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Catalytic Properties of Silica-Supported Molybdenum Catalysts in Methanol Oxidation: The Influence of Molybdenum Dispersion

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Two types of Mo/SiO_2 catalysts prepared by classical impregnation or by the grafting method have been tested in the methanol oxidation reaction, which is known to be structure sensitive. It is shown that there is a dependence of the formation of formaldehyde and methyl formate, the principal products, on the molybdenum content for grafted catalysts with a higher selectivity for methyl formate. In contrast, the dependence is not clear for the impregnated catalysts, and this appears to be due to the lack of reproducibility in their preparation, and to their Mo dispersion being lower than that of the grafted Mo/SiO_2 catalysts. The study of the formation of methyl formate using different reactive mixtures and kinetic calculations led us to propose a mechanism which involves the formation of formaldehyde from methanol on Mo sites, followed by its migration on silica, where it further reacts with methoxy groups to form methyl formate via a hemiacetal intermediate.

INTRODUCTION

The concept of structure sensitivity, well known for metal catalysts, has been recently extended to oxide catalysts (*1–3*). For example, in the case of methanol oxidation on MoO_3, Tatibouët *et al.* (*3–6*) have found that the (010) face of MoO_3 is highly selective for the formation of formaldehyde, whereas the (100) face leads to methylal. This indicates that the selectivity depends on the environment of the molybdenum ion, i.e., on its coordination sphere and on interactions between neighboring molybdenum ions.

In previous work, we have investigated the controlled preparation of Mo/SiO_2 catalysts in order to obtain highly dispersed molybdenum and achieve strong Mo–silica interactions so that the molybdenum dispersion can be maintained during further thermal activation. The catalysts were prepared by the grafting method, which consists of reacting $MoCl_5$ with silica silanol groups. Extensive studies of catalyst characterization confirmed that the expectations had been fulfilled (*7–15a,b*).

It was thus interesting to investigate whether a structure-sensitive reaction such as methanol oxidation (*1–6*) could be influenced by the dispersion of molybdenum. This has been performed by comparing Mo/SiO_2 grafted samples with highly dispersed molybdenum to impregnated samples with lower molybdenum dispersion.

EXPERIMENTAL

Preparation of the Catalysts

The impregnated samples were prepared from an aqueous solution of ammonium heptamolybdate put in contact with silica. The samples were then dried in air at about 80°C with continuous stirring and calcined in oxygen overnight at 500°C.

The grafted catalysts were obtained by reacting $MoCl_5$ either in an organic medium (*7–9*) or in the gas phase (*8, 9, 11, 12*) with silica silanol groups in strict air- and water-free conditions. After reaction, the samples

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TABLE 1

Molybdenum Content of Mo/SiO$_2$ Catalysts

Mo/SiO$_2$	Grafted[a]	Impregnated
Mo content (weight%)	0.07–0.18–0.66–1.05	0.07–0.17–0.63–0.72

[a] A chemical analysis was also performed to detect chlorine after pretreatment in a flow of oxygen at 420°C for 6 h, but no trace of this element was found.

which were brown-orange turned blue in air, indicative of a transformation into molybdenum blues, e.g., molybdenum hydroxides with mixed Mo^{5+}–Mo^{6+} valences, as shown by reflectance spectroscopy (*7–9, 11*). Washing with water or ammonia solution eliminates the loosely bound molybdenum, i.e., the molybdenum blues, and hydrolyzes the chlorides belonging to grafted molybdenum. At the same time, the samples turned brown, which is characteristic of grafted samples (*7, 9*).

The Mo contents of the tested catalysts are given in Table 1.

The silica spherosil XOA 400 (400 m^2/g) supplied by Rhône Poulenc (France) was used as a support. $MoCl_5$ was supplied by Merck (West Germany).

Catalytic Reaction

The catalytic reaction was carried out in an isothermal fixed-bed microreactor under different conditions of atmospheric pressure, between 230 and 280°C, with a mixture of methanol, oxygen, and helium in the ratio 7/19/74 (molar%).

The reactor, a Pyrex tube with an internal diameter of 4 mm, contains the catalyst held between two layers of quartz wool. In this vertical reactor, the gas mixture flows through the catalyst bed from top to bottom.

A line gas chromatographic analysis (FID and TCD) was used to determine the composition of the feed and reaction products. Measurements were performed in the stationary state and at low conversions (<5%). The products thus refer to initial values calculated as the number of moles of ethanol converted.

Before the reaction, the samples are pretreated in a flow of oxygen at 420°C for 6 h. An 8- to 20-mg quantity of catalysts is used to obtain conversions lower than 5%. A blank experiment performed in the absence of catalysts did not lead to any conversion.

TABLE 2

Catalytic Properties[a] of Grafted Mo/SiO$_2$ Samples in Methanol Oxidation ($CH_3OH/O_2/He$)

