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The Formation of Molybdosilicic Acid on Mo/SiO_2 Catalysts and Its Relevance to Methane Oxidation

Renewed interest in silica-supported MoO_3 catalysts has resulted from the report that these catalysts are active and selective in the partial oxidation of methane to methanol and formaldehyde with nitrous oxide (*1–3*). In such work it has been observed that these properties are highly dependent on the method for the preparation of the catalyst (*2, 3*). Such differences may result from the presence of various oxometalate species (*4*) on the surface of the support. In this regard several authors (*5–10*) have previously proposed the existence of 12-molybdosilicic acid on these catalysts. Most recently, further work on the oxidation of methane with molecular oxygen on MoO_3/silica catalysts has been reported and attributed to a promoter effect of the oxide on the bare silica (*11*).

Recent work from this laboratory has shown that silica-supported heteropoly acids such as 12-molybdophosphoric (HPMo) and 12-molybdosilicic acids (HSiMo) are active and selective catalysts for the partial oxidation of methane (*12*). In addition, subsequent work on the silica-supported 12-molybdophosphoric acid catalyst has shown that these species are apparently stabilized by the silica support and exist after calcination at 873 K (*13*). At higher calcination temperatures the species is destroyed and the activity of the catalyst is no longer evident. From this and other observations it has been concluded that these species are active for the oxidation of methane (*13, 14*).

In this note we report a comparison of a $H_4SiMo_{12}O_{40}/SiO_2$ catalyst with MoO_3/SiO_2 catalysts prepared at different pH in order to determine the dependence of the activity of MoO_3/SiO_2 catalysts on the presence of molybdosilicic acid.

The MoO_3/SiO_2 catalysts were prepared by impregnation of the silica support (Grace-Davison, grade 400, specific area 740 $m^2\ g^{-1}$) with a large excess of solution at varying pH produced by the addition of NH_4OH or HNO_3. The HSiMo/SiO_2 catalyst was prepared similarly with a solution of purified $H_4SiMo_{12}O_{40} \cdot 24H_2O$ (Pressure Chemical Co.) at its natural pH (ca. 2.5). After evaporation to dryness overnight at 353 K the catalysts were calcined in air at 773 K for 2 h. The loading values are summarized in Table 1.

The methane oxidation reaction was performed in a fixed bed continuous flow system equipped with a quartz reactor at 773 K with 2 g of catalyst, a flow rate of 15 ml min^{-1}, and a feed composition of 33 and 67% for CH_4 and N_2O, respectively. Additional details on the procedures and catalyst preparation have been reported elsewhere (*12*).

The presence of HSiMo was detected by washing the catalyst samples with acetonitrile (Baker Analyzed) as described previously (*13*) and the filtered solution was analyzed by IR and laser Raman spectroscopy (LRS). The LRS analyses of both the solids and the acetonitrile solutions have been performed with a Ramanor HG2 spectrometer (JOBIN-YVON) using the 488-nm excitation line of an Ar^+ laser (*15*). The IR spectra have been recorded with a double-beam Perkin–Elmer Model 983 spectrometer. Good compensation of the solvent peaks has been obtained. No decom-

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TABLE 1

Catalytic Properties and Characteristics of the Samples

Samples	Loading wt% MoO_3	Conversion[a]		N_2O TON[c]	Selectivities[a]			
		CH_4	N_2O		CO	CO_2	CH_2O	CH_3OH
SiO_2 support[b]	—	0.8	3.0	—	75	25	—	—
MoO_3/SiO_2 (pH 11)	3.0	1.1	4.0	9.8	72	19	9	t
MoO_3/SiO_2 (pH 7)	3.2	2.6	8.4	19.0	67	24	9	t
MoO_3/SiO_2 (pH 2)	3.2	3.3	10.0	22.6	61	37	2	t
$H_4SiMo_{12}O_{40}/SiO_2$	5.7	5.0	19.6	25.2	46	54	t	—

[a] $T = 773$ K, mass of catalyst 2 g, flow rate 15 ml min^{-1}, flow composition CH_4 (33%), N_2O (67%).
[b] SiO_2 Davison-Grace, Grade 400, 750 m^2g^{-1}.
[c] Apparent turnover number (10^{-4} molec/at. Mo/s).

position or synthesis of molybdosilicic acid has been found in acetonitrile under the experimental conditions employed (*13*).

The conversions and product distributions for the oxidation of methane by N_2O at 773 K are reported in Table 1. It is clearly evident that the pH of the Mo solution has a considerable effect on these properties. Both the conversion and the product distribution approach those of the molybdosilicic acid as the pH of the solution decreases. Although under the present experimental conditions methanol and formaldehyde were not produced from the supported acid, these products were detected under other conditions and in particular at higher contact time (*12*).

