

Chemistry of Thiophene, Pyridine, and Cyclohexylamine on Ni/MoS_x and Ni/S/Mo(110) Surfaces: Role of Nickel in Hydrodesulfurization and Hydrodenitrogenation Processes

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Synchrotron-based high-resolution photoemission has been used to study the interaction of thiophene, pyridine, and cyclohexylamine (CHA) with pure and Ni-promoted MoS_x films and S/Mo(110) surfaces. The MoS_x films exhibit Mo 3d and valence spectra that are very similar to those of MoS₂. On the MoS_x systems, the behavior of thiophene closely resembles that seen on MoS₂(0002). The molecules are weakly chemisorbed, and most of them desorb at temperatures around 200 K. A small fraction of the adsorbed thiophene is bonded to Mo sites that have S vacancies and desorbs between 250 and 300 K. A similar behavior is observed for adsorbed pyridine. In contrast, CHA displays a rich chemistry on these surfaces. Mo centers that have a limited number of S vacancies and do not do chemistry with thiophene, pyridine, or H₂ are able to cleave the C–N bond in a nonaromatic H-rich molecule like CHA. The addition of Ni enhances the chemical activity of MoS_x. On the NiMoS_x systems, the adsorption energies of thiophene and pyridine are 5–10 kcal/mol larger than those on pure MoS_x. But no dissociation of these molecules is observed on the NiMoS_x surfaces. The Ni ↔ S interactions reduce the reactivity of nickel, and the presence of this metal alone is not enough to promote or facilitate the cleavage of aromatic C–S or C–N bonds. Hydrogen seems to play an important role in this aspect. Extensive decomposition of thiophene is observed after creating S vacancies in MoS_x and Ni/S/Mo(110) surfaces by reaction with atomic hydrogen ($2\text{H}_{\text{gas}} + \text{S}_{\text{surface}} \rightarrow \text{H}_2\text{S}_{\text{gas}} + \text{vacancy}_{\text{surface}}$). The role of Ni in NiMoS_x catalysts for hydrodesulfurization and hydrodenitrogenation processes is discussed in light of these results.

I. Introduction

In our industrial society, petroleum plays a predominant role as a source of chemicals and fuels.¹ Petroleum consists predominantly of a large series of hydrocarbons (paraffins or alkanes, aromatic ring compounds, naphthenes) but also contains lesser amounts of sulfur and nitrogen in the form of a variety of organic compounds.¹ Catalysts based on molybdenum sulfide are widely used in oil refineries for the hydrotreatment of petroleum-derived feedstocks and the removal of S- and N-containing impurities.^{2,3} Desulfurization and denitrogenation processes are important for two main reasons. First, they prevent sulfur- and nitrogen-containing molecules from reaching and deactivating catalysts used in the reforming of oil.^{2–4} Second, they improve the quality of gasoline related products by reducing the amount of SO_x and NO_x pollutants formed during the combustion of these fuels.⁵

In hydrotreatment, desulfurization and denitrogenation reactions occur simultaneously and can interact with each other in a complicated manner.^{2,3} The conventional industrial catalysts frequently contain a mixture of molybdenum sulfide promoted with Co or Ni on a γ-alumina support.⁶ It is not known what are the active sites in these complex systems.^{3,6} Among the transition-metal sulfides, MoS₂ shows a medium or moderate catalytic activity for hydrodesulfurization (HDS) reactions.^{6,7} The performance of molybdenum sulfide catalysts in desulfu-

rization and denitrogenation processes can be substantially improved by the addition of metal promoters.^{6,8} After comparing the effects of several metals (V, Cr, Fe, Co, Ni, Cu, and Zn) on the HDS activity of molybdenum sulfide catalysts, it was found that nickel was the best promoter.^{9,10} Several proposals have been offered to explain the behavior of NiMoS_x catalysts, from electronic interactions that modify the reactivity of the metal components to unique structural properties.^{6,11–14} In these systems, the active sites probably contain NiMoS units^{2c,14} making it desirable to understand the effects of the Ni ↔ S ↔ Mo and Ni ↔ Mo interactions at a fundamental level.

In recent years, many works have appeared investigating the surface chemistry of sulfur- and nitrogen-containing molecules on metallic Mo and Ni.^{15–24} Metallic nickel is known to have an extremely high chemical affinity for sulfur- and nitrogen-containing molecules.^{15–19} For example, the metal is able to break C–S bonds at temperatures as low as 100 K.^{15,16} But, it is not clear how Ni will behave when in contact with molybdenum sulfide. In this article, we use synchrotron-based high-resolution photoemission to study the effects of Ni on the reactivity of MoS_x and S/Mo(110) surfaces toward thiophene (C₄H₄S), pyridine (C₅H₅N), and cyclohexylamine (C₆H₁₁NH₂, CHA). This type of study has not been done before, and here we take advantage of the sensitivity of photoemission for monitoring the rupture of C–S and C–N bonds.^{4a,18,19,23b} Thiophene and pyridine are frequently used as test molecules in HDS and hydrodenitrogenation (HDN) studies.^{6,10,13,15–17,20–26}

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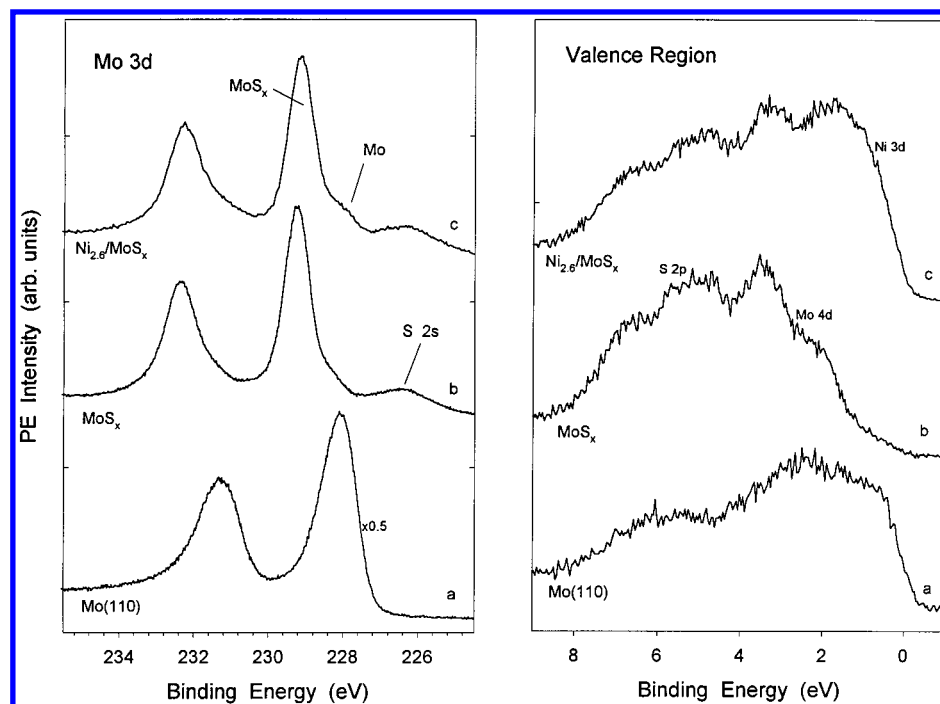


Figure 1. Mo 3d (left) and valence spectra (right) for Mo(110), MoS_x, and Ni_{2.6}/MoS_x. The Ni_{2.6}/MoS_x system was prepared by depositing 2.6 ML of nickel on MoS_x at 300 K and heating to 600 K. All the spectra were acquired using a photon energy of 380 eV.

