Methanol and Formaldehyde Oxidation Study over Molybdenum Oxide

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Formaldehyde oxidation to carbon oxides in conjunction with methanol oxidation was studied to improve understanding about the selectivity of the partial oxidation of methanol to formaldehyde. The good selectivity to formaldehyde over bulk molybdenum trioxide and iron molybdate is attributed to water, a reaction product, and methanol, which retards the further oxidation of formaldehyde. Competitive adsorption experiments monitored by IR indicate that CH_2O, CH_3OH, and H_2O compete for the same site. The loss of the formaldehyde selectivity over the silica-supported catalyst in methanol oxidation can not be attributed to the further oxidation of gaseous formaldehyde. © 1996 Academic Press, Inc.

INTRODUCTION

The partial oxidation of methanol to formaldehyde over MoO_3-based oxides have been studied extensively (1–9). These studies have focused on the reaction mechanism, structure sensitivity, active species and the rate limiting step. MoO_3 and $Fe_2(MoO_4)_3$ are highly selective for the reaction. Mixed $MoO_3 \cdot Fe_2(MoO_4)_3$ has been used industrially and selectivities as high as 91–94% at 95%–99% conversion have been reported (8). Clearly, an important question is why the product formaldehyde is not further oxidized as it is over many metal oxides. To increase the strength of the catalysts for a fluidized bed reactor, supported molybdenum oxides have been studied (10–19). SiO_2 (10–15), Fe_2O_3 (16), Al_2O_3 (17), TiO_2 (18), and ZrO_2 (19) have been used as supports. Many supported Mo oxides have lower selectivity to CH_2O than bulk oxides. For example, Mo oxides supported on high surface area silica give higher selectivity to carbon oxides than unsupported Mo oxides (20, 21). It is interesting to know if the increase in the CO/CO_2 selectivity is caused by the further oxidation of product formaldehyde after its desorption. Thus, I have studied formaldehyde and methanol oxidation over silica, supported and unsupported Mo oxides to investigate catalytic selectivity in the partial oxidation of methanol to formaldehyde. The effect of water and the competitive adsorption of water, methanol, and formaldehyde have also been studied.

EXPERIMENTAL

Some of the catalysts used in this study were commercial ones and are described in Table 1. Polycrystalline MoO_3 was prepared by decomposing molybdenum oxalate obtained from Climax Molybdenum Company. The supported Mo oxide catalysts were prepared by the standard impregnation technique. The surface area of the catalysts used in this study is also described in Table 1. The catalysts were typically conditioned at 350°C for 1 h in air before the methanol or formaldehyde oxidation reaction. Typically, 2 g of catalyst was used for the evaluation unless otherwise indicated.

The formaldehyde reaction study was carried out in a fixed bed reactor (3/8" OD titanium) under a continuous flow. To minimize the concentration of water in the feed, solid paraformaldehyde was used in a formaldehyde saturator heated with an oil bath. Some physical properties of paraformaldehyde have been reported (22). The concentration of formaldehyde was varied by adjusting the saturator temperature between about 60 and 75°C. In a typical run, the saturator temperature was controlled at 72°C to obtain about 10% formaldehyde in air. Feed concentrations were frequently monitored by a GC. The water concentration was constantly below 1% and normally around 0.2%. The formaldehyde concentration could be held constant during a day of study and was relatively independent of the flow rate of carrier gases. Both water and methanol were introduced from liquid pumps. The same reactor was also used for the methanol oxidation study. The IR study was performed using a Nicolet 3600 FTIR. The infrared cell was part of an ultrahigh vacuum system. The system has a base pressure below 1×10^{-8} Torr. The sample was mounted in a cyclindrical open-ended quartz apparatus inside the vacuum system. The preparation of sample pellets for the transmission IR study and the calculation of the difference spectra resulting from subtracting the sample

TABLE 1

Description of the Catalysts Used in the Study

Catalyst	Source	Surface area (m^2/g)
TiO$_2$	Harshaw Ti-0102, Anatase	80.6
Al$_2$O$_3$	Harshaw Al-0104	100
SiO$_2$	Davison Grace, Grade 57	264
MoO$_3$	Decomposition of molybdenum oxalate, orthorombic structure	4.7
MoO$_3 \cdot$ Fe$_2$ (MoO$_4$)$_3$	Harshaw Mo-1907	4.3
15%MoO$_3$/SiO$_2$	Impregnation, SiO$_2$ was Ludox colloidal silica	256 for SiO$_2$ used
38%MoO$_3$/SiO$_2$	Impregnation, SiO$_2$ was Davison Grace, Grade 70	165

FIG. 1. Selectivities in formaldehyde oxidation over 38% MoO$_3$/SiO$_2$.

spectra and the reference spectra obtained without the sample have been described elsewhere (23). The selectivity is expressed as a mole percentage and the catalyst loading as a weight percentage of MoO$_3$. For convenience, the silica-supported molybdenum oxides will be designated as MoO$_3$/SiO$_2$ in this paper and Harshaw MoO$_3 \cdot$ Fe$_2$(MoO$_4$)$_3$ as the Harshaw catalyst.

