

Erratum

Due to a printer's error reproduction of figs. 2a and 3a of the following paper, published in Volume 36 (1996), pp. 87–93, was too dark. The correct version is printed below.

Selectivities in methanol oxidation over silica supported molybdena

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Selectivities in methanol oxidation over silica supported molybdenum oxide catalysts were investigated in relation with the phase distribution. The supported catalysts were prepared by impregnation with ammonium heptamolybdate. In addition to crystalline MoO_3 , Mo containing cluster species of 1–2 nm size were observed by STEM even from a used catalyst with 13% catalyst loading. The percentage of Mo present as crystalline MoO_3 increases with the catalyst loading. An ESCA study indicates that part of surface Mo in the supported catalysts is reduced to Mo^{5+} . The dimethyl ether selectivity increases with the catalyst loading and its formation occurs over the crystalline MoO_3 phase. The selectivities to CO and methyl formate are greatly enhanced because of the presence of support, and are relatively independent of the catalyst loading and phase distribution. The dependence and independence of the selectivities of different byproducts on the loading make the silica supported catalysts with high catalyst loadings less selective for the partial oxidation of methanol to formaldehyde.

Keywords: methanol oxidation; silica; molybdenum oxide; MoO_3 ; cluster; XRD; STEM; methanol; formaldehyde

1. Introduction

The partial oxidation of methanol to formaldehyde over bulk MoO_3 based oxides is an important industrial reaction and has been studied extensively [1–6]. Use of supported molybdenum oxide catalysts for the methanol oxidation reaction was studied to increase the strength of the catalysts for the fluidized bed application. Supports studied include SiO_2 [7–9], Al_2O_3 [10], TiO_2 [11], ZrO_2 [12] and Fe_2O_3 [13].

Unlike alumina support, silica only weakly interacts with molybdenum oxide. Depending on the method of preparation, various types of Mo species have been reported for silica supported catalysts. Impregnation with ammonium heptamolybdate generally yields low dispersions; crystalline MoO_3 was found at Mo loading down to 0.4 wt% [14]. Preparation based on interaction between a silanol group and organometallic compounds such as $\text{Mo}(\eta^3\text{-C}_3\text{H}_5)_4$ and $\text{Mo}_2(\eta^3\text{-C}_3\text{H}_5)_4$ was reported to produce highly dispersed Mo species [15–17]. Polymolybdate, such as heptamolybdate, was identified by Raman spectroscopy for the hydrated state of the catalyst [15–17]. Upon dehydration by thermal heating, spreading of Mo species occurs and yields isolated Mo^{6+} species [18].

Many supported molybdenum oxide catalysts have lower selectivity to formaldehyde than the unsupported catalysts in methanol oxidation [7,19,20]. Yang et al. were even surprised to find that the selectivity to formaldehyde over silica supported molybdena catalysts decreases with the Mo loading although the unsupported MoO_3 is a very selective catalyst [7]. Although a significant amount of studies on the characterization and syn-

thesis of silica supported molybdena catalysts have been conducted, there has been little study on the relation between phases in the supported catalysts and the selectivities in the oxidation of methanol despite of its scientific importance. We report here some selectivity issues over silica supported molybdenum oxide catalysts at high molybdenum loadings in combination with the characterization of Mo phases. This work reveals that the formation of dimethyl ether is phase dependent and occurs from the crystalline MoO_3 phase. On the other hand, the formation of CO and methyl formate over the silica supported catalysts is phase independent.

2. Experimental

Bulk MoO_3 was prepared by decomposing molybdenum oxalate obtained from Climax Molybdenum Company in O_2 at 350°C . It has an orthorhombic structure and surface area of $4.7\text{ m}^2/\text{g}$. The silica supported Mo oxide catalysts were prepared by the impregnation technique using $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24}\cdot 4\text{H}_2\text{O}$ as the Mo source. The silica support was obtained via Ludox[®] colloidal silica. The surface area of the support is $256\text{ m}^2/\text{g}$. The catalysts were dried at 100°C for 16 h and calcined at 350°C for 1 h in O_2 . 2 g of catalysts were loaded in a fixed bed reactor (3/8" o.d. titanium). The catalysts were also conditioned at 350°C for 1 h in air everyday before the reaction study.

