JOURNAL OF CATALYSIS **141**, 430–437 (1993)

The Absence of Molybdenum Precursor Effects for Methanol Oxidation over Molybdenum Oxide Supported on Silica

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Received September 17, 1990; revised December 10, 1992

The partial oxidation of methanol to formaldehyde and methyl formate has been studied at low conversion over Mo/SiO_2. Catalysts up to 1.1 wt% Mo were prepared from $MoCl_5$, $Mo_2(\eta^3\text{-}C_3H_5)_4$, and $(NH_4)_6Mo_7O_{24} \cdot 4H_2O$. Fumed silica (Cab-O-Sil EH-5), silica gel (Davison 952 and Rhone-Poulenc XOA-400), and Davison 952 silica, washed in acid to remove calcium, were used as supports. Iron-doped Cab-O-Sil was also used. Over identical supports, the activity and selectivity of methanol oxidation was similar for samples prepared from all precursors, although some slight differences were observed. More significant differences were observed, however, when the impurity levels were changed by acid washing, iron doping, and using different types of silica. The results suggest that impurities on the silica support, rather than the method of preparation or precursor, have a greater influence on methanol oxidation selectivity for loadings less than 1.1 wt% Mo metal. © 1993 Academic Press, Inc.

INTRODUCTION

Methanol oxidation has been found to be a structure-sensitive reaction over unsupported MoO_3. Tatibout *et al.* (*1*, *2*) have proposed that formaldehyde is selectively formed over the (010) face of MoO_3 and that dimethoxymethane is selectively produced over the (100) face.

Che and co-workers have proposed that methanol oxidation also exhibits structure sensitivity for surface molybdate species supported on silica (*3*, *4*). They have observed high selectivities (>80%) for methyl formate formation over catalysts prepared from $MoCl_5$ (*3–5*). The methyl formate activity increased rapidly at lower Mo loadings and leveled off above 0.2% Mo (*3*). Samples prepared from $(NH_4)_6Mo_7O_{24} \cdot 4H_2O$ (AHM) produced higher quantities of formaldehyde, although some individual samples formed methyl formate with reasonably high selectivity. In contrast to the smooth increase and plateau in methyl formate activity observed with $MoCl_5$-derived samples, the activities for methyl formate and formaldehyde formation were quite erratic as Mo loading was increased on AHM-derived samples.

The mechanism of formaldehyde formation from methanol over molybdenum oxide is widely accepted (*6–8*). In the first step, dissociative adsorption leads to methoxy formation on the molybdena surface. The rate-determining step in formaldehyde formation is cleavage of a C–H bond. For the isolated Mo cations proposed to occur from $MoCl_5$ on silica, Louis *et al.* (*3*) argued that formaldehyde, after forming on the Mo site, would readily spill over and react with the neighboring methoxy groups, which had formed on silica, leading to methyl formate. On clustered Mo cations, in contrast, formaldehyde was proposed to desorb readily without further reaction, because the favorable desorption energetics, characteristic of bulk MoO_3, were proposed to be retained by the clusters.

Yang and Lunsford (*9*) have studied the effect of pH during silica impregnation with

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0021-9517/93 $5.00

AHM on methanol conversion and selectivity to formaldehyde. Samples prepared at pH 2 converted nearly twice as much methanol as samples prepared at pH 11. The low pH Mo/silica sample was thought to contain more polymolybdate and the increased activity was attributed to this species. The selectivity to formaldehyde was lower for the sample prepared at pH 2; however it could not be determined whether this difference in selectivity was due to the difference in conversion or to the intrinsic nature of the catalyst. It was also found that although the conversion of methanol increased with Mo loading up to 9.7%, the selectivity to formaldehyde dropped when the Mo loading was increased from 3.2 to 13.8% Mo.