These aromatic molecules are very stable, and it is difficult to break their C–S or C–N bonds. Cyclohexylamine derivatives are often observed during the HDN of large aromatic heterocyclic nitrogen compounds.^{8,18,19} Compared to pyridine, cyclohexylamine is more susceptible to C–N bond cleavage.^{17,18} Our studies show very interesting differences in the chemistry of these molecules on clean and Ni-promoted MoS_x and S/Mo(110) surfaces. The reactivity of an adsorption site on molybdenum sulfide depends strongly on the type of adsorbate. It is shown that nickel greatly enhances the chemical activity of the MoS_x substrate, but the presence of the admetal alone is not enough to promote the cleavage of C–S or C–N bonds.

II. Experimental Results

The photoemission experiments described in section III were carried out in an ultrahigh vacuum (UHV) chamber located at the U7A beamline of the National Synchrotron Light Source (NSLS) at Brookhaven National Laboratory. This UHV chamber is equipped with a hemispherical electron energy analyzer with multichannel detection. The valence, S 2p and C 1s spectra reported in section III were acquired employing a photon energy of 380 eV to excite the electrons. A photon energy of 500 eV was used for taking the N 1s spectra. The binding energy scale in the spectra was calibrated by the position of the Fermi edge in the valence region.

In this work, MoS_x films and a Mo(110) substrate saturated with chemisorbed S ($\theta_S = 0.9$ monolayer) are used as models for studying desulfurization and denitrogenation reactions on molybdenum sulfide. Films of MoS_x (6–8 layers in thickness) were grown on the Mo(110) substrate using S₂ as a source of sulfur following the methodology described in ref 27. In previous studies,^{27–29} we have found that our MoS_x films exhibit a low reactivity toward H₂, CO, and O₂ that is very similar to that reported for the S basal plane of molybdenum sulfide, MoS₂-(0002). These studies indicate that the MoS_x films expose a limited amount of Mo atoms (0.1–0.2 ML) that are not fully coordinated to sulfur.^{27–29} A standard procedure (ion sputtering

and/or fast heating to 2500 K) was applied to clean the Mo crystal.^{27,28} On the MoS_x and S/Mo(110) systems, the deposition of nickel was performed by resistively heating a W filament wrapped with a high purity wire of Ni. The atomic flux from the metal doser was calibrated following the results of previous studies for the Ni/S/Mo(110) and Ni/Mo(110) systems.^{28,30}

High-purity thiophene (Aldrich), pyridine (Mallinckrodt), and cyclohexylamine (Aldrich) were dosed to the clean and Ni-promoted MoS_x and S/Mo(110) surfaces at 100 K from the background by backfilling the UHV chamber. The coverages of the molecules on the surfaces were determined by measuring the area under the C 1s features, which was scaled to absolute values by comparing it to the corresponding area for the saturation coverage of thiophene on Mo(110), ~ 0.1 monolayer.²⁴ In this work, the coverages of Ni and the adsorbates are reported with respect to the number of Mo(110) surface atoms, i.e., 1.43×10^{15} adatoms or admolecules per cm² corresponds to $\theta = 1$ monolayer (ML).

III. Results

III.1. Adsorption of Thiophene, Pyridine, and Cyclohexylamine on MoS_x. Figure 1 shows Mo 3d and valence photoemission spectra for Mo(110) (a) and a typical MoS_x film (b). It is known that the Mo 3d levels are very sensitive to the formation of Mo–S bonds, with MoS₂ exhibiting a positive binding energy shift of ~ 1.2 eV with respect to metallic Mo.^{31,32} This is the magnitude of the binding energy shift seen in Figure 1 when comparing the 3d_{5/2} peaks of MoS_x and Mo(110). In the Mo 3d spectrum for MoS_x, the 3d_{5/2} signal for unoxidized Mo (at ~ 228 eV) is very small. The valence spectrum for the MoS_x film agrees very well with that reported for bulk MoS₂.^{33,34} The Mo 4d levels appear between 2 and 4 eV, with the S 3p levels in the range of 5 to 8 eV.³³ The electron emissions near the Fermi level (2–0 eV) are very weak.

Figure 2 displays C 1s core-level spectra taken after adsorbing thiophene on the MoS_x film of Figure 1. The spectrum for clean molybdenum sulfide (bottom of the figure) exhibits a weak Mo

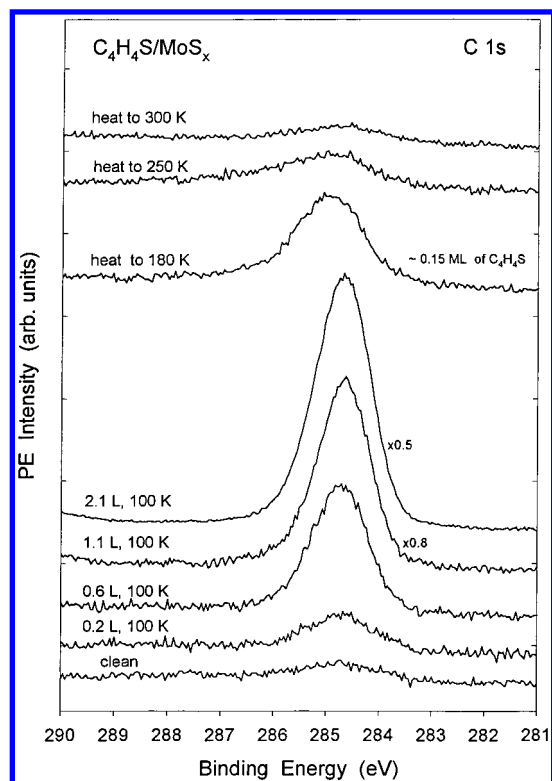


Figure 2. C 1s photoemission spectra ($h\nu = 380$ eV) acquired after dosing thiophene (0.2, 0.6, 1.1, and 2.1 L total exposures) at 100 K. The final C_4H_4S/MoS_x system was heated to 180, 250, and 300 K. The first two thiophene doses produced overlayers dominated by chemisorbed species ($\theta_{C_4H_4S} \approx 0.05$ ML, 0.2 L; and 0.2 ML, 0.6 L), whereas the last two doses led to multilayer systems that contained mainly physisorbed thiophene ($\theta_{C_4H_4S} > 0.5$ ML).

photoemission peak at ~ 284.6 eV.³² This weak peak overlaps with the C 1s features for adsorbed thiophene. As the doses of C_4H_4S increase (0.2–2.1 L, 100 K), there is only one peak in the C 1s region that shifts from 284.8 (submonolayer coverages) to 284.4 eV (multilayer). Heating to 180 K induces desorption of the physisorbed thiophene^{21,24} and leaves ~ 0.15 ML of chemisorbed thiophene on the surface. Most of the chemisorbed molecules desorb upon annealing to 250 K. By 300 K, the spectrum for the C 1s region resembles that of clean MoS_x . In the results of Figure 2, there is no peak that can be assigned to the carbonaceous species formed during the decomposition of thiophene on metals.^{21–24} This type of species, in particular C/Mo³⁵ and C/MoS_x,³⁶ is stable up to very high temperatures (> 500 K). Therefore, we can conclude that the bonding interactions between thiophene and MoS_x are relatively weak and do not lead to decomposition of the organosulfur molecule.