RESULTS

Reaction of Formaldehyde

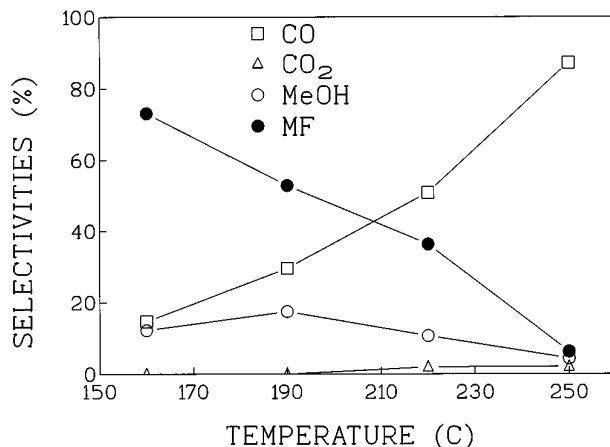The activities and selectivities of several metal oxides and unsupported molybdenum oxides in the reaction of

formaldehyde in air were studied in a fixed bed reactor at various temperatures. The formaldehyde conversions, selectivities, and experimental conditions are shown in Table 2. Reaction rates normalized to the surface area are also given for the above reaction conditions. The average reaction rate is the overall reaction rate in the reactor divided by the total surface area of the catalyst loaded in the reactor. The formaldehyde conversions and reaction rates differ greatly over the catalysts. Al$_2$O$_3$ and TiO$_2$ are very active. SiO$_2$ is a relatively inert material although its

TABLE 2

Conversions of Formaldehyde and Selectivities in Formaldehyde Reaction[a]

Catalyst	Temp. (°C)	Conv. (%)	Selectivities (%)						Average reaction rates[c] $(10^{-4}$ mol/h/m$^2)$	Reaction rates at reactor inlet[d] $(10^{-4}$ mol/h/m$^2)$
			CO	CO$_2$	DME[b]	MeOH[b]	MF[b]	Methylal		
Empty	190	0							0	0
Reactor	300	0							0	0
TiO$_2$	190	80.4	10.5	6.1	0	14.5	68.8	0	1.00	—
	300	100	36.0	23.3	16.0	24.7	0	0	>1.2	—
Al$_2$O$_3$	190	100	11.2	6.7	4.3	18.3	56.4	3.1	>1.0	—
	300	100	48.7	9.1	33.5	8.7	0	0	>1.0	—
SiO$_2$	190	0							0	0
	300	3.8	16.8	16.5	0	38.7	27.9	0	0.01	0.01
MoO$_3$	190	6.7	13.5	2.5	0	20.3	63.7	0	1.43	1.46
	300	18.2	82.9	7.0	0	10.2	0	0	3.87	4.16
MoO$_3 \cdot$ Fe$_2$ (MoO$_4$)$_3$	190	3.7	48.4	0	0	0	51.6		0.86	0.86
	300	15.8	95.7	4.3	0	0	0		3.67	3.91

[a] Standard conditions were 2.0 g catalyst, 3 psig pressure, 75 sccm flow rate and about 10% formaldehyde in air, unless otherwise indicated. The formaldehyde feed rate was equivalent to 1×10^{-2} mole per hour per gram of catalyst.

[b] DME = dimethyl ether, MeOH = methanol, MF = methyl formate.

[c] Average reaction rates of formaldehyde over the entire catalyst bed (i.e., total reaction rates divided by the amount of the catalysts).

