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Dispersion and Activity of Molybdena–Alumina Catalysts Prepared by Impregnation and Solid/Solid Wetting Methods

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Alumina-supported molybdena catalysts were prepared by both the standard incipient wetness method and by mixing MoO_3 and Al_2O_3 (solid/solid wetting), followed by thermal treatment at 500°C under dry or wet O_2 atmospheric conditions. These catalysts were characterized by means of O_2 chemisorption at −78°C, CO_2 uptake at ambient temperature, X-ray diffraction (XRD), and electron spin resonance (ESR) techniques. Activities of the catalysts were determined for partial oxidation of methanol and hydrodesulfurization of thiophene at atmospheric pressure. XRD results suggest high dispersion of Mo-oxide on alumina support irrespective of their method of preparation. However, O_2 and CO_2 uptake measurements reveal partial coverage of the Al_2O_3 support surface by the Mo-oxide phase and appear to depend on the gas atmosphere (wet or dry O_2) during heat treatments in case of solid/solid wetting method. ESR, oxygen and carbon dioxide uptakes and the catalytic properties clearly demonstrate that spontaneous spreading of MoO_3 on the Al_2O_3 support at 500°C in the presence of wet O_2 is a most effective alternative method for preparing molybdena–alumina catalysts.

INTRODUCTION

Molybdena–alumina catalysts are used industrially in both reduced (oxidic) and sulfided forms. These catalysts are active for various reactions, such as metathesis of propene (*1*, *2*), polymerization of ethene (*3*), hydrogenolysis of propane (*4*), and hydrodesulfurization (HDS) of thiophenic compounds (*5–10*). These catalysts are normally prepared by impregnation of the alumina support with an aqueous solution containing $(NH_4)_6 Mo_7O_{24}$ compound followed by drying and calcination at temperatures around 500°C. Catalysts prepared via these methods are considered to give epitaxial monolayer of molybdena phase on an alumina support surface (*9*) consisting of monomeric or polymeric species depending on the concentration and pH of the impregnating solution (*10*, *11*).

Xie and co-workers (*12*) have demonstrated that dispersed supported molybdena/alumina catalysts can also be obtained from simple physical mixtures by the spreading of MoO_3 on the surface of the Al_2O_3 support. On the basis of X-ray diffraction (XRD) and X-ray photoelectron spectroscopic (XPS) measurements they have proved that MoO_3 spontaneously spreads over the surface of Al_2O_3 in physical mixtures of the two oxides when these are subjected to thermal treatments at temperatures around 400–500°C in air for 24 h. Fransen *et al.* (*13*) also reported a similar phenomenon of the spreading of MoO_3 on the surface of Al_2O_3 support by a different method. In this method, MoO_3 and Al_2O_3 were taken in two separate beds and MoO_3 (maintained at 600°C) was transported to the Al_2O_3 support in the form of $MoO_2(OH)_2$ by steam. Leyrer *et al.* (*14*) have extended this study and reported supporting evidence for this spreading phenomena by the application of ion scattering spectroscopy (ISS). Based on laser Raman spectroscopy (LRS) studies, Knozinger and co-workers (*15*, *16*) have further demonstrated the significance of gas

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atmosphere on the resulting dispersed molybdenum species during thermal treatments in the case of simple physical mixtures. Under an absolutely dry O_2 atmosphere only the MoO_3 phase was observed, whereas under an O_2 atmosphere saturated with water vapor, formation of the surface heptamolybdate phase was observed (*10, 15, 16*). Catalysts obtained via the latter method were also found to show comparable catalytic properties with that of a conventionally impregnated catalyst for the HDS of thiophene (*17*). The spreading process was phenomenologically termed as solid/solid wetting and the driving force for this phenomenon was proved to be due to the decrease in surface free energy (*18*).