Over MoS_x/Al_2O_3 catalysts, thiophene is weakly chemisorbed and desorbs in a single peak with a maximum rate of desorption at ~ 240 K.³⁷ On the (0002) sulfur-basal plane of MoS_2 , the adsorption bond of thiophene is extremely weak and desorption takes place at temperatures below 200 K.^{38,39} For the C_4H_4S/MoS_x system, the bonding interactions are somewhat stronger and a few thiophene molecules remain on the surface at 250 K probably attached to Mo sites that have S vacancies. These Mo sites have a low concentration (0.1–0.2 ML^{27–29}). They are still bonded to a significant number of S atoms and are not able to dissociate the molecule. On the (100) and (110) faces of metallic Mo, thiophene completely dissociates leaving C and S atoms on the surface.^{21,24} One can generate a large number of S vacancies (i.e., coordinatively unsaturated Mo atoms) in a MoS_x surface by dosing atomic hydrogen to the system ($2H_{gas} + S_{surface}$

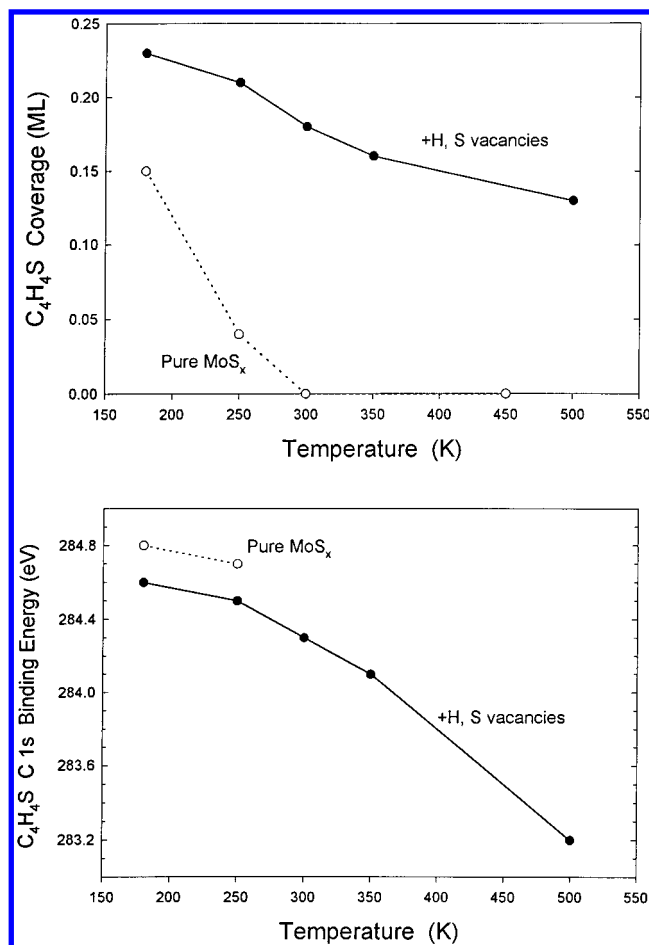


Figure 3. Coverage (top panel) and C 1s binding energies (bottom panel) for the adsorption of thiophene on a pure MoS_x surface, empty circles, and on a surface pre-exposed to a beam of atomic H at 300 K, full circles.^{29,40} The dosing of thiophene was carried out at 100 K and then the samples were heated to the indicated temperatures. The thiophene coverage was calculated by integrating the area under the peaks in the C 1s region (see section II) after subtracting contributions from the Mo features that appear at ~ 284.6 eV. The curves are drawn to guide the eye.

$\rightarrow H_2S_{gas} + vac_{surface}$).^{29,40} Figure 3 compares results for the adsorption of thiophene on the MoS_x film of Figure 1 and on a MoS_x film that was first exposed to atomic hydrogen.^{29,40} The dosing of H produced a decrease of $\sim 10\%$ in the S 2p intensity of MoS_x , 0.3–0.4 ML of S vacancies, and no significant increase in the Mo 3d signal of pure metallic Mo (i.e., no Mo atoms were fully reduced).^{29,40} In Figure 3, both types of surfaces were saturated with a multilayer of C_4H_4S at 100 K and then heated to the indicated temperatures. Thiophene displays stronger bonding interactions with the molybdenum–sulfide surface that is rich in S vacancies: there is an increase in the amount of adsorbed thiophene and most of the C 1s signal does not disappear when the system is annealed to temperatures above 300 K. In fact, at high temperatures (300–500 K), one sees a significant decrease in the C 1s binding energy (bottom panel in Figure 3) which indicates cleavage of the C–S bonds^{23b} and the deposition of C_xH_y fragments on the vacancy-rich molybdenum sulfide. But this system is still much less reactive than clean metallic Mo, where thiophene decomposes extensively at temperatures between 100 and 300 K.²¹

We also investigated the adsorption of pyridine and cyclohexylamine on pure MoS_x films such as the one in Figure 1. Typical results for pyridine adsorption are shown in Figure 4. This adsorbate is a stronger Lewis base than thiophene^{2a,8} but,

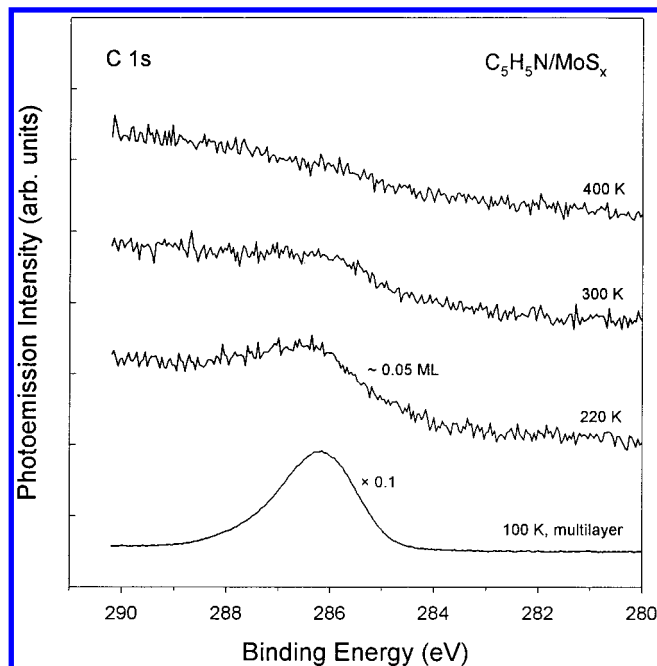


Figure 4. C 1s spectra for the adsorption of pyridine on a MoS_x surface at 100 K with subsequent annealing to elevated temperatures. All the spectra were acquired using a photon energy of 450 eV.

despite this, exhibits weak bonding interactions with the MoS_x. At 300 K, the intensity of the C and N 1s signals was small ($\theta_{\text{pyr}} \approx 0.01$ ML), and no evidence for decomposition of pyridine was found. A completely different picture is seen in the data for the interaction of cyclohexylamine (CHA) in Figure 5. These

results are for adsorption on the MoS_x system of Figure 1. In the first step, a multilayer of CHA was deposited on the molybdenum sulfide surface at 100 K. Heating to 220 K induced desorption of the physisorbed species. A comparison of the relative areas for the C and N 1s peaks at 100 and 220 K shows that the drop in intensity for the N 1s signal is much larger than for the C 1s signal. Thus, *some C–N bond breaking has occurred* with ammonia probably going into the gas phase and hydrocarbon fragments remaining on the MoS_x substrate (this is a typical decomposition pathway for CHA on metals^{18,19}). At 220 K, the broad N 1s features indicate that more than one type of N species is present on the surface. By 400 K, all the nitrogen has disappeared but a large C 1s signal remains (equivalent to 0.1 ML of CHA or 0.6 ML of atomic carbon). Upon further heating to elevated temperatures, there may be desorption of benzene^{18,19} and the C1s signal decreases.