The LRS spectra of the calcined catalysts may be compared with the LRS spectrum of the bulk molybdosilicic acid (Fig. 1). The latter (Fig. 1a) shows characteristic bands at 995, 969, 911, 636, and 252 cm^{-1} which have been assigned to the Mo–O_t symmetric stretching, Mo–O–Mo symmetric stretching, (Mo_3–O) symmetric stretching, and Mo–O bending mode, respectively (*16, 17*). The similarity of the spectrum of the HSiMo/SiO_2 catalyst (Fig. 1b) to that of bulk HSiMo (Fig. 1a) confirms that this species has been deposited and remains as the predominant species after calcination at 773 K.

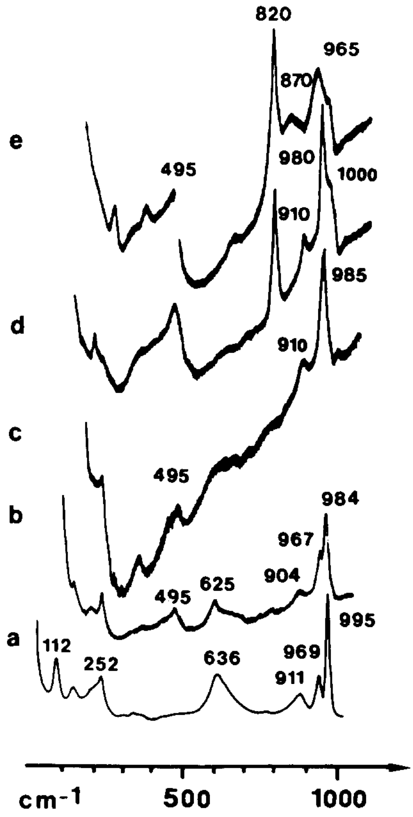

FIG. 1. Raman spectra of a) bulk $H_4SiMo_{12}O_{40}$ calcined at 623 K, 2h, and of supported catalysts calcined at 773 K, 2h, b) $H_4SiMo_{12}O_{40}/SiO_2$, c) MoO_3/SiO_2, pH = 2, d) MoO_3/SiO_2, pH = 7, e) MoO_3/SiO_2, pH = 11.

The increased noise evident in the Raman spectra of the MoO_3/SiO_2 samples (Figs. 1c–1e) is believed to be attributable to the very low Mo loading. Nevertheless, a broad band can be observed at 495 cm^{-1} and attributed to the silica support while the characteristic 995-, 949-, 636-, and 252-cm^{-1} bands of the HSiMo species can be clearly distinguished on the sample prepared at pH 2 and 7. At pH 11 the so-called polymolybdate phase can be identified from the characteristic band at 960 cm^{-1} (*9, 15, 18*). Such a phase is now considered to be a heptamolybdate species (*15, 18–21*). The bands at 1000 and 820 cm^{-1} which are observed for the samples prepared at pH 7 and 11 are due to MoO_3 crystallites.

The existence of molybdosilicic acid is also demonstrated by IR and LRS analyses of the filtered solution obtained from the washing of a calcined sample with acetonitrile to extract the supported HSiMo species selectively. This techique has been previously and successfully employed in the detection of HPMo species present on SiO_2 before and after catalytic testing at 843 K (*13*). It was shown by this method with $HPMo/SiO_2$, which is a system similar to that of $HSiMo/SiO_2$, that the Keggin structure of the anions is largely intact even after use at 843 K (*13*), although after heating to 1000 K for 16 h the intensities of the characteristic bands are sharply reduced (*13*).

The IR spectra (Fig. 2) of the acetonitrile solutions obtained from $HSiMo/SiO_2$ after extraction are clearly characteristic of the molybdosilicic acid with bands at 950, 920, and 810 cm^{-1} (*22*). Evidently this species has been extracted from all samples although only traces are detected for the sample prepared at pH 11.

The Raman spectra of these solutions are shown in Fig. 3. Interestingly the bands of the acetonitrile solvent, at 1045, 925, 750, and 383 cm^{-1} (identified by arrows in Fig. 3), do not interfere with the HSiMo bands (980, 965, 897, 633, 250 cm^{-2}) so that unambiguous identification of this species is possible. It is evident that HSiMo species are present in the acetonitrile solution recovered from the washing of the HSiMo, $HSiMo/SiO_2$, and MoO_3/SiO_2, pH 2 and 7, samples. Furthermore, a characteristic band at 980 cm^{-1} remains detectable for the sample prepared at pH 11.