Methanol feed was introduced from a liquid pump and vaporized. The feed to the reactor contains 10% methanol in air at 75 sccm (standard cm^3/min). These standard catalyst preparation and reaction conditions

Table 1
Methanol oxidation over MoO₃, MoO₃/SiO₂ and SiO₂

Sample	Reaction temp. (°C)	Methanol conv. (%)	Selectivity ^a (%)					
			CH ₂ O	DME	MF	methylal	CO	CO ₂
MoO ₃	300	49.8	78.5	12.4	4.2	3.0	1.8	0
13% MoO ₃ /SiO ₂ ^b	300	94.6	67.2	8.4	2.0	0	21.2	1.3
SiO ₂ ^c	270	6.5	9.0	0	78.4	0	0	12.7
	300	25.8	16.4	0	42.5	0	11.5	29.5
	330	34.3	16.7	0	26.1	0	18.9	38.3

^a DME: dimethylether, MF: methyl formate. ^b Feed was 7.1% methanol in air. ^c 1.7 g of SiO₂ was used.

were used unless otherwise indicated. The catalyst loading is expressed as a weight percent of MoO₃. The selectivity is expressed as a mole percent. For convenience, the silica supported molybdenum oxides will be designated as MoO₃/SiO₂ in this paper.

The STEM study was conducted using a VG HB-501 STEM with a Kevex energy dispersive X-ray spectrometer. The specimen for the STEM study was prepared by grinding up the catalyst in a mortar and pestle and dispersing the dry particles on a carbon film. The IR study was performed using a Nicolet 3600 FTIR. XRD data were obtained from a Rigaku θ/θ diffractometer using Cu K α radiation. ESCA was performed with a Du Pont 650 equipment.

3. Results

3.1. Methanol oxidation

The methanol conversion and selectivities in metha-

nol oxidation over a bulk MoO₃, a silica supported Mo oxide and silica are shown in table 1. Dimethyl ether was observed from the bulk and supported molybdenum oxide catalysts but not from the support silica. Methyl formate is a major product from silica especially at low conversions. Interestingly, little CO₂ is formed over the bulk and supported molybdenum oxide catalysts, but a significant amount of CO₂ is produced from SiO₂ although the activity of SiO₂ is relatively low. The ratio of the CO₂ selectivity to CO selectivity is high over SiO₂. This indicates that most of the surfaces of the supported catalyst no longer possess the intrinsic property of the silica support. The contribution of the bare SiO₂ surfaces to the activity of the supported catalysts is minimal.

Deep oxidation of methanol to CO results in a major loss of the formaldehyde selectivity in the partial oxidation of methanol over the silica supported catalyst at high conversions. However, the selectivities also strongly depend on the conversion. Fig. 1 compares the selectivity to CO over bulk and supported catalysts at