Selective chemisorption of oxygen at low temperatures has been widely employed for the study of supported molybdena catalysts by several groups (*19–35*). Controversial opinions can be found in the literature regarding the property measured by oxygen chemisorption on sulfided Mo/Al_2O_3 catalysts (*24–26, 31,32*). However, oxygen chemisorption on reduced catalysts is widely accepted as an important method for measuring the dispersion of molybdenum on alumina support (*19–21, 29, 31, 33, 35*). Oxygen chemisorption is specific to the molybdena portion of the Mo/Al_2O_3 catalyst. On the other hand, as reported by Hall and coworkers (*36, 37*) from IR studies and by Zmierczak *et al.* (*38*) from adsorption measurements, CO_2 adsorbs exclusively on the alumina portion of the Mo/Al_2O_3 catalyst and not on the Mo-oxide/sulfide phase (*11*). Therefore, the combination of O_2 and CO_2 chemisorption is useful for studying the dispersion of molybdena/alumina catalysts especially when obtained via the nonconventional solid/solid wetting method. In the present study the MoO_3–Al_2O_3 catalysts prepared via the standard impregnation method as well as the nonconventional solid/solid wetting method are characterized by means of O_2 and CO_2 chemisorption, XRD, and ESR. Activities of these catalysts were also evaluated for partial oxidation of methanol (*39, 40*) and hydrodesulfurization of thiophene in order to compare the activities and selectivities of these catalysts.

EXPERIMENTAL

Catalyst Preparation

The materials used were γ-Al_2O_3 from Harshaw (Al-III-61; surface area, 204 m^2 g^{-1}; precalcined at 500°C for 12 h before use), MoO_3 from May & Baker (England, AR grade) and ammonium heptamolybdate from JT Baker (USA, AR grade). The activated alumina support was ground to −200 mesh before use.

Appropriate quantities of physical mixtures of MoO_3 and γ-Al_2O_3 were prepared by first tumbling and then grinding the powders in an agate mortar for 30 min. The physical mixtures thus prepared were divided into three equal portions. The first portion of the mixture was placed into a glass reactor and was calcined at 500°C for 24h in dry O_2atmosphere. Dry N_2 was passed through the reactor during the initial warmup time (10°C min^{-1}). When the final temperature of 500°C was reached, an O_2 flow (30 cm^3 min^{-1}) was admitted. After the completion of heat treatment O_2 was replaced by N_2 and the powder was left to cool to room temperature. A similar heat treatment was given to the second portion of the physical mixture, but under wet O_2 flow conditions. A bubble flow saturator filled with water and maintained at ambient temperature was used to generate water vapor (20 Torr). The remaining third portion of the physical mixture was used as was for comparison purposes.

The impregnatd MoO_3/Al_2O_3 catalyst (Impr) was prepared by impregnation of the support with aqueous ammonium heptamolybdate solution using the standard incipient wetness technique. The impregnated catalyst was dried at 120°C for 16 h and calcined at 500°C for 12 h in an air circulation furnace.

The following notation is used to describe the catalysts: SPM, simple physical mixtures; SSWD, solid/solid wetting under dry O_2 atmosphere, i.e., physical mixtures cal-

TABLE 1

O_2 Chemisorption Results on Mo/Al_2O_3 Catalysts

Catalyst	MoO_3 content[a] (wt%)	O_2 uptake (μmol g^{-1})	BET surface area of reduced catalyst (m^2 g^{-1})	EMA[b] (m^2 g^{-1})	Apparent surface[c] coverage by adsorbed O_2 (%)	Dispersion[d] (%)
Impr	10.73	77.0	147	23.5	16.0	20.66
SPM	10.46	14.8	190	4.5	2.4	4.07
SSWD	10.43	44.7	152	13.6	8.9	12.34
SSWW	10.41	79.0	147	24.1	16.4	21.84

[a] Determined by the ICP technique.

[b] Equivalent molybdenum (MoO_3) area determined from inverse site density for unsupported MoO_3 (Refs. (*19*, *29*)) of 0.305 m^2 μmol^{-1} O_2.

[c] Determined by dividing the values of EMA by BET SA of reduced catalyst.