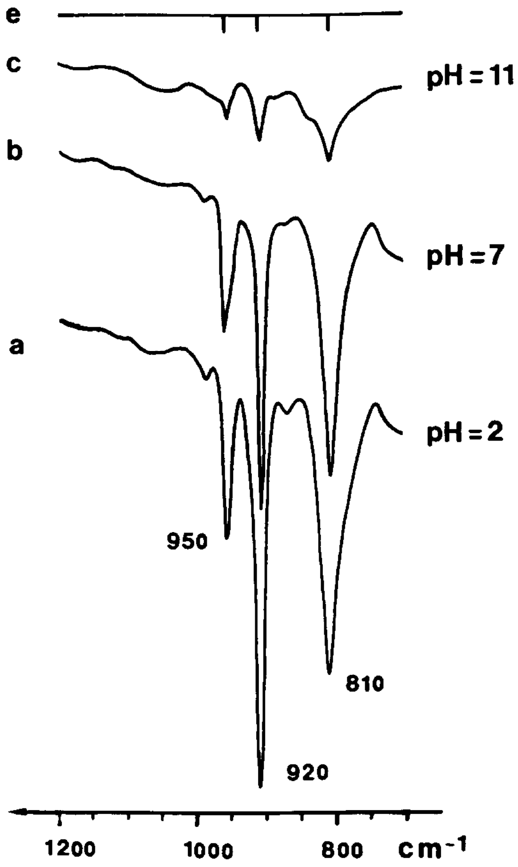

FIG. 2. IR spectra of the acetonitrile solution obtained after washing the catalysts. a) MoO_3/SiO_2, pH = 2, b) MoO_3/SiO_2, pH = 7, c) MoO_3/SiO_2, pH = 11 and e) band position of bulk $H_4SiMo_{12}O_{40}$.

It appears therefore that HSiMo is synthesized during the impregnation of the MoO_3/SiO_2 catalyst at pH 2 and 7 and even at pH 11 although undoubtedly in small amounts in the latter case. This suggests that silica is dissolved during the impregnation in an acidic medium leading to the formation of HSiMo. In addition silica has a strong acidic effect on the solution employed for the impregnation leading to the

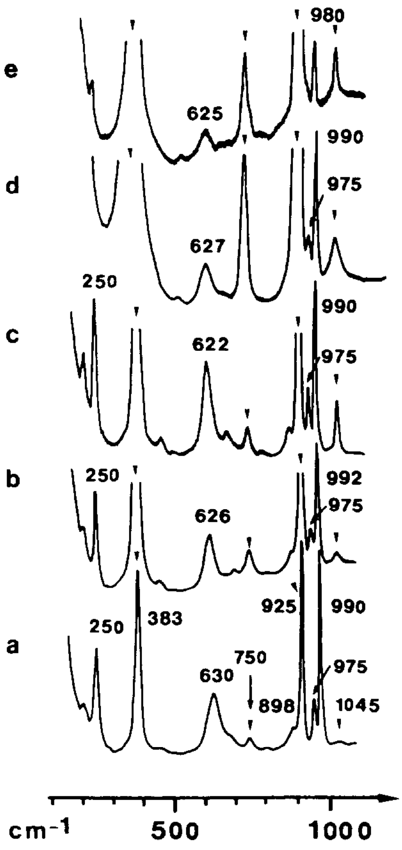

FIG. 3. Raman spectra of the acetonitrile solution obtained after washing the catalysts. a) bulk $H_4Si Mo_{12}O_{40}$, b) $H_4SiMo_{12}O_{40}/SiO_2$, c) MoO_3/SiO_2, pH = 2, d) MoO_3/SiO_2, pH = 7, e) MoO_3/SiO_2, pH = 11.

transformation of the molybdate species present in the basic solution into heptamolybdate and a small amount of molybdosilicic acid. Upon calcination the HSiMo species remain stable and, by analogy with the HPMo species, at least part of the HSiMo species presumably remains stable upon calcination up to 873 K (*13, 14*). However, MoO_3 crystallites are formed either by decomposition of HSiMo at high calcination temperatures or by decomposition of heptamolybdate species at mild calcination temperatures as seen in Raman spectra 1d and 1e.

Thus, at least three species, HSiMo, the heptamolybdate, and MoO_3 crystallites, can be generated on MoO_3/SiO_2, depending on the pH of the solution, and presumably also on the Mo loading and calcination conditions. Although no quantitative analysis has been done it is evident that the amount of HSiMo increases as the pH decreases in parallel with the activity results. Taking into account the activity and selectivity of the silica-supported molybdosilicic acid, as reported here, it may be proposed that the methane oxidation activity of MoO_3/SiO_2 catalysts is primarily due to the molybdosilicic acid and consequently catalysts with better activity will result from preparation at acidic pH. However, as reported in Table 1 the selectivity is not favored by high conversions as is often observed in oxidation reactions. In addition the participation of the remaining oxometalate species in the methane partial oxidation mechanism is ruled out by these results. Further work will be needed to establish the precise role of these species.

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