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Spreading Behavior of Molybdenum Trioxide on Alumina and Silica: A Raman Microscopy Study

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The wetting of alumina by molybdenum trioxide has been demonstrated by Raman microscopy. Special specimens, which consisted of an alumina wafer in contact with a molybdenum trioxide wafer, were prepared for this purpose. Concentration profiles across the sharp dividing line between the two oxides were measured with a Raman microscope after thermal treatment at 800 K in a stream of dry O_2 or O_2 saturated with water vapor. The molybdenum oxide was transported over the alumina surface for several hundred micrometers. In contrast, in a similar wafer with silica no transport of molybdenum oxide could be observed. The results suggest that neither gas-phase transport nor surface diffusion in a concentration gradient provide major contributions to the spreading process. A solid–solid wetting process is considered to best describe the observed phenomena, the decrease in surface free energy being the dominant driving force for the spreading of molybdenum oxide over alumina.

INTRODUCTION

The great current interest in molybdena/alumina catalysts is due to the enormous technological importance of this class of catalyst precursors for hydrodesulfurization (HDS) and other hydrotreating reactions. Typically, these materials are prepared by impregnation (*1, 2*) of the alumina support from aqueous solutions containing an appropriate molybdenum compound (usually $(NH_4)_6\ Mo_7O_{24}$) followed by drying and calcination at temperatures around 770 K. The catalytic materials obtained in this way are frequently considered to develop a monolayer on the support consisting of molybdenum–oxygen polyhedra. The anchoring of three-dimensional $Mo_7O_{24}^{6-}$ islands onto the alumina support surface appears to be a more likely structural model (see Refs. (*1*) and (*3*) and references therein). This surface polyanion must have an unknown number of protons attached to it for charge compensation, the number of protons depending on the number of Mo–O–Al anchoring bonds to the surface. The heptamolybdate anion has been suggested to be the crucial precursor species for an active sulfided catalyst (*1, 4*).

In a series of papers, Xie and co-workers (*5–9*) concluded from X-ray photoelectron spectroscopy (XPS) and X-ray diffraction (XRD) studies that MoO_3 spontaneously spreads over the surface of alumina in physical mixtures of the two oxides when these are thermally treated at temperatures around 670–770 K in air. We have earlier reported (*10–12*) supporting evidence for this phenomenon as obtained by ion scattering spectroscopy (ISS). Raman spectroscopy provided additional information on the structure of the molybdenum–oxygen species present on the alumina surface after the spreading had occurred (*2, 10–13*). The vibrational spectra demonstrated the importance of the gas atmosphere during thermal treatment: only MoO_3 (which was X-ray amorphous) could be detected in absolutely dry O_2 atmosphere, while in the presence of water vapor the surface heptamolybdate was formed. The latter material had the same activity for thiophene HDS as the con-

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ventionally impregnated catalyst having the same molybdenum loading, while the former material was significantly less active (*1, 14*).

Interestingly, spreading could not be observed in mixtures of MoO_3 and SiO_2 (*12*). The observations could be explained phenomenologically (*2, 10–12, 15–18*), but the microscopic mechanism of the spreading process is still unknown.

In the present paper we report on studies carried out by means of a Raman microscope; the aim of the work was to test whether detectable contributions from gas-phase transport would occur, and whether a possible surface transport would occur over macroscopic distances. To answer these questions, special samples were prepared in which wafers of MoO_3 and Al_2O_3 or SiO_2 were brought into contact with a sharp dividing line. Concentration profiles across this dividing line were measured by Raman microscopy after thermal treatments of the wafers with a lateral resolution of ca. 25 μm.

EXPERIMENTAL

1. Materials

γ-Al_2O_3 was prepared by calcination of the hydroxide PURAL SB (Condea, Brunsbüttel, FRG) in air at 1048 K for 24 h. The resulting oxide had a N_2 BET surface area of 123 m^2g^{-1}. The SiO_2 used was Aerosil 200 prepared by flame hydrolysis of the chloride and provided by Degussa (Hanau, FRG). It had a BET surface area of 200 m^2 g^{-1}.

MoO_3 was a Merck product (AR grade). It had a BET surface area of less than 5 m^2 g^{-1}.