Elsewhere (*10*) we have reported the Raman spectra of Mo^{6+} in the hydrated and dehydrated state for samples prepared from $MoCl_5$, $Mo_2(\eta^3\text{-}C_3H_5)_4$, $Mo(\eta^3\text{-}C_3H_5)_4$, $H_2(MoO_3C_2O_4)_2H_2O$, and $(NH_4)_6Mo_7O_{24} \cdot 4H_2O$ over the same silicas used in the studies reported herein and at loadings from 0.1 to 10.0% Mo. The Raman study demonstrated (i) that, when hydrated, the oxidized surface molybdate formed an octahedrally coordinated polymolybdate structure at all loadings and for each precursor investigated, (ii) that the formation of crystalline molybdenum compounds, which was observed for aqueous preparations ($H_2(MoO_3C_2O_4) \cdot 2H_2O$ and $(NH_4)_6Mo_7O_{24} \cdot 4H_2O$), was related to weight loading and support impurities, and (iii) that, when dehydrated, an isolated Mo^{6+} structure formed from the surface polymolybdate. Recent publications have also shown the spreading of the octahedrally coordinated polymolybdate structure to an isolated Mo^{6+} structure on silica (*11–13*), demonstrating the general nature of this process and suggesting that, at the lower Mo loadings employed herein, spreading of the polymolybdates to an isolated structure also occurred. This paper reports a reinvestigation of the role of the method of preparation/precursor on the selectivity of Mo/SiO_2 in methanol oxidation over samples that have been characterized by Raman spectroscopy. We show that the methanol oxidation selectivity is not precursor dependent, with the precursor influencing dispersion, rather that impurities present on the silica support may be responsible for high methyl formate selectivity.

EXPERIMENTAL

Mo/SiO_2 samples were prepared from $MoCl_5$, $Mo_2(\eta^3\text{-}C_3H_5)_4$, and AHM as reported elsewhere (*10*). Some Davison 952 silica was washed with dilute sulfuric acid to remove impurities (*14*) (these samples are referred to as acid-washed). The BET area was 317 m^2/gm before acid-washing and 329 m^2/gm after washing.

Some samples were prepared from AHM and iron-doped Cab-O-Sil. Cab-O-Sil was treated with aqueous $Fe(NO_3)_3 \cdot 9H_2O$ (Aldrich, 99.9%), dried at 120°C for 7 hr, calcined for 3 hr at 500°C, and then impregnated with AHM as usual, followed by drying and calcination. Two different calcium-containing samples were prepared. Cab-O-Sil was treated with aqueous $(CH_3COO)_2Ca \cdot H_2O$ (Baker, analyzed reagent grade), dried at 200°C for 3 hr, and calcined for 18 hr at 500°C to make 0.068 wt% Ca/Cab-O-Sil. The 0.068 wt% Ca/Cab-O-Sil was then impregnated with AHM, dried, and calcined to make 1.0% Mo/0.068 wt% Ca/Cab-O-Sil. The second preparation involved contacting a 0.9 wt% Mo/Cab-O-Sil sample made from AHM with $(CH_3COO)_2Ca \cdot H_2O$, followed by drying and calcination to make 0.068% Ca/0.9 wt% Mo/Cab-O-Sil.

For methanol oxidation, 10 mg samples were contained in a 4-mm i.d. Pyrex tube and calcined *in situ* at 450°C for 1 hr before use. Methanol oxidation was performed at 250°C in hydrocarbon-free air, at a methanol partial pressure of 0.1 atm and a total gas flow of 10 cm^3/min. Methanol partial pressure was maintained with a saturator at 10°C in an automatic cooling bath. The reactions usually required 1 hr to come to steady state. Duplicate runs were preformed for most samples. Gas samples were taken for gas

TABLE 1

Methanol Oxidation on Mo/Cab-O-Sil Samples at 250°C

Molybdenum loading (wt%)	Precursor[a]	Methanol conversion (%)	Activity[b] to methyl formate	Activity to CO_2	Activity to formaldehyde
0.10	AHM	2.32	2.150	2.750	0.791
0.20	AHM	1.60	2.270	0.789	0.865
0.20	AHM	2.56	3.140	1.320	1.070
0.40	AHM	0.87	1.730	0.405	0.000
0.50	AHM	2.19	3.780	0.853	0.746
0.50	AHM	0.57	1.250	0.154	0.000
0.60	AHM	1.76	3.530	0.514	0.280
0.80	AHM	1.91	3.930	0.540	0.220
0.54	allyl	1.09	2.050	0.468	0.157

[a] AHM is $(NH_4)_6Mo_7O_{24} \cdot 4H_2O$; allyl is $Mo_2(\eta^3\text{-}C_3H_5)_4$.

[b] moles-hr^{-1}-(g of catalyst)$^{-1}$ × 10^3.

chromatograph (GC) analysis every 30 min for 3–4 hr.

Air, carbon dioxide, formaldehyde, methyl ether, water, methanol, and methyl formate were separated with a 6 ft × 0.125 in. stainless-steel column packed with Porapak T and were analyzed with the thermal conductivity detector of a Hewlett–Packard 5880 GC. Dimethoxymethane was seen under several reaction conditions but not under those reported herein.