[d] Reaction rates of formaldehyde under the feed concentrations (i.e., at zero conversrion). A power-law kinetics is assumed as described in the discussion.
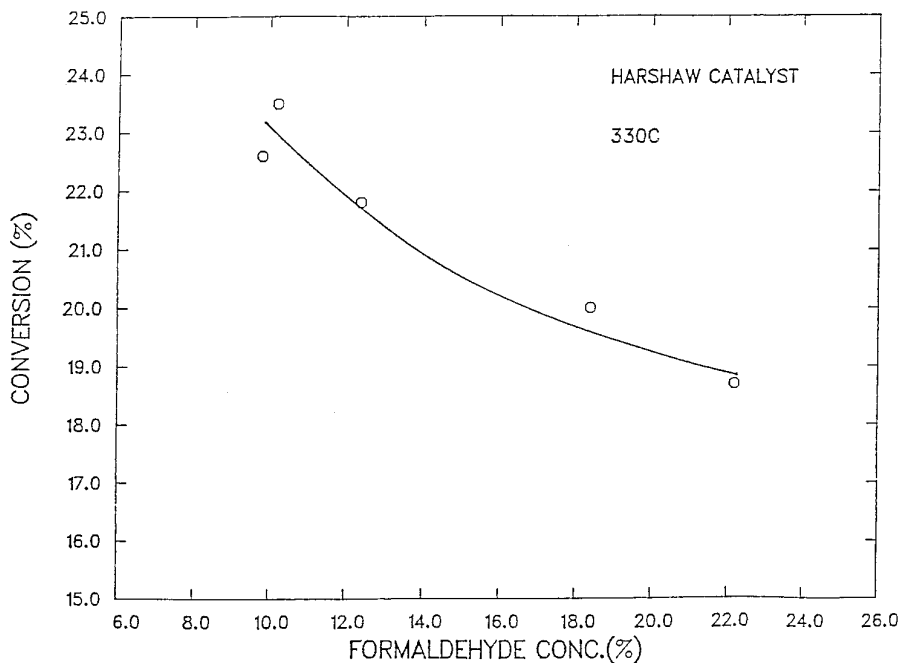
FIG. 2. Effect of formaldehyde concentration on the conversion of formaldehyde in formaldehyde oxidation over the Harshaw catalyst.

surface area is high. Bulk Mo-based oxides are also active for the reaction. Selectivities depend greatly on the temperature and slightly vary with the catalysts. Figure 1 shows the selectivities over 38% MoO_3/SiO_2, as an example. In general methyl formate selectivity decreases with increasing temperature. The selectivity to methanol reaches maximum at an intermediate temperature. CO and CO_2 selectivities increase with temperature.

Formaldehyde oxidation to carbon oxides was studied further over the Harshaw catalyst. Figures 2 and 3 describe the effects of formaldehyde and oxygen concentrations on the reaction. The feed contained formaldehyde in air for the experiments shown in Fig. 2 and 10% formaldehyde in oxygen and nitrogen for Fig. 3. The selectivities are little affected by both formaldehyde and oxygen concentrations. A slight increase in hydrogen selectivity and decrease in CO_2 selectivity were observed, only at very low oxygen concentrations.

Methanol and Formaldehyde Oxidation over Bulk and Supported Molybdenum Oxide

Bulk oxides. As shown in the previous section, bulk oxides such as MoO_3 and $MoO \cdot Fe_2(MoO_4)_3$ are active for the formaldehyde reaction. However, these catalysts are also very selective for the oxidation of methanol to formaldehyde. Selectivities for the oxidation of methanol to formaldehyde over MoO_3 are shown in Figs. 4a and 4b. The selectivities depend on the methanol conversion. The conversion was varied by changing the reaction temperature

and the methanol concentration in air. Formaldehyde selectivity reaches 95% at about 90% conversion. Similar selectivity was also observed for the Harshaw catalyst. Table 3 compares the conversions and yields in methanol and formaldehyde oxidation over MoO_3 and the Harshaw catalyst. Reaction rates and CO production rates are also shown in the table. This comparison indicates that formaldehyde formed in the methanol oxidation reaction is not oxidized to the same degree as in the formaldehyde oxidation reaction. This difference in the carbon oxide yield can be seen clearly, especially over the MoO_3 catalyst at an intermediate methanol conversion.

To understand this retardation of the oxidation of formaldehyde, water was fed with 10% formaldehyde in a formaldehyde oxidation study. Figure 5 demonstrates that the formaldehyde conversion decreases with increasing water concentration. It suggests that water which is coproduced with CH_2O and is present in a significant amount in methanol oxidation reaction retards the further oxidation of formaldehyde produced and contributes to the high selectivity of the methanol to formaldehyde reaction.

The selectivity to CO_2 over the Harshaw catalyst is presented in Fig. 6 at various feed concentrations of water. The balance of carbon products is CO. Although the conversion of formaldehyde is largely affected by water, its selectivity only slightly depends on water.

