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Genesis and Stability of Silicomolybdic Acid on Silica-Supported Molybdenum Oxide Catalysts: *In Situ* Structural-Selectivity Study on Selective Oxidation Reactions

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The formation of silicomolybdic acid (SMA, $H_4SiMo_{12}O_{40}$) on silica-supported molybdenum oxide catalysts has been studied by *in situ* Raman spectroscopy, by TGA measurements, and for the selective oxidation of methane to formaldehyde. The formation of silicomolybdic acid requires exposing the MoO_3/SiO_2 to air saturated with water for several hours at room temperature. The large amount of water deposited on the silica support allows solubilization of part of the silica support in the presence of solvated heptamolybdate species, which leads to the formation of silicomolybdic acid. Desorption of water via thermal treatments breaks the silicomolybdic acid into dehydrated or partial hydrated species which are stable up to ca. 573 K. Above 573 K, only an isolated and distorted mono-oxo surface molybdenum oxide species is observed by *in situ* Raman spectroscopy. Consequently, the silicomolybdic acid species on SiO_2 should not result in catalytic behavior different from that of conventional MoO_3/SiO_2 catalysts for reactions taking place above 573 K. Unlike surface molybdenum oxide species, the surface SMA species on SiO_2 are stable during methanol oxidation at 503 K and do not transform into crystalline β-MoO_3 phase. The selective oxidation of methane to formaldehyde (843–883 K) shows no difference between conventional silica-supported molybdenum oxide and silica-supported silicomolybdic acid catalysts. *In situ* Raman spectroscopy studies during methanol oxidation at temperatures above 573 K reveal that the surface silicomolybdic acid species are not stable and transform into crystalline β-MoO_3.

1. INTRODUCTION

Silica-supported molybdenum oxide catalysts have been studied widely (1–10) and the structure of the supported molybdenum oxides is decisive in their catalytic performance (11–21). However, characterization of the structure of the MoO_3/SiO_2 catalysts by different techniques and under different conditions results in different assignments. Under ambient conditions, the structure of surface molybdenum oxide species is reported as a hydrated surface polymolybdate species ($Mo_7O_{24}^{6-}$) whose structure depends on the surface pH at point of zero charge (PZC) of the catalyst (7). Formation of silicomolybdic acid (SMA) from the surface molybdenum oxide species on SiO_2 has also been observed upon exposure to water vapor at room temperature (12, 14, 16). The silicomolybdic acid is a Keggin-type structure consisting of 12 octahedral MoO_6 surrounding a SiO_4 tetrahedron (22). Cohesion between the Keggin units is achieved by means of hydrated protons and water molecules (23). Upon dehydration, the polymolybdate structures are unstable and spread over the silica surface to form isolated surface molybdenum oxide species possessing one terminal Mo=O bond and four- to six-fold oxygen coordination (8, 9). Crystalline molybdenum oxide (MoO_3) is the dominant species at higher loading of molybdenum oxide on SiO_2 and is stable upon dehydration. However, reaction conditions may also alter the nature of the silica-supported molybdenum oxide species. For example, the bulk β-MoO_3 phase readily forms during the oxidation of methanol from the surface-dispersed molybdenum oxide species on SiO_2, and this surface β-MoO_3 phase transforms easily into the crystalline α-MoO_3 phase upon increase of temperature (9). Therefore, some questions remain as to whether the polymolybdate species or the surface silicomolybdic acid species is the surface species present on the hydrated SiO_2 surface, and to their stabilities at different temperatures and to its effect on different oxidation reactions environments (particularly, methane oxidation to C_1-oxygenates and methanol oxidation (14, 17)). In the present investigation the formation, thermal stability, and structural features of silica-supported silicomolybdic acid species given different treatments and different reaction environments were examined by *in situ* Raman spectroscopy in order to clarify the controversies and to better understand this interesting system.

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2. EXPERIMENTAL SECTION

The silica-supported molybdenum oxide species were prepared by the incipient-wetness impregnation method with an aqueous solution of ammonium heptamolybdate ($(NH_4)_6Mo_7O_{24} \cdot 4H_2O$). Prior to impregnation, the fumed silica (Cabosil EH-5, 380 m^2/g) was wetted by excess water and further dried at 393 K and calcined at 773 K to make the handling of silica easier. This wetting procedure does not change the BET surface area of the SiO_2 support. After impregnation, the samples were dried overnight under ambient conditions and at 393 K overnight in air. The dry samples were subsequently calcined in dry air at 773 K for 4 h. The silica-supported molybdenum oxide species is referred to as the MoSi series, and each specific sample is identified by a number denoting the MoO_3 loading as a weight percentage. The experimental procedure for the generation of the silica-supported silicomolybdic acid is based on previous works by Roberge and co-workers (12, 16). However, the transformation process of surface molybdenum oxide on SiO_2 to the SMA is followed for the first time using *in situ* Raman spectroscopy. Oxygen gas (Linde, 99.99%) was passed through a saturator containing water at room temperature and the water-saturated oxygen flowed through an *in situ* sample cell with a pellet of silica-supported molybdenum oxide catalyst held in the center of the cell at room temperatures for at least 12 h which results in the SMA series. Identification of specific SMA samples follows a nomenclature similar to that of the MoSi series.