	Silica XOA 400		Grafted Mo/SiO$_2$ samples											
	wt% Mo		wt% Mo											
	0		0.07			0.18			0.66			1.05		
	T (°C)		T (°C)			T (°C)			T (°C)			T (°C)		
	230	260	230	260	280	230	260	280	230	260	280	230	273	294
A_{CO_2}	0.074	0.11	0.112	0.435	0.920	0.068	0.360	0.84	0.051	0.406	1.08	0.468	0.613	0.926
$A_{CH_3OCH_3}$	0.029	0.07	0.035	0.103	0.179	0.032	0.134	0.243	0.071	0.219	0.378	0.175	0.436	0.704
A_{CH_2O}	—	—	—	—	—	—	—	—	—	0.96	2.32	—	1.70	3.55
A_{HCOOCH_3}	0.09	0.36	3.21	7.44	11.83	4.03	11.48	18.07	6.05	12.98	18.59	5.91	19.07	28.43
A_{DHG}	0.05	0.18	1.61	3.72	5.92	2.02	5.74	9.04	3.03	7.45	11.62	2.96	11.24	17.77
$A_T = \Sigma A_x$	0.193	0.54	3.36	7.98	12.93	4.13	11.97	19.15	6.17	14.56	22.37	6.55	21.82	33.67
S_{CO_2}	38.8	25.6	3.3	5.5	7.1	1.6	3.0	4.4	0.9	2.8	4.8	7.1	2.8	2.9
$S_{CH_3OCH_3}$	15.1	16.1	1.0	1.3	1.4	0.8	1.1	1.3	1.1	1.5	1.7	2.7	2.0	2.1
S_{CH_2O}	—	—	—	—	—	—	—	—	—	6.6	10.4	—	7.8	10.5
S_{HCOOCH_3}	46.1	58.3	95.7	93.2	91.5	97.6	95.9	94.3	98	89.1	83.1	90.2	87.4	84.4

[a] The activities A_x are expressed in mol h^{-1} (g of catalyst)$^{-1}$ × 10^3; the selectivities S_x are expressed in percentages.

TABLE 3

Catalytic Properties[a] of Impregnated Mo/SiO$_2$ Samples in Methanol Oxidation (CH$_3$OH/O$_2$/He)

	wt% Mo											
	0.07			0.17			0.63			0.72		
	T (°C)			T (°C)			T (°C)			T (°C)		
	230	260	280	230	260	280	243	273	294	230	260	280
A_{CO_2}	0.265	0.856	2.087	1.809	3.697	6.08	0.052	1.60	2.0	0.121	0.446	0.764
$A_{CH_3OCH_3}$	0.077	0.028	0.372	0.029	0.166	0.26	0.085	0.200	0.391	—	—	—
A_{CH_2O}	—	1.29	4.52	9.47	19.17	27.15	0.53	8.0	10.5	1.125	3.53	4.62
A_{HCOOCH_3}	2.77	7.16	12.09	1.885	12.33	18.13	6.86	18.8	34.2	0.32	4.22	7.60
A_{DHG}	1.39	4.87	10.57	10.41	25.34	36.22	3.96	17.40	27.60	1.29	5.64	8.42
$A_T = \Sigma A_x$	3.04	9.33	18.73	13.2	35.36	51.62	7.53	28.6	47.09	1.57	8.20	12.98
S_{CO_2}	8.7	9.2	11.2	13.7	10.4	11.8	0.7	5.6	4.2	7.7	5.5	5.9
$S_{CH_3OCH_3}$	0.3	0.3	0.2	0.2	0.5	0.5	1.1	0.7	0.8	—	—	—
S_{CH_2O}	—	13.8	24.1	71.8	54.2	52.6	7.1	28.0	22.4	72.0	43.0	35.0
S_{HCOOCH_3}	91.0	76.7	64.5	14.3	34.9	35.1	91.1	65.7	72.6	20.3	51.5	58.5

[a] The activities A_x are expressed in mol h^{-1} (g of catalyst)$^{-1}$ × 10^3; the selectivities S_x are expressed in percentages.

RESULTS AND DISCUSSION

For all the samples tested, the stationary state is reached within an interval of 0.5–1 h. This time depends neither on the amount of molybdenum nor on the preparation method. The experimental results (activities and selectivities) obtained with the grafted and impregnated Mo/SiO$_2$ samples in the stationary state are presented in Tables 2 and 3, respectively, which indicate that the reaction produces methyl formate (HCOOCH$_3$), formaldehyde (CH$_2$O), carbon dioxide, and dimethyl ether ((CH$_3$)$_2$O). Dimethoxymethane ((CH$_3$O)$_2$CH$_2$) is not mentioned in Tables 2 and 3 since only traces of it are detected.

Figure 1 shows the activities in formaldehyde and methyl formate versus Mo content for the two types of samples. In this figure, the experimental values obtained at 243, 273, and 294°C have been corrected from Arrhenius plots to values at 230, 260, and 280°C for grafted and impregnated samples with molybdenum contents of 1.05 and 0.63 wt%, respectively (Table 4). The apparent activation energies calculated from Arrhenius plots are equal to 15.5–13.1 kcal mol^{-1} for grafted Mo/SiO$_2$ and 22.0–23.0 kcal mol^{-1} for impregnated Mo/SiO$_2$.

The results clearly indicate that there is a dependence of the formation of formaldehyde and methyl formate, the principal products, on the molybdenum content for grafted catalysts with a higher selectivity for methyl formate (Fig. 1a). By contrast, the dependence is not clear for the impregnated catalysts (Fig. 1b). It must be stressed that the scattering of the points for the latter samples is fully reproducible, since each catalytic experiment was repeated several times, leading to the same result within experimental error (0.03 mol h^{-1} g^{-1} × 10^3). It can thus be inferred that the scattering of the points is due to the

TABLE 4

Activity Values Extrapolated from Arrhenius Plots

	Impregnated 0.63 Mo wt%			Grafted 1.05 Mo wt%		
	T (°C)			T (°C)		
	230	260	280	230	260	280
A_{CH_2O}[a]	0.13	2.0	6.1	0.47[b]	1.4	2.5
A_{HCOOCH_3}[a]	4.3	12.4	23.3	5.9	13.6	23.0
A_{DHG}[a]	2.3	8.2	17.8	3.4	8.2	14.0

[a] Activities are expressed in mol h^{-1} g^{-1} × 10^3.

