# Photoelectron Spectromicroscopic Study of the Spreading Behavior of MoO<sub>3</sub> on Titania and Alumina Model Supports<sup>†</sup>

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The spreading of micron-sized  $MoO_3$  particles deposited on model supports, alumina and titania thin films, has been studied by scanning photoemission spectromicroscopy. It was shown that Mo species released from the  $MoO_3$  crystals spread over the thin oxide film under conditions (heating to 720 K for 6 h in air) similar to those used for catalysts on powdered supports. The changes in the surface morphology were followed by elemental mapping and photoelectron spectroscopy from submicron spots where the intensities and kinetic energies of the Mo 3d, Al 2p, Ti 3d, and O 1s photoelectrons were used as fingerprints for the chemical composition of the surface. The high spatial resolution when imaging the spread phase on the laterally inhomogeneous samples made it possible to throw light onto the active transport mechanism of the wetting Mo oxide species during heat treatment of the model systems.

#### Introduction

Many industrially important solid catalysts consist of at least two different compounds: an oxidic support material and the usually highly dispersed active phases, which are often metals, oxides, or sulfides. At high temperatures and in the presence of reactive gases, e.g., under catalytic conditions, these active phases can develop surface mobility, which may result in sintering of the active phase (catalyst deactivation) or in wetting and spreading across the support surface (activation or reactivation). The following well-known phenomena are a consequence of this surface mobility at high temperatures: (i) sintering and redispersion of the active catalyst phase (often a function of the reactive gas phase); (ii) strong metal-support interaction (SMSI), where the active noble metal catalyst is partially encapsulated by an overlayer of the support oxide, or (iii) spreading of salts or oxides across support surfaces.<sup>1-3</sup> Although surface mobility strongly affects catalytic properties, e.g., catalyst aging and deactivation, it has not been considered frequently in the literature. All these processes are strongly related and are suggested to depend on the surface and interface free energies of the phases present and the mean free paths of the diffusing entities. The mechanisms on an atomic level that lead to mobility are not fully understood yet, and a physicochemical theory is still missing that completely describes the evolution of surface mobility. This motivated the increasing number of fundamental UHV–STM studies dealing with the mobility of metal overlayers on metal surfaces, surface alloy formation, or their segregation.<sup>4–6</sup> Comparably well-defined experiments, however, on the mobility of oxide overlayers on oxide supports have not been conducted yet.

Xie and co-workers were the first to report that the XRD reflections of MoO<sub>3</sub> in physical mixtures with Al<sub>2</sub>O<sub>3</sub> are disappearing upon calcination at about 700 K.7-9 XPS investigations supported their interpretation of a Mo oxide monolayer formation during this treatment. Stampfl et al. also concluded from Raman and IR spectra that Mo oxide monolayers were formed in physical mixtures of MoO<sub>3</sub> with various support oxides upon calcination in air at 720 K.<sup>10</sup> ISS studies revealed that MoO<sub>3</sub> in physical mixtures with alumina or titania was spontaneously spreading over the support surface at temperatures close to its Tammann temperature and even in dry oxygen.<sup>11,12</sup> Raman spectroscopy was additionally used to characterize the surface Mo species formed under spreading conditions.<sup>11-13</sup> After heat treatment at 720 K (and 800 K) in dry oxygen only crystalline MoO<sub>3</sub> could be detected, whereas under the presence of H<sub>2</sub>O vapor the formation of surface molybdates (Mo<sub>7</sub>O<sub>24</sub><sup>6-</sup> on y-Al<sub>2</sub>O<sub>3</sub>) was observed. Thus, it was concluded that spreading on one hand and the chemical conversion into polymolybdates on the other were two independent processes. This observation was further confirmed by EXAFS.<sup>14</sup> Raman microscopy demonstrated that the transport of MoO<sub>3</sub> across the alumina surface occurred over several hundred micrometers.<sup>15</sup>

 $<sup>^\</sup>dagger$  Dedicated to Prof. Sir J. M. Thomas on the occasion of his 65th birthday.