A comparison of the results in Figures 2, 4, and 5 indicates that Mo centers that have a limited number of S vacancies and do not do chemistry with thiophene or pyridine can break C–N bonds in nonaromatic or H-rich molecules such as cyclohexylamine.

III.2. Adsorption of Thiophene, Pyridine, and Cyclohexylamine on Ni/MoS_x. Metallic nickel is very efficient for breaking C–S or C–N bonds in organic compounds.^{15–19} In principle, one can try to enhance the reactivity of molybdenum sulfide toward thiophene and pyridine by depositing Ni on the surface. Previous studies have examined the deposition of Ni on MoS_x films²⁸ and a MoS₂(0002) surface.⁴¹ The results are similar in many aspects. At temperatures between 80 and 300 K, the Ni adatoms remain on top of the Mo substrate essentially in a metallic state (i.e., the admetal is not able to remove S from

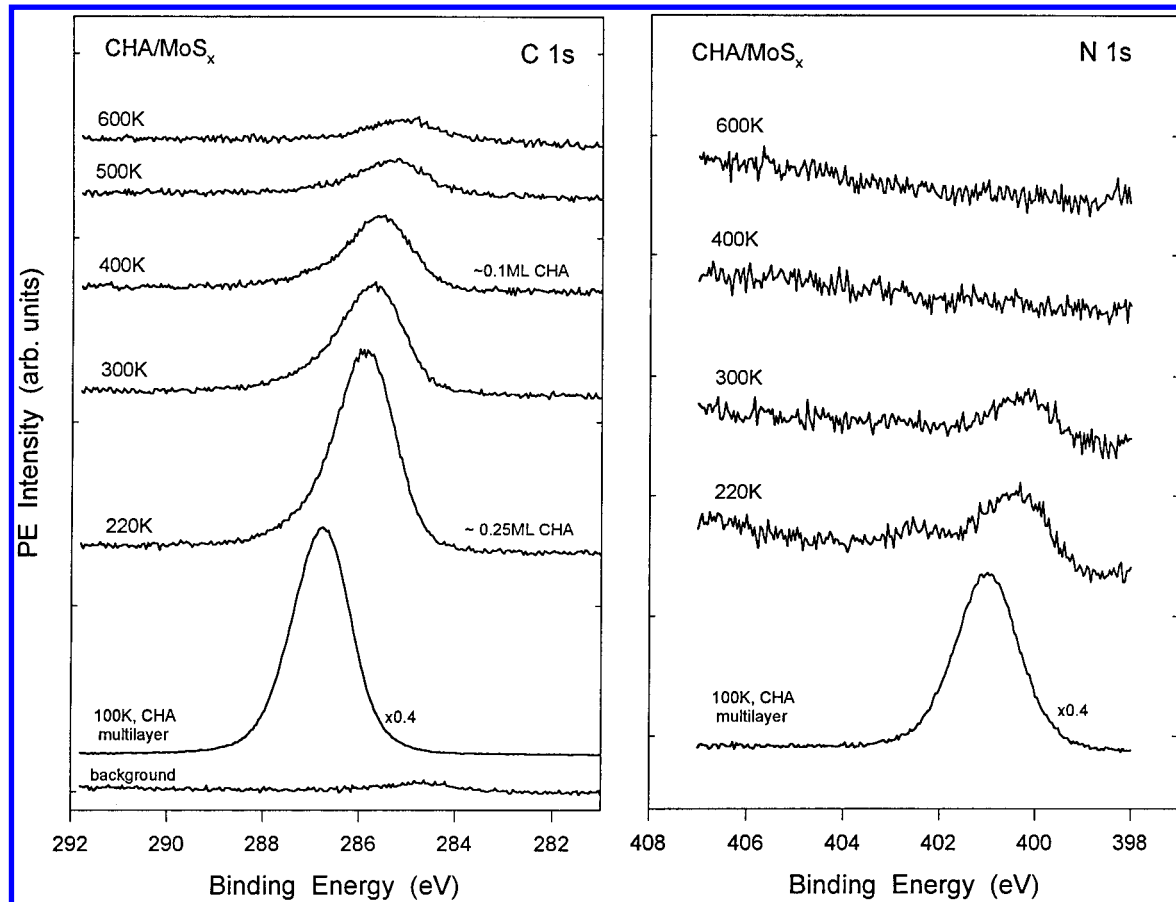


Figure 5. C 1s (left panel, $h\nu = 380$ eV) and N 1s (right panel, $h\nu = 500$ eV) spectra taken after dosing a multilayer of cyclohexylamine (CHA) to a MoS_x surface at 100 K followed by annealing to higher temperatures.

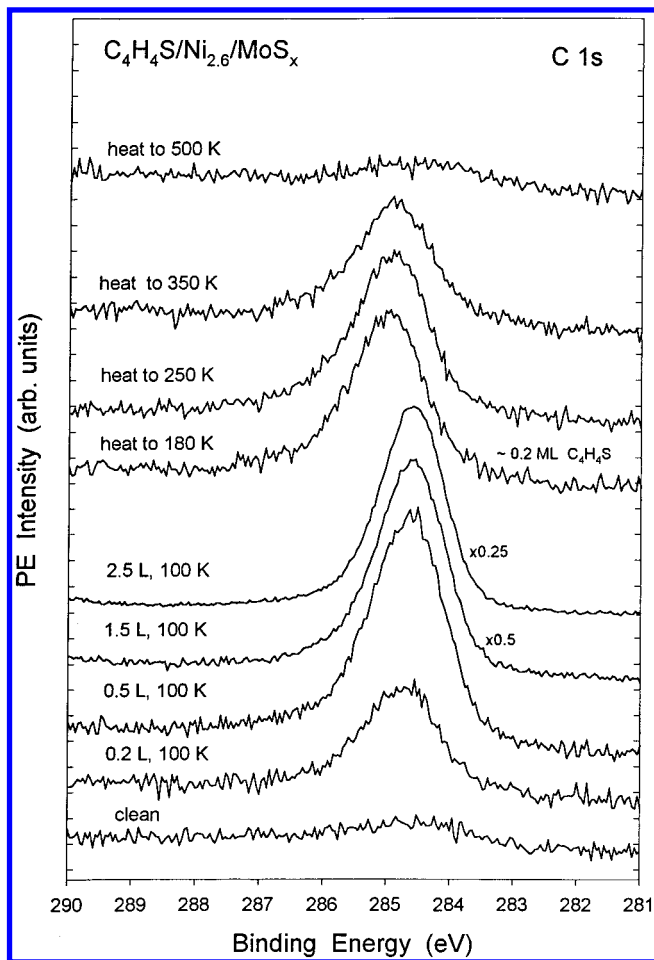


Figure 6. C 1s photoemission spectra ($h\nu = 380$ eV) for the adsorption of thiophene on $\text{Ni}_{2.6}/\text{MoS}_x$. Before dosing thiophene, the sample was heated to 600 K. Then, it was cooled to 100 K and exposed to thiophene. After a total dose of 2.5 L (multilayer coverage), the $\text{C}_4\text{H}_4\text{S}/\text{Ni}_{2.6}/\text{MoS}_x$ system was heated to the indicated temperatures.

