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Scanning tunneling microscopy investigations of cluster sizes of molybdenum-based catalysts on graphite

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Surface morphologies of molybdenum-based catalysts supported on graphite were investigated with a scanning tunneling microscope. The oxide phases of Mo, Co, and Mo–Co were observed to form distinct types of clusters on graphite. MoOx clusters appeared to be elliptical, with sizes ranging from 100 to 200 Å in length and 60 Å in width, while CoOx formed round and needle-shaped clusters, about 200 Å in size. Oxidized Co–Mo was observed to form ring-type structures which were uniformly 100 Å in diameter. This ring-type structure was attributed to the CoMoOx structure with Co decorating the edges of Mo. Sulfided phases of these catalysts were observed to form large slabs on graphite. Sulfided MoOx formed large islands (100 Å × 150 Å). These may be formed from the aggregation of small MoS_2 crystallites. Besides forming large patches, CoS also formed needle-type clusters similar to CoOx, but smaller (120 Å) in length. These clusters and patches are believed to be bulk Co_9S_8. Sulfided CoMoOx formed CoMoS islands similar to the needle-type clusters observed in CoS, but much larger in size, from 300 to 600 Å. No MoS_2 and CoS types of clusters were observed on this sample. No apparent movement of the clusters was observed during repeated scanning, suggesting that there is an interaction between the cluster and the graphite support.

Keywords: STM; molybdenum catalyst; graphite support; catalyst morphology

1. Introduction

Several studies have aimed at analyzing the structure of carbon-supported Mo sulfide catalysts and their Co-promoted phases. The motivation behind these studies is that carbon-supported molybdenum catalysts have been reported to possess higher HDS activity compared to their alumina-supported counterparts, and it is believed that the superior activity of these catalysts is due to the presence of Mo sulfide on carbon support, which is different from those on alumina support. Advanced surface analytical tools such as XPS, HRTEM, and EXAFS have been used to study the structures of oxidic and sulfided Mo catalysts on carbon. The results of these studies have led to disagreement: XPS observations by Vissers et al. [1] revealed that sulfided Mo/C catalysts exist as tiny three-dimensional MoS_2 par-

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ticles, less than 4.6 nm in size even with the highest Mo loading (up to 14.1 wt%); but HRTEM study of MoS_2 supported on graphite by Hayden et al. [2] showed that MoS_2 exists in toroidal form, with sizes ranging from 150 to 2000 nm. The structures gradually transform into the rag phase of MoS_2 upon heating at higher temperature; small, dense particles of 5 nm then start to collect at the rag phase structure. The immobility of the MoS_2 structures also led these authors to suggest that there is a strong sulfide–graphite interaction. EXAFS studies by Bouwens et al. [3] also suggest that some kind of interaction must exist between MoS_2 and the carbon support. Moreover, they also showed that MoS_2 particles formed on carbon support are smaller than those on alumina support, which may indicate that this interaction is not weaker than in alumina. While investigators have relied heavily on numerous surface science techniques for catalyst characterization, scanning tunneling microscopic (STM) technique has not been used extensively for this purpose. Advances in STM technique allow direct imaging of supported clusters. Unlike EXAFS, which mainly measures local order structures, and TEM, which relies on the thickness contrast of images mainly on a two-dimensional scale, STM had the advantage of being able to resolve a three-dimensional image of a surface structure with possible atomic resolution. The technique is non-destructive and surface-sensitive, so that the structure of an adsorbate and its orientation with respect to the support can be characterized. Several investigators have been successful in obtaining STM images of supported metal catalysts [4–7]. Usually, the substrates used are conducting graphite or carbon film. Chu et al. [4] studied gasification of graphite catalyzed by Pt, Pd, V_2O_5, K_2CO_3, and NO/Rh, and were able to obtain images of these particles on graphite. They have shown that not only images of metals on graphite can be obtained with STM, but also images of metal oxides on graphite. Recent STM investigation of MoS_2 formed by thermal decomposition of $(NH_4)_2[Mo_3S_{13}]\cdot H_2O$ on carbon film has shown that MoS_2 is oriented on the carbon surface with its metal plane perpendicular to the surface of carbon support, tilted at an angle larger than 100° [5]. This suggests that STM can be used to identify the orientation of MoS_2 directly on carbon.

In this study, our objectives are: (1) to demonstrate whether STM can be used to distinguish different surface morphologies of graphite-supported Mo, Co, and Mo–Co clusters; (2) to provide direct evidence on the size of MoS_2 on graphite; and (3) to address the question of support interaction. Under our experimental conditions, we find that Mo, Co, Co–Mo oxide, and sulfide phases have characteristic morphologies. Moreover, the rag-like phase of MoS_2 can be clearly observed. No apparent movement of the clusters was observed during repeated scanning, suggesting that there is an interaction between the cluster and the graphite support.