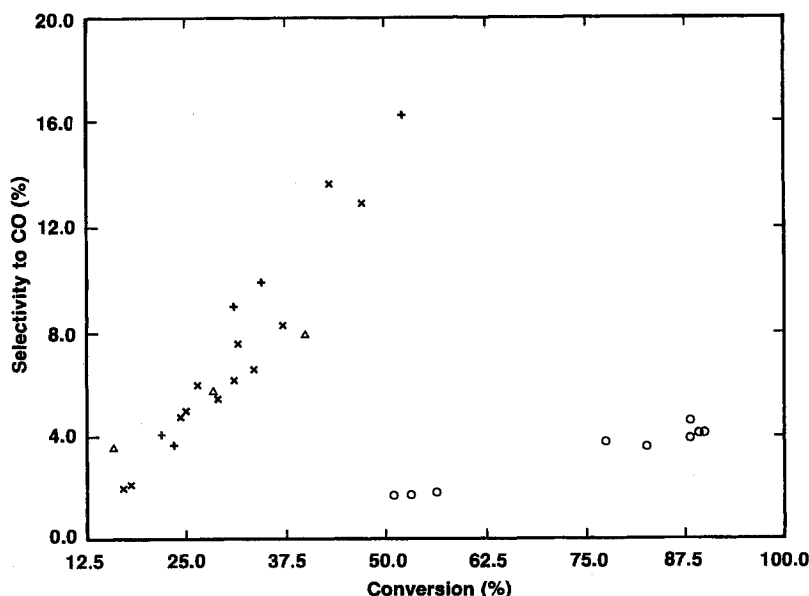


Fig. 1. The CO selectivity in methanol oxidation at various conversions over 9% MoO₃/SiO₂ (Δ), 13% MoO₃/SiO₂ (+), 38% MoO₃/SiO₂ (×), and bulk MoO₃ (○).

various methanol conversions which were varied by changing reaction temperatures and methanol feed concentrations. The selectivity to CO over the supported catalysts is much higher than that from the bulk MoO_3 catalyst at all conversion levels. However, there is no significant and consistent difference in the CO selectivity between the supported catalysts at different loadings.

The 13% $\text{MoO}_3/\text{SiO}_2$ was studied further for the effect of the crystallite size of MoO_3 on the selectivity. The crystallite size was varied by changing the calcina-

tion time. The only crystalline phase indicated by XRD was orthorhombic MoO_3 . The average crystallite size of MoO_3 determined by X-ray line broadening technique was 9.7 nm after 13% $\text{MoO}_3/\text{SiO}_2$ was calcined at 350°C for 1 h. The crystallite size increased to 19.8 nm after calcination at 350°C for 15 h. However, little difference in the dependence of the CO selectivity on the conversion was observed between these two supported catalysts with different MoO_3 crystallite size. The CO selectivity is relatively independent of the catalyst loading as well as

