

Mobile Promoters on Anisotropic Catalysts: Nickel on MoS₂

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We have imaged the MoS₂ basal plane bare and with adsorbed Ni atoms at 298, 77, and 4 K using a low-temperature ultrahigh vacuum scanning tunneling microscope. Ni atoms freely diffuse across the surface even at 77 K. At 4 K, isolated atoms and small clusters of Ni are stable and can be imaged. At 4 K, Ni atoms can be easily manipulated with the microscope tip. Spectroscopic measurements reveal that Ni adatoms create favorable electronic structures for binding nucleophilic reactants. In addition to this, our observations suggest two new roles for the Ni promoter atoms: (1) increasing the sticking probability of sulfur-containing hydrocarbons by binding them to the unreactive basal planes of MoS₂ and (2) transporting these hydrocarbons as inorganic complexes to the active sites for reaction.

I. Introduction

Molybdenum disulfide (MoS₂) promoted with Ni or Co is an important hydrodesulfurization (HDS) catalyst used to remove sulfur from petroleum feedstock.^{1–5} Despite widespread study of heterogeneous catalytic HDS, the functions of the promoter species on MoS₂ remain unclear. Topsøe and co-workers have shown that promoter atoms locate at MoS₂ sheet edges in the form of Ni(Co)–Mo–S structures.^{1,2} These structures are known to dominate the catalytic reactivity of the system.³ The anisotropy of the catalytic system stems from the saturated bonding of the MoS₂ basal plane. The catalytic activity is strongly dependent on the specific dispersion of the MoS₂ crystal—the ratio of edge sites to basal plane area.⁴ The reactivity of a specific catalyst is a complicated function of not only exposed edge and promoter coverage but also of the MoS₂ stacking.⁵ While the basal plane is largely inert,⁶ sheet edges expose Mo and S atoms for reaction and attachment of Ni and Co.² The prototypical reactant molecule thiophene desorbs from MoS₂ basal planes at 168 K,⁶ far below reaction temperatures. In this work we explore the behavior and possible roles of Ni on the basal plane.

We propose that metal promoters, adsorbed to the unreactive basal planes of the MoS₂, increase catalytic reactivity by binding and transporting sulfur-containing molecules as inorganic complexes to the catalytically active edge sites, as described below. We have previously discussed how electronegative species can diffuse across other surfaces by forming complexes with metal atoms.⁷ Promoters in heterogeneous catalysis are generally thought to modulate the binding interaction between reactant or intermediate and surface, typically increasing the reactivity by modifying the electronic or morphological properties of the catalyst surface. We are able to show such an electronic effect for Ni on MoS₂ directly from scanning tunneling spectroscopy data. On the basis of our data, we also propose two additional roles for promoters that appear to have been neglected to date—binding a reactant to and transporting it across unreactive portions of the catalyst surface.

The scanning tunneling microscope (STM) is an attractive tool for elucidating catalytic processes owing to its ability to

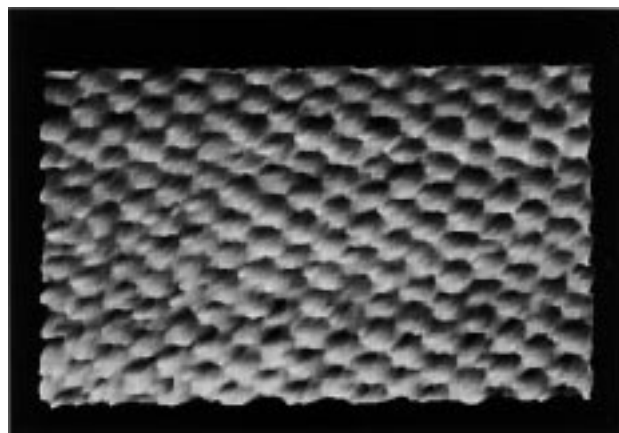


Figure 1. Typical atomic resolution STM image of the clean basal plane of MoS₂ recorded at 77K (55 Å × 35 Å image area, sample bias = −200 mV, tunneling current = 200 pA).

image surfaces in real space with atomic resolution, as well as to measure local electronic structure. The STM is thus ideal for probing heterogeneous minority sites that cannot be investigated by surface spectroscopies that average over macroscopic or even microscopic areas.