In situ Raman spectroscopy experiments were performed in order to study the structural changes taking place for the silica-supported molybdenum oxide catalysts under different conditions. These experiments were performed with an *in situ* Raman apparatus consisting of an Ar^+ laser (Spectra Physics, Model 165), a triple-grating spectrometer (Spex, Model 1877), a photodiode array detector (EG&G, Princeton Applied Research, Model 1420), and a specially designed sample cell. The 514.5-nm line of the Ar^+ laser with 10–100 mW of power was focused on the sample disc in a right-angle scattering geometry. The *in situ* cell was equipped with a spinning sample holder which was generally rotated at ca. 1000 rpm inside a quartz cell, which allows working under a controlled atmosphere and temperature. Sample discs of 100–200 mg are held by the cap of the metallic alloy sample holder. A cylindrical furnace surrounding the quartz cell heats the sample and is controlled by an internal thermocouple. The MoO_3/SiO_2 samples had to be calcined at 773 K for at least 2 h before the Raman measurement to eliminate the fluorescence from the SiO_2 support. The *in situ* Raman spectra were initially obtained under continuous flow of a He/O_2 gaseous mixture with pressure ratio near 11/6. The Raman spectra of the dehydrated MoSi samples were recorded *in situ* after heating the sample at 773 K for half an hour and cooling to 503 K, which is the methanol oxidation reaction temperature employed in the present study. The Raman spectra of the SMA samples were taken under ambient conditions. The Raman spectra under reaction conditions were collected after the He/O_2 gaseous mixture was passed through a methanol reservoir in a 273K water–ice bath for at least 1 h. The Raman spectra after the methanol oxidation reaction were taken after the catalyst used was reoxidized in a flow of the He/O_2 gas at 503 and 773 K for 1 h.

The thermogravimetric analysis was performed on a Cahn 2000 Microbalance operating at a sensitivity of 10 μg. Catalyst samples were heated at 4 K min^{-1} to 773 K in air flowing at 150 ml/min.

Measurements of the selective oxidation of methane were carried out at atmospheric pressure in a fixed-bed quartz microcatalytic reactor (6 mm o.d.) by cofeeding CH_4 (99.95% vol.) and O_2 (99.98% vol.) without diluent. The CH_4/O_2 ratio was adjusted to 7 by means of mass flow controllers and the methane residence time was adjusted to 2 g h/mol (referenced to the weight of the dehydrated catalyst). The reactor effluent was analyzed by an on-line Hewlett–Packard Gas Chromatograph 5890 Series-II fitted with a thermal conductivity detector. Chromosorb 107- and Molecular Sieve 5A-packed columns were used with a column isolation analysis system.

3. RESULTS

Figure 1 shows the *in situ* Raman spectra of the 5% MoO_3/SiO_2 catalyst at different temperatures under a flow of oxygen saturated with water vapor (O_2/H_2O). The Raman features at ca. 480, 603, and 804 cm^{-1} are characteristic of the silica support (9). An intense Raman band is observed at ca. 980 cm^{-1} at 773 K, which corresponds to the stretching mode of the terminal bond Mo=O (24) of the dehydrated monomeric surface molybdenum oxide species on the silica support. A weaker Raman band at 360 cm^{-1} is due to the corresponding bending mode of this species (Fig. 1a). This Raman spectrum is identical to that obtained for a dehydrated MoO_3/SiO_2 catalyst (7, 8). No significant changes can be observed upon lowering the temperature from 773 to 443 K (Figs. 1a–1d), which suggests that the catalyst remains in a dehydrated state at these temperatures under the flow of water vapor. However, at room temperature, new Raman bands at 240, 370, 867, and 941 cm^{-1} appear after 2 h (Fig. 1e). These Raman bands are characteristic of heptamolybdate species (7) and are formed by the adsorption of water on the silica support, in agreement with previous observations (8). Further changes are observed in the *in situ* Raman spectra of the MoO_3/SiO_2 sample upon longer exposure to oxygen saturated with water at room temperature overnight. Un-