2. Experimental

The support used was a highly oriented pyrolytic graphite (HOPG), grade ZYH, obtained from Union Carbide. Graphite is used in our studies because it can be cleaved easily to obtain a flat area, and its atomic resolution image can be obtained routinely by STM. Thus there should be good contrast between the metal clusters and the graphite support. Six 10 mm × 5 mm HOPG samples were impregnated with appropriate amounts of ammonium heptamolybdate (AHM) and cobalt nitrate solution to prepare the Mo, Co, and Mo–Co samples. The concentrations of Mo and Co atoms deposited on the sample are 1.132×10^{-7} mol/mm^2, respectively. The ratio of Co/Mo in Mo–Co/HOPG is 1 and the ratio in Mo–Co–S/HOPG sample is 0.5. Before impregnation, the graphite sample was cleaned by cleaving several layers with adhesive tape. For the Co-promoted sample, the AHM solution was introduced first. After each impregnation step the sample was oven-dried at 110°C for 16 h. The sample was then treated in flowing H_2 (10 cm^3/min) in a reactor tube. The temperature was increased from 25 to 400°C in 30 min, followed by heating at 400°C for 2 h. Then the sample was cooled to 25°C in 30 min under flowing He or Ar. Sulfidation of graphite supported Mo, Co, and Mo–Co was carried out in 10% H_2S/H_2 at the flow rate of 60 cm^3/min. The temperature was increased from 25 to 600°C in 30 min, followed by sulfidation at 600°C for 2 h. Then the sample was cooled in flowing He to 25°C in 30 min, followed by purging in He flow at room temperature for 48 h to remove excess H_2S. The STM used in this study is a UHV-compatible commercial unit from Omicron. All measurements were performed in constant current mode in air, with typical bias voltage $= -0.015$ V and tunneling current= 1.02 nA. A typical image was obtained in approximately 2–3 min. The images presented here, which are selected from a large number of images, are representative for a particular sample. Various bias voltages and tunneling currents were also used to explore possible electronic effects. The tip used was made from an 80% Pt–20% Ir wire, which was electrochemically etched in a mixture of 3 M NaCN and 1 M KOH solution.

XPS spectra (C 1s, S 2p, Mo 3d, and Co 2p) peaks were obtained using a Surface Science Instrument model M-Probe ESCA spectrometer, with Al Kα radiation (1486 eV). For each element region, typically 40 scans were collected with a detector path energy of 50 eV and a total scanning time of 20 min.

3. Results and discussion

3.1. MoOx/HOPG, CoOx/HOPG, AND CoMoOx/HOPG

Attempts to investigate the fully oxidized samples (oven-calcining at 400°C for 2 h) were unsuccessful. In most cases, the oxide layers or contaminants on the surface of graphite act as an insulating barrier between the conducting graphite and the tip, thus making tunneling very difficult. Even when tunneling was obtained initially in some cases, presumably due to the probing of the conductive support, further scanning was not possible, because of the extremely unstable signal when the tip is scanning over an insulating layer. Treating the samples in H_2 resulted in a cleaner oxide sample or partially reduced clusters on HOPG surface, so that tunneling between tip and sample could be achieved.

Table 1 shows the binding energies of Mo, Co, and S of these catalysts in the oxidized and sulfided states. For the MoOx/C sample, the Mo is clearly in Mo^{6+} state (232.8 eV) suggesting the sample is mainly molybdenum oxides. In the STM image (fig. 1a), MoOx forms three-dimensional islands on HOPG surface. The clusters appear to be elliptical or rod-like in shape, with lengths varying from 100 to 200 Å, and widths of about 60 Å. The heights of the clusters vary from 5 to 60 Å. Similar elliptical structures were also observed for vanadia/HOPG [4]. These results agree with the notion that Mo oxides form long-chain polymerized polymolybdate clusters on support surfaces. Assuming a repeating unit of molyoxide of 5.2 Å, the typical cluster is about fifteen molyoxide units in width and 26 to 53 units in length. The large variation in the height can be attributed to the fact that the observed images are actually aggregations of MoOx clusters. It can be seen that the real cluster heights are around 10–12 Å, assuming that these clusters are stacked up one over the other. A cross-section profile in fig. 1b clearly illustrates this point. Thus, distribution of Mo clusters is quite uneven, i.e., some areas of HOPG are covered with Mo oxide clusters, entirely while totally uncovered HOPG surface can also be observed. Our results showed that MoOx is aligned diagonally along the [100] direction on the basal plane of graphite. Our observation on a scarcely covered surface revealed that although some clusters aggregate near a step, MoOx clusters do not necessarily anchor themselves on the graphite steps. Many clusters are observed to form aggregations on a flat graphite surface. In this experiment, no gasification reaction of graphite was observed. This can be attributed to the low reduction temperature (400°C).

CoOx/HOPG exhibits two types of clusters: needle-type and round, as shown in figs. 2 and 3, respectively. The needle-type clusters have interesting behavior: they always exist as doublets, more like mirror images of one another. The needle-type clusters are about 200 Å in length and 60 Å in width, while the round clusters

Table 1
XPS analysis of oxidized and sulfided Mo, Co, and Mo–Co catalysts supported on HOPG

	Binding energy (eV)			Oxidation state		
	Mo	Co	S	Mo	Co	S
Mo–O/HOPG	232.8			6+		
Co–O/HOPG		780.6			2+, 3+	
Co–Mo–O/HOPG	232.3	780.7		6+	2+, 3+	
Mo–S/HOPG	229.1		162.1	4+		2–
Co–S/HOPG		778	161.5		2+	2–
			162.5			0
			168.4			6+
Co–Mo–S/HOPG	229.9	778.2	161.8	4+	2+	2–