[b] This figure corresponds to the value extrapolated from the experimental points obtained at 273 and 294°C. No formol was detected at 230°C (Table 2).

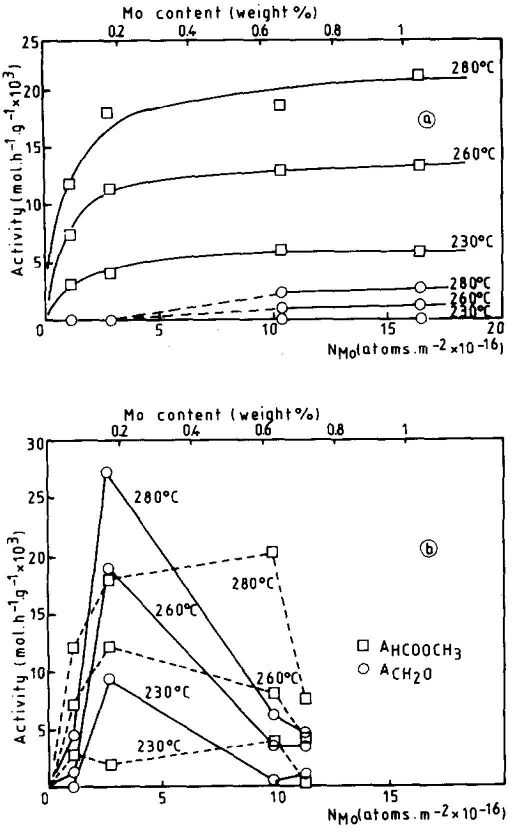


FIG. 1. Activity of Mo/SiO$_2$ catalysts in methanol oxidation as a function of Mo content (N_{Mo}: number of Mo atoms per m^2 of silica support). (a) Grafted samples; (b) impregnated samples. Circles and squares represent the activities for CH$_2$O and HCOOCH$_3$, respectively.

difficulty of preparing reproducible catalysts, i.e., of getting the same molybdenum dispersion for a given molybdenum content. It is well known indeed (*16*) that the sample drying step is important since it determines the distribution of the molybdenum salt within the pores of silica. In contrast to this, the kinetic results of the grafted samples are very homogeneous, so it is worth investigating why there is such a drastic difference from the impregnated catalysts and whether this is due to the effect of molybdenum dispersion.

Several experiments (*7–9*) (tests of solubility in HF–H$_2$SO$_4$ acid solutions, measurements of molybdenum reducibility) performed with impregnated and grafted samples showed that the molybdenum–silica interactions are stronger on grafted samples.

The simplest quantitative method for determining the molybdenum dispersion in supported catalysts has been described by Weller *et al.* (*17*). It consists of measuring the amount of chemisorbed oxygen at 77 or 195 K on prereduced catalysts. This method has been criticized recently (*18*) because it is difficult to apply when the molybdenum content of the catalyst is very low ($\leq$1 wt%). This led us to use two other methods: one qualitative, the second quantitative.

The UV–visible reflectance spectra of the blue samples obtained after preparation exhibit a Mo^{5+}–Mo^{6+} intervalence band at around 1000 nm. After being washed the samples are brown and this band no longer exists, although the two Mo^{5+} and Mo^{6+} oxidation states can still be observed by EPR and reflectance spectroscopies, respectively (*7–9, 11*). It means that on the grafted samples, no interaction exists between the Mo^{5+} and Mo^{6+} ions, suggesting that those ions are isolated ones from the others on the silica surface (*7–9, 11*).

EPR revealed the existence of three types of Mo^{5+} ions on thermally reduced grafted Mo/SiO$_2$ samples; one of those is new and has been identified as tetracoordinated Mo$^{5+}_{4c}$ ions in distorted tetrahedral symmetry (*8, 9, 11, 14*). Those Mo$^{5+}_{4c}$ ions are present on impregnated Mo/SiO$_2$ samples also (*14*) but had never before been observed. We have used EPR to measure the dispersion of Mo^{5+} ions (*7, 9, 11*). The method involves the chemisorption of oxygen on prereduced samples, leading to the following electron transfer reaction:

$$Mo^{5+} + O_2 \rightarrow Mo^{6+}O_2^- \qquad (1)$$

The EPR signal of Mo^{5+} decreases in intensity while that of O$_2^-$ appears. By measuring the Mo^{5+} EPR signal intensity before and after oxygen chemisorption, it is possible to derive the relative fraction of Mo^{5+}

ions accessible to oxygen. Care was taken to perform the adsorption of oxygen at 77 K in order to restrict reaction (1) to surface Mo^{5+} ions only and to avoid any electron transfer from Mo^{5+} ions in positions not accessible to oxygen (*19*). For samples with a Mo content of 1 wt%, the dispersion, measured as the fraction of Mo^{5+} ions accessible to oxygen at 77 K, was found to be 80% for grafted samples but only 30% for impregnated samples. Values as high as 100% could be obtained for grafted samples with molybdenum contents below 1 wt%. The sample with 0.18 wt% Mo exhibits 3.8% of its molybdenum as Mo^{5+} ions.

The absence of the Mo^{5+}–Mo^{6+} intervalence band in the UV–visible reflectance spectra and the EPR measurements of the Mo^{5+} dispersion indicate that the molybdenum on grafted samples is highly and better dispersed than on impregnated samples. Recent photoluminescence studies on grafted and impregnated Mo/SiO_2 samples have confirmed this high dispersion for grafted samples (*15*).