RESULTS

Cairati and Trifiro (*15*) have observed the formation of CO, CO_2, CH_2O, and CH_3OCHO during methanol oxidation over a fluidized bed of a commercial silica. The temperatures used in that study were generally higher (>300°C) than those used in this study, although one silica (*15*) showed activity at temperatures as low as 240°C. Silica activity experiments were performed with all of the silica types used in this study, including those doped with iron and calcium. Only traces of water and carbon dioxide were formed over silica and the activity of silica was unchanged with acid washing (Ca and Fe removal), Fe doping, or Ca doping. Methanol oxidation caused by the support alone was therefore minimal under the conditions used in this study.

Tables 1–3 summarize the methanol oxidation results over Cab-O-Sil, Davison 952, and acid-washed Davison 952. The selectivities for carbon dioxide, formaldehyde, and methyl formate were 5 to 48%, 0 to 22%, and 38 to 89%, respectively. As the methanol conversion increased, the selectivity to methyl formate increased as well. As the methanol conversion decreased, the selectivities to carbon dioxide and formaldehyde approached the higher limits of the ranges listed above. Selectivities were defined on the basis of molecules of methanol that are converted to a given product, after Louis *et al.* (*3*).

The methyl formate activity for these catalysts is illustrated in Figs. 1–3. Each support produced different results. The methyl formate activity was lowest over Mo supported on Cab-O-Sil and increased from 1 to 4 moles-hr^{-1}-(g cat)$^{-1}$ × 10^3 for the loadings investigated. The methyl formate activity was higher over Davison 952 and highest over acid-washed Davison 952.

One or more surface impurities was suspected as the cause for the different activity to methyl formate. Iron was selected for study because $FeMoO_4$ has been shown to be an effective catalyst for methanol oxidation (*16*). The iron impurity levels for the silicas used herein are listed in Table 4. The iron content of Cab-O-Sil is more than two orders of magnitude lower than over any of

TABLE 2

Methanol Oxidation on Mo/Davison 952 Samples at 250°C

Molybdenum loading (wt%)	Precursor[a]	Methanol conversion (%)	Activity[b] to methyl formate	Activity to CO_2	Activity to formaldehyde
0.13	$MoCl_5$	1.59	2.100	1.580	0.221
0.26	$MoCl_5$	4.80	9.580	1.077	1.118
0.26	$MoCl_5$	4.99	10.160	0.880	1.178
0.80	AHM	4.19	8.030	0.707	1.540
0.80	AHM	5.08	9.840	0.964	1.660
0.06	allyl	2.95	5.325	1.368	0.550
0.41	allyl	5.96	11.300	1.005	2.316
0.42	allyl	6.11	12.110	0.847	2.020
0.62	allyl	3.42	6.880	0.524	0.970
0.62	allyl	5.23	9.851	0.999	1.973
1.11	allyl	2.19	4.106	0.497	0.760
1.11	allyl	2.34	4.650	0.362	0.720

[a] AHM is $(NH_4)_6Mo_7O_{24} \cdot 4H_2O$; allyl is $Mo_2(\eta^3\text{-}C_3H_5)_4$.

[b] moles-hr^{-1}-(g of catalyst)$^{-1}$ × 10^3.

the other supports. Molybdenum was present in excess for the iron-doped Cab-O-Sil samples, with a molar ratio ranging from 3.9 to 29.1 Mo/Fe. There was no evidence from Raman of either iron–molybdenum compounds or crystalline phases over any of the samples investigated. The catalytic performance of these samples is listed in Table 5 and shows that methyl formate activity increased when iron was present on the surface of Cab-O-Sil.