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#### MoO<sub>3</sub> on Titania and Alumina

In situ high-temperature Raman spectroscopy suggested that the actual spreading phase was surface molten  $MoO_3$ , which seemed to consist of  $MoO_3$  monomers or small oligomers.<sup>16</sup> This surface molten phase was highly reactive toward H<sub>2</sub>O as proved by in situ exposure to water vapor at room temperature which led to the formation of surface polymolybdates. The reduction of the surface free energy of the whole system, support/MoO<sub>3</sub>, was discussed as the driving force for this solid wetting.<sup>1,2</sup>

One of the disadvantages of the previous wetting and spreading studies was the disperse nature of the oxide powders used as supports. In this case the amorphizity of the support particles affects the spreading due to the existence of altered surface free energies. This introduces uncertainty when studying the spreading phenomena. That is why the experiments, reported in this paper, were performed using model supports, namely, thin Al<sub>2</sub>O<sub>3</sub> and TiO<sub>2</sub> films on Al or Ti foils. Using these supports, we reduced the possible effects of the support polydispersity and expect to get direct experimental evidence for the molecular nature of the spreading of MoO<sub>3</sub> across support oxides. The high lateral resolution and analytical capabilities of the used scanning photoelectron microscope allowed us to image directly this spreading process and to examine the variations in the local surface composition and morphology of the spread layer.

#### **Experimental Section**

The experiments were performed using a conventional XPS system (VSW ESCA 100) and the scanning photoelectron microscope (SPEM) on the ESCAMICROSCOPY beam line of the ELETTRA synchrotron radiation source.<sup>17</sup> In the SPEM the photon beam, provided by an undulator and monochromatized by a spherical grating monochromator, was demagnified to a spot of 0.15  $\mu$ m diameter by using a zone plate optical system. The emitted photoelectrons (PEs) were collected by a 100 mm hemispherical analyzer with a large acceptance angle, mounted at  $70^{\circ}$  with respect to the sample normal and the incident photon beam. The microscope can work in imaging mode, collecting photoelectrons with chosen kinetic energy while scanning the sample, and in spectroscopy mode, measuring energy distribution curves (EDC) with the beam focused to a feature selected from the maps. The contrast in the maps due to variation of the photoelectron intensity is a fingerprint for the local chemical composition of the imaged surface. The lateral resolution of the SPEM is limited by the spot size of the demagnified photon beam. All photoemission measurements in this study were performed with photon energy between 580 and 590 eV and energy resolution of 0.4 eV.

As support samples, Al and Ti foils (Goodfellow, purity 99.999% and 99.6%, respectively) were used which were mechanically mirror polished and anodically oxidized following a recipe described elsewhere.<sup>18,19</sup> Subsequent heat treatment of the foils (823 K for Al<sub>2</sub>O<sub>3</sub> and 623 K for TiO<sub>2</sub>) for 4 h provided the transformation of the amorphous oxide layer into a thin, polycrystalline oxide film resulting in a ~20 nm thick Al<sub>2</sub>O<sub>3</sub> film on the Al foil and a ~50 nm thick TiO<sub>2</sub> film (anatase modification) on the Ti foil. These oxidized foils provide surfaces comparable to those of real catalysts, having the advantage not to charge up severely when being illuminated with soft X-rays. While single sapphire crystals charge up to ~200 V under the highly focused X-ray beam of the SPEM, the charging on the thin Al<sub>2</sub>O<sub>3</sub> oxide films was less than 10 V whereas it was negligible on the TiO<sub>2</sub> films.

In order to prepare a model surface for a monolayer type catalyst, small molybdena particles were placed on the support foil. For this purpose, a drop of a suspension of the  $MoO_3$ 



**Figure 1.** Conventional XP spectra taken before (i) and after heat treatment (ii) (660 K for 5 h) of model samples where a small amount of MoO<sub>3</sub> crystals is dispersed on an  $Al_2O_3$ —Al (A) or a TiO<sub>2</sub>—Ti (B) support foil, respectively. For determining the binding energy in system A charging of 2 eV had to be considered (see text). No charging occurred for system B.

crystals in methanol was taken with a pipet and placed on a moderately heated (320 K) support foil. The methanol evaporated instantaneously, and the small MoO<sub>3</sub> particles remained fairly homogeneously dispersed on the surface. By this procedure we obtained a model system that is comparable to samples where supported MoO<sub>3</sub> model catalysts were produced by physical mixing of MoO<sub>3</sub> crystals with Al<sub>2</sub>O<sub>3</sub> support powder.<sup>11–13</sup> One of the advantages of our model samples is the very defined geometry, because the support is a flat oxide film. This makes the samples suitable for spectromicroscopic studies, where the topography artifacts become important. The MoO<sub>3</sub> crystals stick well on the support so that the sample can be transferred into or outside the SPEM without loss of material.