In summary, one can conclude that the catalytic results for the grafted catalysts depend on the molybdenum dispersion. This is due to the grafted reaction itself, which generates strong molybdenum–silica interactions and to the additional washing step, which eliminates the molybdenum loosely bound to silica. In this way, the dispersion of molybdenum can be controlled. This is not possible for impregnated samples, as is reflected by the catalytic results (Table 2), which vary monotonically for the grafted samples (Fig. 2) but are scattered for the impregnated ones (Fig. 3).

Inspection of Table 2 indicates that CO_2 and dimethyl ether are essentially formed on silica because the activities in these products at 230 and 260°C on pure silica are close to those observed for the grafted samples at the same temperature and whatever the molybdenum content. The formation of methyl formate on pure silica may be neglected since at 230 and 260°C the corresponding activity is less than 5% of that on grafted samples at the same temperatures.

Since the yields of CO_2 and dimethyl ether do not depend on the presence of molybdenum, we shall consider only the formaldehyde and methyl formate selectivities. On impregnated samples, formaldehyde is produced whatever the Mo amount and the reaction temperature, with a selectivity which can reach 72% (Fig. 2a). On grafted catalysts, formaldehyde is detected only for Mo amounts above 0.66% and for temperatures higher than 260°C (Fig. 2b). Its selectivity remains lower than 10%, whereas for methyl formate it varies between 83 and 98%. These results show that formaldehyde, which is the main reaction product on pure MoO_3 (*3*, *20*) and Fe–Mo oxides (*21*, *22*), is not formed when Mo is highly dispersed as in grafted Mo/SiO_2 catalysts with low Mo content. In the latter case, methyl formate is the main product.

The formation of methyl formate may be

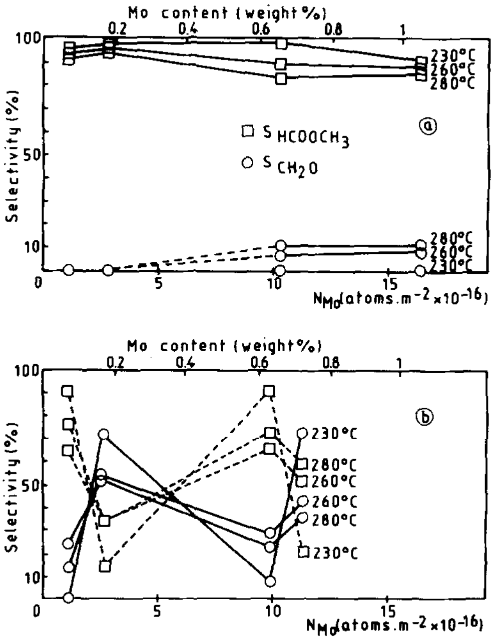
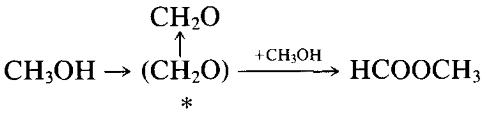


FIG. 2. Selectivity of Mo/SiO_2 catalysts in methanol oxidation as a function of Mo content (N_{Mo}: number of Mo atoms per m^2 of silica support). (a) Grafted samples; (b) impregnated samples. Circles and squares represent the selectivities for CH_2O and $HCOOCH_3$, respectively.

formally described as a two-step reaction in which only the first step is an oxidative dehydrogenation:



$$CH_3OH \rightarrow \underset{*}{\overset{\overset{CH_2O}{\uparrow}}{(CH_2O)}} \xrightarrow{+CH_3OH} HCOOCH_3$$

The subscript * refers to the adsorbed state. If the activities are expressed with respect to the methanol consumption, the activity for methanol dehydrogenation (A_{DHG}) may then be defined as the sum of the activity in formaldehyde (A_{CH_2O}) and half of the activity in methyl formate (A_{HCOOCH_3}) since only one mole of methanol is dehydrogenated to produce methyl formate. One can thus write

$$A_{DHG} = A_{CH_2O} + \tfrac{1}{2}A_{HCOOCH_3}$$

The activity in CO$_2$ is not taken into account since CO$_2$, as stated above, is essentially produced on silica for the grafted catalysts. The graphs showing A_{DHG} of grafted Mo/SiO$_2$ versus the Mo concentration N_{Mo} (expressed by the number of Mo atoms per m^2 of silica) are shown in Fig. 3.

As stated above, the results are more homogeneous for the grafted than for the impregnated catalysts, owing to the better control of preparation. The discussion that follows is, therefore, essentially concerned with the grafted catalysts for which A_{DHG} is equal to A_{HCOOCH_3}, since A_{CH_2O} is negligible. The graphs do not yield straight lines passing through the origin. This fact may be explained as follows:

- either molybdenum forms clusters whose size increases with the molybdenum content. Methyl formate is formed on molybdenum sites, as is formaldehyde on pure MoO$_3$,
- or molybdenum is highly dispersed, probably as isolated ions, as our previous results show (*7–9, 11, 12*). Since the plot $A_{DHG} = f(N_{Mo})$ does not yield a straight line, one has to assume that molybdenum is not the only active site and that silica also participates in the catalytic reaction (see Appendix).