[d] Apparent dispersion (D = O/Mo) = 100 × (No. of chemisorbed O atoms)/(total number of Mo atoms).

cined under dry O_2 atmosphere; and SSWW, physical mixtures calcined under O_2 saturated with water vapor.

Chemical Analysis

The Mo content of the finished catalysts were determined by an inductively coupled plasma emission spectrophotometry (Lab Tam Instruments, Australia) and are reported as wt% of MoO_3 on Al_2O_3 (Table 1). For ICP analysis about 0.5 g of catalyst sample was dissolved in a 3 : 1 mixture of concentrated HCl and HNO_3 (aquaregia) and digested for 1 h on a hot plate. The resulting slurry was filtered, washed with deionized water, and made up to 500 ml in standard flask. As observed from analysis results (Table 1) no appreciable loss of molybdenum, upon heating under dry or humid O_2 atmospheres, was noted.

O_2 and CO_2 Chemisorption

Oxygen and carbon dioxide adsorptions were conducted on a standard static volumetric all-glass high-vacuum system equipped with a mercury diffusion pump and an in-line liquid nitrogen cold trap. Details of the setup and oxygen chemisorption procedure have been published (*32*). Chemisorption of oxygen was determined as the difference between two oxygen adsorption isotherms at −78°C. Prior to the first adsorption isotherm, the catalyst was prereduced for 4 h at 500°C in flowing purified hydrogen (35 cm^3 min^{-1}), pumped for 1 h at 500°C, and cooled to −78°C under vacuum (1×10^{-6} Torr). Between the first and the second oxygen adsorption isotherms, the catalyst sample was evacuated for 1 h at −78°C.

Carbon dioxide adsorption was measured adopting the same procedure of O_2 chemisorption, but at ambient temperature. A fresh catalyst, ca. 0.5 g, was loaded each time and evacuated at ambient temperature for 2–3 h before CO_2 chemisorption measurements. The adsorbed amount of CO_2 was determined as the difference between the two successive adsorption isotherms at room temperature. In between the two adsorption isotherms, the sample was evacuated for 1 h at ambient temperature.

BET surface areas were measured for all fresh and hydrogen-reduced catalysts by adsorption of nitrogen at −195°C assuming 0.162 nm^2 as the area of cross section of the N_2 molecule.

X-ray Diffraction

The X-ray diffraction profiles were recorded on a Philips PW 1051 instrument using Ni-filtered Cu$K\alpha$ radiation and standard conditions.

Electron Spin Resonance

The ESR spectra of the reduced and unreduced catalysts were recorded on a Bruker ER 200D-SRC X-band spectrometer with 100 kHz modulation at ambient temperature. DPPH was used for the calibration ($g = 2.0036$) of the magnetic field and for the calculation of g values. Reduced catalysts for ESR study were prepared according to the procedure described elsewhere (*41*). After hydrogen reduction at 500°C for 4 h the sample was evacuated at the same temperature for 2 h and sealed off under vacuum.

Activity Measurements

A vertical flow microreactor operating under normal atmospheric pressure and interfaced with a gas chromatograph by a six-way gas sampling valve was used to study the catalytic properties of the catalysts. Partial oxidation of methanol was studied at a constant temperature of 225°C. The feed gas consisted of 72, 24, and 4% by volume nitrogen, oxygen, and methanol vapor, respectively. For each run about 0.25 g of catalyst was used and the products were analyzed with a 10% Carbowax 20 M column (2 m long). The major products observed were dimethyl ether (DME) and formaldehyde (HCHO) with some traces of methyl formate, CO and CO_2, respectively (*42*).

Thiophene HDS was studied at 400°C temperature and the products were analyzed with the help of a 2-m-long stainless-steel column packed with 10% OV-17, maintained at 90°C. A carrier-gas (nitrogen) flow of 40 $cm^3\ min^{-1}$ and an FID were used in both cases. Before introducing the thiophene feed by means of bubblers, all the catalysts were presulfided at 400°C for 2 h with a stream of hydrogen saturated with CS_2. The conversions were kept within the 15% level and the rates were measured under steady-state conditions in the absence of any diffusional effects. Further details of the experimental procedure and the activity calculations can be found elsewhere (*32*).