The spreading of molybdena on the support was investigated by characterizing the samples before and after heat treatment in air (660–800 K for 5–7 h), using either a standard XPS system or the laterally resolving SPEM. For the latter measurements, we placed small scratches as markers on the support foil. With the help of an optical microscope (OLYMPUS BH2, resolution <1  $\mu$ m), the position of the MoO<sub>3</sub> particles could be determined relative to the markers. Thus, it was possible to reproducibly position the X-ray beam of the SPEM onto specific MoO<sub>3</sub> particles and to image the Mo distribution on a selected area of the model surface before and after the heat treatment. The surface sensitivity of the laterally resolving XPS enabled us to determine the evolution of very thin surface layers as expected for spreading systems.

#### Results

The first characterization of the model samples consisting of a few MoO<sub>3</sub> crystals placed on a flat Al<sub>2</sub>O<sub>3</sub>-Al or a TiO<sub>2</sub>-Ti support substrate was performed using a conventional photoelectron spectroscopy system. Figure 1 shows the Mo 3d core level spectra taken from both model systems before (i) and after annealing (ii) at 660 K for 5 h in air. A significant increase of the Mo 3d core level peak intensity after the heat treatment is clearly visible for both supports, the alumina (A) and the titania (B) thin oxide film. The same effect is also visible, if the experiment is repeated when the support material is replaced by a sapphire single crystal (not shown here), which confirms that the thin oxide films serve as a suitable support material. Due to the surface sensitivity of integrative XPS, one can attribute the enhanced intensity of the Mo 3d core level peak



**Figure 2.** (a) Image of a big MoO<sub>3</sub> crystal (length 40  $\mu$ m) on an Al<sub>2</sub>O<sub>3</sub>-Al support foil; the analyzer was tuned to the Mo 3d core level peak. The imaged area is identical before and after heat treatment (720 K for 6 h) of the sample. (b) Reversed image of the nonannealed sample when tuning the analyzer to the Al 2p core level peak. (c) XP spectra taken from the big crystal (i) and from the support before (ii) and after annealing the sample (iii).

to the existence of molybdena species released from the  $MoO_3$  crystals and spread over the support surface, because before the spreading the  $MoO_3$  particles cover only a small fraction of the surface. To clarify this picture, which is in agreement with the previous investigations of powder catalysts,<sup>11–13</sup> we followed the spreading of the Mo species on a micron scale with the help of photoelectron emission microscopy. Therefore, a sample with small  $MoO_3$  particles dispersed on an  $Al_2O_3$ –Al foil was imaged by SPEM before and after annealing at 720 K for 6 h in air.

The SPEM experiments included two-dimensional elemental mapping with the analyzer tuned to a selected photoelectron kinetic energy and photoelectron spectroscopy from a submicron spot positioned on the  $MoO_3$  particles or away from them. The contrast of the maps was determined by the surface and near surface concentration of the probed element and by topographic

artifacts due to the anisotropic angular distribution of the emitted photoelectrons. For the present system, because of the large height of the  $MoO_3$  particles the topographic effects are significant. However, they affect negligibly the spectroscopic measurements because the size of the  $MoO_3$  particles allowed us to choose spots for taking EDC spectra away from the edges.

A fairly large MoO<sub>3</sub> crystal (length 40  $\mu$ m) can be seen in the Mo 3d two-dimensional micrograph shown in Figure 2a. Surprisingly, the image of this area was identical prior and after annealing in air. Even the small, micron-sized particles covering the big crystal were not affected by the heat treatment within our resolution limit. Microspot core level spectroscopy proved that these particles were molybdena crystals as well. The shadow on the left side of the particles is a typical topographic effect. Since the analyzer is mounted at a grazing angle on the right side of the displayed image, the particles prevent the photoelectrons emitted beneath their left edge to reach the analyzer in direct line-of-sight.