Competitive adsorption. To further elucidate how water retards the reaction of formaldehyde, the competitive adsorption of various molecules was monitored by IR spec-
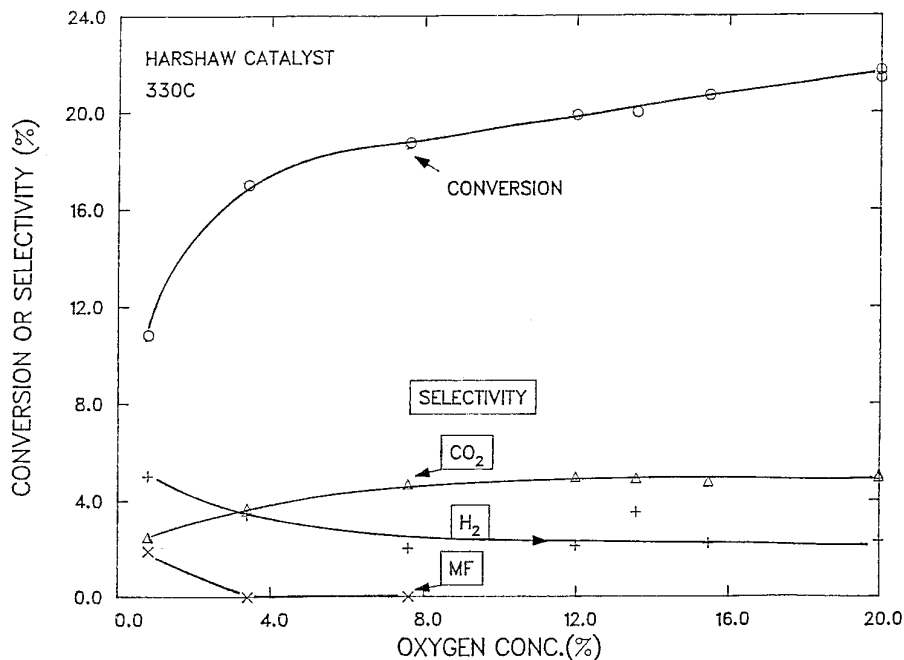
FIG. 3. Effect of oxygen concentration on the conversion and selectivity in formaldehyde oxidation over the Harshaw catalyst. The balance of the carbon products is CO.

troscopy at room temperature. The MoO_3 catalyst was first exposed to 3 mTorr CH_2O at room temperature. A difference spectrum before and after introducing formaldehyde is shown in Fig. 7a. Since the lattice contribution has also been subtracted, the spectrum shows adsorbed formaldehyde molecules (e.g., CH bending at about 1490 cm^{-1}, C=O stretching at about 1720 cm^{-1}). The sample was then further exposed to 10 mTorr H_2O at room temperature. The bands corresponding to adsorbed formaldehyde disappear and new bands corresponding to adsorbed water (e.g., OH bending at about 1650 cm^{-1}) appear as shown in Fig. 7b. The sample was then further exposed to 10 mTorr CH_3OH. Figure 7c reveals that the 1650 cm^{-1} band significantly reduces. New bands can be attributed to adsorbed methanol and methoxy species (e.g., the 1070 and 1445 cm^{-1} bands for $-O-C$ stretching and CH_3 deformation vibrations, respectively, of both methanol and methoxy species; the 1360, 2850, and 2960 cm^{-1} bands for OH deformation, CH_3 symmetric stretch, and CH_3 asymmetric stretch of methanol, respectively; and the 2825 and 2925 cm^{-1} bands for CH_3 symmetric and asymmetric stretches of methoxy, respectively). The 2825 and 2850 cm^{-1} bands overlapped and showed a single peak at about 2835 cm^{-1} in this study. The peak assignment of IR bands for adsorbed methanol and methoxy species over MoO_3 has been reported by Groff with the assistance of various methanol isotopes (23).

Supported molybdenum oxides. It is interesting to know the reactivities of materials in formaldehyde oxidation that may be used as supports in the partial oxidation of methanol. Molybdenum oxides supported on TiO_2, Al_2O_3, and silica have been studied for the partial oxidation of methanol (10–15, 17, 18). Our study shows that TiO_2 and Al_2O_3 are quite active for the formaldehyde reaction (Table 2). Their use as supports in the partial oxidation of methanol with good performance would suggest that the surfaces of the supports no longer possess their intrinsic properties. This is consistent with the monolayer morphology reported for the TiO_2- and Al_2O_3-supported molybdenum oxide catalysts (17, 18).