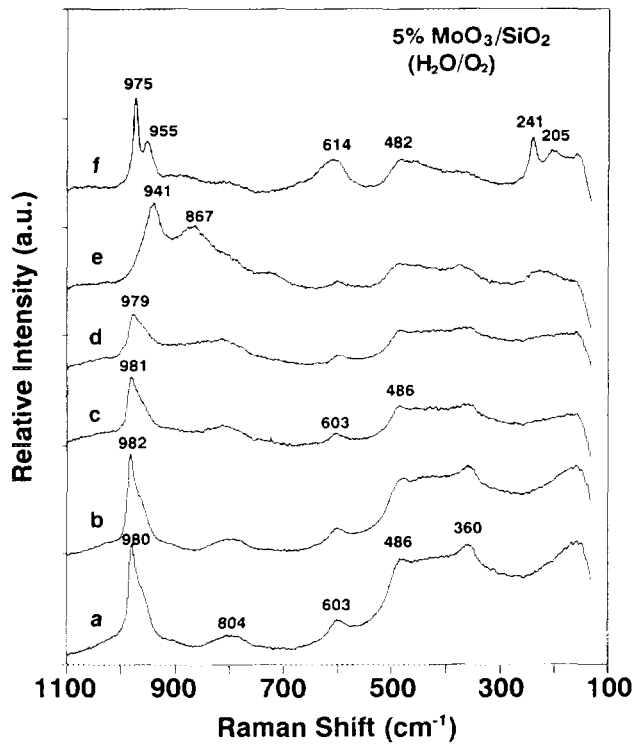

FIG. 1. *In situ* Raman spectra of 5MoSi in flowing air saturated with water at different decreasing temperatures: (a) 773 K, (b) 623 K, (c) 503 K, (d) 443 K, (e) room temperature for 2 h, and (f) room temperature overnight.

der these conditions, new Raman bands are observed at 241, 614, 955, and 975 cm^{-1}, which correspond in wavenumber and relative intensity to β-silicomolybdic acid (25) (Fig. 1f).

Addition *in situ* Raman spectra were recorded by increasing the temperature of the above SMA/SiO_2 sample (Fig. 1f) to evaluate the thermal stability of the silica-supported β-silicomolybdic acid in oxygen/water and dry oxygen environments and are shown in Figs. 2 and 3, respectively. In both cases, the trends observed are very similar, but the SMA/SiO_2 sample in Figs. 2 and 3 also exhibits a small Raman band at 818 cm^{-1} due to traces of crystalline α-MoO_3. At 443 K, Raman features are observed at ca. 996 and 240 cm^{-1} as well as a shoulder at ca. 977 cm^{-1} (Figs. 2b and 3b). The 996, 977, and 240 cm^{-1} bands are assigned to a dehydrated surface β-silicomolybdic acid species and the shift of the 980 cm^{-1} Raman band to higher frequency is consistent with shortening of the Mo=O bond upon dehydration. The presence of the 240 cm^{-1} Raman band also reveals that the β-silicomolybdic acid species is still present on the SiO_2 surface. Similar features can be observed at 503 K (Figs. 2c and 3c). At 573 K, the 996 cm^{-1} Raman band has essentially disappeared and the band at ca. 240 cm^{-1} has broadened considerably (Figs. 2d and 3d). The Raman spectrum at 773 K exhibits a band at ca. 980 cm^{-1} and possesses no 240 cm^{-1} band, which is characteristic of isolated surface molybdenum oxide species on silica and no band at 240 cm^{-1}, characteristic of β-silicomolybdic acid species (Fig. 2e). Thus, the β-silicomolybdic acid species decomposes above 573 K in both dry and wet oxidizing environments.

The *in situ* Raman spectra of the above prepared silica-supported β-silicomolybdic acid sample during methanol oxidations are presented in Fig. 4. The Raman bands observed at room temperatures are those previously reported for silicomolybdic acid supported on silica (25). Under methanol oxidation reaction conditions at 443 and 503 K Raman features at ca. 998, 978, and 235 cm^{-1} are observed (Fig. 4b and 4c) and assigned to the dehydrated surface β-silicomolybdic acid species. The strong Raman band at 235 cm^{-1} suggests that methanol is perturbing the vibrations of the silicomolybdic acid species. When the methanol oxidation reaction is operated at higher temperatures (573 K), new changes can be observed in the *in situ* Raman spectra since additional features appear at ca. 838 and 487 cm^{-1} (Fig. 4d). These new bands are characteristic of crystalline β-MoO_3, a low-temperature phase of bulk MoO_3. The corresponding shift of the 980 cm^{-1} band to 973 cm^{-1} appears to be associated with the formation of isolated surface molybdenum oxide species