II. Experimental Section

We imaged the basal plane of a natural MoS₂ crystal both bare and with adsorbed Ni at room temperature, 77 K, and 4 K using a low-temperature ultrahigh vacuum (UHV) STM.⁸ The MoS₂ sample was prepared by cleaving in air with adhesive tape followed by annealing to 600 °C in UHV to remove surface contaminants. All images were acquired in constant current mode, with the sample biased with respect to the tip, and are presented unfiltered. Atomic resolution images of the clean MoS₂ surface (Figure 1) exhibited the hexagonal symmetry and 3.2 Å lattice constant of the exposed sulfur atoms. Ring structures, which are imaged as apparent protrusions from the MoS₂ surface with diameters of 50–100 Å, similar to those previously reported, were also observed.⁹ These ring structures have been attributed to impurities, trapped between MoS₂ layers during formation, and not to surface species.^{9a}

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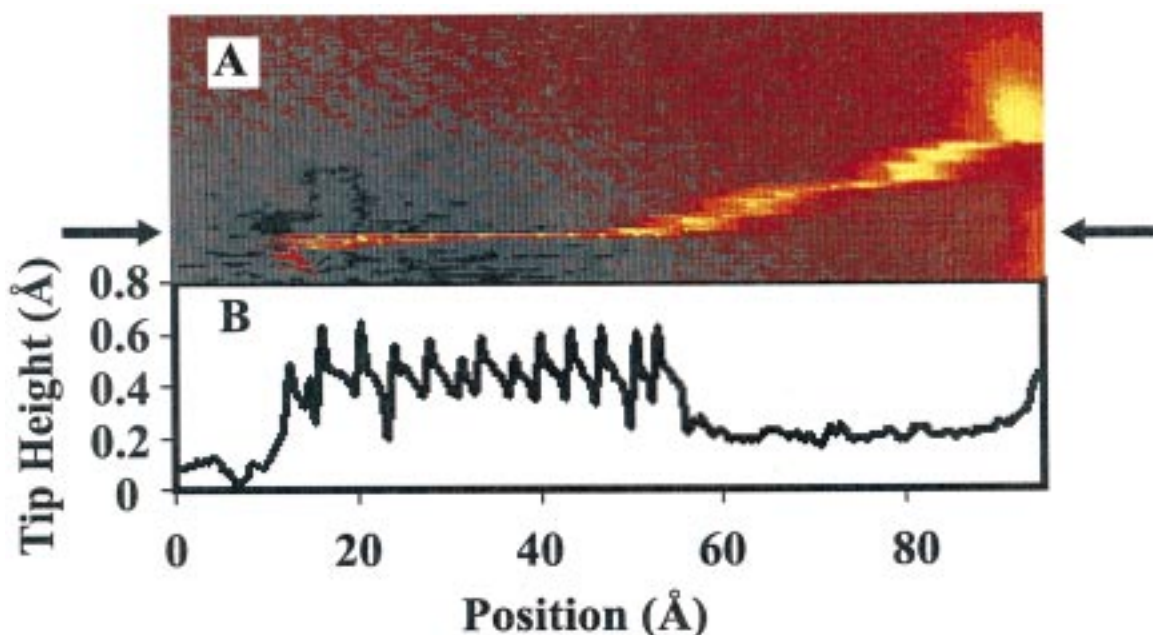


Figure 2. (A) STM image showing the manipulation of a Ni adsorbate by the probe tip at 4K ($30 \text{ Å} \times 95 \text{ Å}$ image area, sample bias = -1.5 V , tunneling current = 100 pA). Images are acquired line by line, from the bottom to the top as shown here. Data were collected as the tip moved from left to right in this image, and then the tip was quickly moved back to the start of the next line. (B) Tip-sample separation during Ni motion is plotted. The line is indicated by the two arrows in Figure 2A. The motion of the tip indicates that the Ni adsorbate hops to neighboring lattice sites owing to an attractive interaction with the STM probe tip.