O_2 and Ar were from Linde AG and had 99.998% nominal purity. The gases were further dried by passing them through a column containing freshly activated 4Å molecular sieve (Merck).

2. Sample Preparation

γ-Al_2O_3 or SiO_2 were first pressed at 200 kp cm^{-2} (1kp = 9.81*N*) between two mica sheets for ca. 30 s to obtain a thin wafer. A sharp edge was prepared by cutting the wafer with a scalpel. MoO_3 powder (ground in an agate mortar for 5 min) was then placed on the mica sheet, homogeneously distributed, and brought into close contact with the sharp γ-Al_2O_3 or SiO_2 edge. Care was taken not to place any MoO_3 powder onto the surface of the γ-Al_2O_3 or SiO_2 wafer. A short piece of Pt wire (0.5 mm in diameter) was also placed at the edge. This could later be used as the zero of the distance scale. This combination of wafer and MoO_3 powder was then covered with a second mica sheet and pressed at 100 kp cm^{-2} for ca. 30 s. Sufficiently stable wafers in which the two oxides were in contact across a well-defined dividing line were thus obtained.

These samples were placed in a glass reactor for thermal treatments at 770–800 K for up to 200 h. A dry argon flow (50 cm^3 min^{-1}) was passed over the sample during the initial warm-up period. When the temperature of 800 K was reached, an oxygen flow (50 cm^3 min^{-1}), either dry or saturated with water vapor at a partial pressure of 56 hPa, was admitted (to avoid reduction of MoO_3). The saturation of the O_2 flow with water vapor was performed with a temperature-controlled saturator, which was described earlier (*19*).

3. Raman Spectroscopy

Laser Raman spectra were recorded in the wavenumber range 800–1200 cm^{-1} on a computer-controlled Dilor OMARS 90 spectrometer, the design of which was described by Deffontaine *et al.* (*20*). The spectrometer was equipped with an optical multichannel analyzer (OMA) Model IRY 512 from Spectroscopy Instruments. For Raman microscopy, an Olympus microscope Model BHT was connected to the spectrometer and in this way laterally resolved spectra of the specimen were obtained. The sample wafer was kept in ambient atmosphere in these studies.

The 514.5-nm line of a Spectra Physics Ar^+ ion laser Model 2025-03 was used for excitation. The laser power at the sample was typically limited to 15 mW. The lateral