Despite the strong topographic effects, the Al 2p image in Figure 2b shows the expected reverse contrast, consistent with the different chemical composition of the support and the deposited active phase. This is confirmed by the microspot photoelectron spectra shown in Figure 2c. The top two spectra are measured on the large crystal (i) and on the support away of it (ii) before annealing the sample. Before annealing, the spectra from the MoO<sub>3</sub> crystal (i) contain only the O 1s (not shown in Figure 2c), the Mo 3d, and the O(*KLL*) Auger peaks. The spectra taken from the uncovered support surface (ii) contain only the O 1s (not shown), the Al 2s, Al 2p, and the O(*KLL*) Auger peaks, which proves the absence of any Mo species dispersed away from the deposited MoO<sub>3</sub> crystals.

The different status of the sample before and after annealing can be characterized by following the spectroscopic information of Figure 2c. While spectrum i, taken from the big crystal of Figure 2a, does not change after the heat treatment of the sample, the spectra taken from the free support show distinct differences. As was mentioned, we can rule out the presence of Mo species on top of the support before the heat treatment (spectrum ii). After annealing, the Mo 3d core level peak is clearly detected on top of the support (spectrum iii). This indicates that a small amount of Mo species is released from the MoO<sub>3</sub> crystals and spreads over the Al<sub>2</sub>O<sub>3</sub>-Al support foil as a thin film or as highly dispersed MoO<sub>x</sub> species. Since the MoO<sub>3</sub> particles contain a lot of material, the loss of Mo species due to spreading is not visible within the resolution limit of the microscope.

To obtain information about the lateral distribution, we have to tackle a problem. As can be seen for the case of  $MoO_3$  on the Al<sub>2</sub>O<sub>3</sub>-Al support in Figure 2c, there was a notable difference (up to  $\sim 10 \text{ eV}$ ) between the kinetic energies of the Mo 3d photoelectrons emitted from the large crystal and from the spread Mo oxide phase. As will be discussed in the next section, these energy shifts are due to a mixture of charging effects and changes in the Mo oxidation state. The different kinetic energy of the Mo 3d photoelectrons accounts for the preserved contrast of the Mo 3d maps measured before and after annealing: in both cases the analyzer was tuned to the Mo 3d levels corresponding to the compact MoO<sub>3</sub> particles. Since the deposited large Mo oxide particles and the spread phase cannot be imaged at the same time when tuning to the Mo 3d core level, more precise quantitative information on the surface morphology can be obtained from the contrast of the Al 2p maps. The contrast of the Al 2p maps varies with the local thickness of the spread molybdena phase. In the Al 2p images of the support the darker areas correspond to stronger attenuation of the Al 2p emission due to local enrichment of Mo oxide species covering the support foil, as will be seen below.

Figure 3a,b shows Al 2p PE maps of the nonannealed and annealed sample in which the contrast shows a conglomerate of one big and several small  $MoO_3$  particles. The larger area image of the same region, displayed in Figure 3b, reveals the appearance of darker areas on the support foil after the heat treatment. In order to emphasize the contrast variation, inserts i and ii show zoomed images of the areas marked in Figure 3b. Figure 3c shows the spectra taken from the center of these two areas. The inverse Mo 3d and Al 2p intensity from the darker and brighter spots confirm the lateral inhomogeniety of the spread phase. The dark spots in Figure 3b can be described as islands, where the amount of Mo oxide species, covering the support, is enhanced. The maps evidence that the islands are homogeneously distributed. The exact nature of these islands in the spread molybdena phase is unclear. No influence of mesoscopic support defects, such as holes or scratches, on the island distribution can be detected within our resolution. The spectromicroscopic data also ruled out a Mo concentration gradient in the close vicinity of the deposited  $MoO_3$  particles: within the resolution limit no dark circle around the small  $MoO_3$  particles can be seen in the Al 2p maps in Figure 3b.