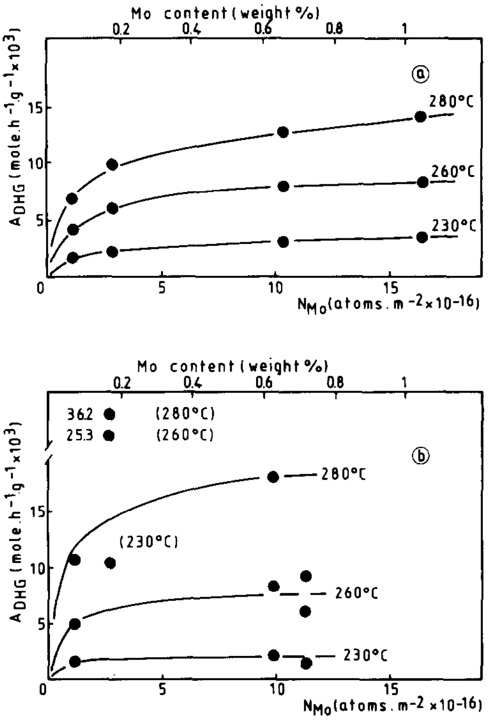


FIG. 3. Activity of Mo/SiO$_2$ catalysts in methanol dehydrogenation as a function of Mo content (N_{Mo}: number of Mo atoms per m^2 of silica support). $A_{DHG} = A_{CH_2O} + \tfrac{1}{2}A_{HCOOCH_3}$. (a) Grafted samples; (b) impregnated samples.

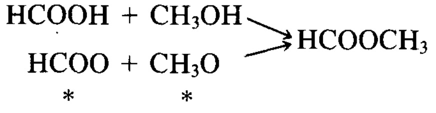
To our knowledge, three mechanisms may explain the formation of methyl formate from methanol or from intermediate compounds produced by its oxidative dehydrogenation:

1. The formaldehyde dimerization:

$$2\,CH_2O \rightarrow HCOOCH_3$$

The mechanism explains the formation of methyl formate on mixed oxides such as SnO$_2$–MoO$_3$ and SnO$_2$–WO$_3$ (*23*) and also on copper wire surfaces (*24*).

2. The esterification of formic acid or of adsorbed formate:

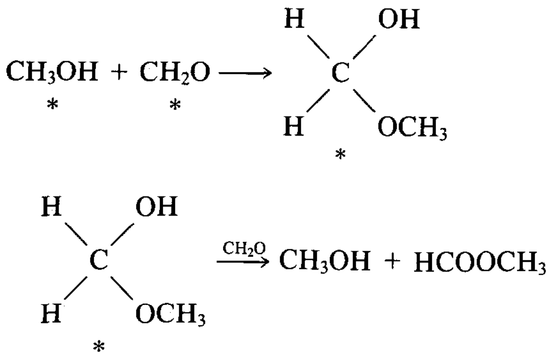


$$\left.\begin{array}{l} HCOOH + CH_3OH \\ \underset{*}{HCOO} + \underset{*}{CH_3O} \end{array}\right\rangle \rightarrow HCOOCH_3$$

where the subscript * refers to the adsorbed state.

This reaction was used by Cairati and Trifirò (*25*) and Liu *et al.* (*26*) to explain the formation of methyl formate during methanol oxidation on silica at temperatures above 300°C and on TiO_2, respectively.

3. The heterogeneous analog of the Tischenko reaction via a surface hemiacetal intermediate:



This mechanism was first proposed by Wach and Madix (*27a*) to explain the formation of methyl formate on Ag(110) and later by Takahashi *et al.* (*27b*) in the case of copper–silica catalysts prepared by ion exchange.

Mechanism 1

To test the hypothesis of formaldehyde dimerization and the role of silica, two samples, grafted Mo/SiO_2 catalyst and pure silica were put in a flow of helium and formaldehyde containing or not containing oxygen ($CH_2O/O_2/He$ or CH_2O/He). The results presented in Table 5 show that the activity of methyl formate on grafted Mo/SiO_2 or silica is negligible in comparison to that on Mo/SiO_2 for methanol oxidation. Hence, it is deduced that methyl formate is not produced by formaldehyde dimerization on grafted Mo/SiO_2 and mechanism 1 can be discarded.

TABLE 5

Formaldehyde Reactivity on Grafted Mo/SiO_2 Samples (0.18 wt% Mo) and Pure Silica: Comparison with Activities for Methanol Oxidation

	Grafted Mo/SiO_2 (0.18 wt% Mo)			Silica XOA 400		
	CH_2O/He (2.3/97.7)	$CH_2O/O_2/He$ (2.3/18/79.7)	$CH_3OH/O_2/He$ (7/19/74)	CH_2O/He (2.3/97.7)	$CH_2O/O_2/He$ (2.3/18/79.7)	$CH_3OH/O_2/He$ (7/19/74)
		T (°C)			T (°C)	
	260	260	260	260	260	230
A_{CO_2}[a]	0.07	3.5	0.36	0.09	3.6	0.074
Y_{CO_2}[a]	0.07	3.4				
A_{HCOOCH_3}[a]	0.7	0.8	11.48	1	1	0.09
Y_{HCOOCH_3}[b]	0.7	0.8				
Y_T	1	23				

[a] A_x is the activity in product x and is expressed in mol h^{-1} g^{-1} × 10^3.

[b] Y_x is the conversion of formaldehyde in product x and is expressed in percentages.

According to Table 5, the total conversion (Y_T) is larger than or nearly equal to the sum of the conversions of CO_2 and $HCOOCH_3$ (Y_{CO_2}, Y_{HCOOCH_3}) when experiments on Mo/SiO_2 are performed in the presence or absence of oxygen, respectively. These results may be explained either by the formation of formic acid, which cannot be detected with our experimental set-up, or by the accumulation of formaldehyde or of its oxidation products, such as formic acid, on the catalyst surface when the $CH_2O/O_2/He$ mixture is brought into contact with Mo/SiO_2. It must be kept in mind that formic acid and formaldehyde are the reactants in the reactions of mechanisms 2 and 3, respectively, to which we now turn.