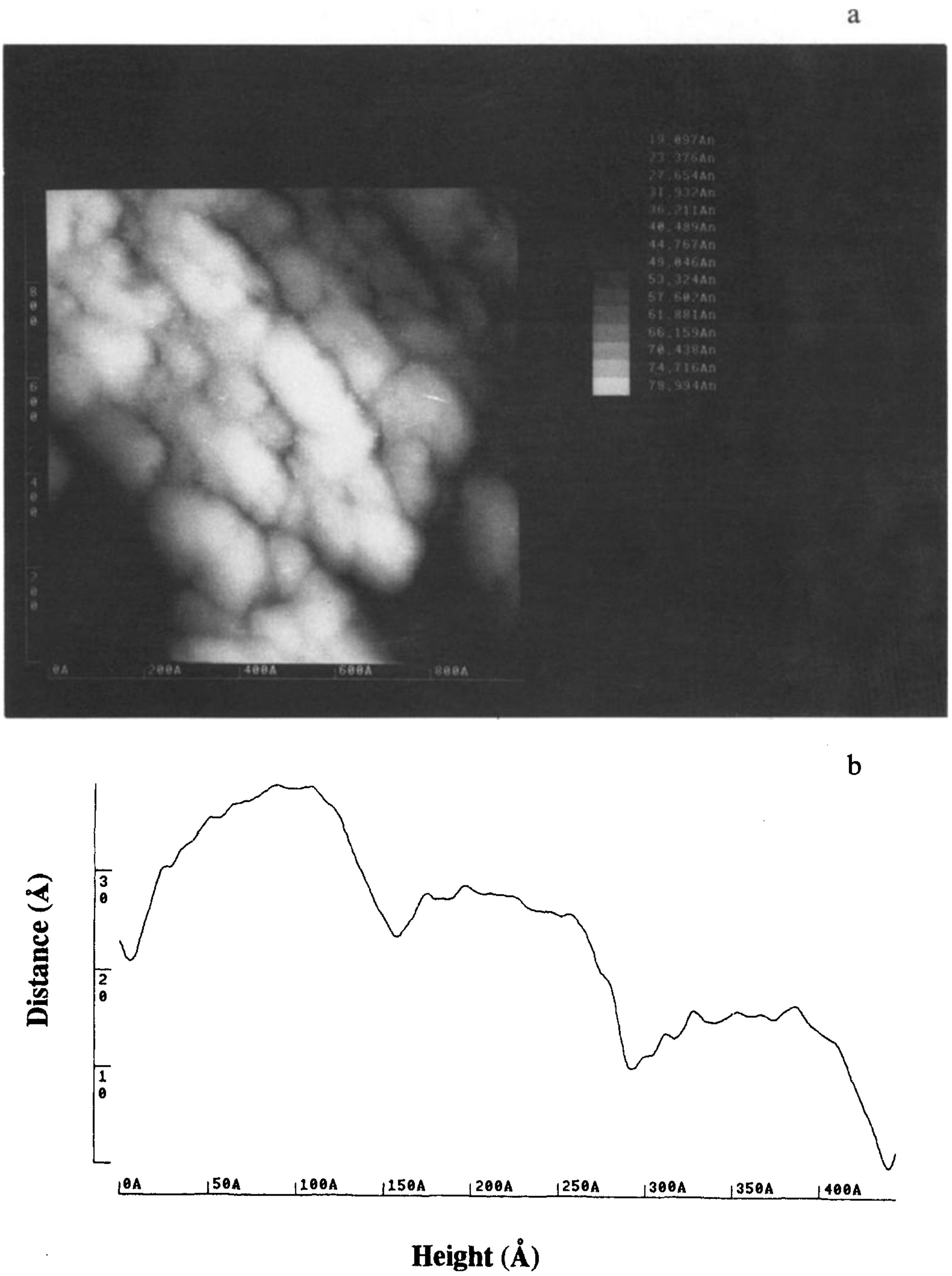

Fig. 1. (a) A 1000 × 1000 Å^2 area of MoOx/HOPG sample. MoOx forms bulkly elliptical clusters on HOPG, with sizes varying from 60 to 200 Å in width and 5 to 60 Å in height. MoOx tends to aggregate together to form a large mass on HOPG. (b) A cross section profile of an area in (a). This figure illustrates that the image in (a) is actually an aggregation of several clusters of 10–12 Å high.

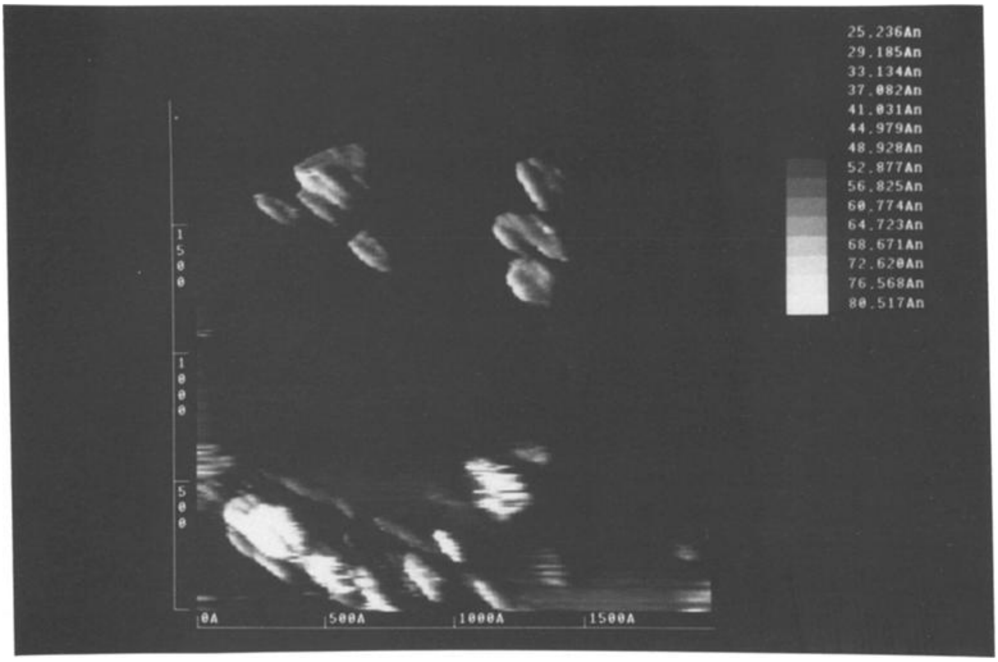

Fig. 2. CoOx forms needle-type clusters on HOPG. These clusters are 200 Å in length and 60 Å in width. Interestingly, these clusters tend to exist as doublets.