Mo to form NiS_y).^{28,41} Heating to temperatures above 300 K induces a reduction in the Ni photoemission peaks as a consequence of three-dimensional clustering and penetration of the admetal into the molybdenum sulfide substrate.^{28,41} At 600 K, there is significant intermixing between the admetal and substrate. *This is the type of state that is most relevant for modeling NiMoS_x catalysts.*^{6,11,42} Figure 1 shows Mo 3d and valence spectra (c) acquired after depositing 2.6 ML of Ni on a MoS_x film at 300 K and annealing to 600 K ($\text{Ni}_{2.6}/\text{MoS}_x$ in our notation). The mixing with Ni induces a small decrease in the binding energy of the Mo 3d levels for MoS_x and a minor increase in the signal for metallic Mo around 228 eV. In the valence region, there is a large density of states (DOS) near the Fermi level that is not seen in pure MoS_x . This effect has been predicted by theoretical studies,¹³ which also indicate that this change should lead to a significant enhancement in the chemical activity with respect to pure molybdenum sulfide.

Thiophene was adsorbed on $\text{Ni}_{1.3}/\text{MoS}_x$ and $\text{Ni}_{2.6}/\text{MoS}_x$. Both Ni/MoS_x systems were preannealed at 600 K before dosing $\text{C}_4\text{H}_4\text{S}$ at 100 K. Figure 6 shows C 1s spectra for thiophene on $\text{Ni}_{2.6}/\text{MoS}_x$. As in the case of $\text{C}_4\text{H}_4\text{S}/\text{MoS}_x$, there is only one C 1s peak and the difference in binding energy between chemisorbed and physisorbed thiophene is less than 0.5 eV. At 180 K, upon desorbing the physisorbed thiophene,^{21,24} the coverage of the molecule on the surface is ~ 0.2 ML. In this case, the adsorption bonds are relatively strong and most of the chemi-

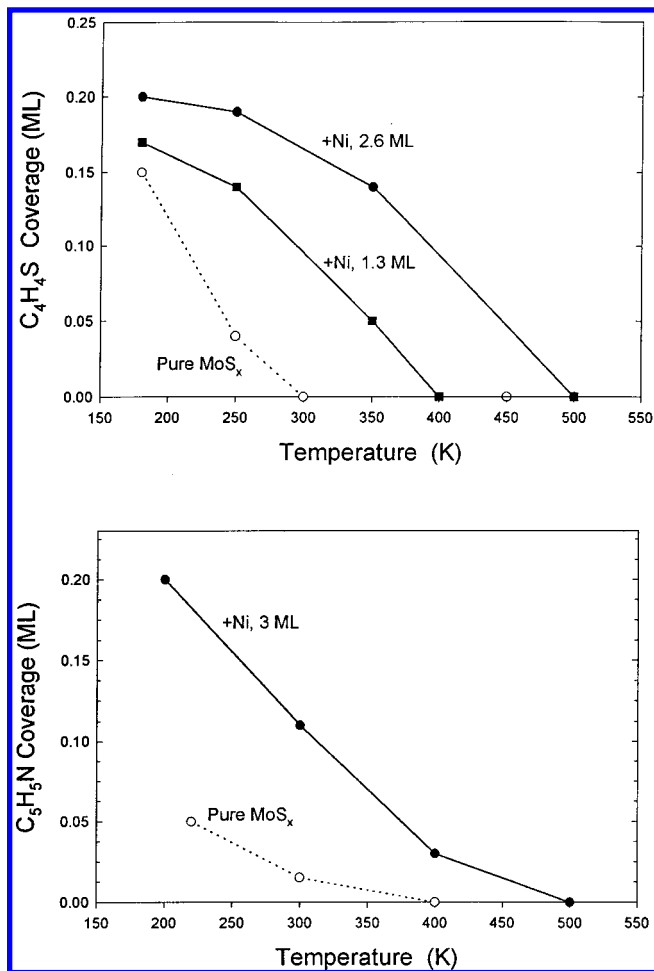


Figure 7. Coverages of thiophene (top panel) and pyridine (bottom panel) on MoS_x and Ni/MoS_x systems as a function of temperature. 1.3, 2.6, or 3 ML of Ni were deposited on MoS_x surfaces at 300 K, and the resulting Ni/MoS_x systems were heated to 600 K before depositing a multilayer of the organic molecules at 100 K. The thiophene and pyridine coverages were calculated by integrating the area under the peaks in the C 1s region (see section II) after subtracting contributions from the Mo features that appear at ~ 284.6 eV. The curves are drawn to guide the eye.

sorbed thiophene (~ 0.15 ML) is still present on the surface after heating to 350 K. By 500 K, all the adsorbed thiophene has disappeared and one sees the C 1s spectrum of clean MoS_x . No evidence is seen here for the dissociation of thiophene and the deposition of C or CH_y groups on molybdenum sulfide^{35,36} and Ni.^{15,16}

The trends in the results for the $\text{C}_4\text{H}_4\text{S}/\text{Ni}_{1.3}/\text{MoS}_x$ system were identical to those described for $\text{C}_4\text{H}_4\text{S}/\text{Ni}_{2.6}/\text{MoS}_x$, in the sense that the presence of Ni enhanced the adsorption energy of thiophene without inducing decomposition of the molecule. The top panel in Figure 7 compares the coverages of thiophene on pure and Ni-promoted MoS_x as a function of temperature. At 250 K, the coverage of thiophene on pure MoS_x is very small, whereas significant coverages are found on $\text{Ni}_{1.3}/\text{MoS}_x$ and $\text{Ni}_{2.6}/\text{MoS}_x$. Furthermore, the coverages of $\text{C}_4\text{H}_4\text{S}$ at 350 K on the Ni-promoted systems are bigger than that at 250 K on pure MoS_x . The larger the amount of Ni in the system, the bigger the coverage of thiophene and the more stable the molecule on the surface.