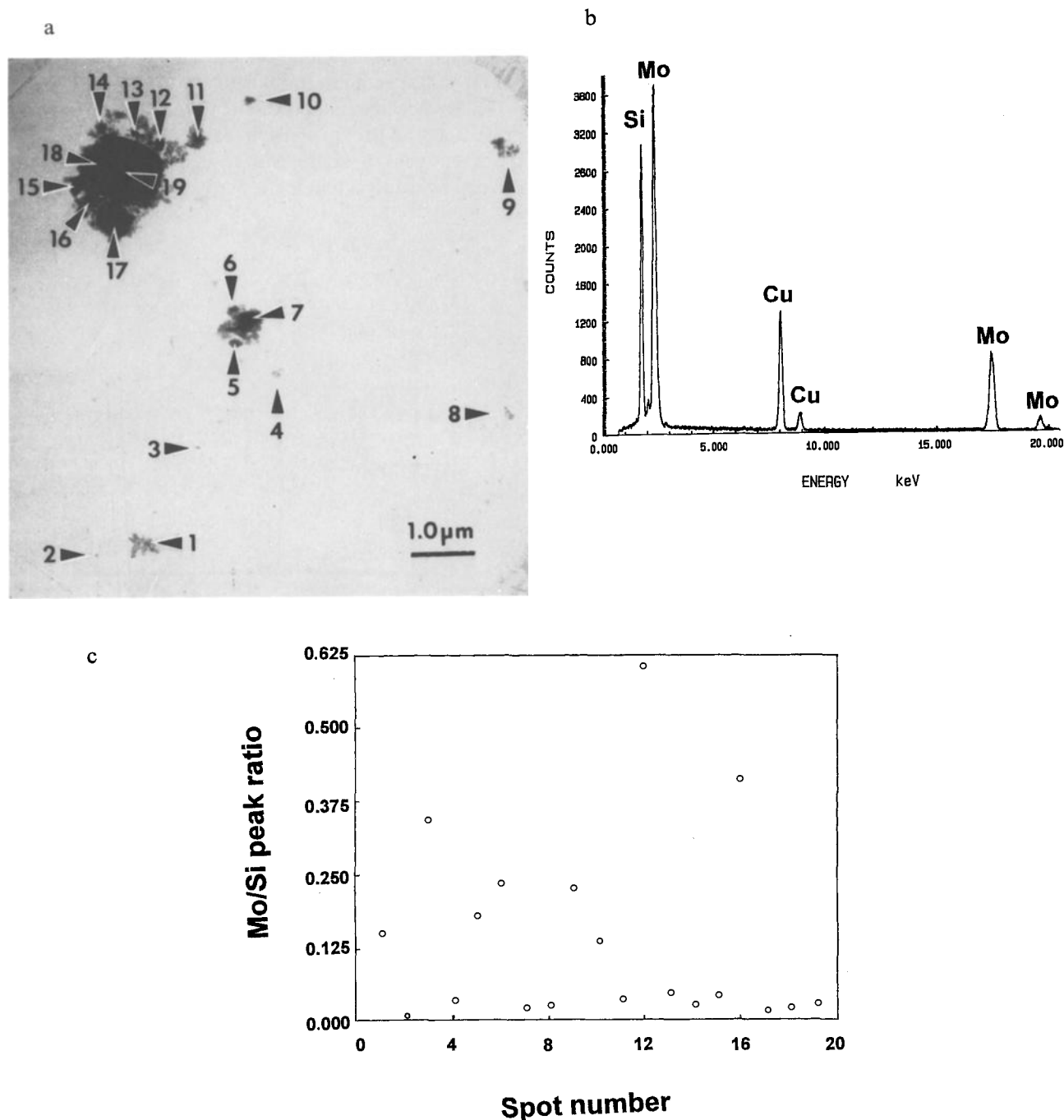


Fig. 2. (a) Bright-field STEM survey image of the used 13% $\text{MoO}_3/\text{SiO}_2$ specimen. (b) X-ray spectrum of spot 12. (c) The intensity ratio of low-energy Mo-to-Si peaks for the spots indicated on (a).

the crystallite size of MoO_3 for the silica supported catalysts, but the support greatly increases the selectivity to CO.

3.2. Characterization of supported Mo oxides

To study the morphology of the supported molybdenum oxide catalysts, a used 13% $\text{MoO}_3/\text{SiO}_2$ catalyst previously calcined for 15 h before the reaction was investigated by STEM. Fig. 2a shows a bright field image for a survey analysis. X-ray analysis was conducted in the STEM equipment. As an example, the X-ray spectrum taken with the raster size of about 200 nm square area for dark spot #12 is given in fig. 2b. Cu peaks in the spectrum were originated from a Cu grid used to support the carbon film. The intensity ratios of the Mo K_α to Si K_α peaks are shown in fig. 2c for the spots indicated on fig. 2a. The intensity ratio of Mo to Si varies over a wide range. The dark spots with high Mo/Si ratios

probably contain crystalline MoO_3 as revealed by XRD indicated in the previous section. To avoid electron scattering and bremsstrahlung generation creating detectable Mo X-rays even in areas free of Mo, a 20 nm single well-separated Ludox[®] sphere was used for the further study under a high magnification as shown in fig. 3. Some dark spots of 1–2 nm size can be clearly visualized (fig. 3a). X-ray analysis from just the dark spot shows the presence of Mo by scanning a very small raster of 2 nm square area over the particle (fig. 3b). Very little Mo was found in the adjacent clear area (fig. 3c). The STEM and XRD results clearly show that at least two morphologically distinct phases are present in the silica supported molybdenum oxide catalyst: crystalline MoO_3 and Mo containing clusters.