The calcium levels in the silicas are also presented in Table 4. A doping level of 0.068 wt% Ca was selected to test the effect of Ca on catalyst activity over Cab-O-Sil. The 1.0% Mo/0.068 wt% Ca/Cab-O-Sil, 0.068% Ca/0.9 wt% Mo/Cab-O-Sil, and 0.9 wt% Mo/Cab-O-Sil samples had average methyl

TABLE 3

Methanol Oxidation on Mo/Davison 952 (Acid-Washed) Samples at 250°C

Molybdenum loading (wt%)	Precursor[a]	Methanol conversion (%)	Activity[b] to methyl formate	Activity to CO_2	Activity to formaldehyde
0.20	AHM	7.68	15.480	1.440	1.917
0.20	AHM	4.57	8.800	1.600	0.802
0.20	AHM	8.32	13.810	3.810	2.770
0.40	AHM	9.24	18.740	1.490	2.440
0.40	AHM	6.10	12.088	1.700	1.180
0.40	AHM	7.68	14.620	1.670	2.540
0.60	AHM	7.13	14.300	1.339	1.838
0.60	AHM	7.23	14.660	1.100	1.970
0.80	AHM	6.53	9.130	3.350	3.530
1.00	AHM	5.74	11.930	0.878	1.260
1.00	AHM	3.91	7.800	0.982	0.809

[a] AHM is $(NH_4)_6Mo_7O_{24} \cdot 4H_2O$.

[b] moles-hr^{-1}-(g of catalyst)$^{-1}$ × 10^3.

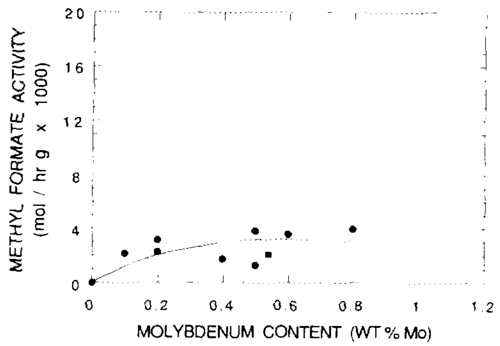

FIG. 1. Methyl formate activity over Cab-O-Sil-supported Mo prepared from AHM (●) and $Mo_2(\eta^3\text{-}C_3H_5)_4$ (■).

formate activities of 2.26, 1.36, and 2.33 moles-$hr^{-1}(g\ cat)^{-1} \times 10^3$.

Table 5 also lists the activity of two catalysts prepared in the laboratories of M. Che using $MoCl_5$ and Rhone-Poulenc XOA-400. The Rhone-Poulenc silica was not the same batch as was used to prepare the samples in Ref. (*3*). The Mo/Rhone-Poulenc samples have comparable activities to the Mo/Davison and Mo/Davison acid-washed samples. The methyl formate activity measured for the Rhone-Poulenc samples compared well with the activities reported earlier (*3*), when interpolated to account for the different temperatures used here and in Ref. (*3*).

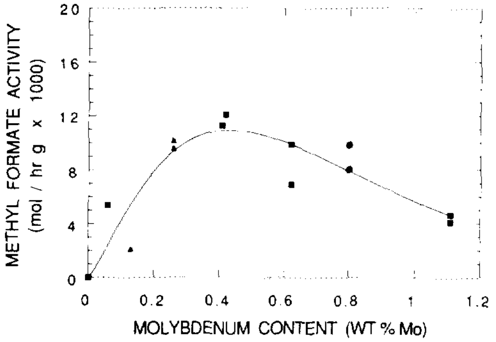

FIG. 2. Methyl formate activity over Davison 952-supported Mo prepared from AHM (●), $Mo_2(\eta^3\text{-}C_3H_5)_4$ (■), and $MoCl_5$ (▲).

TABLE 4

Iron and Calcium Content of Silica Supports Used for Methanol Oxidation

Silica	% Fe	% Ca
Davison 952	0.0062[a]	0.053[a]
Davison 952 (acid-washed)	0.0043[a]	0.013[a]
Rhone-Poulenc XOA-400[b]	0.0105[a]	0.010[a]
Cab-O-Sil	<0.0001[c]	<0.0002[c]

[a] Determined by Galbraith Laboratories.

[b] Not the same batch used by Louis *et al.* (*3*).

[c] Determined by supplier.

DISCUSSION

A separate Raman study (*10*) revealed that, when hydrated, a polymolybdate structure formed over the silicas used here and that crystalline compounds, MoO_3 and $CaMoO_4$, could also be formed at loadings as low at 0.1 wt% Mo when aqueous preparation methods, such as AHM, were employed. The formation of $CaMoO_4$ can be prevented (*10*) by removing the Ca impurity from supports such as Davison 952 with acid washing prior to impregnation with AHM. On the basis of Raman studies only a surface polymolybdate structure was present, when hydrated, for samples made from $Mo_2(\eta^3\text{-}C_3H_5)_4$ and $MoCl_5$, while the same polymolybdate structure and MoO_3 were present for samples made from AHM. Isolated Mo^{6+} on the silica surface should be formed