Ni was deposited onto a room-temperature MoS_2 surface by sublimation of a 1.0 mm diameter $99.99\%+$ Ni wire in UHV. An exposure of 6×10^{-8} Torr-s yielded a dilute coverage of $\sim 6\%$, suggesting a sticking coefficient near unity. The MoS_2 sample was then transferred (within UHV) to the STM maintained at 298 , 77 , or 4 K .

The low-temperature STM has been described previously.⁸ The base pressure at room temperature is in the 10^{-11} Torr range, and decreases at reduced temperature to the 10^{-14} Torr range. The stability is such that we are able to image surface features repeatedly for days at a time (passive drift rates have been reduced below 1 atomic site per day, 0.1 Å/h).

III. Results and Discussion

The MoS_2 basal plane can be imaged routinely with atomic resolution as shown in Figure 1. After metal deposition, STM imaging directly revealed the low barrier to diffusion for Ni on the basal plane of MoS_2 . Rapid diffusion of adsorbed Ni atoms prevented acquisition of stable images at 298 and at 77 K . The Ni species diffused across the surface on a submillisecond time scale inaccessible to our STM,¹⁰ and thus the images were dominated by apparent current noise as atoms moved rapidly on the surface through the tunnel junction.^{11,12}

At 4 K isolated atoms and small clusters of Ni are stable and can be imaged. Even at 4 K , single Ni atoms can be easily manipulated with the microscope tip. By lowering the tunnel gap impedance, the tip can be moved close enough to move the adsorbates across the surface.¹³ Figure 2a is a representative image demonstrating tip-induced motion of a Ni adatom. The Ni atom is pulled from its adsorption site at a surface defect and dragged across the surface by the scanning tip. The Ni atom initially travels ca. 45 Å across the surface, and then moves smaller amounts on each successive scan until it attaches to a preexisting cluster. Larger clusters can be constructed in this way for further study. Atomic clusters are more energetically stable and thus less affected by the microscope tip.

Examining the initial 45 Å slide reveals that it is not one continuous motion but consists of the Ni atom hopping between neighboring lattice sites.¹⁴ The tip-sample separation, as the Ni atom is moved, is plotted in Figure 2b. This line is taken from the data shown in Figure 2a (between the points indicated by arrows). The tip initially approaches the Ni atom and retracts suddenly. The tip then begins to scan down the contour of the Ni atom but retracts again when the Ni atom hops—one lattice site at a time—back under the tip. It is the shape of the tip motion that indicates that the Ni atom is being dragged by attractive interactions.¹⁴ This sequence is repeated until the Ni atom has traversed 45 Å across the surface. The distance between tip jumps, and thus Ni adsorption sites, is 3.3 Å , in good agreement with the lattice constant of 3.2 Å for this surface.

Spectroscopic investigations of Ni clusters reveal the electronic origins for binding the S-containing nucleophilic molecules. Figure 3A–E shows a Ni_3 cluster imaged at three sample biases. Parts A–C show perspective views of the data at sample biases of $+2$, $+1.4$, and -2 V from top to bottom, respectively. Imaging at these different bias voltages allows us to measure the effect the Ni cluster has on electronic states as a function of both position and energy.¹⁵ At $+2 \text{ V}$ sample bias (electrons tunneling into the empty states on the surface), the Ni_3 cluster appears as a significant three-lobed protrusion from the MoS_2 basal plane (Figure 3A,D), indicating that it increases the local density of empty electronic states at this energy. Likewise, we see from Figure 3C,E that the cluster depletes the density of filled states at 2 V below the Fermi level (electrons tunneling from the filled sample electron states to the tip), electronic states that would repel electron-rich reactants.