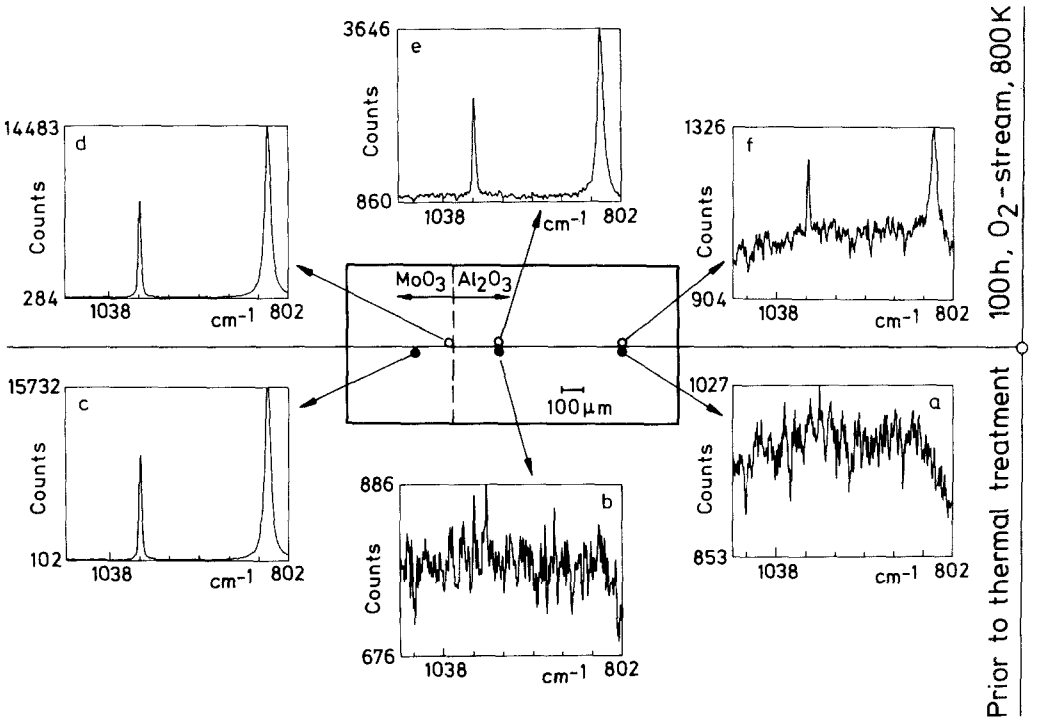

FIG. 1. Raman spectra of an untreated MoO_3/Al_2O_3 wafer (a–c) and after thermal treatment (d–f) at 800 K in a dry O_2 flow for 100 h at the indicated positions.

resolution was estimated to be ca. 25 μm. The spectra were recorded with a spectral resolution of 2.5 cm^{-1} and the wavenumber accuracy was ± 2 cm^{-1}.

RESULTS

Laterally resolved Raman spectra were recorded across the dividing line of the specimens prior to and after thermal treatments. Typical spectra for MoO_3/Al_2O_3 prior to thermal treatment (spectra a–c) and after calcination at 800 K in dry flowing O_2 for 100 h (spectra d–f) are shown in Fig. 1. A schematic representation of the MoO_3/Al_2O_3 wafer is illustrated in the center of the figure which indicates the locations at which the spectra shown were taken. As expected, only noisy background without any characteristic features is recorded on the Al_2O_3 part of the wafer prior to thermal treatment (spectra a and b), while the two strongest Raman bands of MoO_3 at 819 and 999 cm^{-1} (*22*) are clearly detected on the MoO_3 half of the wafer (spectrum c). In contrast, after thermal treatment at 800 K in dry O_2 flow for 100 h these Raman bands are clearly detectable at distances of ca. 170 μm (spectrum e) and even 660 μm from the dividing line (spectrum f). This indicates that MoO_3 was transported during the thermal treatment over macroscopic distances across the dividing line and that the only detectable chemical species formed on the Al_2O_3 surface is MoO_3. The absolute intensities of the characteristic MoO_3 Raman lines and the signal-to-noise ratio clearly decrease with increasing distance from the dividing line in the direction of the Al_2O_3 part of the wafer (see Fig. 1, spectra d–f), suggesting that a concentration profile has developed across the dividing line. A typical profile is shown in Fig. 2, where the relative peak intensity of the MoO_3 Raman line at 999 cm^{-1} (referenced to the intensity of this line in the MoO_3

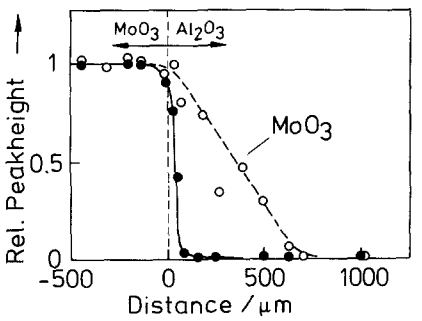

FIG. 2. Relative peak heights of the characteristic MoO_3 band at 999 cm^{-1} of a MoO_3/Al_2O_3 wafer prior to (●) and after (○) thermal treatment for 100 h at 800 K in dry O_2 flow plotted vs the distance from the dividing line between MoO_3 and Al_2O_3.

part of the wafer) is plotted against the distance from the dividing line for samples prior to and after thermal treatment. Comparison of the two profiles in this figure clearly demonstrates the transport of MoO_3 over several hundred micrometers under the experimental conditions applied. It is important to note that almost identical profiles were obtained irrespective of the direction of the O_2 flow.