Results for pyridine on Ni/MoS_x are shown at the bottom of Figure 7. In these experiments, a multilayer of $\text{C}_5\text{H}_5\text{N}$ was deposited at 100 K on a Ni_3/MoS_x surface which was prean-

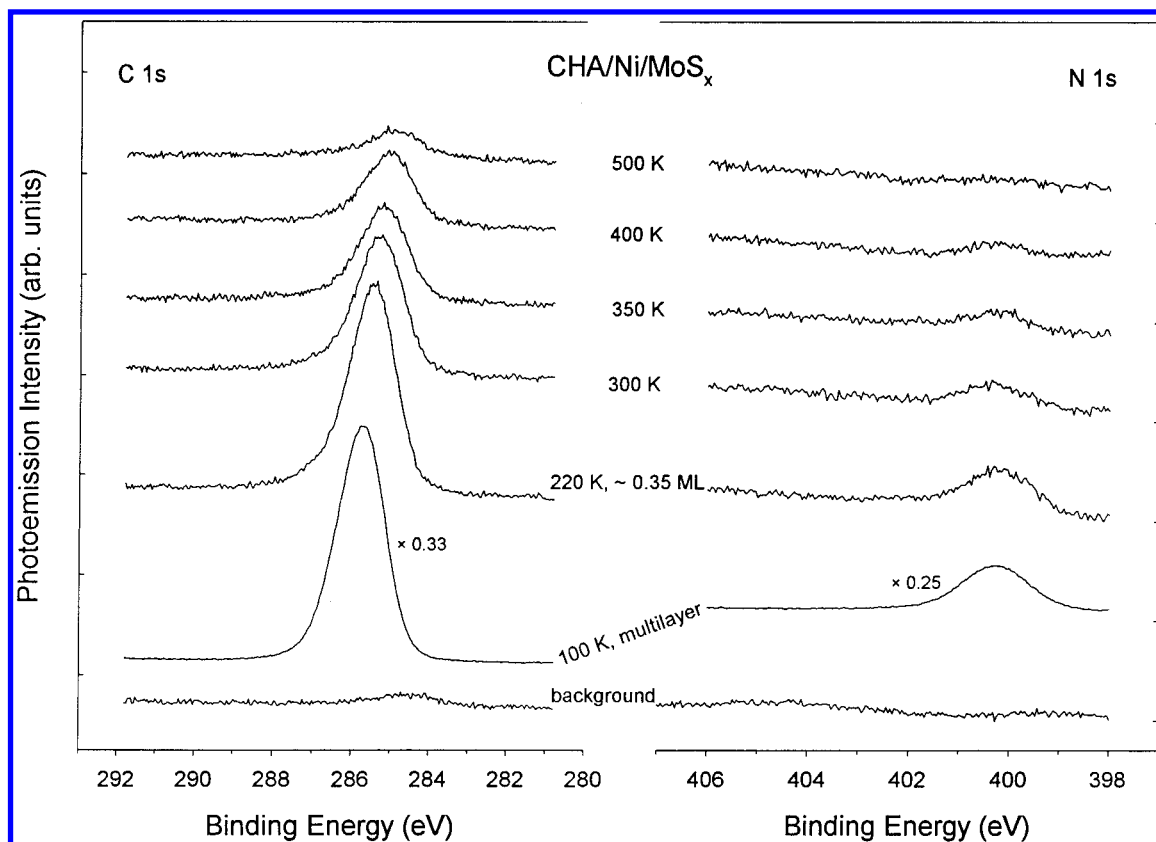


Figure 8. C 1s ($h\nu = 380$ eV) and N 1s ($h\nu = 500$ eV) spectra for the adsorption of cyclohexylamine (CHA) on a $\text{Ni}_{2.6}/\text{MoS}_x$ surface. The Ni/MoS_x system was preannealed to 600 K before depositing a multilayer of CHA at 100 K. Then, the surface was heated to the indicated temperatures.

nealed to 600 K. The Ni/MoS_x system clearly bonds pyridine much stronger than pure MoS_x , but we did not find evidence for the dissociation of the molecule. The C and N 1s features were always around 286 and 400.5 eV (respectively) and decreased simultaneously when the temperature was raised from 100 to 500 K.

In contrast to the behavior of thiophene and pyridine, cyclohexylamine undergoes extensive C–N bond cleavage on the Ni/MoS_x surfaces. Figure 8 displays C and N 1s spectra for the adsorption of CHA on the $\text{Ni}_{2.6}/\text{MoS}_x$ system of Figure 1. At 100 K, a multilayer of the molecule is on the surface. Upon heating to 220 K, the relative drop in intensity for the N 1s signal is larger than for the C 1s signal, which indicates that in addition to desorption of physisorbed CHA there was decomposition of part of the chemisorbed molecules ($\text{C}_6\text{H}_{11}\text{NH}_{2,\text{ads}} \rightarrow \text{NH}_{3,\text{gas}} + \text{C}_x\text{H}_{y,\text{ads}}$ ^{18,19}). From 220 to 300 K, again the decrease in the N 1s intensity is larger than in the C 1s intensity. At temperatures above 400 K, the N 1s signal was negligible or undetectable, while there was still a significant amount of carbon on the surface. As happened in the case of pure MoS_x , sites in the Ni/MoS_x system that do not activate thiophene or pyridine do chemistry with cyclohexylamine.

III.3. Adsorption of Thiophene and Cyclohexylamine on $\text{Ni}/\text{S}/\text{Mo}(110)$. For the Ni/MoS_x systems investigated in the previous section, it may be argued that the lack of chemistry with thiophene and pyridine is due to the fact that many of the Ni atoms are embedded deep in the molybdenum sulfide and not close enough to the surface to respond to the presence of the molecules. When Ni atoms are deposited on a $\text{Mo}(110)$ surface saturated with chemisorbed sulfur ($\theta_{\text{S}} \approx 0.9$ ML), they grow forming three-dimensional clusters and a substantial fraction of the sulfur moves from Mo to on top of the Ni

adlayer.²⁸ In a $\text{Ni}/\text{S}_{0.9}/\text{Mo}(110)$ system, the Ni atoms are always at or near the surface.²⁸

The bottom of Figure 9 shows S 2p spectra taken before and after depositing 1.3 ML of Ni on a $\text{S}_{0.9}/\text{Mo}(110)$ surface at 600 K. The deposition of Ni induces a change in the line shape and binding energy of the S 2p features. The dosing of thiophene at 100 K produces a C 1s peak centered around 284.5 eV and new features appear in the S 2p region between 163 and 165 eV. After annealing to 180 K, the physisorbed species desorb and ~ 0.1 ML of thiophene are left on the surface. This thiophene is weakly bound and desorbs upon further heating to 250 K. At the end, one gets C 1s and S 2p spectra that are almost identical to those seen before dosing thiophene. In the $\text{Ni}_{1.3}/\text{S}_{0.9}/\text{Mo}(110)$ system, although the Ni is close to the surface, the S prevents any strong interaction with the thiophene.

Sulfur can be removed from $\text{Mo}(110)$ ^{29,40} and Ni surfaces⁴³ by reaction with atomic hydrogen ($2\text{H}_{\text{gas}} + \text{S}_{\text{surface}} \rightarrow \text{H}_2\text{S}_{\text{gas}}$). Figure 10 shows C 1s spectra acquired after dosing thiophene at 300 K to a $\text{Ni}_{1.1}/\text{S}_{0.9}/\text{Mo}(110)$ surface that was previously exposed to a beam of atomic hydrogen.^{29,40} The treatment with hydrogen removed $\sim 40\%$ of the sulfur. Thiophene reacts with this surface. At 300 K, the C 1s features are broad and can be fitted by two peaks.^{23b,44} These can be assigned to chemisorbed thiophene and a decomposition product which does not contain C–S bonds.^{23b} By 400 K, the molecular thiophene has disappeared but hydrocarbon fragments remain on the surface.