To further understand the relative percentage of Mo present as the MoO_3 phase in each supported catalyst, the XRD peak area for MoO_3 at 0.326 nm d spacing divided by catalyst loading is used as an indicator. Simi-

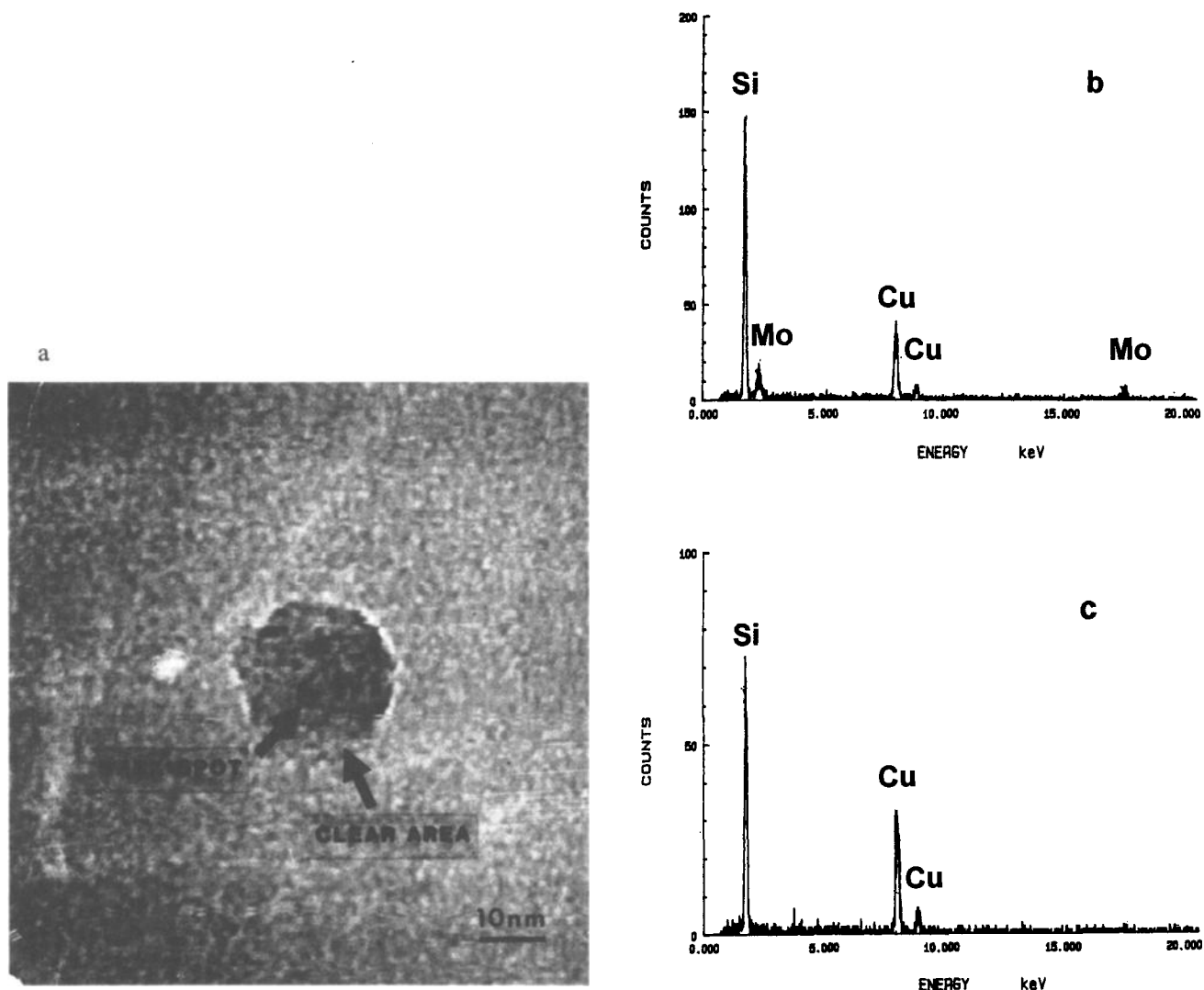


Fig. 3. (a) STEM image of a single Ludox sphere in the 13% $\text{MoO}_3/\text{SiO}_2$ catalyst used showing dark spots of 1–2 nm size. (b) X-ray spectrum of the dark spot. (c) X-ray spectrum of the clear area.