On the other hand, silica is relatively inert toward the formaldehyde reaction (Table 2). However, it is known that silica support increases the carbon oxide selectivity in the methanol oxidation compared with unsupported molybdenum oxides (20, 21). To understand which reaction path causes the increase of CO_x formation and the loss of CH_2O selectivity, Table 4 compares the conversions, selectivities, and carbon oxide yields in methanol and formaldehyde oxidation over the bulk MoO_3 and a SiO_2-supported molybdenum oxide. The supported catalyst has a much higher selectivity to carbon oxides in methanol oxidation reaction, but lower conversion and carbon oxides yields in formaldehyde oxidation reaction than the bulk oxide. Clearly, the increase in the carbon oxide selectivity over the supported catalyst can not be attributed to the further oxidation of gas-phase formaldehyde.
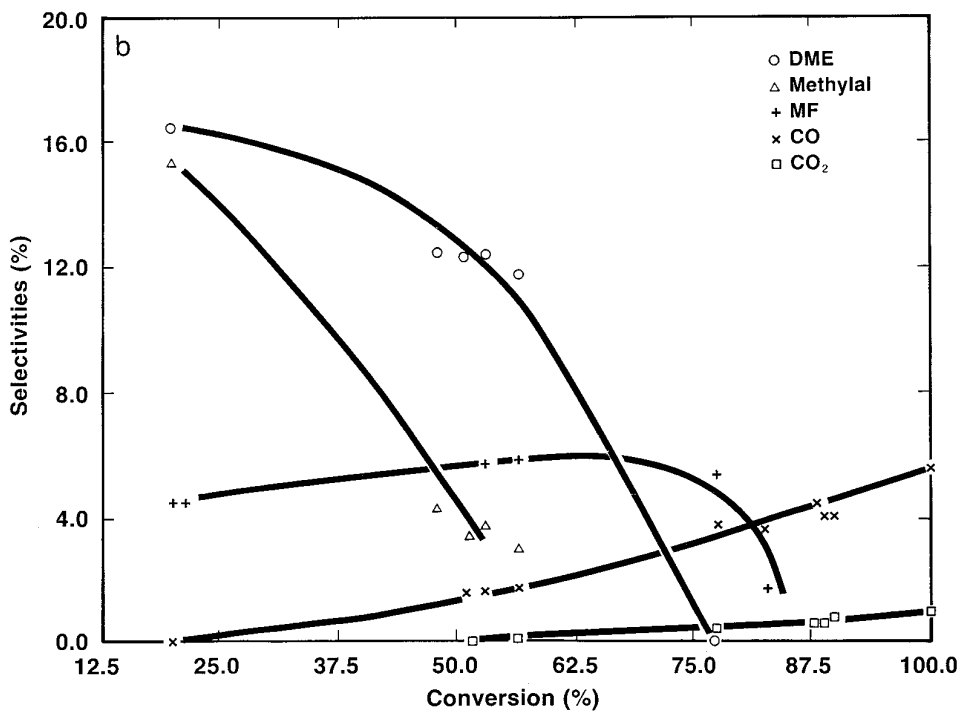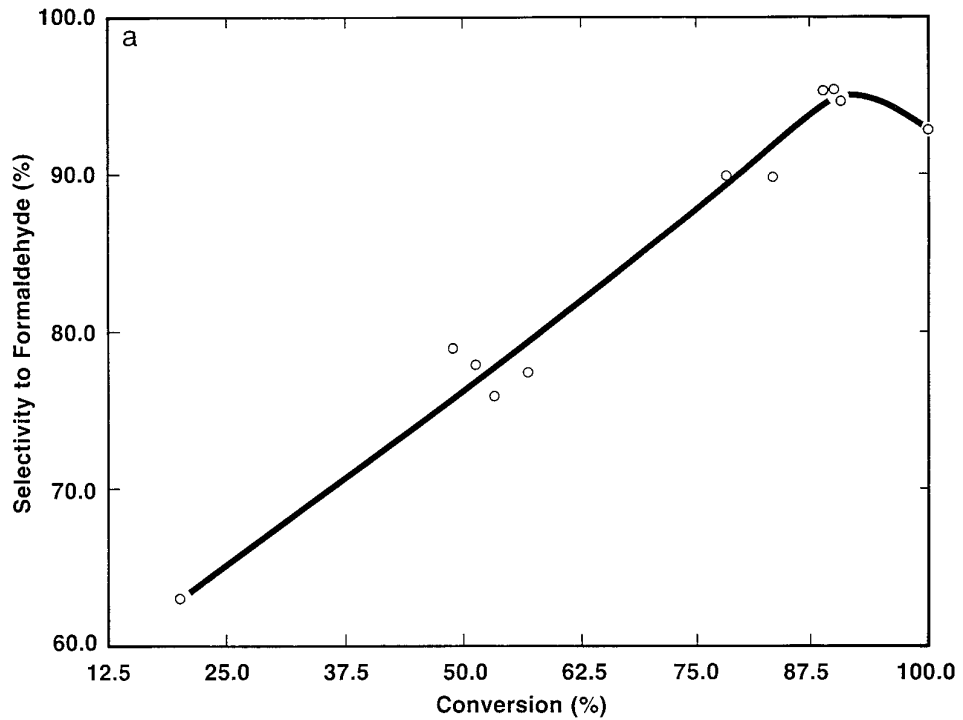
FIG. 4. Selectivities in methanol oxidation over MoO_3.