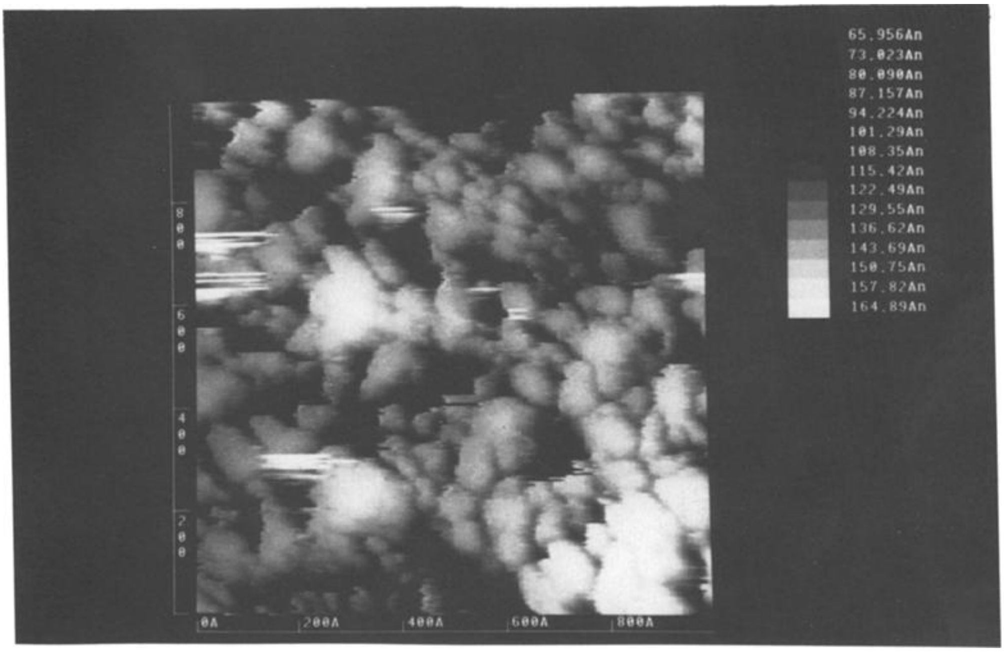

Fig. 3. Round clusters are also observed on another area of the CoOx/HOPG sample. These clusters are 200 Å in diameter. The different shapes observed on this sample can be attributed to different CoOx species.

are about 200 Å in diameter. One would suspect that the doublets might be due to instrument artifacts, as reported in the literature [8], but the fact that we observed round clusters on the same area with no doublet appearance is convincing evidence that the images of these doublets are real. Like Mo oxide on graphite, the round clusters also aggregate together on graphite surface. The different shapes of clusters we observed on our sample may be due to the different CoOx species formed on the graphite sample, such as Co_3O_4 or CoO. However, due to instrumental limitations, at present we are not able to probe the chemical identity of each cluster. We can only speculate that the round clusters are likely due to CoO, since this species is known to have a bulky structure [9]. From XPS spectra (not shown), the Co $2p_{3/2}$ peak appears broad, together with a satellite peak. This suggests Co exists in a mixture of oxidation states (2+, 3+). Fig. 4 shows that Co species also promoted gasification on the graphite support. In certain areas we observed pits two to three monolayers deep (6–10 Å). The pits are usually 150–300 Å in width, and the length varies widely. This phenomenon is expected on this sample, since Co is known as a catalyst for graphite–H_2 reaction [10]. No specific orientation of the pits could be determined, because the pits were only scarcely observed on the graphite surface. This could be due to the low Co loading or the low temperature we used in H_2 reduction, which did not lead to extensive gasification.