Mechanisms 2 and 3

Pure silica was subjected to a flow first of $CH_2O/O_2/He$ for 2 h at 230°C, then of helium to eliminate residual CH_2O and O_2. When a flow of $CH_3OH/O_2/He$ is then passed over the catalyst, methyl formate is formed with an initial activity of 4.5 10^{-3} mol h^{-1} g^{-1}, which decreases with time (Fig. 4). This result indicates that the compounds adsorbed on the surface, while the mixture of $CH_2O/O_2/He$ flows on the catalyst, can react further with methanol and produce methyl formate.

TABLE 6

Reactivities of Various Mixtures on Pure Silica

	Reactive mixture (molar %)	
	$CH_2O/CH_3OH/O_2/He$ (3.4/5.2/18.2/73.2)	$HCOOH/CH_2OH/O_2/He$ (0.3/6.5/18.6/74.6)
T (°C)	260	230
A_{CO_2}[a]	0.4	0.29
A_{HCOOCH_3}[a]	22.9	3.52

[a] A_x is the activity in product x and is expressed in mol h^{-1} g^{-1} × 10^3.

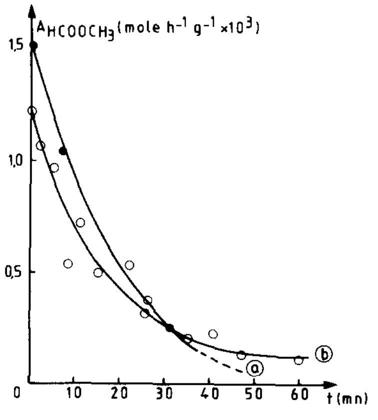


FIG. 4. Activity of pure silica for methyl formate formation as a function of time on stream (CH_3OH/O_2He). (a) Silica first swept by CH_2O/O_2He and then by He (solid circles); (b) after adsorption of HCOOH, silica was swept by He (open circles).

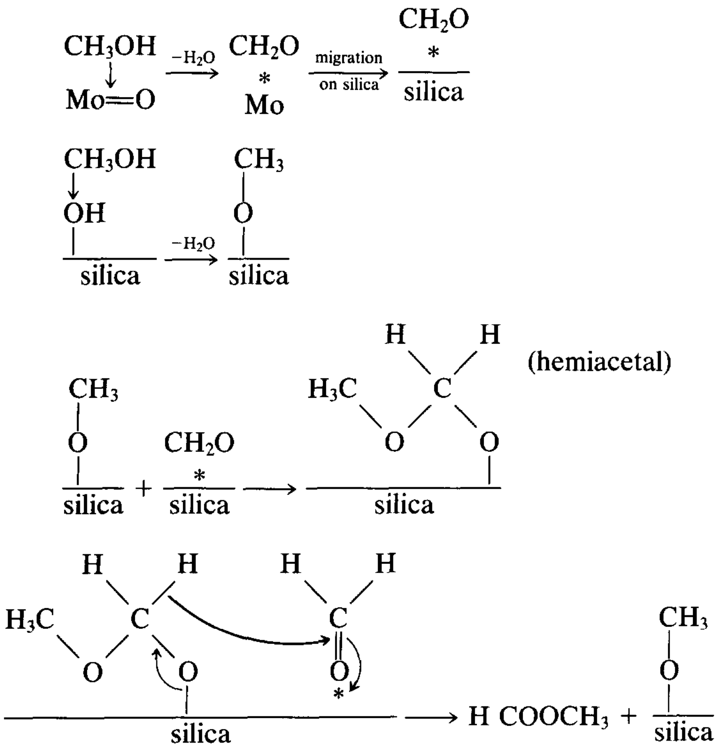
In the same way, preadsorption of formic acid on pure silica at 230°C, followed by first a flow of helium (in order to eliminate the residual vapors) and then of the $CH_3OH/O_2/He$ or CH_3OH/He mixture, induces the formation of methyl formate within an activity that decreases with time. The initial activities were about 1.2–1.4 10^{-3} mol h^{-1} g^{-1}. These last two experiments support the explanation proposed above, i.e., that methyl formate can be produced by reaction of methanol with either formaldehyde (mechanism 3) or adsorbed formic acid (mechanism 2).

To determine which reaction is the most probable, pure silica was subjected to a flow of the following mixtures: $HCOOH/CH_3OH/O_2/He$ and $CH_2O/CH_3OH/O_2/He$. The results summarized in Table 6 show that the activity in methyl formate is larger for the formaldehyde–methanol mixture than for the formic acid–methanol mixture. Furthermore, the activity in methyl formate in the latter case is found to decrease when the reaction temperature increases, in agreement with Cairati and Trifirò's work (*25*) with methanol oxidation on silica, whereas it increases with temperature in methanol oxidation on grafted Mo/SiO_2 catalysts (Table 2, Fig. 1a). These results, which indicate that the reaction between adsorbed formaldehyde and methanol dominates the formation of methyl formate, show that mechanism 2 is the most likely.