larly, the intensity of an IR peak for MoO_3 at about 995 cm^{-1} with respect to the peak intensity at about 1170 cm^{-1} for SiO_2 after loading adjustment is used as the second indicator. The results are given in table 2. Each value was the average value of two repeated analyses. It can be drawn from these two studies that the relative composition of the MoO_3 phase with respect to total Mo content generally increases with the Mo loading although the increase becomes slower at higher loadings.

ESCA was used to study the oxidation state of surface Mo in the bulk and supported molybdenum oxide catalysts. The ESCA spectrum of the fresh, bulk MoO_3 catalyst shows the presence of Mo^{6+} only (fig. 4a). Its spectrum does not change after the reaction. However, the ESCA spectrum of the fresh 13% $\text{MoO}_3/\text{SiO}_2$ catalyst shows the overlapping peaks of Mo^{6+} and Mo^{5+} (fig. 4b). Binding energy values were based on the Si 2p peak of SiO_2 at 103.5 eV [21]. Binding energies of the 3d doublets of Mo^{6+} and Mo^{5+} have been reported [22]. Part of surface Mo in the supported catalyst was in the reduced state. Mo^{5+} species still exists for the 13% $\text{MoO}_3/\text{SiO}_2$ catalyst calcined at 350°C for 15 h.

3.3. Relation of morphology with selectivities

Although the selectivity to CO is relatively independent of the catalyst loading (fig. 1), the selectivity to dimethyl ether increases with the catalyst loading when compared at the same conversion. Fig. 5 gives an example at 40% conversion level. The selectivity to formaldehyde decreases with the catalyst loading because of the corresponding increase in the dimethyl ether selectivity. However, low selectivity to CO over the bulk MoO_3 catalyst makes it a selective catalyst for the formaldehyde production. Similar dependence of the selectivities to CO, dimethyl ether and formaldehyde on the catalyst loading was observed when comparisons were made at low conversions at the same 270°C (table 3). Similar to CO, the selectivity to methyl formate is also relatively unaffected by the molybdenum loading; the selectivity is much higher over the supported catalysts than that from the bulk MoO_3 catalyst. Table 3 also shows that the activities of these samples only vary within a limited range. From these results it can be

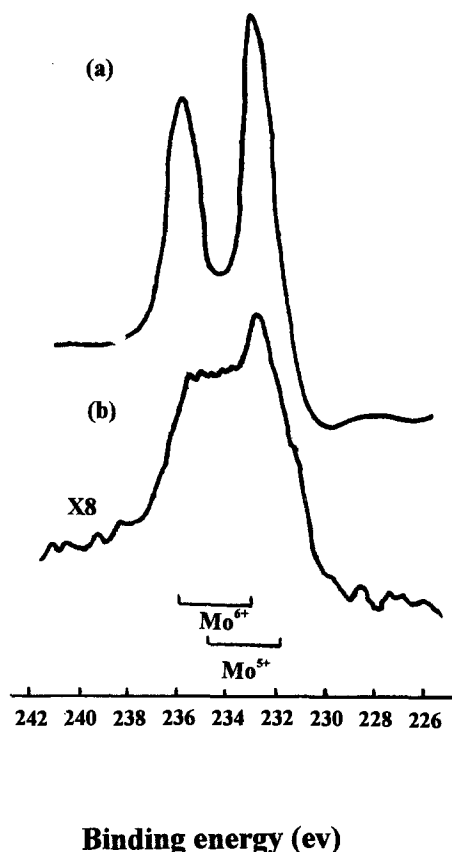


Fig. 4. (a) ESCA spectrum of the bulk MoO_3 catalyst. (b) ESCA spectrum of the 13% $\text{MoO}_3/\text{SiO}_2$ catalyst.

deduced that the dimethyl ether selectivity parallels with the relative composition of MoO_3 . The selectivity is also highest for the bulk MoO_3 catalyst.