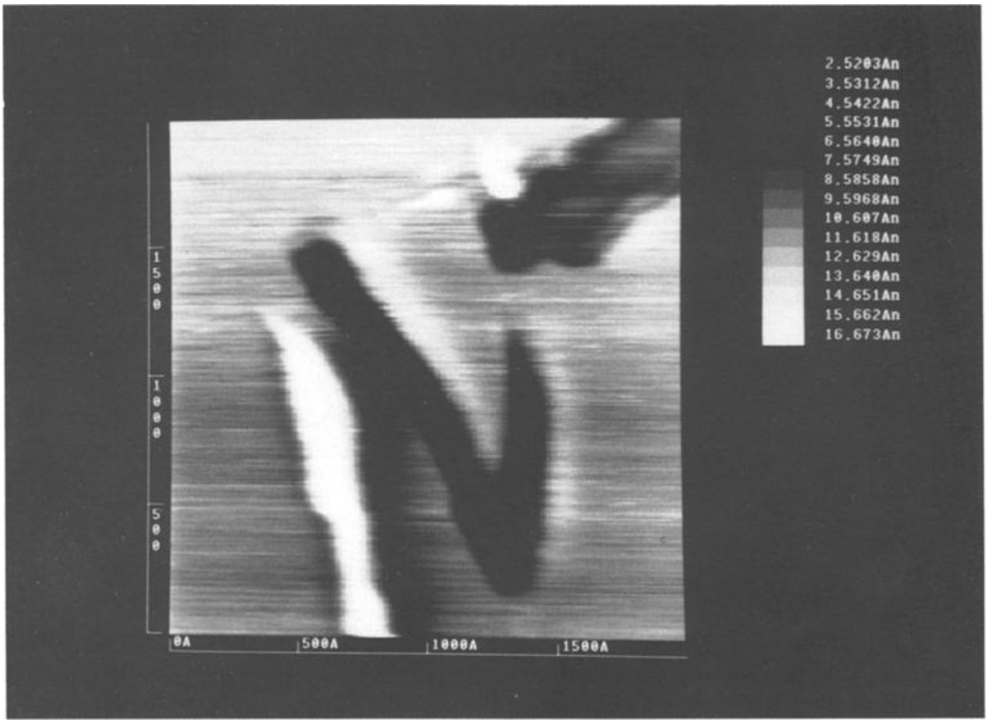

Fig. 4. Another area of the CoOx/HOPG sample shows that Co species also promoted gasification on the graphite support. The pits, a result of gasification, are 6–10 Å deep, with various widths and lengths.

The STM images of CoMoOx/HOPG are distinct compared to those of MoOx/HOPG and CoOx/HOPG. Round clusters and donut-shaped structures were frequently observed on this sample. The ring-type structures shown in fig. 5 have uniform diameter of about 100 Å. The height of the protrusion around the center is 6–10 Å, and the height of the indentation in the middle is 3–5 Å. The formation of the ring-type structure for the CoMoOx species is rather interesting, and has never been reported before in the literature. We have previously reported the observation of ring-type structures on natural MoS_2 sample, which we attributed to the electronic effect of the impurities in the sample [11]. However, the ring-type structures on the graphite-supported Mo–Co are not the result of the electronic effects of impurities, since no ring-type structures (thus no impurities) were observed on the Mo/C or Co/C samples. Moreover, when the bias voltage is varied from +0.030 to −0.030 V, the image persists, suggesting that it is not due to electronic effects. We propose that these structures are formed from Co atoms decorating the edges of MoOx clusters, forming a miscible CoMoOx phase. Most of the ring-type structures exist as isolated species, but in some instances they aggregate together or stack on top of each other, forming a chain. The chain formations are most often observed near a step or at the edge of a step, and they are usually observed together with round clusters. The round clusters in fig. 6, with an average

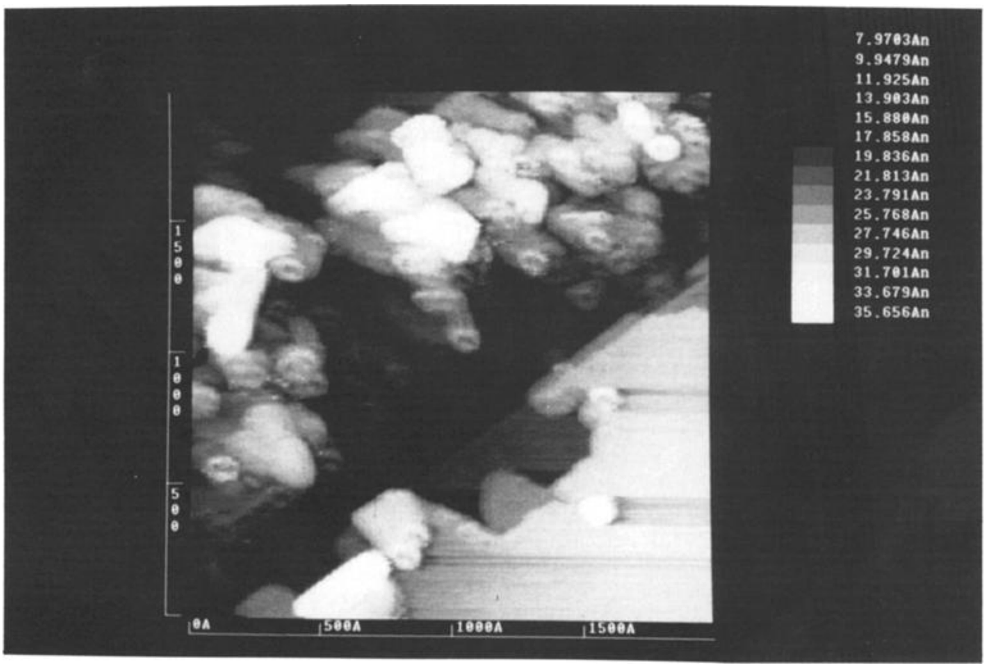

Fig. 5. CoMoOx forms ring-type structures on HOPG. These clusters are about 100 Å in diameter and 10 Å in height. These structures are believed to be images of CoMoOx with Co decorating the edges of MoOx clusters.