RESULTS AND DISCUSSION

X-ray diffraction patterns of MoO_3/Al_2O_3 catalysts obtained via the conventional impregnation method as well as solid/solid wetting method along with simple physical mixtures are shown in Fig. 1. As can be noted from Fig. 1, in the case of simple physical mixtures, sharp diffraction lines due to the well crystalline orthorhombic MoO_3 phase (JCPDS, Card No. 5-0508) with the background of the γ-Al_2O_3 phase (JCPDS, Card No. 29-1486) can be seen. When this simple physical mixture was calcined in dry or wet O_2 atmosphere, a total disappearance of peaks due to MoO_3 phase can be noted. Only the broad diffraction peaks due to the γ-alumina phase can be seen. Similarly the XRD pattern of the impregnated Mo/Al_2O_3 catalyst also shows no diffraction lines due to the crystalline MoO_3 phase. The absence of characteristic XRD lines due to the crystalline MoO_3 phase can be taken as an indication of high dispersion of MoO_3 on the Al_2O_3 support or the crystallites formed are less than 4 nm size, i.e., beyond the detection capability of the XRD technique. According to the literature, the Mo/Al_2O_3 catalyst of no more than 12 wt% MoO_3 on the Al_2O_3 support of 196 $m^2\ g^{-1}$ surface area generally yields a highly dispersed monolayer of the Mo-oxide phase on the surface of the alumina support (*9*). It is interesting to note, from Fig. 1, that no significant differences can be seen, as observed from XRD data, beween the two different methods of preparation irrespective of their treatment procedures.

Table 1 shows static volumetric oxygen uptake results for Mo/Al_2O_3 catalysts of different origin at −78°C. After the O_2 adsorption measurement, the reduced sample was saved and degassed for several hours and the N_2 BET surface area was determined. From O_2 uptake and BET surface area data it is possible to estimate the equivalent molybdenum surface area, apparent surface coverage, and apparent dispersion according to the procedures described by Parekh and Weller (*19*). The equivalent molyb-

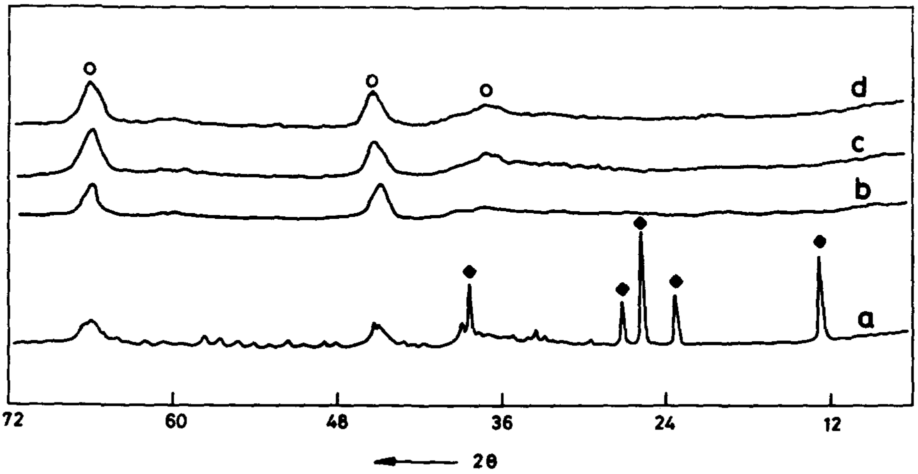

FIG. 1. XRD patterns of MoO_3/Al_2O_3 catalysts: Characteristic peaks due to MoO_3 (◆) and Al_2O_3 (○) phases. (a) SPM; (b) SSWD; (c) SSWW; (d) Impr.