On the basis of the previous results, the mechanism proposed by Wachs and Madix (*27a*) and by Takahashi *et al.* (*27b*) has been completed so as to include the participation of both the molybdenum and silica components of the catalyst: methanol, dissociatively adsorbed on molybdenum sites, is transformed into formaldehyde according to a mechanism of oxidative dehydrogenation similar to that occurring on MoO_3 (*28–30*), and this has been confirmed recently by EPR of Mo/SiO_2 grafted samples (*31*). Simultaneously, methanol can react with surface hydroxyl groups of silica to form adsorbed methoxy groups (*32, 33*):

$$SiOH + CH_3OH \rightarrow SiOCH_3 + H_2O$$

As the molybdenum ions are highly dispersed on grafted catalysts, one can assume that formaldehyde, rather than desorbing as in the case of pure MoO_3 catalysts characterized by molybdenum ions in close interaction, can spillover to silica and react with methoxy groups to form methyl formate via a hemiacetal intermediate:



The role of oxygen in the reaction mixture is to reoxidize the molybdenum ions that have been reduced by methanol during its transformation into formaldehyde.

This mechanism does not take into account the activation of molecular oxygen since oxygen species adsorbed on the catalyst have not been investigated in this work. However, it is supported by kinetic calculations described in the Appendix. Furthermore, according to the bond-strength model of active sites on MoO_3 catalysts proposed by Ziołkowski (*34*), the formation of formaldehyde from methanol dehydrogenation requires the presence of two adjacent Mo=O bonds. This was recently supported by Allison and Goddard (*30*), who showed that the formation of free formaldehyde is thermodynamically favored by the presence of a dual set of adjacent dioxomolybdenum units. It means that the Mo ions should interact with each other to allow the release of CH_2O. This explains why formaldehyde is formed on impregnated catalysts with poorly dispersed Mo but not on grafted catalysts, on which Mo is highly dispersed. On the latter, the interactions between neighboring molybdenum ions are strongly inhibited. In this case, to explain the formation of methyl formate, we have to suppose that the desorption of formaldehyde is more difficult than the spillover to silica. This is supported by the variation of selectivities as the reaction temperature is increased: the selectivity in methyl formate decreases whereas that in formaldehyde increases. The desorption of formaldehyde is more favored by a rise of temperature than its migration.

CONCLUSION

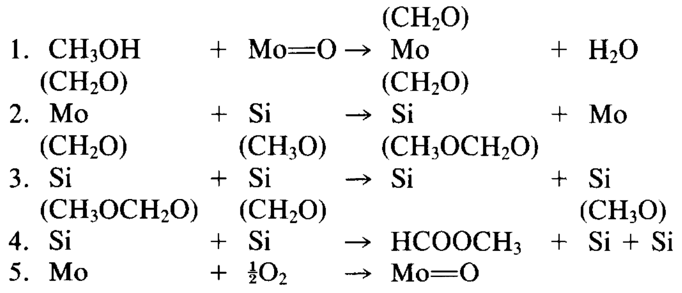
Silica-supported molybdenum catalysts prepared by different techniques (impregnation or grafting) have been compared by means of methanol oxidation, which is structure sensitive (*2–5*). The results indicate that it is sensitive also to dispersion. When Mo ions are interacting, as in pure MoO_3, formaldehyde is formed, whereas when they are highly dispersed (grafted samples), methyl formate is the principal product. For intermediate dispersion states (impregnated samples), both products are formed, but in amounts that do not appear to be related to the molybdenum loading in a consistent way. The preparation of the catalyst, not correctly controlled for the impregnated samples, appears to determine the selectivity.

Based on kinetic calculations and experimental results involving the use of different gas mixtures, a mechanism for the formation of methyl formate on grafted catalysts is proposed, which involves the reaction of adsorbed formaldehyde with methoxy groups adsorbed on silica via a hemiacetal intermediate. While this mechanism is known to occur on silver (*27a*) and Cu/SiO_2 catalysts (*27b*), it had not been demonstrated previously for supported oxides. An important aspect of the mechanism is the migration of adsorbed CH_2O from its formation site (Mo ions) toward silica sites, where it can react further. Work is in progress to investigate the nature of the adsorbed species by magnetic and optical spectroscopies.

APPENDIX

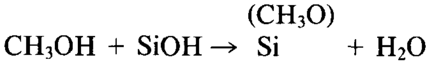
Kinetic Model for the Formation of Methyl Formate on Grafted Mo/SiO₂ Catalysts

The reaction mechanism proposed above involves the following kinetic steps. Parentheses refer to the adsorbed state:



$$\begin{array}{lllll}
1. & CH_3OH & + \; Mo{=}O & \rightarrow \; \overset{(CH_2O)}{Mo} & + \; H_2O \\
2. & \overset{(CH_2O)}{Mo} & + \; Si & \rightarrow \; \overset{(CH_2O)}{Si} & + \; Mo \\
3. & \overset{(CH_2O)}{Si} & + \; \overset{(CH_3O)}{Si} & \rightarrow \; \overset{(CH_3OCH_2O)}{Si} & + \; Si \\
4. & \overset{(CH_3OCH_2O)}{Si} & + \; \overset{(CH_2O)}{Si} & \rightarrow \; HCOOCH_3 & + \; \overset{(CH_3O)}{Si} + Si \\
5. & Mo & + \; \tfrac{1}{2}O_2 & \rightarrow \; Mo{=}O &
\end{array}$$

The completeness of the mechanism involves the noncatalytic reaction of methoxy regeneration occurring during the transient state.



$$CH_3OH + SiOH \rightarrow \overset{(CH_3O)}{Si} + H_2O$$

Let θ_{Mo}^{Ox}, θ_{Mo}, and θ_{Mo}^{F} be the percentages of Mo sites oxidized, reduced, and covered by formaldehyde, respectively, and let θ_{Si}, θ^{F}_{Si}, and θ^{HA}_{Si} be the percentages of Si sites, free, covered by formaldehyde, by methoxy groups and by hemiacetal, respectively.