In a set of experiments, we studied the adsorption of cyclohexylamine on the $\text{Ni}_{1.3}/\text{S}_{0.9}/\text{Mo}(110)$ surface that interacted weakly with thiophene. In agreement with the trends found on the MoS_x and Ni/MoS_x systems, the amine reacted readily with the $\text{Ni}_{1.3}/\text{S}_{0.9}/\text{Mo}(110)$ surface with some C–N bond breaking taking place below room temperature. At temperatures

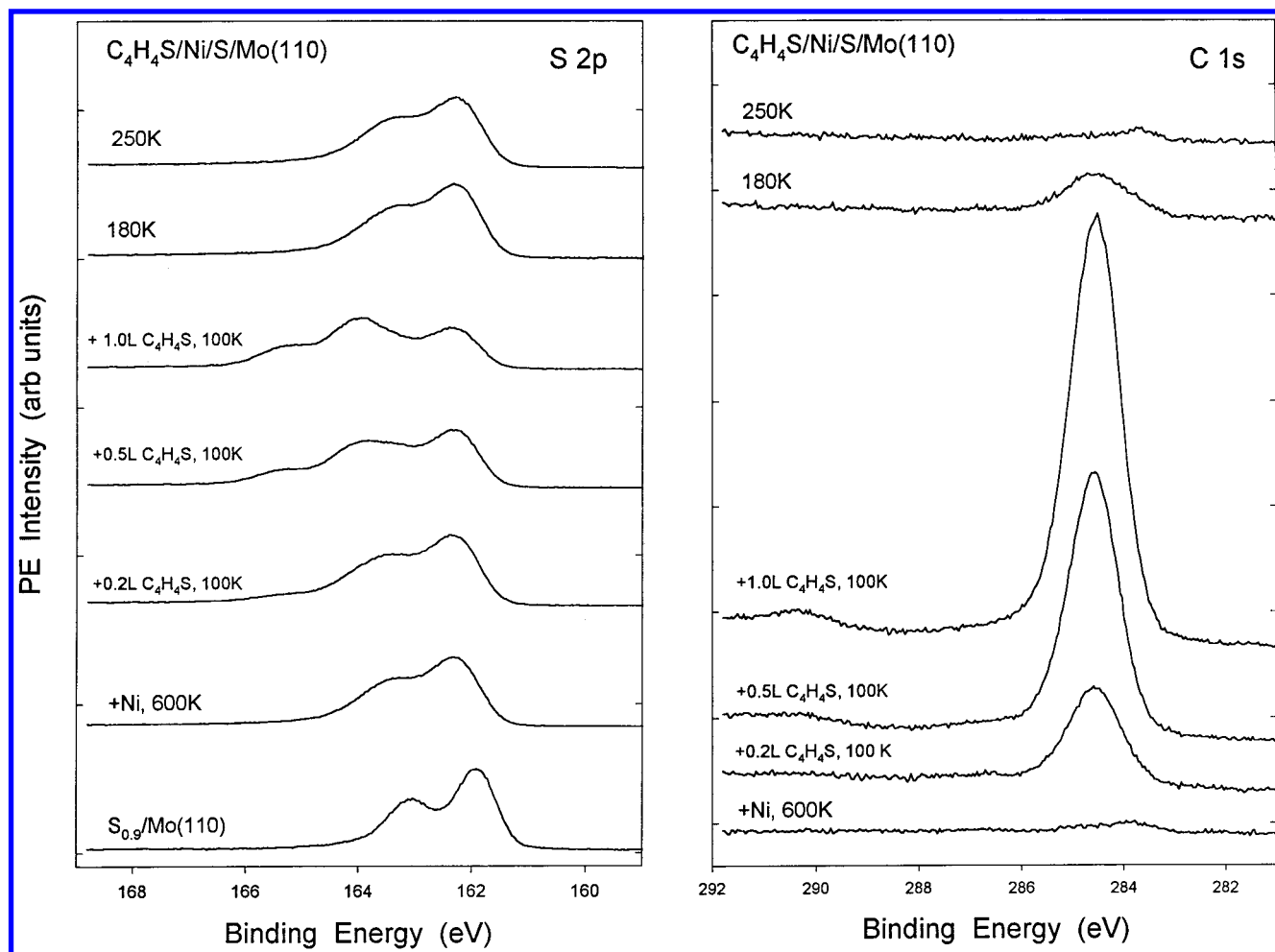


Figure 9. S 2p (left panel) and C 1s (right panel) data for the adsorption of thiophene on a Ni_{1.3}/S_{0.9}/Mo(110) surface at 100 K and subsequent annealing to 180 and 250 K. All the spectra were acquired using a photon energy of 380 eV.

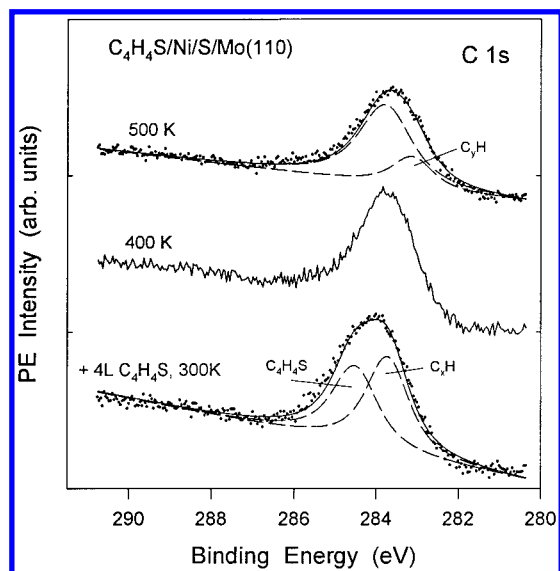


Figure 10. C 1s spectra for the adsorption of 5 L of thiophene on a Ni/S/Mo(110) surface at 300 K. Before dosing thiophene a Ni_{1.1}/S_{0.9}/Mo(110) system was exposed to a beam of atomic hydrogen^{29,40} and ~40% of the sulfur was removed from the surface. The C 1s spectra were curve fitted following the procedure described in refs 23b and 44.

between 300 and 400 K, two types of N-containing species with N 1s binding energies of ~400 and 401.5 eV were present on the surface. The behavior seen for the N 1s signal at temper-

atures lower than 400 K indicates that there was cleavage of the C–N bonds with NH₃ probably evolving into gas phase. Upon heating above 400 K, there was a continuous decrease in the C 1s signal likely as a consequence of the desorption of benzene.^{18,19}

IV. Discussion

Thiophene and pyridine are frequently used in HDS and HDN studies.^{6,10,13,15–17,20–26} On most metals, including Mo, these molecules undergo extensive decomposition leaving hydrocarbon fragments and S or N on the surface.^{15–19,21,22,45} Much weaker interactions have been observed for thiophene on oxides,^{23b,46} where there is no decomposition and the molecule generally desorbs below room temperature. This behavior is similar to that seen here for the adsorption of thiophene on MoS_x. In previous works,^{27–29} we have found that the type of MoS_x films used in this study exhibit a low reactivity toward H₂, CO, and O₂ that is very similar to that reported for the S basal plane of molybdenum sulfide, MoS₂(0002). These works indicate that the MoS_x films expose a limited amount of Mo atoms (0.1–0.2 ML) that are not fully coordinated to sulfur.^{27–29} It is known that the MoS₂(0002) surface interacts weakly with thiophene.^{38,39} The adsorption energy of the molecule is only 9.5 kcal/mol, and desorption takes place at temperatures below 200 K.^{38,39} For the C₄H₄S/MoS_x system, the bonding interactions are somewhat stronger and a few thiophene molecules remain on the surface at 250 K probably attached to Mo sites that have S vacancies. On such Mo sites, the adsorption energy of the

molecule can be as large as 15 kcal/mol. These Mo sites are still bonded to a significant number of S atoms and are not able to dissociate the molecule like pure metallic Mo.^{21,24} On MoS_x/Al₂O₃ catalysts, thiophene is weakly chemisorbed via S and desorbs in a single peak with a maximum rate of desorption at ~240 K and no decomposition.³⁷

Pyridine is a harder Lewis base than thiophene^{2a,8} and can form relatively strong bonds with pure and sulfided oxides (MoO_x/Al₂O₃, for example).⁴⁷ This is not the behavior seen for the molecule on the MoS_x surfaces, where the adsorption bonds are not much stronger than those of thiophene. This difference with respect to pure and sulfided oxides⁴⁷ may result from lack of a significant amount of S vacancies on the MoS_x substrate, and also the Lewis acidity of the metal centers in the sulfide can be smaller than that of similar centers in an oxide^{2,12,13} due to the fact that S is less electronegative than O.