denum area was calculated for reduced catalysts based on inverse site densities of 0.305 m^2 μmol^{-1} O_2 reported for MoO_3 on the Al_2O_3 support (*19, 29*). These data, along with estimates of apparent MoO_3 coverages and apparent dispersion, are listed in Table 1. As can be noted from Table 1, the numerical values of oxygen uptake, MoO_3 coverage, and the apparent dispersion on both the impregnated sample and the wet O_2-treated solid/solid wetting sample are the same within experimental error. These values are also higher than those observed on the other two samples. A large difference, approximately a factor of 2, can be seen between the wet and dry O_2-treated samples. Practically no uptake of O_2 was observed on the Al_2O_3 support under the experimental conditions employed in this study. A reasonable uptake of O_2 can be seen on the SPM catalyst, which is due to the reduced MoO_3 alone in that sample. The O_2 uptakes and the apparent dispersions observed on the impregnated sample as well as on the wet O_2-treated solid/solid wetting sample are close to the values reported by Muralidhar *et al.* (*29*). Several other investigators (*19, 21, 22, 29, 35*) have also reported that the amount of chemisorbed oxygen for the reduced MoO_3/Al_2O_3 catalyst corresponds to an O/Mo atomic ratio of 0.18–0.35. On the basis of Hall's (*7*) "patchy monolayer model," the observed oxygen uptake trends on a series of Mo/Al_2O_3 and Mo/SiO_2 catalysts were envisaged recently by Reddy *et al.* (*33, 43*). This model is consistent with the observed alumina surface hydroxyl groups by IR and NMR spectroscopy (*43–45*) on an Mo/Al_2O_3 catalyst with an Mo loading near the monolayer capacity of the support. Under the tenet of this model, it was proposed that the coordinatively unsaturated Mo sites (CUS) generated upon reduction in hydrogen on the patchy monolayer phase of Mo-oxide are the locations for dissociative O_2 chemisorption at low temperatures. The overall reduction behavior of the supported catalyst also expected to have an important bearing on the oxygen chemisorption capacity. This is because low-temperature oxygen chemisorption is possible on the prereduced catalyst that contains the CUS, generated by the removal of oxygen by H_2 reduction, and that can hold adsorbed oxygen more strongly (*35*). This study is, of course, not the primary objective of the present investigation. However, an interesting point to mention here is that the sample obtained via the solid/solid wetting method appears to show

TABLE 2

CO_2 Chemisorption Results on Mo/Al_2O_3 Catalysts

Catalyst	CO_2 uptake (μmol g^{-1} cat.)	BET surface area[a] (m^2 g^{-1})	Apparent surface coverage[b] by adsorbed CO_2 (%)
Al_2O_3	81.7	196	100
Impr	14.8	151	23.5
SPM	69.9	191	87.8
SSWD	44.6	166	64.5
SSWW	13.2	149	21.3

[a] BET surface area after CO_2 uptake measurements. After CO_2 uptake sample was evacuated for several hours before the BET SA measurement.

[b] Area covered by CO_2 molecule (assuming 2.4 m^2 μmol^{-1} CO_2, from the results on Al_2O_3) to the BET surface area.

an O_2 uptake capacity similar to that of a standard impregnated catalyst.