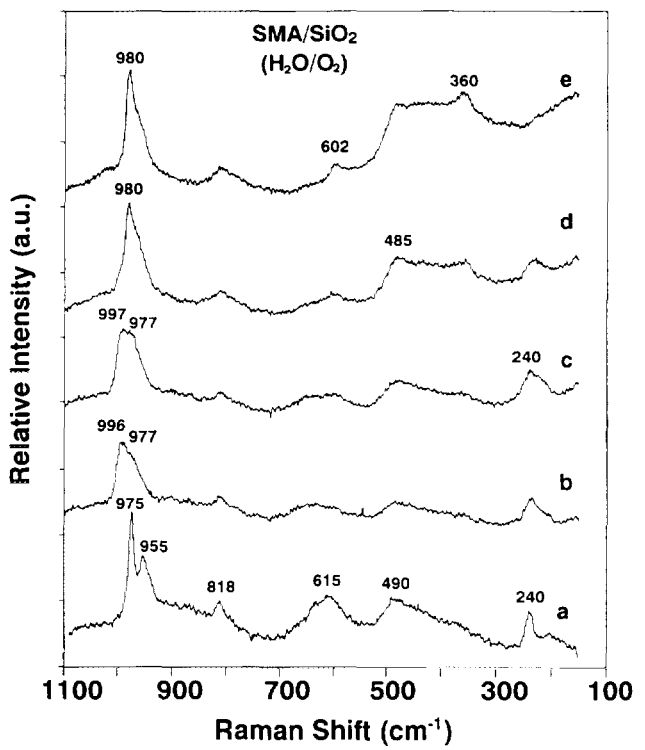

FIG. 2. *In situ* Raman spectra of 5SMA in flowing oxygen saturated with water at different increasing temperatures: (a) room temperature, (b) 443 K, (c) 503 K, (d) 573 K, and (e) 773 K.

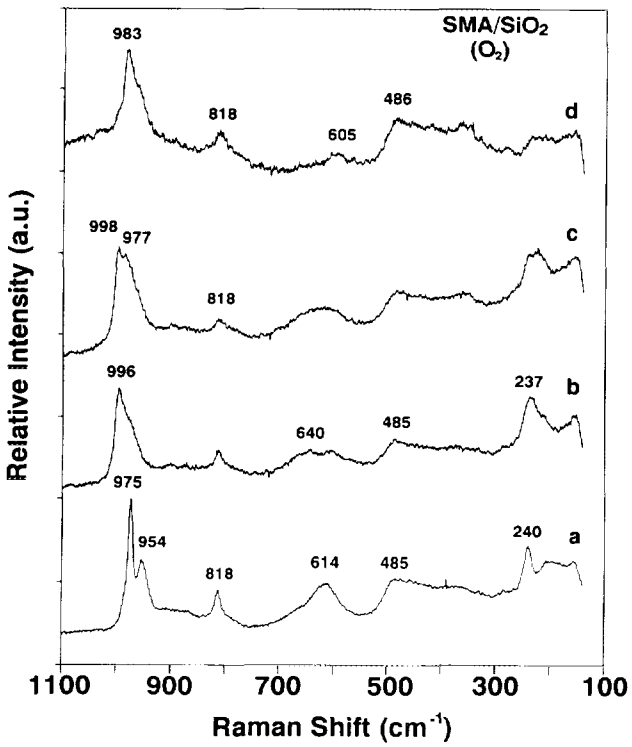

FIG. 3. *In situ* Raman spectra of 5SMA in flowing dry oxygen at different increasing temperatures: (a) room temperature, (b) 443 K, (c) 503 K, and (d) 573 K.

linked to methoxide species (9), since further treatment in flowing oxygen (Fig. 4e) causes the Raman band at 973 cm^{-1} to shift back to 986 cm^{-1}, which is characteristic of isolated surface molybdenum oxide species (7, 24). In addition, in the flowing oxygen atmosphere the conversion of the low-temperature crystalline β-MoO_3 into the high-temperature crystalline α-MoO_3 phase is evidenced by the onset of new Raman bands at 815, 460, 393, 348, and 296 cm^{-1}.

The results from the TGA experiments are presented in Fig. 5 in the form of percentage weight loss for the different samples for samples heated in air. The main feature is the remarkably higher weight loss observed on the SMA series (ca. 45%) as compared to the MoSi series (<5%). The difference in weight loss is due to the higher amount of water present on the SMA series. Most of the moisture is desorbed by approximately 443 K. In addition, the SMA series also exhibits a small additional weight loss at ca. 543 K for high molybdenum oxide loadings. This is illustrated by the inset to Fig. 5 for the 5SMA catalyst. This feature becomes less evident as the molybdenum oxide loading decreases and becomes hardly noticeable for low-loading SMA samples. This additional weight loss takes place in the same temperature range at which the silicomolybdic acid species completely decomposes to isolated surface molybdenum oxide species.