Analogous experiments were carried out applying an O_2 flow which was saturated with 56 hPa H_2O vapor. Typical spectra obtained at various positions of the wafer prior to and after thermal treatment are shown in Fig. 3. The spectra for the untreated sample wafer match those shown in Fig. 1, indicating that the MoO_3 concentration steeply decays across the dividing line (see Fig. 4). After thermal treatment a new broad spectral feature with a maximum at 965 cm^{-1} develops on the Al_2O_3 part of the wafer up to distances of ca. 1000 μm from the dividing line. This band corresponds to the Mo=O stretching mode of a surface polymolybdate (probably $Mo_7O_{24}^{6-}$) as reported earlier (*12, 22–24*). Hence, in agreement with our previous results obtained on mixtures of oxide powders (*10–13*), not only spreading but also chemical transformation of the MoO_3 into a surface polymolybdate occurs in the presence of water vapor. As indicated by

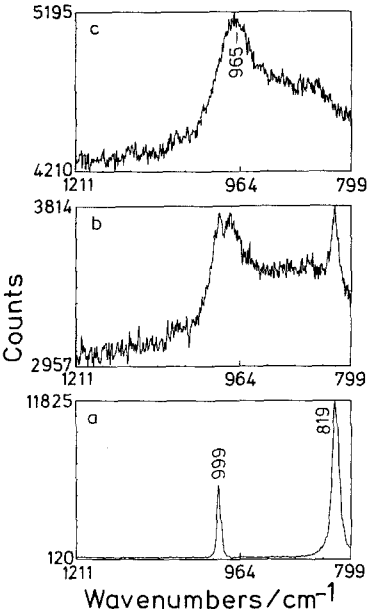

FIG. 3. Raman spectra of a MoO_3/Al_2O_3 wafer after thermal treatment for 100 h at 800 K in a water vapor-saturated O_2 flow taken at (a) the dividing line, (b) 200 μm from the dividing line, and (c) 900 μm from the dividing line.

the dependence of the relative intensities on distance from the dividing line (concentration profiles) as shown in Fig. 4, the polymolybdate formation occurs only on the Al_2O_3 surface, while the MoO_3 profiles are identi-

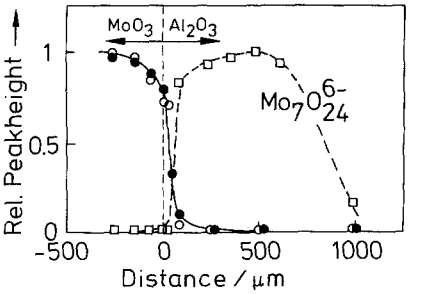

FIG. 4. Relative peak heights of the characteristic Raman bands of MoO_3 at 999 cm^{-1} and of the surface polymolybdate at 965 cm^{-1} prior to (●) and after (○ and □) thermal treatment for 100 h at 800 K in water vapor-saturated O_2 flow plotted vs the distance from the dividing line between MoO_3 and Al_2O_3.

cal before and after thermal treatment. The relative intensities of the polymolybdate bands at 965 cm^{-1} as plotted in Fig. 4 were referenced to the maximum intensity of this band measured at ca. 500 μm from the dividing line.

Entirely different results were obtained with the MoO_3/SiO_2 wafer. Even after thermal treatment for 200 h under otherwise identical conditions in either dry or water vapor-saturated O_2 flow, neither MoO_3 nor polymolybdate species could be detected on the SiO_2 part of the wafer. As an example of this behavior, the concentration profiles after calcination at 770 K in dry O_2 flow for 100 and 200 h are compared in Fig. 5 with that of the wafer prior to thermal treatment. Within the limits of the lateral resolution of the technique, all three profiles are identical. This undoubtedly suggests that transport of MoO_3 across the dividing line between the two oxides has not occurred in this case under the applied experimental conditions. Even in the presence of water during thermal treatment the concentration profile for MoO_3 was identical to those shown in Fig. 5 and no indication for a surface molybdate could be detected. These observations are in complete agreement with earlier results obtained for physical mixtures of MoO_3 and SiO_2. ISS had shown that spreading did not occur in this system and the only detectable species in the Raman spectra even in the presence of water vapor during thermal treatment was MoO_3 (*12*).

