes in the total methoxy amount.

We have not observed any oscillatory behavior on pure silica, showing that the active phase ( $CaMoO_4$ ) plays a major role (1, 10). Nevertheless, two important questions remain unanswered: how are the methoxy groups on silica oxidized into formate species and why does this rapid oxidation start?

By assuming an activation energy of the catalytic methanol oxidation of about 85 kJ/mol, as reported by many authors (19), we can estimate an increase of the formation rate caused by temperature growth during oscillation. For a  $\Delta T$  of 40°C at 260°C, the reaction rate appears to be multiplied by a factor of 4, showing that the oscillation phenomenon affects only the formate formation (multiplied by a factor of 47), the carbon oxides being partly formed by the formate decomposition.

The temperature increase could play the role of synchronization factor, triggering an increase in the reaction rate, from place to place until it affects all the catalyst (5), a heat front moving through the catalyst bed, as demonstrated by Sant and Wolf (20, 21) for CO oxidation on a Pt/Al<sub>2</sub>O<sub>3</sub> catalyst.

The experimental data (Table 4) obtained by diluting the catalyst with silica and with the 2 wt% Mo catalyst seem to show that the heat transfer phenomena are not at the origin of the oscillation behavior. The period appears to be on the same order of magnitude whatever the ratio between active phase and support is (obtained by diluting with pure silica or by a lower amount of active phase on the support). Moreover, the larger width of the methyl formate (or temperature) peak observed for the diluted catalyst, while the maximum is about the same for the undiluted catalyst, and the larger amount of methyl formate formed by oscillation (the amount is multiplied by a factor of 1.75 when 50 mg of catalyst are diluted by 50 mg of pure silica) are fully consistent with the proposed mechanism which supposes that the methyl formate formed during the oscillation originates from the methoxy groups on the silica surface.

In summary, by following continuously the composition of the feed exiting a catalytic reactor, we have observed an oscillatory behavior in the reaction of methanol oxidation. This unusual behavior in such a type of reaction seems to concern only the methyl formate formation, the increase of the formation rate of the other reaction products being possibly due to the increase of the catalyst bed temperature observed simultaneously with the growth of the reaction rate. The mechanism of the oscillation was investigated by the combination of various *in situ* techniques (transient isotopic experiments, IR of adsorbed species under the reaction conditions). The results indicate clearly that the methyl formate is formed by the fast reaction of the gas phase methanol with a formate species issuing from the oxidation of the silica surface methoxy groups. The variation of the catalyst bed temperature amplifies these phenomena and could play the role of synchronization factor. The study of the mechanism which starts the oscillation behavior is in progress.

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