The results of the selective oxidation of methane are presented in Table 1 and Fig. 6 for the catalysts 5MoSi and 5SMA. The weight of the 5SMA catalyst was higher than that of 5MoSi in the proportion determined by the TGA experiments due to the presence of moisture, so that the molybdenum loading of both catalysts in the reactor (dehydrated) was maintained about the same. In fact, no significant differences in weight were observed between the two catalysts (less than 1%) after reaction. For both catalysts, formaldehyde and carbon monoxide were the main oxidation products and minor amounts of carbon dioxide were also produced. In addition, the conversion and selectivity values were very similar for both catalysts. The selectivity trends presented in Fig. 6 indicate that formaldehyde is the main reaction product and that it is further oxidized to carbon monoxide. The almost constant selectivity to carbon dioxide, even at very low conversion levels, appears to indicate that it originates directly from methane rather than from further oxidation of carbon monoxide. These mechanistic observations are in agreement with previous kinetic (29) and isotopic (30) measurements. The most remarkable feature of this plot is the essentially identical selectivity trends for both catalysts. This very similar catalytic behavior suggests that a similar active center is probably present on both catalysts.

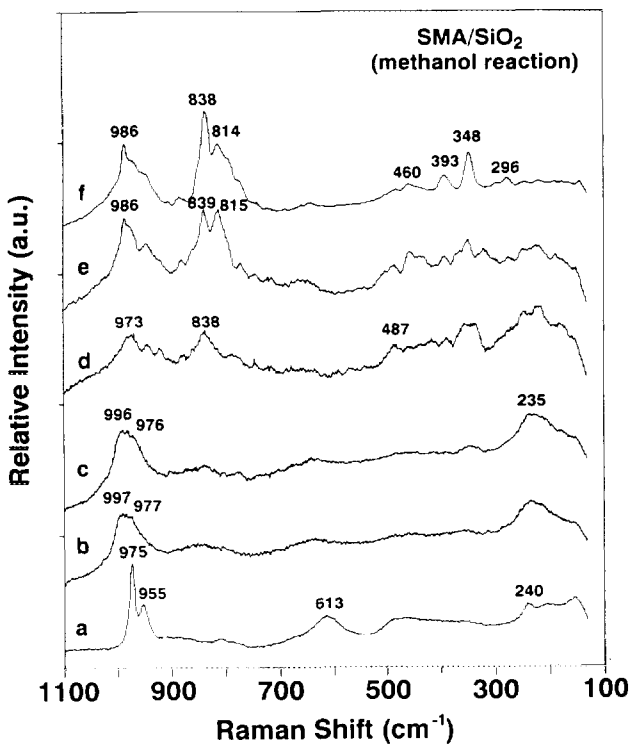

FIG. 4. *In situ* Raman spectra of 5SMA during the methanol oxidation reactions at different increasing temperatures: (a) room temperature, ambient; (b) flowing $CH_3OH/He/O_2$ at 443 K, (c) at 503 K, and (d) at 573 K; and (e) flowing pure oxygen at 573 K and (f) at 773 K.

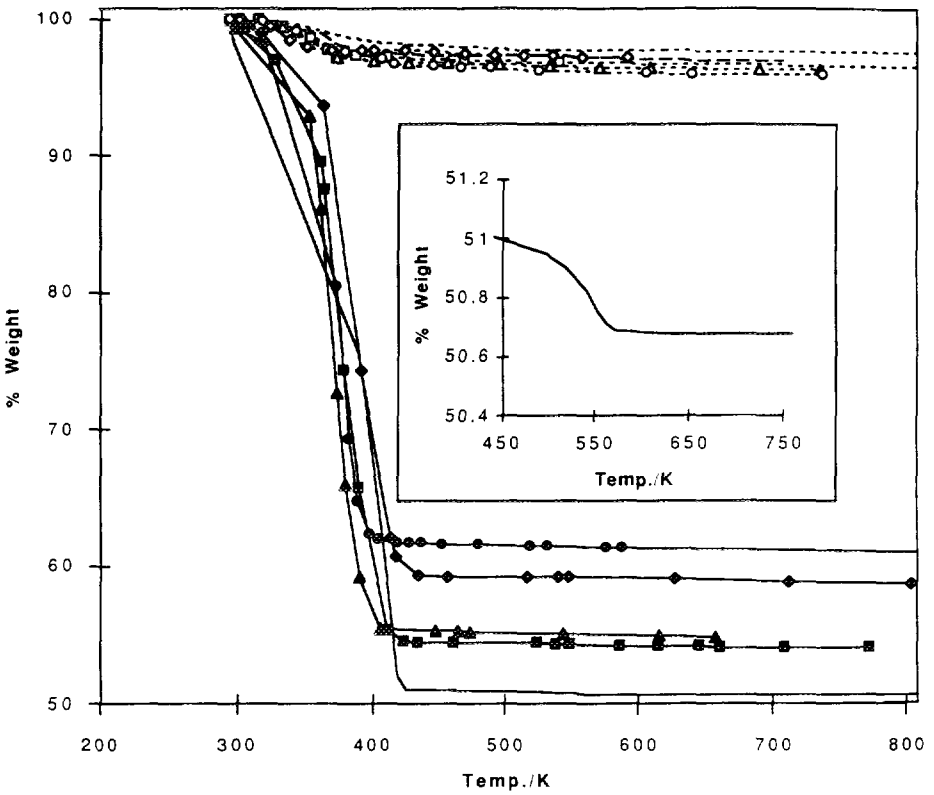

FIG. 5. TGA measurements of the weight loss patterns in dry air of the MoSi series (open symbols, dotted lines) and SMA series (closed symbols, solid lines): Square, 1% MoO_3; diamond, 2% MoO_3; triangle, 3% MoO_3; circle, 4% MoO_3; no symbol for 5% MoO_3. The inset is for 5SMA.