The hypothesis of pseudo-first-orders may be written as

$$v_1 = k_1 P_M \theta^{Ox}_{Mo} \tag{1}$$

$$v_2 = k_2 \theta^{F}_{Mo} \theta_{Si} \tag{2}$$

$$v_3 = k_3 \theta^{F}_{Si} \theta^{M}_{Si} \tag{3}$$

$$v_4 = k_4 \theta^{HA}_{Si} \theta^{F}_{Si} \tag{4}$$

$$v_5 = k_5 P_{O_2} \theta_{Mo}, \tag{5}$$

where k_1 to k_5 are rate constants and P_M and P_{O_2} are the partial pressures of methanol and oxygen, respectively.

In the steady state, one can write

$$v_1 = v_2 = v_5 \quad \text{(transformation on Mo sites)} \tag{6}$$

$$v_2 = v_3 + v_4 \quad \text{(formaldehyde consumption)} \tag{7}$$

$$v_3 = v_4 \quad \text{(methoxy consumption)} \tag{8}$$

Using equations (3) and (4), relation (8) can be expressed as

$$\frac{\theta^{M}_{Si}}{\theta^{HA}_{Si}} = \frac{k_4}{k_3} \tag{9}$$

Assuming the following relation to apply to the silica surface free and covered by the adsorbed species,

$$\theta_{Si} + \theta^{M}_{Si} + \theta^{F}_{Si} + \theta^{HA}_{Si} = 1, \tag{10}$$

relation (9) can be rewritten as

$$\theta_{Si} = 1 - \theta^{M}_{Si}\left(1 + \frac{k_3}{k_4}\right) - \theta^{F}_{Si}. \tag{11}$$

By combining relations (7) and (8) one obtains the equation

$$v_2 = 2v_4, \tag{12}$$

which, connected to (9) and (11), leads to the expression

$$\theta^{F}_{Si} = \frac{k_2\theta^{F}_{Mo}[1 - \theta^{M}_{Si}(1 + k_3/k_4)]}{k_2\theta^{F}_{Mo} + 2k_3\theta^{M}_{Si}}. \tag{13}$$

The rate of methyl formate formation (v_{MF}), expressed with respect to methanol consumption (v_1), is $v_{MF} = v_1 = 2v_3$. This means that

$$v_{MF} = \frac{2k_2k_3\theta^{M}_{Si}\theta^{F}_{Mo}[1 - \theta^{M}_{Si}(1 + k_3/k_4)]}{k_2\theta^{F}_{Mo} + 2k_3\theta^{M}_{Si}}. \tag{14}$$

Because of the high Mo dispersion on grafted catalysts, it may be assumed that formaldehyde can migrate easily over to silica and that in consequence θ^{F}_{Mo} is nearly constant, whatever the Mo amount. The possibility of methoxy regeneration by methanol reaction with hydroxyl groups of silica leads us to suppose that θ^{M}_{Si} remains unchanged when the Mo content varies. With $P = \theta^{F}_{Mo}$ and $Q = \theta^{M}_{Si}$, the inverse of the rate of methyl formate formation may be written as

$$\frac{1}{v_{MF}} = \frac{1}{2k_3Q[1 - Q(1 + K_3/K_4)]} + \frac{1}{k_2P[1 - Q(1 + K_3/K_4)]}. \tag{15}$$

The rate constants can be expressed by $k = KN_i$ where K is the rate per each reaction site (turnover) and N_i is the reaction site density. Hence

$$k_2 = K_2 N_{Mo} N_{Si} \tag{16}$$

$$k_3 = K_3 N_{Si} \tag{17}$$

$$k_4 = K_4 N_{Si} \tag{18}$$

The expression of the rate of methyl formate formation becomes

$$\frac{1}{v_{MF}} = \frac{1}{2N_{Si}K_3Q[1 - Q(1 + K_3/K_4)]} + \frac{1}{N_{Mo}N_{Si}K_2P[1 - Q(1 + K_3/K_4)]} \tag{19}$$

The Mo amount is low ($\leq 1\%$) and the silica surface area is large (400 m^2/g) so that N_{Si} is larger than N_{Mo} and may be considered constant. The above expression can then be simplified to

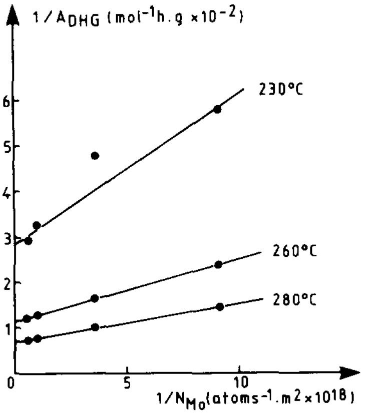


FIG. 5. Reciprocal of the activity for methyl formate formation as a function of the reciprocal of Mo amount for grafted catalysts.

$$\frac{1}{V_{\mathrm{MF}}} = A + \frac{B}{N_{\mathrm{Mo}}}, \qquad (20)$$

where A and B are constants.

The reciprocal of the methyl formate formation rate versus the reciprocal of Mo amount gives a straight line characterized by a positive slope and a positive intercept. Figure 5 shows that our results agree with these calculations and justifies the hypothesis of the migration of adsorbed formaldehyde from molybdenum sites over to silica, where it can react to form methyl formate via a hemiacetal intermediate.

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