4. Discussion

The activity of silica in methanol oxidation is relatively low and its deep oxidation yields mainly CO_2 instead of CO. Contribution of the SiO_2 surface to the formation of CO from the supported catalysts would be low. On the other hand, if we assume that CO_2 is produced only from the SiO_2 surface for the supported catalysts, the percentage of the bare SiO_2 surface can be calculated by comparing the production of CO_2 from the supported catalysts and the CO_2 activity of silica. The result shows that less than 20% of the support surface of 13% $\text{MoO}_3/\text{SiO}_2$ is intrinsic SiO_2 . Most of the SiO_2 surface is covered or modified by molybdenum.

At least two morphologically distinct phases, crystalline MoO_3 and cluster, were evidenced in the silica supported catalysts. XRD shows the presence of crystalline MoO_3 ; STEM analysis reveals the presence of Mo containing, small clusters of 1–2 nm size. Furthermore, the normalized IR and XRD intensities for the MoO_3 phase per unit loading vary with the catalyst loading. It suggests that more than one phase is present in the sup-

Table 2
Relative composition of the MoO_3 phase indicated by XRD and IR

Catalyst	XRD I_{MoO_3}/L^a	IR $(I_{\text{MoO}_3}/L)^a$ $I_{\text{SiO}_2}/(1-L)$
5% $\text{MoO}_3/\text{SiO}_2$	18	—
9% $\text{MoO}_3/\text{SiO}_2$	36	48
13% $\text{MoO}_3/\text{SiO}_2$	100	100
38% $\text{MoO}_3/\text{SiO}_2$	95	125

^a Normalized with respect to 13% $\text{MoO}_3/\text{SiO}_2$ at 100; $L = \text{MoO}_3$ loading.

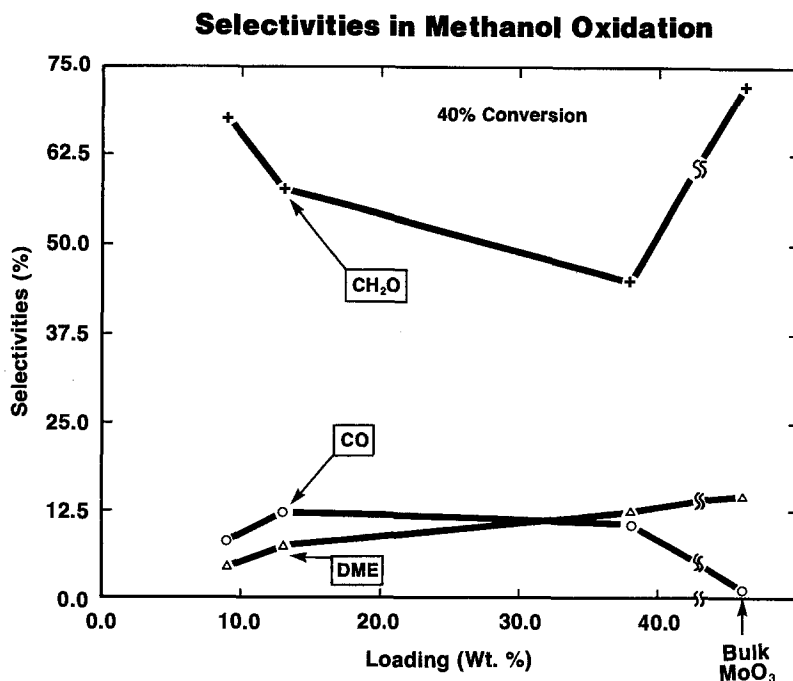


Fig. 5. Dependence of selectivities in methanol oxidation on catalyst loading at a constant 40% conversion.