Uptakes of CO_2 on the Al_2O_3 support and on Mo/Al_2O_3 catalysts are shown in Table 2. In agreement with earlier findings (*11, 36, 37*), no uptake of CO_2 was observed on a pure and evacuated MoO_3 sample at ambient temperature. A maximum uptake of 81.7 μmol g^{-1} was observed on the Al_2O_3 support used in this study. A similar uptake of 81.1 μmol g^{-1} (within experimental error) was reported by Zmierczak *et al.* (*38*) for an Al_2O_3 support (194 m^2 g^{-1} surface area) calcined at 500°C. To calculate the apparent surface coverages by adsorbed CO_2 on Mo/Al_2O_3 catalysts a conversion factor was defined (2.4 m^2 μmol^{-1} CO_2) by taking into consideration the observed CO_2 uptake on the Al_2O_3 support used in this study and also reported by Zmierczak *et al.* (*38*). The apparent surface coverages thus derived are shown in Table 2. As can be seen, this value gives meaningful information about the free accessible support available for the adsorption of CO_2 molecule. In case of simple physical mixtures the calculated apparent surface coverage by adsorbed CO_2 is about 88%. This sample also contains about 89 wt% of Al_2O_3 and 11 wt% of MoO_3. On those lines, the impregnated Mo/Al_2O_3 catalyst contains at least 24% free alumina uncovered by molybdenum species. In other words, the molybdenum species coverage on Al_2O_3 support surface is about 76%. A similar (slightly higher) surface coverage of Mo species on the Al_2O_3 surface can be seen in the case of the wet O_2-treated sample. However, in the case of the SSWD sample, the Mo species coverage on the Al_2O_3 support surface is only about 35.5%. This observation is in agreement with the earlier Raman spectroscopic study (*15, 16*), which showed intense Raman bands at 820 and 996 cm^{-1} characteristic of MoO_3. The CO_2 uptake results thus give an impression that the MoO_3 in the case of SSWD preparation has not lost its identity; however, it is in a highly dispersed (from XRD) state, probably not interacting with Al_2O_3 surface hydroxyls.

The ESR spectra of reduced Mo/Al_2O_3 catalysts recorded at ambient temperature are shown in Fig. 2. The spectra of the oxidized samples recorded at room temperature did not reveal any significant presence

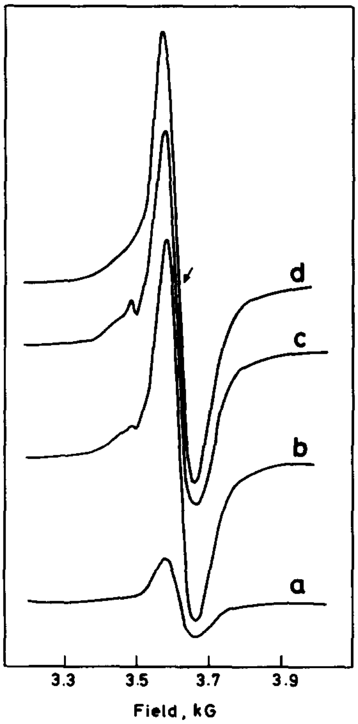

FIG. 2. ESR spectra of reduced Mo/Al_2O_3 catalysts recorded at room temperature. (a) SPM; (b) SSWD; (c) SSWW; (d) Impr.

TABLE 3

ESR Parameters of the signals

Catalyst	Average *g*	ΔH (G)
Impr	1.956	77
SSWW	1.957	76
SSWD	1.925	84
SPM	1.924	87

of Mo^{5+} ions, whereas the samples reduced in flowing hydrogen and subsequently evacuated at 500°C exhibited an ESR spectrum characteristic of Mo^{5+}. The shape of the spectrum in Fig. 2 is identical to the one shown by Hall (*7*) for a reduced molybdena–alumina catalyst of similar composition to that used in the present study and prepared by the impregnation method. The average *g* values and line widths at peak to peak maximum (ΔH) are presented in Table 3. These values are also very close to those values reported by other workers (see for example (*7, 46*)). Based on *g* and ΔH values these catalysts can be divided into two group, i.e., Impr, SSWW as one group and SPM, SSWD as the other group. One must be cautious about making such a comparison on the basis of ESR spin concentrations since Mo^{5+} signal is antiferromagnetically coupled and the spin concentrations actually seen by ESR represent very small fraction of the total Mo^{5+} (*47*). However, the observation of similar *g* and ΔH values gives an impression that the surface structure of Mo-oxide species on the impregnated sample and that on the wet O_2-derived solid/solid wetting sample are the same, in agreement with the findings of Knozinger and co-workers (*15*). From Raman spectroscopic measurements Knozinger and co-workers (*15*) have observed the formation of surface heptamolybdate phase in the presence of O_2 atmosphere saturated with water vapor in the case of the solid/solid wetting method. This surface heptamolybdate phase formed was also identical to the one observed on the impregnated sample.