Compared to pyridine, cyclohexylamine is more susceptible to C–N bond cleavage on the molybdenum sulfide surfaces. On metals, CHA undergoes disproportionation to form ammonia and benzene.^{18,19} A high reactivity is also observed on MoS_x, and in some cases the breaking of the C–N bond occurs below room temperature. Thus, Mo centers that have a limited number of S vacancies and do not do chemistry with thiophene, pyridine, H₂,²⁹ or O₂.^{27,29} are able to split the C–N bond in a nonaromatic (or H rich) molecule like cyclohexylamine. Simple thiols (RSH) also decompose on defective MoS₂(0002)³⁹ and MoS_x.⁴⁸ Thus, it appears that the activation of single C–S or C–N bonds does not require a lot of S vacancies in a molybdenum sulfide surface, and is easier than the activation of the bond in H₂.

Reaction with atomic hydrogen leads to a large number of S vacancies (i.e., coordinately unsaturated Mo atoms) in MoS_x.^{29,40} The vacancy-rich systems bond thiophene strongly and dissociate the molecule, but they are still less reactive than clean metallic Mo.²¹ Theoretical studies indicate that Mo centers of MoS₂ which are coordinated to only a few (≤4) S atoms can interact with thiophene and pyridine via a ring bonding configuration that is a good precursor for dissociation of the molecules.^{12,13,25} On the other hand, Mo centers that are pentacoordinated (one S vacancy) interact with thiophene and pyridine through the S or N lone pairs and, therefore, the distortions in the aromatic rings are negligible^{12,13,25} making very difficult the breaking of C–S or C–N bonds.

The deposition of Ni enhances the chemical activity of MoS_x surfaces. On the Ni/MoS_x systems, the adsorption energies of thiophene and pyridine are 5–10 kcal/mol larger than on pure MoS_x. The Ni/MoS_x systems have a heterogeneous nature with Ni embedded in the MoS_x substrate and also probably forming clusters on top of the surface.^{28,41} Ni 2p XPS spectra²⁸ indicate that the nickel does not form bulklike NiS_x compounds. Some “metallic” Mo sites are created as a result of the Ni ↔ MoS_x interactions (see left panel in Figure 1). Thus, several factors could contribute to the chemical activity of the Ni/MoS_x systems. The results of theoretical studies¹³ predict that Ni adatoms substantially increase the chemical activity of MoS₂ by providing active sites for the chemisorption of molecules on S-terminated terraces or by making Mo more reactive toward organosulfur molecules through Ni ↔ Mo and Ni ↔ S ↔ Mo interactions. Depending on the type of adsorption site, the theoretical studies predict that the enhancement in the bonding energy of thiophene varies between 4 and 12 kcal/mol.¹³ These values are consistent with the trends seen in the experimental results of Figure 7.

Metallic nickel is well-known for its high reactivity toward thiophene. On Ni(100)¹⁶ and Ni(111),¹⁵ sulfur is easily removed from the ring with the scission of the C–S bonds (C₄H₄S_{gas} →

S_{ads} + C₄H_{4,ads}) taking place at temperatures between 100 and 150 K. For pyridine on Ni(100),^{17b} molecular adsorption is observed at low temperatures and the adsorbate transforms into an α-pyridil species around 300 K, with the breaking of the C–N bonds occurring at temperatures higher than 450 K. For pyridine and aniline derivatives, the cleavage of the C–N bonds usually takes place at temperatures between 200 and 400 K on surfaces of metallic nickel.^{17–19} Interestingly, no dissociation of thiophene or pyridine is observed on the Ni/MoS_x systems. The Ni ↔ S interactions reduce the chemical reactivity of nickel. Thus, the presence of the admetal alone is not enough to promote or facilitate the cleavage of C–S or C–N bonds during HDS or HDN reactions over molybdenum sulfide catalyst. The extra and necessary element that is missing is probably hydrogen.

There is a commonly held notion that HDS and HDN reactions for molecules such as thiophene and pyridine probably proceed via hydrogenation of the aromatic ring, followed by hydrogenolysis of the C–S or C–N bonds.^{11,49,50} This is consistent with the trends seen in this work for the denitrogenation of pyridine and cyclohexylamine. From this viewpoint, Ni is a promoter of HDS and HDN processes because it provides the H atoms that react with the S- and N-containing molecules on the catalysts. Previous studies have shown that in Ni/MoS_x the metal adatoms help to increase the coverage of H on the surface.^{28,51} For the Ni/MoS₂ system, ab initio SCF calculations indicate that Ni greatly enhances the probability for H₂ dissociation by increasing the stability of the transition state and products of this reaction.¹³ The H provided by Ni can hydrogenate the aromatic C–S and C–N bonds and facilitate their rupture. Or, it can remove sulfur from the surface (2H_{ads} + S_{ads} → H₂S_{gas}) creating vacancies around the metal centers^{14,28,29} and enhancing in this way their ability for breaking C–S and C–N bonds.

V. Conclusions

We have examined the adsorption of thiophene, pyridine, and cyclohexylamine on MoS_x films that exhibit Mo 3d and valence spectra that are very similar to those of MoS₂. On the MoS_x systems, the behavior of thiophene closely resembles that seen on MoS₂(0002). The molecules are weakly chemisorbed, and most of them desorb at temperatures around 200 K. A small fraction of the adsorbed thiophene is bonded to Mo sites that have S vacancies and desorbs between 250 and 300 K. A similar behavior is observed for adsorbed pyridine. In contrast, adsorbed cyclohexylamine displays a rich chemistry. Mo centers that have a limited number of S vacancies and do not do chemistry with thiophene, pyridine, or H₂ are able to cleave the C–N bond in a nonaromatic H-rich molecule like cyclohexylamine.

The addition of Ni enhances the chemical activity of MoS_x. On the Ni/MoS_x systems, the adsorption energies of thiophene and pyridine are 5–10 kcal/mol larger than on pure MoS_x. But no dissociation of these molecules is observed on the Ni/MoS_x surfaces. The Ni ↔ S interactions reduce the reactivity of nickel, and it appears that the presence of the admetal alone is not enough to promote or facilitate the cleavage of aromatic C–S or C–N bonds in HDS or HDN reactions. Hydrogen probably plays an important role in this aspect. Extensive decomposition of thiophene is seen after creating S vacancies in MoS_x and Ni/S/Mo(110) surfaces by reaction with atomic hydrogen (2H_a + S_{surface} → H₂S_{gas} + vacancy_{surface}).

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