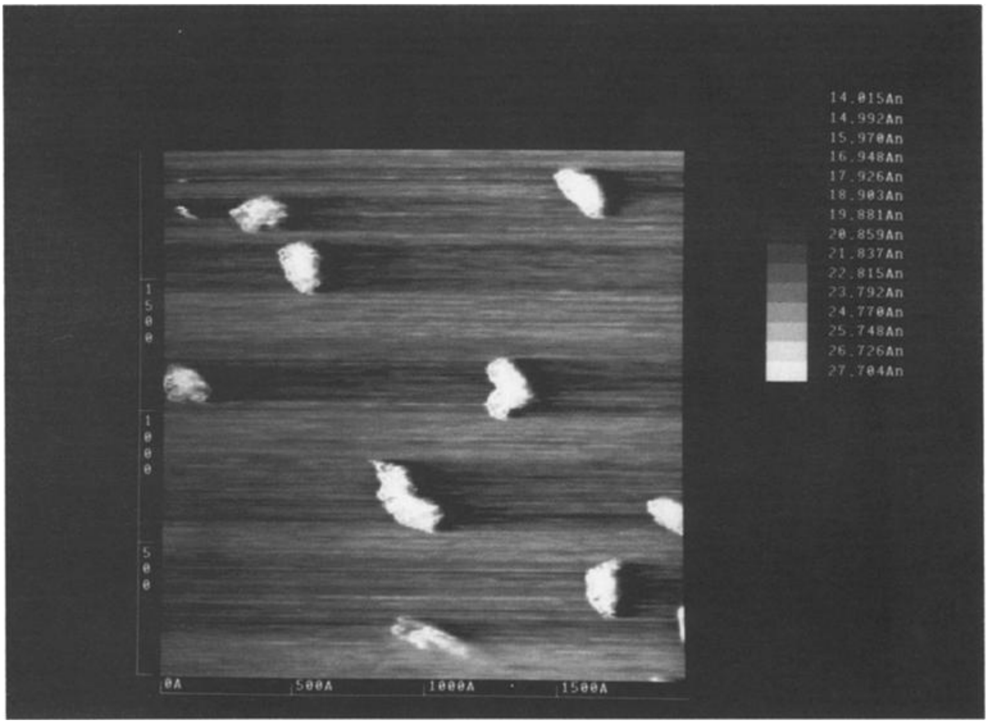

Fig. 6. Round clusters with an average diameter of 200 Å are also observed on the CoMoOx/HOPG sample. These structures are attributed to excess CoOx clusters that did not react with MoOx to form CoMoOx phase.

diameter of about 200 Å, are similar to the ones observed on the CoOx/HOPG sample (fig. 3). Because the Co/Mo ratio in this sample is 1, these round clusters can be attributed to the excess CoOx clusters that did not react with MoOx to form CoMoOx phase. The binding energies (table 1) of Mo and Co on this sample are essentially the same as the Mo/C and Co/C samples. Crajé et al. [12] have reported that full edge occupation of Co on Mo is achieved at Co/Mo of 0.5. Higher than this ratio, Co will segregate as separate CoOx, which then turns into Co_9S_8 crystallites upon sulfidation.

During the STM investigation, we did not observe any apparent movements of the clusters. Repeated scanning of a specific area consistently resulted in the same image. This is an indication that some interaction exists between the oxide phases and the graphite support.

3.2. MoS_2/HOPG, CoS/HOPG, AND CoMoS/HOPG

The XPS analysis of sulfided Mo/C sample indicated Mo^{4+} and S^{2-} on the surface, which strongly suggested the formation of MoS_2 (table 1). In the STM image, MoS_2 was observed to exist as large slabs (100 Å × 150 Å) on graphite surface.

The appearance of large slabs of MoS_2 on graphite is an indication that the MoS_2 is a poorly crystalline phase, as reported by Hayden et al. [2] in their TEM study. However, according to Vissers et al. [1] the weak interaction between carbon support and Mo could result in the formation of small three-dimensional MoS_2-like particles at low temperature sulfidation (400°C). Thus, it is possible that the slabs observed in this study (fig. 7) are due to aggregation of small MoS_2 crystallites. Bouwens et al. [3] reported that, after sulfidation, small MoS_2 crystallites (10–13 Å) agglomerate together to form large slabs of MoS_2 particles. Though graphite atoms at the edge of the islands and pure MoS_2 [11] can be imaged routinely with atomic resolution, atomic resolution of the patches could not be obtained easily, probably because: (1) the MoS_2 formed upon the sulfidation of MoOx on graphite did not exhibit a well-ordered structure, or (2) sulfidation caused the replacement of the bridging O atoms between the surface and Mo by S atoms, which then resulted in a basal plane of MoS_2 crystallites oriented perpendicular to the basal plane of the graphite [1]. STM studies by Diemann et al. [5] have also suggested that MoS_2 on carbon is oriented with the metal plane perpendicular to the carbon film, similar to $MoS_2/\gamma\text{-}Al_2O_3$.