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TABLE 3

Methanol and Formaldehyde Oxidation over MoO$_3$ and the Harshaw Catalyst

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Catalyst	Feed[a]	Conv. (%)	Average reaction rates[b] (10^{-4} mol/hr/m^2)	Reaction rates at reactor inlet[b] (10^{-4} mol/hr/m^2)	Yields (%)[c]							CO production rates[d] (10^{-4} mol/h/m^2)
					CO	CO$_2$	CH$_2$O	DME	MeOH	MF	Methylal	
Harshaw	MeOH	99.7	23.19	36.87	10.0	0.5	87.0	2.5	—	—	—	2.33
Harshaw	CH$_2$O	15.8	3.67	3.91	15.1	0.7	—	—	—	—	—	3.51
MoO$_3$	MeOH	49.8	10.60	12.51	0.9	—	39.1	6.2	2.1	—	1.9	0.19
MoO$_3$	CH$_2$O	18.2	3.87	4.16	15.1	1.3	—	—	—	1.9	—	3.21

[a] Feed was 10% MeOH or 10% formaldehyde in air at 75 sccm. The reaction temperature was 300°C.
[b] Reaction rates of methanol or formaldehyde. Please also see footnotes (c) and (d) of Table 2.
[c] Yield = conversion × selectivity.
[d] Average production rates of CO over the catalyst bed in the reactor.

DISCUSSION

The formaldehyde oxidation over the bulk MoO$_3$-based catalyst is shown to follow a power-law kinetics with 0.7 order in the formaldehyde concentration and 0.15 order in the oxygen concentration (29). If we assume this kinetics for MoO$_3$-based catalysts used in this study, we can estimate the reaction rates over the catalysts at very front of the catalyst beds using the reaction data of the integral reactor in this study. This is the reaction rate under the feed concentrations. The results are also given in Table 2.

The results are in line with those shown earlier and again show high activities of bulk MoO$_3$-based catalysts and low activity of SiO$_2$. The reaction kinetics for methanol oxidation over MoO$_3$-based catalysts has been studied. The kinetics follows a power-law model with about 0.5 order in the methanol concentration and 0.1 order in the oxygen concentration (2). Using this kinetic model, the reaction rates of methanol under the feed concentrations in this study are also estimated and are given in Table 3.

The competitive adsorption study reveals that adsorbed formaldehyde is readily displaced by water. This suggests
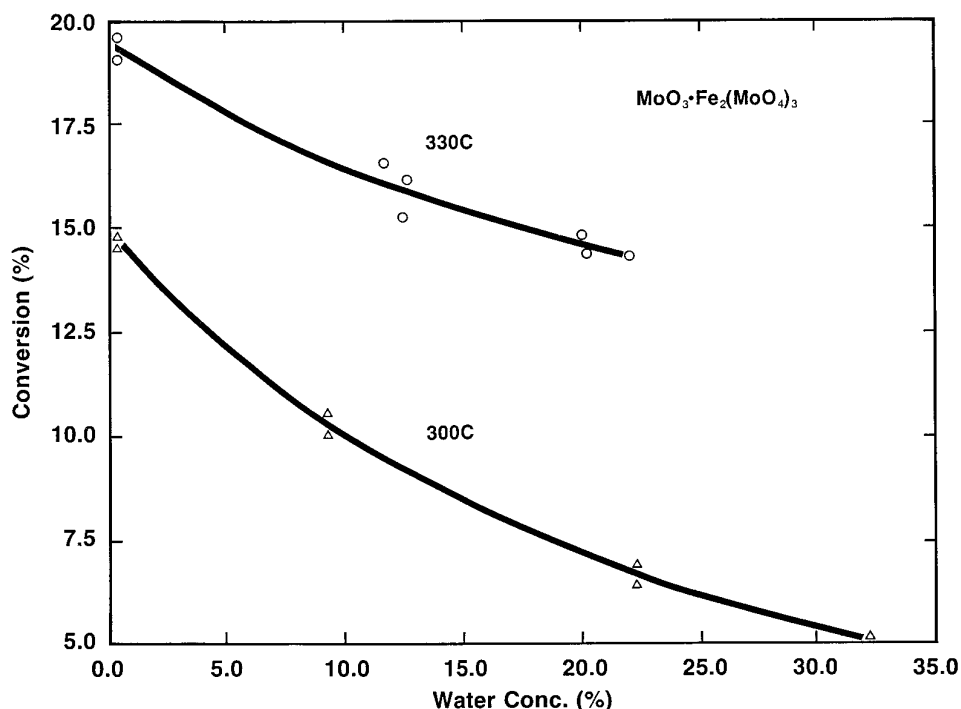