This result is expected since under the methane oxidation reaction conditions (863 K) both catalysts possess only dehydrated surface molybdenum oxide species on SiO_2. The slightly higher activity of the 5MoSi catalyst is partially associated with the additional MoO_3 present in this sample.

4. DISCUSSION

The hydration/dehydration behavior of the MoO_3/SiO_2 catalysts has been extensively studied (7, 8, 26) and will not be further discussed in this paper. The results presented above demonstrate that the formation of silicomolybdic acid takes place upon exposure of silica-supported

TABLE 1

Methane Conversion on Silica-Supported Molybdenum Oxide and Silicomolybdic Acid

	% Conversion		% Selectivity		
Catalyst	CH_4	O_2	HCHO	CO	CO_2
5SMA	0.7	5.3	72	21	5
5MoSi	0.8	6.8	69	26	4

Note. Reaction conditions: 863 K, CH_4/O_2 = 7, W/F = 2 g h/mol.

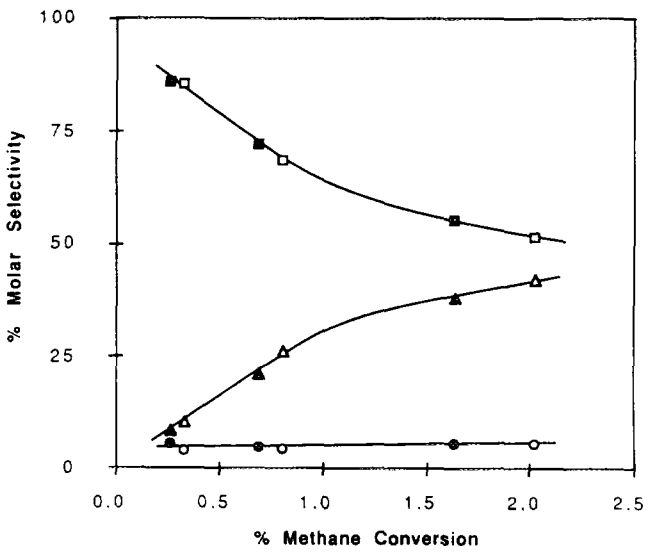

FIG. 6. Selectivity vs methane conversion plots for the representative catalysts 5SMA and 5MoSi. Reaction conditions: CH_4/O_2 = 7 molar ratio; W/F = 2 g h/mol; reaction temperature 843–883 K. Closed symbols, 5SMA; and open symbols, 5MoSi. Square, HCHO; triangle, CO; and circle, CO_2.

molybdenum oxide to large amounts of water for several hours at room temperature. The presence of water is fundamental for the formation and stabilization of silicomolybdic species, as has previously been demonstrated (12, 16, 18, 27, 28). Initial exposure to air saturated with water at room temperatures has an effect similar to that of exposing silica-supported molybdenum oxide material to ambient humidity. Under these initial conditions, hydrated heptamolybdate ($Mo_7O_{24}^{6-}$) species are formed as demonstrated by *in situ* Raman spectroscopy. These hydrated heptamolybdate species are dissolved in the thin water layer covering the surface of the MoO_3/SiO_2 catalysts (7). Previous research by Che *et al.* shown that the presence of MoO_3 and SiO_2 stirred in water for a period of time results in the formation of silicomolybdic acid (14). The same phenomenon is taking place on the surface of the silica support between Mo and Si for the SMA series. TGA measurements reveal the presence of large amounts of water on the SMA series (ca. 45% weight) and significant amounts of water (many layers) which allow solubilization of a portion of the silica support. These conditions are similar to those reported by Che *et al.* (14) and *in situ* Raman spectroscopy directly reveals the formation of silicomolybdic acid.