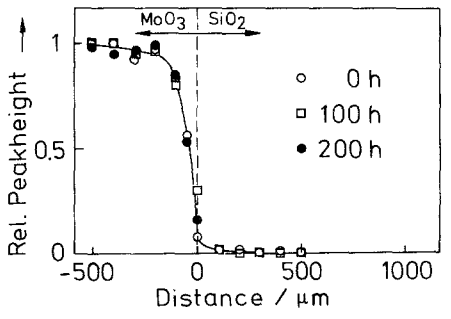

FIG. 5. Relative peak height of the characteristic Raman band of MoO_3 at 999 cm^{-1} of a MoO_3/SiO_2 wafer prior to (○) and after thermal treatment for 100 h (□) and 200 h (●) at 770 K in dry O_2 flow plotted vs the distance from the dividing line between MoO_3 and SiO_2.

DISCUSSION

The present studies clearly demonstrate that spreading of MoO_3 occurred on the Al_2O_3 surface in the presence and absence of water vapor, while this was not the case with the SiO_2 surface. In addition, MoO_3 was converted into a surface polymolybdate on the Al_2O_3 surface when water was present. These results are in complete agreement with previous results obtained for physical mixtures of the oxide combinations by means of ISS and Raman spectroscopy (*10–13*).

The chemical transformation of MoO_3 on the Al_2O_3 surface was described (*10–13*) as being due to the intermediate formation of $MoO_2(OH)_2$, a reaction which does occur with low but nonnegligible yields under the experimental conditions (*25, 26*):

$$MoO_3 + H_2O \rightleftharpoons MoO_2(OH)_2. \quad (1)$$

This oxyhydroxide is then assumed to react with hydroxyl groups $[OH^-]_s$ to form a surface molybdate $[MoO_4^{2-}]_s$:

$$MoO_2(OH)_2 + 2[OH^-]_s \rightleftharpoons [MoO_4^{2-}]_s + 2H_2O. \quad (2)$$

The $[MoO_4^{2-}]_s$ species have been detected as intermediates (*13*). They undergo condensation with formation of the surface polymolybdate provided their local concentration becomes sufficiently high.

The spreading phenomenon itself was interpreted phenomenologically as a solid–solid wetting process (*10–12, 15–18*). The change in the surface free energy ΔF_s was considered to be the driving force for the spreading process,

$$\Delta F_s = \gamma_{M,g}\Delta A_M - \gamma_{S,g}\Delta A_S + \gamma_{MS}\Delta A_{MS}, \quad (3)$$

where $\gamma_{M,g}$ and $\gamma_{S,g}$ are the areal surface free energies of MoO_3 and the support oxide, respectively, in contact with the gas phase and γ_{MS} is the specific free interface energy.

The ΔA_M, ΔA_S, and ΔA_{MS} are the corresponding changes in surface and interface areas. Spreading will occur if $\Delta F_s < 0$. Assuming $|\Delta A_M| = |\Delta A_S| = |\Delta A_{MS}|$, this requires

$$(\gamma_{M,g} + \gamma_{MS}) < \gamma_{S,g}. \quad (4)$$

Approximate surface free energies are known (*27*), and $\gamma_{M,g}$ turns out to be smaller by about an order of magnitude than $\gamma_{S,g}$ of both Al_2O_3 and SiO_2. The interface free energies are unknown. It has been argued (*12*), however, that "chemical" interactions are likely to occur between MoO_3 and Al_2O_3 ($Al_2(MoO_4)_3$ is formed in a solid state reaction at higher temperatures) while such interactions are not to be expected between MoO_3 and SiO_2 (no solid state reaction reported in the literature). Hence, γ_{MS} in Eq. (4) is favorable for spreading in the case of Al_2O_3 and presumably unfavorable in the case of SiO_2. The different behaviors of the MoO_3/Al_2O_3 and MoO_3/SiO_2 could thus be explained on a thermodynamic basis.

The microscopic mechanism of the spreading process in those cases where it is thermodynamically possible, is, however, still unknown. Also, the present study cannot establish such transport mechanisms at a molecular level. However, certain processes can be excluded based on the present results.