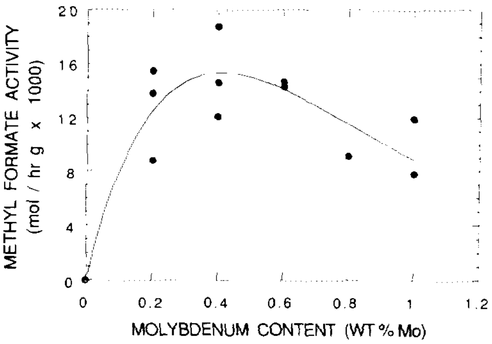

FIG. 3. Methyl formate activity over acid-washed Davison 952-supported Mo prepared from AHM.

TABLE 5

Methanol Oxidation on Mo(VI) Supported on Iron-Doped, Cab-O-Sil and Rhone-Poulenc XOA-400[a]

Molybdenum loading (wt%)	Support[b]	Precursor[a]	Methanol conversion (%)	Activity[b] to methyl formate	Activity to CO$_2$	Activity to formaldehyde
0.20	0.01%-Fe	AHM	4.26	7.350	1.850	1.260
0.20	0.01%-Fe	AHM	2.47	3.870	1.570	0.608
0.20	0.01%-Fe	AHM	1.73	3.100	0.793	0.360
0.20	0.03%-Fe	AHM	3.37	7.070	0.345	0.842
0.50	0.01%-Fe	AHM	6.98	7.800	6.108	3.200
0.50	0.01%-Fe	AHM	2.56	4.230	1.097	0.940
0.50	0.03%-Fe	AHM	4.22	8.490	1.010	0.850
0.07	XOA-400	MoCl$_5$	4.88	9.600	1.620	0.752
0.07	XOA-400	MoCl$_5$	5.48	10.100	1.830	1.500
0.84	XOA-400	MoCl$_5$	5.36	10.670	1.320	1.160
0.84	XOA-400	MoCl$_5$	6.06	12.300	1.940	0.628
0.84	XOA-400	MoCl$_5$	6.21	12.880	1.770	0.570

[a] Samples provided by M. Che.

[b] 0.01%-Fe were loaded with 0.01 wt% Fe; 0.03%-Fe were loaded with 0.03 wt% Fe.

[c] AHM is $(NH_4)_6Mo_7O_{24} \cdot 4H_2O$.

[d] moles-hr^{-1}-(g of catalyst)$^{-1}$ × 10^3.

(*10–13*) from the polymolybdate structure during the *in situ* calcination step preformed prior to methanol oxidation.

Figure 4 summarizes the results over all of the samples investigated. The curves from Figs. 1–3 are shown, without data, along with the methyl formate activity results over iron-doped Cab-O-Sil and Rhone-Poulenc samples. This figure reveals several features of Mo. First, Mo has a rather low activity for methanol oxidation when supported on silica, and because of this other factors can influence the catalytic properties. Second, the support and most likely the impurities on the support had the greatest effect on the catalytic performance of Mo for methanol oxidation. Finally, there does not appear to be a unique method of preparation or precursor that leads to high activity to methyl formate provided the comparisons are made at the same coverage.

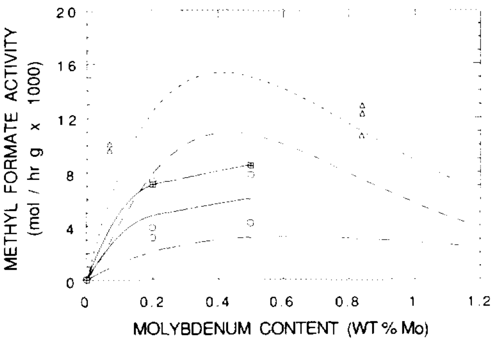

FIG. 4. Methyl formate activity over Mo supported on Cab-O-Sil (————), Davison 952 (– – –), or acid-washed Davison 952 (---) or prepared from 0.01 wt% Fe-doped Cab-O-Sil and AHM (—○—) 0.03 wt% Fe-doped Cab-O-Sil and AHM (—□—), and MoCl$_5$ and Rhone-Poulenc XOA-400 (△).