ported catalysts. These results are consistent with Raman studies from similar impregnated catalysts showing MoO₃ and the polymolybdate (i.e. heptamolybdate) cluster when the catalyst was in the hydrated state (e.g. in ambient environment) [16,17]. Heating the catalyst during the calcination converts polymolybdate to an isolated monodispersed Mo⁶⁺ species [18]. The polymolybdate cluster is reformed after rehydration. The spreading phenomenon on silica suggests that monodispersed Mo would also be present during the methanol oxidation reaction. Although the monodispersed Mo species was not directly observed in this study, its presence is consistent with the observation that bare SiO₂ surface in the supported catalysts is very limited.

The IR and XRD study indicates that the composition of Mo present as crystalline MoO₃ increases with the catalyst loading (table 2). It is clear from this study that dimethyl ether is largely produced from the MoO₃ phase based on the direct correlation between the phase composition and the dimethyl ether selectivity. Since the selectivities in methanol oxidation strongly depend on

the methanol conversion, the comparison was made at the same or similar conversion levels. This correlation indicates the dehydration activity of acidic MoO₃. The selectivities to CO and methyl formate from the supported catalysts are much higher than those from the bulk MoO₃ catalyst. It implies that these two products are largely produced from the dispersed species in the supported catalysts. Williams and Ekerdt recently reported that impurities on silica support, rather than the method of preparation or precursor, influence the selectivity (mainly methyl formate, formaldehyde and CO₂) in methanol oxidation at low conversions for loading less than 1.1 wt% Mo metal [9]. The absence of the precursor effect suggests that the phases of Mo species would not affect the selectivity at low catalyst loadings. Our results extend the absence of the effect of Mo phases to high Mo loadings for the CO and methyl formate selectivities. The dimethyl ether selectivity was not addressed in Williams' study. Also contrary to their study, CO instead of CO₂ was produced significantly from the supported catalysts. High ratios of CO to CO₂

Table 3
Activity and selectivities in methanol oxidation at 270°C

Catalyst	Activity (mmol/(h g-sample))	Selectivity (%)				
		CO	DME	MF	methylal	CH ₂ O
9% MoO ₃ /SiO ₂	1.53	3.7	~0	28.5	14.0	53.8
13% MoO ₃ /SiO ₂	2.18	3.6	9.7	34.9	11.2	40.6
38% MoO ₃ /SiO ₂	1.77	3.7	16.0	34.4	11.1	34.8
bulk MoO ₃	2.01	~0	16.6	4.6	15.6	63.2

selectivities were also found from the unsupported catalyst from this study and others [3].

The selectivity to formaldehyde decreases with the catalyst loading although the unsupported MoO_3 is a highly selective catalyst. This result confirms the early observation by Yang and Lunsford [7]. Our study further points out that the supported molybdenum oxide catalysts with high loadings are not very selective for the partial oxidation reaction because of high selectivities to CO and methyl formate due to the support effect and high dimethyl ether selectivity due to high compositions of the crystalline MoO_3 phase. It also suggests that the formation of formaldehyde from the MoO_3 phase in the supported catalysts does not occur as much as in the case when the support would not have been present. There are two possibilities for this: (1) formaldehyde produced is further oxidized to CO by dispersed species. This possibility is less likely because our separate study showed that the loss of the selectivity to formaldehyde over the supported catalysts is largely attributed to the deep oxidation of methanol rather than further oxidation of the product formaldehyde after it is produced in the gas phase [23]. (2) The production of formaldehyde is retarded over the MoO_3 phase when the support is present. 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 [6]. Pulse experiments show that formaldehyde selectivity decreases when a bulk MoO_3 based catalyst is reduced [6]. Furthermore, the ESCA result in this study indicates that surface Mo in the supported catalyst tends to be reduced. Although our ESCA study cannot distinguish whether the reduction occurs only in the dispersed species or also in the crystalline MoO_3 phase, the reaction study implies that the support may also facilitate the reduction of MoO_3 and hence retard the production of formaldehyde.

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