Experiments similar to those described above (for the Al<sub>2</sub>O<sub>3</sub>-Al support) were performed with samples where MoO<sub>3</sub> crystals were deposited on a TiO<sub>2</sub>-Ti foil. Here a treatment was applied where the crystals were intended to be modified on a lateral scale detectable with the SPEM. A smaller initial amount of MoO<sub>3</sub> crystals and a more severe heat treatment of the sample (annealing at 720 K for 4 h and increasing the temperature to 800 K for 3 h) were chosen. Since charging in this system is very low, the energy position of the Mo 3d core level peak is mainly determined by the chemical state of the surface species. These effects will be discussed in more detail in the next section. The Mo 3d PE maps of Figure 4a,b reveal the extinction of the MoO<sub>3</sub> microcrystals (size  $\sim 2 \mu m$ ) after the above-described heat treatment of the sample. The long vertical line in the right side of the larger area image is the end of a scratch that served as a marker to find the same area, where the MoO<sub>3</sub> particle appears as a bright spot before heating. The zoomed images clearly confirm that the MoO<sub>3</sub> particle has completely vanished after the heat treatment. Spot PE spectra (not shown here) proved that no traces of the particle (enhanced local Mo oxide content) were left at its former position. To rule out the observation of an exceptional event, we confirmed this finding for six different areas containing MoO<sub>3</sub> particles. As in the case of a Al<sub>2</sub>O<sub>3</sub>-Al support, local spectroscopy proved again that the TiO<sub>2</sub>-Ti foil was completely covered by a thin spread molybdenum oxide phase after the heat treatment. Again, mesoscopic defects of the substrate, like the imaged scratch in Figure 4, do not seem to promote inhomogeneities in the spread phase.

#### Photoinduced Reduction of the Mo Oxide Species

As was mentioned already, the energy position of the PE core level peaks have to be studied in detail. Due to the nonconductive character of the active phase and the supports and the morphology of our samples, effects such as differential charging and Fermi level decoupling should be considered when evaluating the core level binding energies from the measured photoelectron kinetic energies.<sup>20</sup>

First, we will focus on the peak positions of the spectra obtained with a standard laboratory Al K $\alpha$  X-ray source where (differential) charging is less severe. For this experimental setup the work function of the analyzer was determined in a separate experiment. Thus, an absolute energy scale is obtained and the peak shifts due to charging can be evaluated. The charging of the different substrates was measured very reproducibly from experiment to experiment within a scatter of less than 0.4 eV. The energy position of the Mo 3d core level peak was cross-checked by measuring relative to the O 1s (530 eV for TiO<sub>2</sub> and 531 eV for Al<sub>2</sub>O<sub>3</sub>)<sup>21</sup> and relative to the C 1s peak (284.4 eV),<sup>21</sup> in fair agreement with the determined absolute energy scale. Therefore, an error of ~0.4 eV for the peak position of the Mo 3d core level (and thus the chemical state of the Mo oxide species on the model surfaces) seems to be realistic.

For the system  $MoO_3/TiO_2$  charging of the substrate and the  $MoO_3$  crystals definitely remained below 0.5 eV. Referencing to the binding energy of O 1s (530 eV) and C 1s (284.4 eV) confirms a Mo  $3d_{5/2}$  peak position at 232.6 eV for spectra taken from samples with  $MoO_3$  crystals placed on the  $TiO_2-Ti$  support at room temperature and samples after heat treatment. This proves an oxidation state of +6 for both Mo oxide species,





**Figure 3.** (a) Al 2p image (size  $30 \times 30 \ \mu\text{m}^2$ ) of a conglomerate of small MoO<sub>3</sub> crystals on the Al<sub>2</sub>O<sub>3</sub>-Al support before annealing (720 K for 6 h). (b) The same area imaged after the heat treatment (size  $50 \times 50 \ \mu\text{m}^2$ ). Zoom i and ii emphasize the occurrence of dark spots on the support foil. (c) XP spectra taken from the center of zoom i (bright area) and of zoom ii (dark spot).

the MoO<sub>3</sub> crystals and the spread phase.<sup>21</sup> Oxygen loss of the Mo oxide species in vacuum or induced during the X-ray irradiation were not detectable in the PE spectra.

In the MoO<sub>3</sub>/Al<sub>2</sub>O<sub>3</sub> system the substrate and the MoO<sub>3</sub> particles charged up to  $\sim$ 2 eV. By referencing again to O 1s (531 eV) and C 1s (284.4 eV), the peak position of the Mo 3d<sub>5/2</sub> core level was determined as 232.6 eV for all samples.

Thus, again it is confirmed that the oxidation state of the  $MoO_3$  crystals and the spread phase on the  $Al_2O_3$ -Al substrate is +6.