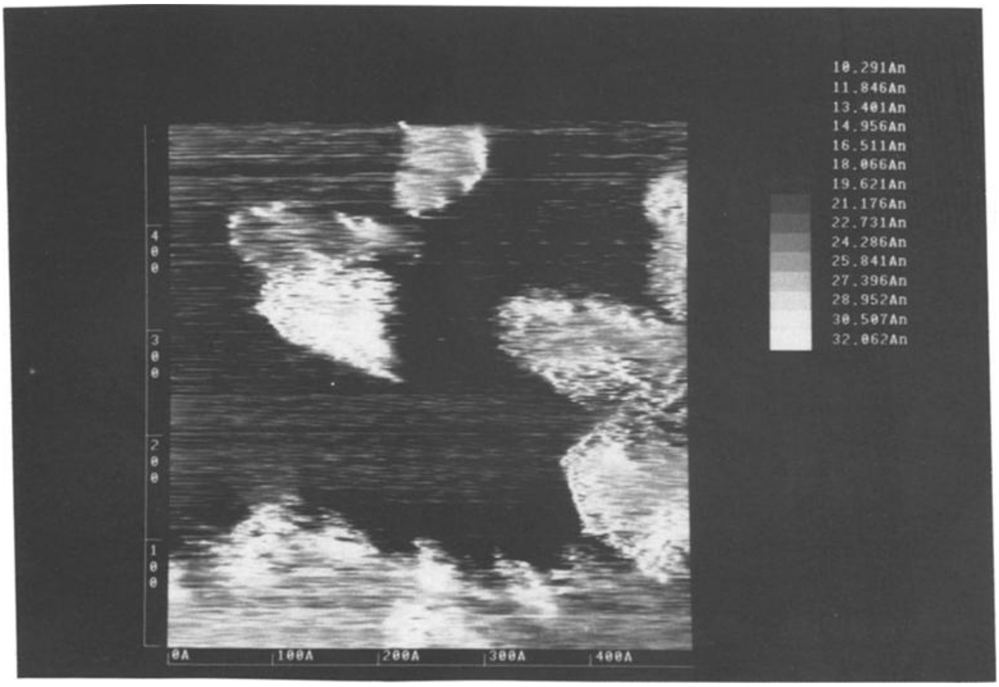

Fig. 7. A 500 × 500 $Å^2$ area of MoS_2/HOPG formed from sulfidation of MoOx/HOPG. MoS_2 formed from this process was observed as large patches. Scanning across the patches did not yield any atomic resolution image, which may indicate that the MoS_2 formed is not an ordered structure, or that it may be oriented with its basal plane perpendicular to the graphite surface.

Cobalt sulfides also form large patches and needle-type clusters on graphite. These needle-type clusters are similar to the ones we observed on the CoOx samples, but are smaller in size, about 120 Å in length. Unlike those in CoOx, where the needles are found to make doublets, these structures align themselves so as to make a long chain (fig. 8). The XPS S 2p peak is very broad suggesting that various forms of sulfur may be present. The Co 2p peak shifted slightly as compared to the oxide sample. The sulfide clusters in our experiment are most likely due to bulk Co_9S_8, since MES observation by Crajé et al. [12] showed that at high Co loading and at sulfidation temperature higher than 400°C, Co–S may exist as bulk Co_9S_8. This finding was also confirmed by EXAFS observation by Bouwens et al. [13] which showed that the Co atoms in the sulfided Co/C catalysts have Co–S and Co–Co coordination as in Co_9S_8. It is unlikely that CoS_2 is formed in our sample, since these authors have found that at sulfidation temperatures higher than 400°C, all Co species in Co–S/C exist in the form of Co_9S_8.

Fig. 9 shows the STM image of sulfided CoMoOx/graphite. The Co/Mo ratio in this sample is 0.5. We observed that sulfidation of CoMoOx has transformed the ring-type structures into elongated islands. The formation of large islands agrees with Bouwens et al.'s suggestion that, after sulfidation, sulfided Co–Mo particles

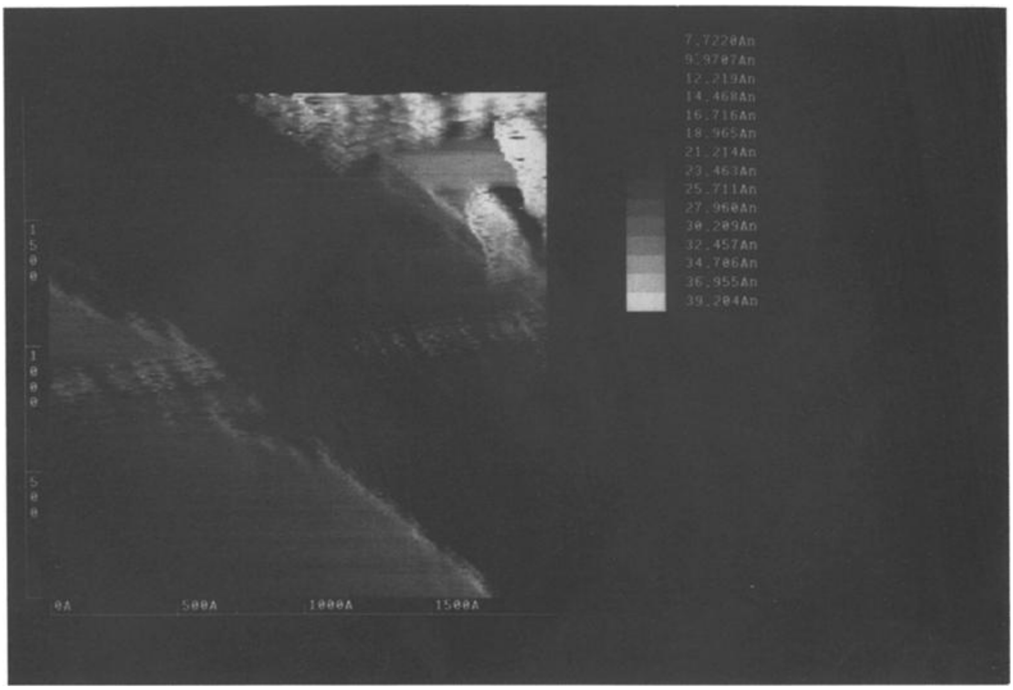

Fig. 8. A 500 × 500 $Å^2$ image of CoS/HOPG. Similar to CoOx/HOPG, needle-like structures were observed on this sample. However, instead of forming doublets like those on CoOx/HOPG sample, these structures tend to align themselves to form a long chain.