Cab-O-Sil-supported Mo showed the lowest activity and the activity increased slowly with Mo loading. (A similar loading dependence was reported by Louis *et al.* over a different Mo catalyst (*3*). When impurity levels on Cab-O-Sil were changed, by iron doping, the activity increased dramatically (Table 5, Figure 4). Also, other supports, which contained impurity concentrations higher than that of Cab-O-Sil, displayed a higher activity even though the same hydrated, polymolybdate phase was present over all the silicas. Since Cab-O-Sil was the purest support examined, the results over this support are probably an indication of inherent catalytic activity of dispersed Mo^{6+}.

Impurities on the silica supports are suspected as the principle cause for the different methyl formate activities. In the studies reported here only two support impurities were investigated, Fe and Ca, and Fe was found to alter the activity significantly over Cab-O-Sil. An increase in methanol conversion and possibly methyl formate activity was anticipated because $FeMoO_4$ has been shown to oxidize methanol (*12*); however, iron–molybdate phases could not be detected using Raman spectroscopy. It is not possible to associate the activities reported by others (*3–5, 9*) to this impurity, nor is it possible to establish that the iron impurity on Davison 952 and Rhone-Poulenc XOA-400 caused the methyl formate activity seen in Fig. 4 to be higher than that in Cab-O-Sil. Our study does demonstrate that when iron was added to a system where it was initially absent, the activity increased. The study also indicates that support impurities should be considered when the inherent activity of the catalyst (in this case Mo^{6+}) is very low.

Acid washing removed Ca from Davison 952 and thereby prevented the formation of $CaMoO_4$ on the samples prepared from AHM (Table 3, Fig. 3). The hydrated Mo on acid-washed Davison 952 was present as MoO_3 and polymolybdate. The hydrated Mo on Davison 952 was present as polymolybdate for samples made with $Mo_2(\eta^3\text{-}C_2H_5)_4$ and $MoCl_5$, and as the polymolybdate, MoO_3 and $CaMoO_4$ for samples made with AHM. The results over the two Davison 952 supports suggest that the MoO_3 and $CaMoO_4$ crystallites do not contribute to the formation of methyl formate and that they may be spectators under the conditions of the catalytic reactions. The calcium-doped Cab-O-Sil samples are expected to contain some $CaMoO_4$. The activity did not increase above that observed with Mo/Cab-O-Sil when calcium was added before or after the deposition of Mo, rather it decreased somewhat. A decrease is expected if the Mo, in the form of $CaMoO_4$, is not available for reaction.

Louis *et al.* (*3*) have reported significant differences in the activity to methyl formate over different Mo/Rhone-Poulenc samples than we examined herein. They prepared catalysts from $MoCl_5$ and AHM. The methyl formate selectivity increased rapidly at low loadings and increased smoothly with loading for samples prepared from $MoCl_5$. The samples they prepared from AHM, while reproducible, displayed an erratic methyl formate activity with increasing Mo loading. The differences in catalytic performance were associated with differing degrees of Mo^{6+} dispersion. Grafting Mo onto the support via $MoCl_5$ was reasoned to give a uniform dispersion, while impregnation from AHM was proposed to lead to some form of Mo clustering.

The samples we prepared from AHM over acid-washed Davison 952 were of comparable methyl formate selectivity to those samples supplied by M. Che. Following *in situ* calcination, the samples prepared from AHM had MoO_3 crystallites along with a dispersed Mo^{6+}, whereas samples prepared from $MoCl_5$ only had the dispersed Mo^{6+} species. We agree that there is a higher dispersion of Mo^{6+} when using $MoCl_5$ to support Mo on silica because MoO_3 formation is avoided. However, the same molybdate phase is formed by all the precursor routes investigated here and differences seen in Fig. 4 are not associated with different degrees of dispersion of noncrystalline molybdenum.

CONCLUSIONS

(i) The CO_2, CH_2O, and CH_3OCHO selectivities of Mo^{6+}/SiO_2 prepared from AHM, $MoCl_5$, and $Mo_2(\eta^3\text{-}C_3H_5)_4$, on all silica samples studied, are largely independent of the Mo precursor and the silica type.

(ii) The overall methanol oxidation activities and the specific methyl formate activities are largely independent of the Mo precursor.

(iii) The inherent activity of dispersed

Mo^{6+} is low enough that impurities on the support can enhance the activity of Mo.

ACKNOWLEDGMENTS

This work was supported by the Robert A. Welch Foundation and the U.S. Department of Energy, Office of Basic Energy Sciences. We thank M. Che for providing the samples prepared with Rhone-Poulenc silica.

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