MoO_3 is known to sublime slowly at temperatures around 800 K, the temperature applied during the thermal treatments as described above. Therefore, gas-phase transport might contribute to the transport of MoO_3 onto the support surface. The experimental results, however, permit us to exclude measurable contributions of gas-phase transport. First, if gas-phase transport had occurred, S-shaped concentration profiles as shown in Fig. 2 would hardly have been built up, but rather the entire alumina part of the wafer would have been covered by MoO_3. Moreover, deposition of MoO_3 would also have been expected on the SiO_2 wafer, which was not observed. Second, if gas-phase transport were important, the deposition of MoO_3 on the Al_2O_3 part of the wafer would have been dependent on the direction of the O_2 flow, which was not the case.

The oxyhydroxide $MoO_2(OH)_2$ has a higher vapor pressure than MoO_3 (*25, 26*). This fact has been used to load MoO_3 onto support oxides in packed columns by Sonnemans and Mars (*28*). We had therefore originally assumed (*13*) that the $MoO_2(OH)_2$ species was the mobile species. This assumption, however, cannot explain the MoO_3 mobility in the absence of water vapor. Gas-phase transport mediated by the oxyhydroxide can be excluded by the same arguments given in the previous paragraph. It must therefore be concluded that gas-phase transport is negligible and that surface transport must be responsible for the observed spreading phenomenon.

The Raman microscopy studies reported here indicate that the spreading of MoO_3 is not a local phenomenon occurring exclusively at or very close (on an atomic scale) to a contact zone between a MoO_3 particle and an Al_2O_3 particle, but transport rather occurs over macroscopic distances (several 100 μm under the applied experimental conditions). This observation is in good agreement with the elegant high-resolution TEM results of Hayden *et al.* (*29*).

The melting point T_m of MoO_3 is 1068 K, and hence, the Tammann temperature $T_T \cong 0.5\ T_m$ is calculated to be 534 K. Therefore, mobility of MoO_3 at the temperatures of the present experiments is undoubtedly expected and one might describe the surface transport in terms of diffusion in a concentration gradient across the dividing line between the two oxides. This mechanism, however, must also be rejected, since in this case the driving forces would be the same for the MoO_3/Al_2O_3 and MoO_3/SiO_2 combinations and a broadening of the concentration profile across the dividing line would be expected in both cases. This, however, was not observed (compare Figs. 2 and 5). Haber (*17*) also concluded that surface diffusion should be slow in the temperature range

concerned due to the relatively high values of the lattice energy of oxides.

It must therefore be concluded that a significant decrease in surface free energy ΔF_s in the case of MoO_3/Al_2O_3 acts as the dominant driving force for the spreading, which can thus be described as wetting of one solid by a second solid. Close inspection of the concentration profiles of Figs. 2 and 4 shows that in the presence of water vapor under otherwise identical conditions the molybdenum species are transported over a somewhat larger distance than those in the absence of water vapor. Although the reason for this observation is not entirely clear, it is probably due to a modification of the surface free energies by adsorption of water.

CONCLUSIONS

The results of the present Raman microscopy study permit the following conclusions to be drawn:

1. MoO_3 spreads on the surface of alumina. The transport can occur over macroscopic distances, i.e., several hundred micrometers in the present case.

2. In contrast, spreading does not occur on silica surfaces.

3. Gas-phase transport can be excluded as the dominant mechanism, at least at the temperatures applied in the experiments described. This applies also when thermal treatments are carried out in the presence of water vapor, under which conditions $MoO_2(OH)_2$ is formed and acts as an intermediate in surface polymolybdate formation.

4. Surface diffusion in a concentration gradient can also be rejected as a major mechanism of spreading.

5. The experimental results can best be explained by a solid–solid wetting process, in which the decrease in surface free energy is to be considered as the dominant driving force for spreading. The different behavior of Al_2O_3 and SiO_2 can be understood on these grounds by assuming "chemical" interactions between MoO_3 and Al_2O_3 which lead to a favorable interface energy, which is not the case for MoO_3 and SiO_2. These considerations are in full agreement with experimental results obtained for physical mixtures of powders of the various oxide combinations (*10–12*).

6. Wetting processes of this kind have been reported to be important steps in the mechanisms of solid state reactions (*30, 31*).

7. It is suggested that solid–solid wetting may play an important role in catalyst preparation and regeneration, particularly for supported oxides.

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