As could be seen already in Figure 2c, the situation changes if the samples are illuminated with the intense and highly focused X-ray beam of the SPEM. For the system MoO<sub>3</sub>/TiO<sub>2</sub>, the charging of the substrate was almost negligible (below 1 eV), and more importantly, no differential charging occurred.





Figure 4. Mo 3d images of a MoO<sub>3</sub> crystal on top of a  $TiO_2-Ti$  support foil before (a) and after heat treatment (b) (720 K for 4 h + 800 K for 3 h).

Using as a reference the kinetic energy measured for the C 1s peak (if present) and the O 1s core level (assuming a binding energy of 531 eV for MoO<sub>3</sub> and 530 eV for TiO<sub>2</sub>),<sup>21</sup> we evaluated a binding energy of the Mo  $3d_{5/2}$  core level of ~230 eV for the MoO<sub>3</sub> particles before and after spreading. The binding energy for the spread Mo oxide phase after annealing was ~228 eV. Using the results of the already-described conventional XPS analysis, we can rule out oxygen loss due to the vacuum environment. Therefore, we can state that the reduction is initiated by the photon beam. The MoO<sub>3</sub> particles are reduced to an oxidation state of +4 whereas the spread phase is almost completely reduced to its metallic state.<sup>21</sup>

The illuminating photon beam affects equally the Mo oxide species on the Al<sub>2</sub>O<sub>3</sub>-Al support although the analysis is more complex since differential charging occurs. While the charging of the substrate is low (since the oxide film is only ~20 nm thick) the micrometer-thick crystals are charged up to ~10 eV relative to the substrate. Again, referencing against C 1s (if present) or O 1s (binding energy 531 eV for both Al<sub>2</sub>O<sub>3</sub> and MoO<sub>3</sub>)<sup>21</sup> proves that the MoO<sub>3</sub> crystals (before and after annealing) are reduced to an oxidation state of +4 (Mo 3d<sub>5/2</sub> at 230 eV) while the spread Mo oxide phase reaches nearly its metallic state (Mo 3d<sub>5/2</sub> at 228 eV) when being illuminated. The energy shift of the differential charging (up to +8 eV for

the  $MoO_3$  particles) and the different photoinduced reduction of the islands and the spread phase (+2 eV for the  $MoO_3$ particles) account for the observed shift of the Mo 3d core level in Figure 2c) which prevented reliable imaging of the spread phase on the  $Al_2O_3$ -Al support when tuning the analyzer onto Mo 3d core level photoelectrons.

The fact that the MoO<sub>3</sub> particles were reduced equally before and after the heat treatment of the samples confirms that the spreading process does not change the stability of this species against photoreduction. On the other hand, the spread phase loses oxygen more easily, resulting in a complete reduction when illuminated by the focused X-ray beam. As a process inducing the oxygen loss, we propose a Knotek–Feibelman mechanism which has been found for WO<sub>3</sub> which is structurally and chemically comparable to MoO<sub>3</sub>.<sup>22</sup> The reason why the spread phase loses oxygen easier might be related to the amorphous nature of this phase. The fact that before illumination the oxidation state of the spread Mo oxide is +6 (as for MoO<sub>3</sub>) still provides the possibility of a Knotek–Feibelman mechanism although the oxygen atoms interacting with the spread Mo might be bonded to the metal atoms of the substrate as well.

In the last section we will discuss our data with regard to the transport mechanisms that govern the spreading of the Mo oxide species during the heat treatment of the model samples.

# Discussion of the Transport Mechanism during Spreading

As mentioned in the Introduction, the described experiments aimed at providing deeper insight into spreading phenomena by replacing the support powder by a flat support film. We outlined in the previous section that spreading of Mo species on the support foil could be observed by standard XPS and additionally characterized by SPEM.

There are three possible transport mechanisms for Mo oxide species that spread across the support surface after being released from the  $MoO_3$  crystals:<sup>1</sup> (a) Unrolling carpet mechanism: Mo oxide species, diffusing on top of crystalline  $MoO_3$  particles, are trapped at the edge of the crystal when reaching the support surface. (b) Surface diffusion on the support: Mo oxide species, detached from the  $MoO_3$  crystals, diffuse and nucleate on the surface of the support foil and eventually recrystallize at certain spots. (c) Transport via gas phase: Mo oxide species from the  $MoO_3$  crystals evaporate in the gas phase and via subsequent recondensation spread on the support foil and eventually recrystallize at certain spots. (d) A combination of processes b and c is also possible.