FIG. 5. Effect of water on the conversion of formaldehyde over Harshaw MoO$_3$ · Fe$_2$(MoO$_4$)$_3$ in formaldehyde oxidation.
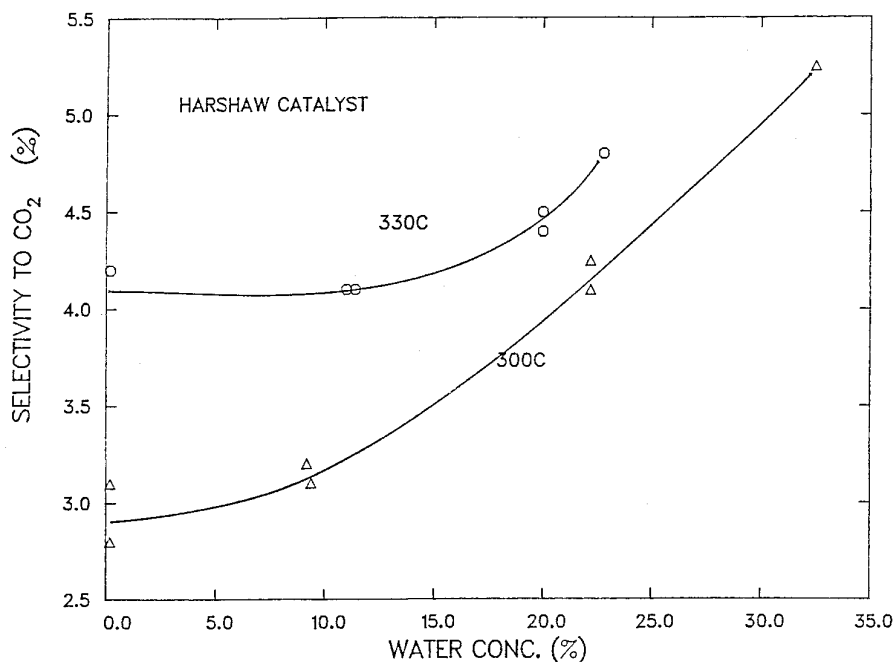
FIG. 6. Effect of water on the selectivity to CO_2 in formaldehyde oxidation over the Harshaw catalyst. The balance of the carbon products is CO.
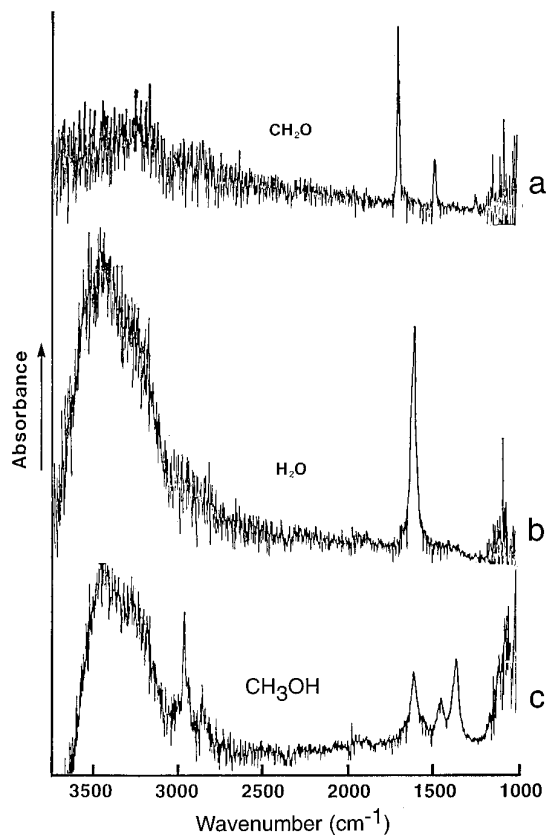

FIG. 7. IR spectra during competitive adsorption of CH_2O, H_2O, and CH_3OH on MoO_3.

that water and formaldehyde adsorb on the same site in MoO_3. Water can also be displaced by methanol. Further experiments show that water and methanol can be displaced each other. Therefore, in addition to water, methanol could also suppress the adsorption of formaldehyde.

Although it is also interesting to see if the above displacement also holds at reaction temperatures, heating the sample above 125°C in methanol caused the reduction of MoO_3 (23). It resulted in increases in overall absorbance and caused the signal-to-noise ratio to be insufficient. However, a link has been established between the reactor data in methanol oxidation at reaction temperatures and temperature-programmed desorption data following adsorption of methanol at room temperature over MoO_3 (24). For example, (i) the activation energy obtained by varying the heating rate for TPD of formaldehyde following methanol adsorption at room temperature is 20.6 kcal/mol which is comparable to the value of 20.5 kcal/mol obtained from the kinetic study of the reaction (2) and (ii) Farneth *et al.* (24) also showed that values for the number of active sites and the Arrhenius parameters for the rate-limiting C-H bond cleavage, both obtained by TPD following room temperature adsorption of methanol, can be combined to predict the reaction rate in excellent agreement with reactor data using a working MoO_3 catalyst. Although the remarkably quantitative agreement of the values shown above between the TPD following room temperature adsorption and the reactor study should not be taken too seriously because of simplifications used in their analysis, it can be concluded that surface methoxy concentrations after the

TABLE 4

Bulk and SiO$_2$ Supported Molybdenum Oxide for Methanol and Formaldehyde Oxidation[a]