The silica-supported silicomolybdic acid is not stable at temperatures above 573 K. Initial heating of the SMA series results in dehydration of the materials and the Raman bands characteristic of β-silicomolybdic acid (975, 955, ~630, and 241 cm^{-1}) are no longer present. However, dehydrated or partially hydrated surface silicomolybdic acid species appear to form below 573 K and exhibit Raman bands at 998, 977, and ~235 cm^{-1}. When the sample is heated above ca. 573 K, the dehydrated silicomolybdic acid species do not appear to be stable and spread on the silica support as isolated surface molybdenum oxide species (characterized by the Raman bands at ca. 980 and 360 cm^{-1}) (7, 8). Similar behavior can be observed during the decomposition of surface heptamolybdate species by dehydration of the silica-supported molybdenum oxide materials (2, 8, 26). In both cases, the same isolated and distorted surface molybdenum oxide species are formed after decomposition.

No catalytic differences are expected between the MoSi and SMA series during reactions above 573 K, since silicomolybdic acid is not stable above 573 K and the resulting material is identical to silica-supported molybdenum oxide species. Results presented above for the selective oxidation of methane at 863 K (Table 1 and Fig. 6) suggest that the same catalyst results from reactions from loading either a MoSi or a SMA catalyst into the reactor. However, the increase in the loadings of surfce molybdenum oxide and surface SMA results in a higher level of methane conversion as a consequence of the greater number of active sites (10, 17, 19). The conversion of methane has a very important effect on the selectivity (Fig. 6 and, e.g., Ref. 31) and, consequently, the less selective behavior of the SMA/SiO_2 catalyst may be due to its higher loading of molybdenum oxide rather than to a different active site. The overall lower selectivity toward partial oxidation products also originates from the use of N_2O as oxidant, which is less selective than molecular oxygen for methane oxidation (10). *In situ* Raman studies during methane oxidation over MoO_3/SiO_2 catalysts have shown that the isolated surface molybdenum oxide species are present during reaction (15).

For reactions operating below 573 K, however, the silicomolybdic acid may be present in a dehydrated or partially hydrated state and catalytic differences should be expected between the MoSi and SMA series. The *in situ* Raman spectra during methanol oxidation at 443 and 503 K (see Figs. 4b and 4c) show structures similar to those of the dehydrated surface silicomolybdic acid and no crystalline MoO_3 was detected. Furthermore, this used surface SMA species recovers after rehydration in a flow of the H_2O/O_2 gas. These behaviors reveal that the silica-supported silicomolybdic acid is more stable than the silica-supported molybdenum oxide species. The *in situ* Raman spectrum of surface silicomolybdic acid during methanol oxidation at higher temperature (573 K; Fig. 4d) reveals the presence of silicomolybdic acid, surface molybdenum oxide species, and small amounts of β-MoO_3. However, the *in situ* Raman spectra of the 5% MoO_3/SiO_2 catalyst during methanol oxidation at 503 K revealed a complete transformation of the surface molybdenum oxide species to the crystalline β-MoO_3 phase (9). Very extensive work on the selective oxidation of methanol on silica-supported silicomolybdic acid at 503 K shows a marked acidic character (14, 29). This suggests that the silicomolybdic acid species must be more reactive than the surface molybdenum oxide species, which accounts for the acidic activity observed by Che *et al.* on silica-supported silicomolybdic acid during the oxidation of methanol (23, 29). *In situ* Raman spectroscopy reveals that treatments of the SMA/SiO_2 catalyst above ca. 573 K break the surface silicomolybdic acid species into isolated surface molybdenum oxide species which are identical to those observed on dehydrated silica-supported molybdenum oxide catalysts. Oxidation of methanol over the silica-supported surface molybdenum oxide species has a redox character (9, 23, 29) and the redox catalysis observed on the silica-supported silicomolybdic acid after a treatment at 573 K is expected since the acidic silicomolybdic acid species are no longer present at this temperature.

5. CONCLUSIONS

1. Formation of silicomolybdic acid requires adsorption of large amounts of water at room temperature that allow

solubilization of silicon and molybdenum oxide species for the formation heteropolyacid.

2. Upon dehydration, silica-supported silicomolybdic acid forms a dehydrated or partially hydrated surface silicomolybdic acid species with an acidic character.

3. At ca. 573 K, the silicomolybdic acid species completely breaks into an isolated surface molybdenum oxide species which possesses a redox property during the oxidation of methanol.

4. During the selective oxidation of methane, at ~863 K, the same isolated and distorted mono-oxo surface molybdenum oxide species are present on the silica surface for the silica-supported silicomolybdic acid and surface molybdenum oxide species, independent of the initial presence of silicomolybdic acid.

5. During methanol oxidation at 503 K, the dehydrated silicomolybdic acid species are present on the silica surface, which are more stable than the dehydrated molybdenum oxide species on SiO_2 toward the formation of crystalline β-MoO_3. Reaction with methanol at above 573 K also transforms dehydrated silicomolybdic acid species into crystalline MoO_3.