Steady-state activities and selectivities for partial oxidation of methanol to formaldehyde on various Mo/Al_2O_3 catalysts are presented in Figure 3. The results clearly indicate that the formation of the main products, formaldehyde and DME, depends on the Mo/Al_2O_3 catalyst origin. Alumina support also shows some small conversion and total selectivity to DME under the experimental conditions employed in this study. The activity results on the MoO_3 + Al_2O_3 mixture sample resembles the results of the Al_2O_3 support. The increase in the conversion and the observation of the HCHO product in addition to DME are due to the presence of MoO_3 in this sample. The DME product selectivities on various samples follow the following trend Al_2O_3 > SPM > SSWD > Impr ≃ SSWW and HCHO as SPM < SSWD < SSWW ≃ Impr. An interesting observation from Fig. 3 is that activity and selectivity trends observed are the same within experimental error on both the impregnated sample and the wet O_2 calcined solid/solid wetting sample. In addition, the SSWD catalyst also shows activity comparable to that of the SSWW sample; however, the product selectivities are different. The SSWD catalyst shows more DME than the SSWW catalyst. These results are in agreement with the observation of Tatibouet *et al.* (*39, 40*) that methanol oxidation is a

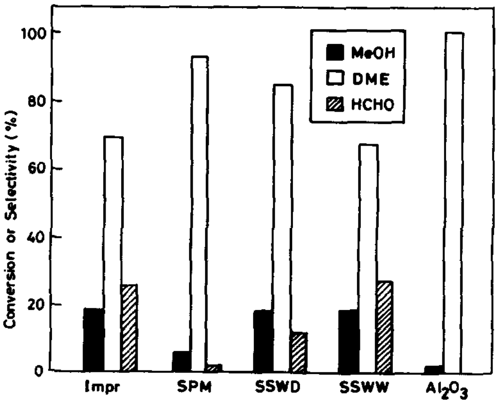

FIG. 3. Activities and selectivities of various samples for partial oxidation of methanol.

TABLE 4

Thiophene HDS activity of Mo/Al_2O_3 catalysts

Catalyst	HDS activity, 10^3 r_{HDS} (mol g^{-1} cat. h^{-1})
Impr	14.8
SPM	1.2
SSWD	6.8
SSWW	15.1

highly structure-sensitive reaction and depends on the dispersion of molybdenum and on the environment of the molybdenum ion, i.e., on its coordination sphere and on interactions between neighboring molybdenum ions.

The HDS activity of various catalysts, reported as the steady-state rate, are presented in Table 4. All the samples were prefulfided under identical conditions before their activities for thiophene HDS at 400°C were measured. As can be noted from Table 4, the impregnated sample and the SSWW catalyst show identical catalytic activity and are both more active than the SSWD and SPM samples. The thiophene HDS activity sequence is SSWW = Impr > SSWD > SPM. A similar observation was made earlier by Koranyi *et al.* (*17*) on various Mo/Al_2O_3 catalysts obtained by conventional impregnation and solid/solid wetting methods. As envisaged by Koranyi *et al.*(*17*), the identical and higher HDS activities on both the conventional impregnated catalyst and the wet O_2-derived solid/solid wetting sample are primarily due to the presence of identical surface heptamolybdate species in the oxide precursor state. Upon presulfiding, the heptamolybdate ion, being chemically anchored to the support surface, leads to a highly dispersed active sulfide phase. Thiophene HDS rates on various samples are thus in line with other results observed on these samples.

Thus, thermal treatment of mechanical mixtures of $MoO_3 + Al_2O_3$ at 500°C in the presence of water vapor saturated O_2 atmosphere can be considered an alternative route toward the preparation of alumina-supported molybdate catalyst. Further study is needed to understand fully the role of alumina surface hydroxyls in the spreading phenomena and the nature of Mo species after thermal treatments especially, under dry O_2 atmospheric conditions.

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