The unrolling carpet mechanism a was favored in ref 16, because a surface melting of the MoO<sub>3</sub> phase could explain the recorded high-temperature in situ Raman spectra, whereas no accordance was found with published spectra for the gas-phase Mo oxide species. If mechanism a is the active transport mechanism, we would expect the MoO3 crystals to wet the support in the direct vicinity of a crystalline particle. Thus, the radius of the wet surface around a crystal would increase at the expense of the crystal height, which should result in a Mo oxide concentration gradient moving away from the crystal. The reported spectromicroscopic data do not provide any evidence for a higher Mo oxide density around the MoO<sub>3</sub> crystals within our resolution. Thus, it seems unlikely that the unrolling carpet mechanism a is the active one. Our data can be explained in the frame of an unrolling carpet mechanism only assuming a very efficient wetting mechanism of the moving Mo oxide species that nearly instantaneously stops after the surface is completely covered by a thin molybdena film. In this case one would not expect a thickness gradient of Mo oxide species in the vicinity of the  $MoO_3$  crystals, in agreement with the described experiments. In this case, it would still be a problem to explain the fairly homogeneously distributed islands of enhanced Mo density on the spread molybdena film, which cannot be correlated to the position of the  $MoO_3$  crystals. Therefore, the transport mechanism a as the only spreading process seems to be unlikely for the systems investigated.

The important new finding in the present study is the lateral inhomogeneity of the spread Mo oxide phase: formation of islands of higher Mo oxide concentration of a size up to a few microns. These islands are almost homogeneously distributed with an island-island distance of  $1-10 \,\mu\text{m}$ . In order to explain these lateral inhomogeneities by the diffusion mechanism b, the surface mobility or the stability of the initial island nucleus should be taken into account. Since the island-island distances are large on an atomic scale, this suggests fairly mobile surface species or/and very unstable nuclei, i.e., the Mo oxide species. travel rather long distances on the surface before being trapped in an island. A common feature in diffusion-controlled surface processes is that the mobility and the adsorption energy are influenced by surface defects, resulting in an uneven island density distribution, e.g., as step decoration. The absence of variations in the island density due to visible surface defects of our samples can be used as an argument that questions the determining role of surface diffusion in the spreading process. However, the nucleation centers are not necessarily the visible micron-sized topographic features, but might be structural and/ or compositional defects on a nanoscale or atomic scale, not detectable with our spatial resolution.

If the spreading process follows the gas phase transport mechanism c, it is needed to find out whether the recondensation of the Mo oxide species takes place at special locations on the surface and how these can be related to the observed islands.

In order to distinguish unambiguously between the active transport mechanisms, further experiments are necessary; e.g., the effect of the gas phase composition and the humidity during heat treatment should be studied in detail.

#### Conclusion

The results on MoO<sub>3</sub> spreading on Al<sub>2</sub>O<sub>3</sub>-Al and TiO<sub>2</sub>-Ti support surfaces obtained by synchrotron radiation photoemission spectromicroscopy have manifested the power of laterally resolved compositional surface analysis in understanding the transport processes on supported catalyst surfaces. It has been shown that, after heat treatment in air, the model samples, containing MoO<sub>3</sub> particles on an Al<sub>2</sub>O<sub>3</sub>-Al or a TiO<sub>2</sub>-Ti support surface, respectively, were covered with a thin molybdena phase that included islands of higher Mo concentration. These islands are fairly homogeneously distributed on the support, and their formation cannot be correlated with preferential nucleation at mesoscopic topographic defects of the support or at the deposited MoO<sub>3</sub> particles. The presented results suggest that the unrolling carpet mechanism can be considered as a transport mechanism controlling the spreading only assuming a very efficient wetting mechanism of the moving Mo oxide species that nearly instantaneously stops after the surface is completely covered by a thin molybdena film. In this case the island formation observed under the described preparation conditions has to be governed by a second process. Future experiments using the new SPEM technique might help to separate the leading transport and formation mechanisms of the Mo oxide species during spreading of supported MoO<sub>3</sub> catalysts.

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