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REFERENCES

1. Barbaux, Y., Elamrani, A. R., Payen, E., Gengembre, L., Bonnelle, J. P., and Gryzbowska, B., *Appl. Catal.* **44,** 117 (1988).
2. Liu, T.-C., Forissier, M., Coudurier, G., and Vèdrine, J. C., *J. Chem. Soc. Faraday Trans I* **85,** 1607 (1989).
3. Ono, T., Anpo, M., and Kubokawa, Y., *J. Phys. Chem.* **90,** 4780 (1986).
4. Cheng, C. P., and Schrader, G. L., *J. Catal.* **60,** 276 (1979).
5. Jeziorowski, H., Knözinger, H., Grange, P., and Gajardo, P., *J. Phys. Chem.* **84,** 1825 (1980).
6. Seyedmonir, S. R., Abdo, S., and Howe, R. F., *J. Phys. Chem.* **86,** 1233 (1982).
7. Williams, C. C., Ekerdt, J. C., Jehng, J.-M., Hardcastle, F. D., Turek, A. M., and Wachs, I. E., *J. Phys. Chem.* **95,** 8781 (1991).
8. de Boer, M., van Dillen, A. J., Koningsberger, D. C., Vuurman, M. A., Wachs, I. E., and Geus, J. G., *Catal. Lett.* **11,** 227 (1991).
9. Bañares, M. A., Hu, H., and Wachs, I. E., *J. Catal.* **150,** 407 (1994).
10. Bañares, M. A., Fierro, J. L. G., and Moffat, J. B., *J. Catal.* **142,** 406 (1993).
11. Thomas, R., Moulijn, J. A., de Beer, V. H. J., and Medema, J., *J. Mol. Catal.* **8,** 161 (1980).
12. Stencel, J. M., Diehl, J. R., D'Este, J. R., Makovsky, L. E., Rodrigo, L., Marcinkowska, K., Adnot, A., Roberge, P. C., and Kaliaguine, S., *J. Phys. Chem.* **90,** 4739 (1986).
13. Giordano, N., Meazzo, M., Castellan, A., Bart, J. C., and Ragaini, V., *J. Catal.* **50,** 342 (1977).
14. Rocchiccioli-Deltcheff, C., Amirouche, M., Che, M., Tatibouët, J. M., and Fournier, M., *J. Catal.* **125,** 2892 (1990).
15. Bañares, M. A., Spencer, N. D., Jones, M., and Wachs, I. E., *J. Catal.* **142,** 206 (1994).
16. Marcinkowska, K., Adnot, A., Roberge, P. C., and Kaliaguine, S., *J. Phys. Chem.* **90,** 4773 (1986).
17. Kasztelan, S., Payen, E., and Moffat, J. B., *J. Catal.* **112,** 320 (1988).
18. Marcinkowska, K., Kaliaguine, S., and Roberge, P. C., *J. Catal.* **90,** 49 (1984).
19. Bañares, M. A., and Fierro, J. L. G., *Catal. Lett.* **17,** 205 (1993).
20. Bañares, M. A., and Fierro, J. L. G., *in* "Catalytic Selective Oxidation" (S. T. Oyama, and J. W. Hightower, Eds.), Chap. 27, ACS Symp. Ser. Vol. 253. Amer. Chem. Soc., Washington, DC, 1993.
21. Bañares, M. A., and Fierro, J. L. G., *An. Quím.* **87**(2), 223 (1991).
22. Greenwood, N. N., and Earnshaw, A., "Chemistry of the Elements." Pergamon Press, Elmsford, NY, 1989.
23. Tatibouët, J. M., Che, M., Amirouche, M., Fournier, M., and Rocciccchioli-Deltcheff, C., *J. Chem. Soc. Chem. Commun.*, 1260 (1988).
24. Hardcastle, F. D., and Wachs, I. E., *J. Raman Spectrosc.* **21,** 683 (1990).
25. Kasprzak, M. S., Leroi, G. E., and Crouch, S. R., *Appl. Spectrosc.* **36,** 285 (1982).
26. Roark, R. D., Kohler, S. D., and Ekerdt, J. G., *Catal. Lett.* **16,** 71 (1992).
27. Castellan, A., Bart, C. J., Vaghi, A., and Giordano, N., *J. Catal.* **42,** 162 (1976).
28. Leyrer, J., Mey, D., and Knözinger, H., *J. Catal.* **124,** 349 (1993).
29. Rocchiccioli-Deltcheff, C., Amirouche, M., Hervé, G., Fournier, M., Che, M., and Tatibouët, J. M., *J. Catal.* **126,** 591 (1990).
30. Spencer, N. D., Pereira, C. J., and Grasselli, R. K., *J. Catal.* **126,** 546 (1990).
31. Bañares, M. A., Rodríguez-Ramos, I., Guerrero-Ruíz, A., and G. Fierro, J. L. G., *in* "Proceedings, 10th International Congress on Catalysis" (L. Guczi *et al.*, Ed.), p. 1131. Elsevier, Amsterdam, 1994.