Two point defects in the MoS_2 surface are also found within this area (apparent in Figure 3C–E). The point defects have previously been assigned as single S vacancies in the MoS_2 surface.¹⁶ Such vacancies may stabilize the cluster and thus determine its position.^{13c,17}

In the image acquired at a sample bias of $+1.4 \text{ V}$, the cluster is not apparent but a diffuse ring $\sim 30 \text{ Å}$ in diameter surrounding

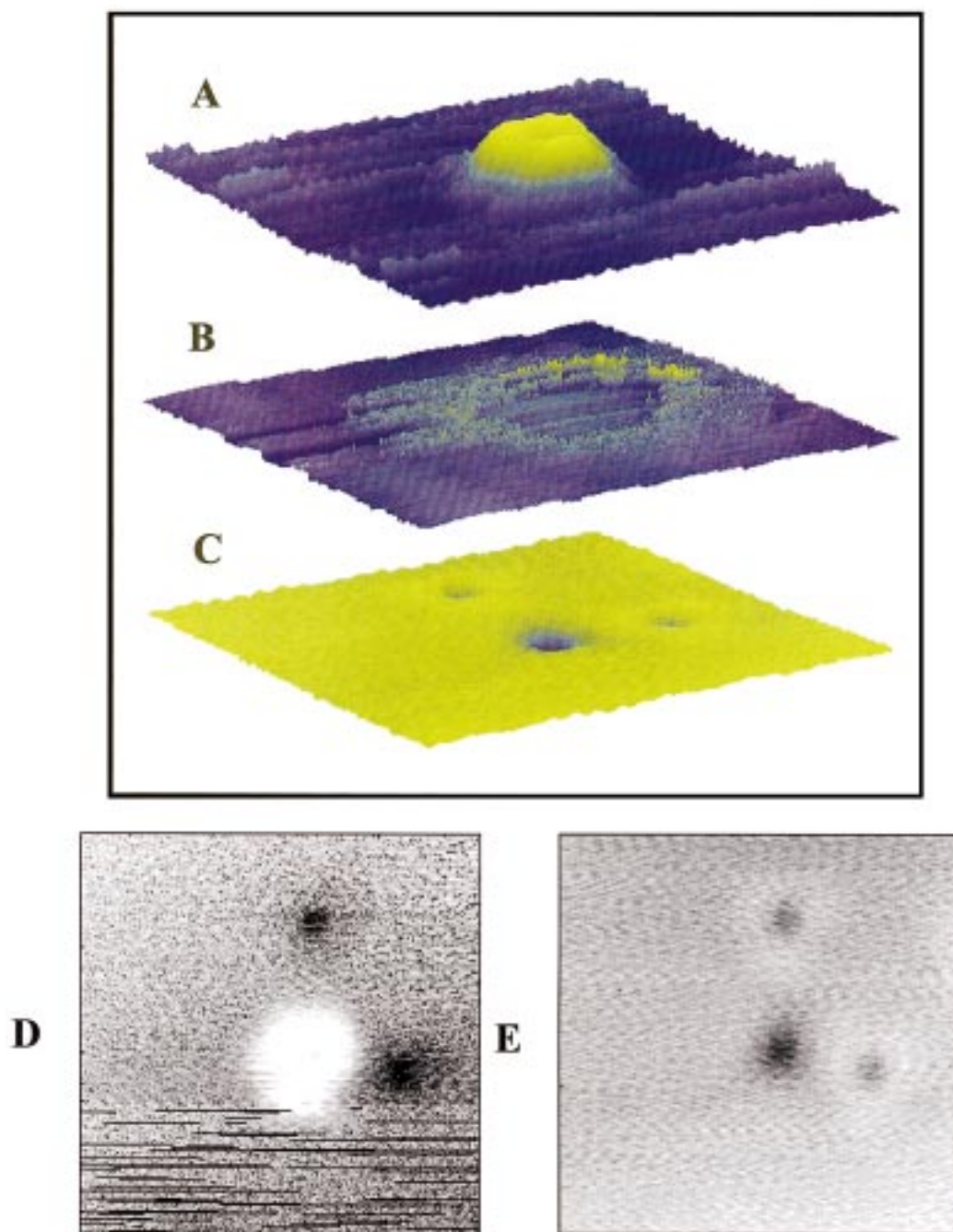


Figure 3. Three STM images of a Ni₃ cluster adsorbed on a MoS₂ basal plane at 4 K. All three images show a 60 Å × 60 Å area and are plotted as perspective views with the same aspect ratio and angle of view. The images were acquired with sample biases of +2 (A), +1.4 (B), and -2 V (C) and tunneling currents of 100, 100, and 200 pA, respectively. The Ni₃ clusters effect on the local density of electronic states—both filled and empty—can be seen and is explained in the text. Topographic views of the data at sample biases of +2 and -2 V are shown in (D) and (E), respectively.

it is found. This ring is well outside the geometric (physical) extent of the protrusion (~16 Å diameter) measured at +2 V sample bias. This ring results from a perturbation of the MoS₂ surface electronic structure by the Ni₃ cluster. This ring is substantially different from those observed around intercalation impurities mentioned earlier. Locally perturbed electronic structures by defects, steps, and adsorbates have been observed by STM to direct molecular adsorption,^{12,18} affecting both adsorbate structures and chemistry.

IV. Implications

The Ni₃ cluster increases the density of empty states, creating a favorable adsorption site for electron-rich molecules, such as

the thiophenic compounds.¹⁹ Thiophene and its derivatives form transition-metal complexes by coordinating through either their p electrons (η^5 bonding) or the S atom's lone pair of electrons (η^1 bonding).²⁰ Studies of thiophene adsorption on single-crystal surfaces of Ni report that bonding occurs through the sulfur atom.²¹ Recently a dinuclear nickel phosphine complex was found that activates and inserts into the C—S bond of dibenzothiophene.²² We hypothesize that Ni species adsorbed on the MoS₂ basal plane bond to the sulfur atom of thiophenic compounds, creating adsorbed inorganic complexes. These inorganic complexes, owing to their expected low barrier to diffusion, are able to diffuse about the surface until reaching active sites at the MoS₂ sheet edges.⁷ Binding the thiophenic