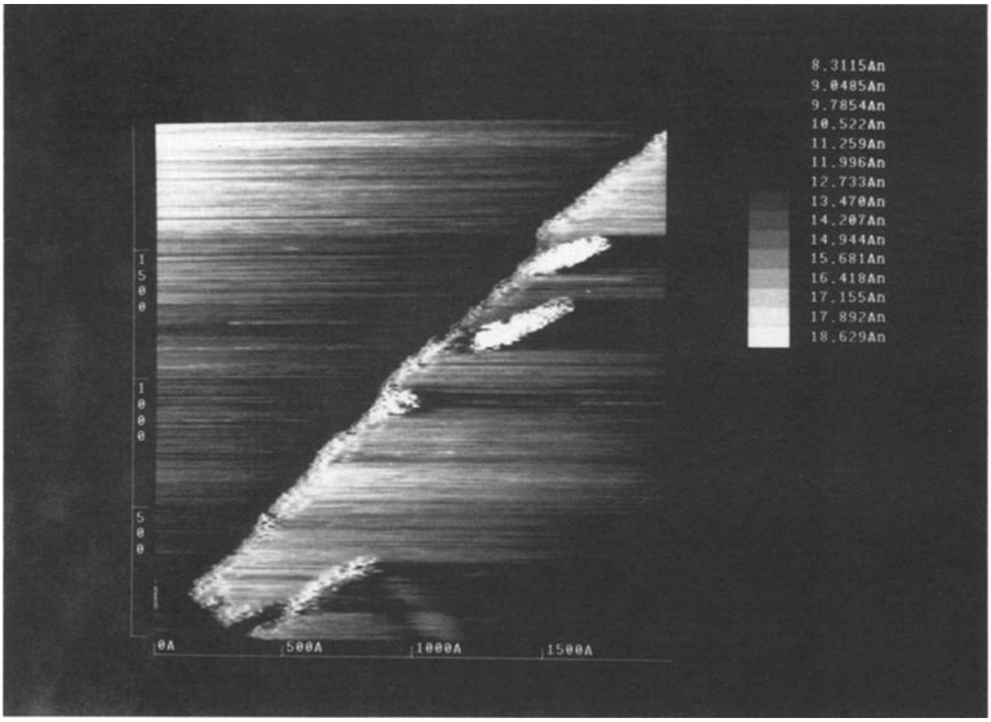

Fig. 9. A 2000 × 2000 Å^2 image of CoMoS/HOPG shows that sulfidation of CoMoOx may have transformed the ring-type structures into two-dimensional islands with elongated shapes on HOPG.

(12–15 Å) agglomerate together to form large patches [3]. There are a number of studies concerning the types of species on Co–Mo–S/carbon surface. Topsøe et al. [14] observed that Co–Mo–S structures are only weakly bound to the carbon support surface, which is similar to type II Co–Mo–S on alumina support. Duchet et al. [15] proposed that in Co–Mo–S/C, Co ions form a well dispersed phase, either as a separate sulfide species (Co_9S_8) attached to MoS_2 or as separate cobalt ions at the surface of MoS_2. The XPS data (table 1) again indicate that the Co and Mo in the Co–Mo–S sample have the same oxidation states as in Mo–S/C and Co–S/C, with the exception that the S 2p becomes more uniform in the 2– state. Also, Bouwens et al. [13] observed that Co atoms in sulfided Co–Mo were partly present in a Co_9S_8-like structure and partly in a Co–Mo–S structure. They also proposed that in the Co–Mo–S/C catalysts the Mo sulfide phase is also present in the form of fully sulfided MoS_2 particles, with the Co atoms located at the MoS_2 edges in the plane of the Mo atoms. In our experiment with sulfided Co–Mo sample, we did not observe any rough patches similar to those observed in MoS_2/HOPG sample. The elongated islands (300–600 Å) observed are much larger than the needle-type clusters observed in the CoS/HOPG sample. Thus, the islands we observed on our sample can be attributed mainly to a CoMoS phase. This is consistent with the report that the 0.5 ratio of Co to Mo yields full edge occupation of Co on Mo [12].

Similar to the oxide species, the sulfide phases also did not move during repeated scanning. Therefore, there is an interaction between the sulfide phases and the carbon support, as reported by previous investigators [2,3,15].

4. Summary

Our results show that we can use STM to image supported molybdenum-based catalysts, both in their oxidic and sulfidic forms. With STM, we were also able to identify distinct types of clusters for each species that we investigated. MoOx on graphite was observed as elliptical or rod-like clusters which tend to aggregate together to form large clusters. Round clusters and needle-type clusters were observed on the CoOx/HOPG sample. The round clusters were observed to behave more like MoOx, they form agglomerations on the graphite surface, while the needle-type structures were observed to exist as doublets. The STM image of CoMoOx/HOPG showed distinct ring-type clusters, which have never been reported before. We attribute these structures to the CoMoOx phase, where the Co are decorating the edges of MoOx clusters. The round clusters are thought to be CoOx clusters that did not react to form CoMoOx.

The sulfided phase of the oxide species seems to form large patches on the graphite support. These patches are believed to be the aggregation of individual sulfide crystallites. Scanning over the large slabs of MoS_2 did not yield any atomic resolution image. This could be due to the fact that the MoS_2 formed on graphite did not exhibit any well-ordered structures, or because the MoS_2 is oriented with its edge plane parallel to the graphite surface. The large patches of Co–S that we observed could be the result of the agglomeration of Co_9S_8 crystallites, while those observed on the sulfided CoMoOx consist mainly of Co–Mo–S phase, and no clusters similar to CoS/HOPG and MoS_2/HOPG were observed.

Our experiment suggests that there is some interaction between the oxide and sulfide phases with carbon support. This interaction was evident during the STM investigation, since no apparent movement of the clusters was observed during repeated scanning of the same area.

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