			Selectivities (%)							Carbon oxides[c]
Reactions	Catalysts	Conv. (%)	CO	CO$_2$	CH$_2$O	DME	MF	MeOH	Methylal	yields (%)
Methanol oxidation	15% MoO$_3$/SiO$_2$[b]	94.6	21.2	1.3	67.2	8.4	2.0	—	—	21.3
Methanol oxidation	MoO$_3$	49.8	1.8	—	78.5	12.4	4.2	—	3.8	0.9
Formaldehyde oxidation	15% MoO$_3$/SiO$_2$	10.9	96.4	3.6	—	—	—	—	—	10.9
Formaldehyde oxidation	MoO$_3$	18.2	82.9	7.0	—	—	—	10.2	—	16.4

[a] Standard reaction conditions: see note (a) of Table 3.
[b] Feed was 7.1% methanol in air.
[c] This is the sum of CO and CO$_2$ yields.

adsorption of methanol at room temperature gives a number for the active site population of the working MoO$_3$ catalyst (24). In fact, it was also shown that the surface methoxy concentration before TPD differed by only a factor of 2 following equivalent exposures at 25, 100, or 200°C. Furthermore, it has also been shown that the methanol conversion rate is suppressed by water in methanol oxidation over MoO$_3$ at reaction temperatures (2, 12). Our results show that the formaldehyde conversion is also suppressed by water in the formaldehyde oxidation reaction at 300–330°C (Fig. 5). The negative effect on the conversions by water may be because of three possibilities: (a) They compete for the same sites. (b) The rate limiting step is inhibited by water. In the case of methanol oxidation, abstraction of hydrogen from methoxy species was shown to be the rate-limiting step (2, 12). (c) An intermediate or product reacts with water and is reversed to form a reactant. This last possibility is less likely for the formaldehyde reaction since the formaldehyde oxidation is largely a combustion reaction to form CO$_x$ and water. Its reverse reaction is thermodynamically unfavored at reaction conditions. However, in view of the spectroscopic observation of displacement between methanol, water, and formaldehyde and the link of reactor data with TPD following room temperature adsorption mentioned above, it is probable that the competitive adsorption also occurs at reaction temperatures although other possibilities can not be completely ruled out in this work. This is also consistent with the suppression of methanol oxidation by water (12) and suppression of formaldehyde oxidation by water with little change in the selectivity described in this work. Therefore, it is concluded that the high selectivity to formaldehyde in the partial oxidation reaction of methanol over MoO$_3$, and (presumably molybdate in general) can be attributed to water, a reaction product, and methanol, which suppress the further oxidation of formaldehyde likely by blocking formaldehyde adsorption sites.

Methanol oxidation over silica-supported molybdenum oxides have also been studied at low conversions and low molybdenum loadings (about 1% or less) (14, 25). High selectivity to methyl formate was reported in addition to the product formaldehyde. This was attributed to highly dispersed Mo species (25) and the nature of the silica support (14). Significant amounts of carbon oxides are formed at high conversions or higher Mo loadings, as found in this study and others (12, 20, 21). However, it has not been demonstrated which reaction path causes the increase of carbon oxide selectivity. This work combining the study of formaldehyde and methanol oxidation clearly indicates that the increase of the carbon oxide production is not caused by the further oxidation of product formaldehyde after its desorption. However, it can not be determined in this study whether it is via adsorbed formaldehyde as an intermediate. Our characterizations of the supported catalysts by STEM and other techniques indicate that dispersed species exist in addition to crystalline MoO$_3$ (26) when the supported catalysts are in the ambient state. This is consistent with the formation of heptamolybdate (10, 27), and silicomolybdic acid (28) suggested by Raman and ESR studies. Upon thermal heating, the polymolybdate is converted to isolated monodispersed Mo^{6+} species (10). An ESCA study indicates that surface Mo in the silica-supported molybdenum oxide catalyst tends to be reduced (26) but the bulk MoO$_3$ catalyst is at fully oxidized Mo^{6+} state before and after the methanol oxidation reaction. It has been shown that C-H bond breaking is the slowest step in the production of formaldehyde over the bulk catalyst and lattice oxygen is involved in the formaldehyde production process (2). Fully oxidized MoO$_3$ is most selective (9). The loss of selectivity to formaldehyde over the supported catalyst may be attributed to the presence of the dispersed non-MoO$_3$ species and the reduction of the catalyst (26).

CONCLUSIONS

(1) The formaldehyde oxidation study complements the methanol to formaldehyde reaction study in understanding

some selectivity issues of the partial oxidation reaction of methanol. Good selectivity in the partial oxidation of methanol over unsupported MoO$_3$ is because of water, a reaction product, and methanol, which retard the further oxidation of formaldehyde.

(2) A competitive adsorption study suggests that the above suppressing effect is caused by water and methanol blocking or occupying the adsorption site of formaldehyde.

(3) The loss of formaldehyde selectivity over the silica-supported catalyst in methanol oxidation can not be attributed to the further oxidation of product formaldehyde after its desorption.

ACKNOWLEDGMENTS

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