ligands to Ni should reduce the barrier to diffusion from the value found for the unattached metals.⁷ Thus, our measurements for the bare metal diffusion on MoS₂ are *lower limits* of the values expected for these inorganic complexes. The ability to form these complexes would effectively increase the sticking probabilities and surface mobilities of thiophenes. Without such a mechanism the weak interactions of thiophenes with the MoS₂ basal plane would dictate that only molecules which impinge upon the MoS₂ surface at (or near) sheet edges would react.

Such a mechanism is analogous to phase-transfer catalysis in two-phase liquid media.²³ A phase-transfer catalyst (often a complexing agent such as a crown ether) increases reactivity by shuttling reactants across the interface between aqueous and organic phases. In both mechanisms the transfer agent (in our case Ni adatoms) increases the reactant concentration at the active site, which in turn increases the catalytic activity.

We do expect that the majority of promoter atoms will be tied up at step edge sites known to dominate reactivity.¹⁻⁴ From such sites and other binding sites for promoters we also expect a two-dimensional vapor pressure of promoters on the basal planes. The chemical forms and cluster sizes of these will depend on the specific reaction conditions.

We therefore propose that in addition to their classic role in modifying the surface chemistry, metal promoters on MoS₂ HDS catalysts (1) bind reactants to unreactive portions of the catalytic surface and (2) transport reactants to active sites on the anisotropic catalytic surface. These two new roles in conjunction with their conventional electronic and structural effects could more fully explain the function of Ni and Co promoters on MoS₂ HDS catalysts. Experiments are underway to show the capture and motion of thiophenes by these mechanisms.

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