Infrared Spectroscopic Investigation of Thiophene Adsorption on Silica-Supported Nickel Phosphide Catalysts

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The surface chemistry of thiophene on reduced and sulfided Ni/SiO_2 and Ni_2P/SiO_2 catalysts has been investigated by using infrared (IR) spectroscopy. Thiophene is quite reactive on Ni_2P/SiO_2 catalysts; even at 190 K, cleavage of some C−S bonds was observed, forming 1,3-butadiene-like species on the surface. Annealing this thiophene-dosed Ni_2P/SiO_2 catalyst to 250 K resulted in the formation of adsorbed butenes and other thiophene decomposition products on the surface. In the presence of H_2 and elevated temperatures, the reactivity of thiophene on Ni_2P/SiO_2 catalysts increased, producing adsorbed butenes and saturated hydrocarbon fragments. Coadsorption experiments indicate that CO and thiophene compete for the same sites on the Ni_2P/SiO_2 catalysts, as preadsorbed CO blocked the adsorption of thiophene on Ni_2P sites. The IR spectroscopic data for the adsorption and reactivity of thiophene on reduced and sulfided Ni/SiO_2 and Ni_2P/SiO_2 catalysts correlate well with the trend of HDS activity of the catalysts. Specifically, the Ni_2P/SiO_2 catalysts are more reactive toward thiophene than reduced and sulfided Ni/SiO_2 catalysts in UHV and in an atmospheric pressure flow reactor. The increased reactivity of thiophene on Ni_2P/SiO_2 catalysts in UHV may explain the high turnover frequency previously reported for Ni_2P/SiO_2 catalysts relative to sulfided Ni/SiO_2, Mo/SiO_2, and $Ni−Mo/SiO_2$ catalysts.

Introduction

Environmental regulations requiring a dramatic reduction in the allowable sulfur levels in transportation fuels and the need to process lower quality petroleum feedstocks have prompted research focused on developing highly active hydrotreating catalysts.[1,2] A new class of materials, the transition metal phosphides (e.g., MoP,[3−8] WP,[8−10] and Ni_2P[8,11−17]), has shown high hydrodesulfurization (HDS) activity. Silica-supported nickel phosphide (Ni_2P/SiO_2) has shown particular promise as a future hydroprocessing catalyst. Specifically, Ni_2P/SiO_2 catalysts have demonstrated the highest HDS activity among the transition metal phosphides tested,[8,13,14,16] and have been reported to have a higher activity, under industrial conditions, than commercial $Ni−Mo/Al_2O_3$ and $Co−Mo/Al_2O_3$ catalysts for the HDS of a model feed containing quinoline (2000 ppm N), dibenzothiophene (3000 ppm S), tetralin (20 wt %), and tetradecane (balance).[8] Therefore, obtaining a detailed understanding of the HDS catalytic properties of Ni_2P/SiO_2 catalysts is of primary importance. To this end, Ni_2P/SiO_2 catalysts have been characterized by using a variety of techniques including chemisorption,[15] X-ray photoelectron spectroscopy (XPS),[15] solid-state NMR spectroscopy,[18] transmission electron microscopy (TEM),[15] extended X-ray absorption fine structure,[11,12,16] and X-ray diffraction (XRD).[13−15,18] These studies led to the conclusion that Ni_2P has metallic properties and that the high HDS activity of Ni_2P/SiO_2 catalysts can be traced to both a high site density and a high turnover frequency (TOF).[15]

In a previous study, we performed an IR spectroscopic investigation of CO adsorption on Ni_2P/SiO_2 catalysts to characterize the sites available on these catalysts for the HDS

of thiophene.[17] The IR spectroscopic data for the adsorption of CO on reduced and sulfided Ni/SiO_2 and Ni_2P/SiO_2 catalysts correlated well with the trend of HDS activity of the catalysts. Specifically, we observed a higher site density and higher ΔH_{ads} for CO adsorption on the Ni_2P/SiO_2 catalysts compared to reduced and sulfided Ni/SiO_2 catalysts. The IR spectroscopic data also verified that Ni_2P has metallic-like properties. At 298 K, CO adsorbed on *cus* $Ni^{\delta+}$ ($0 < \delta < 1$) sites on reduced Ni_2P/SiO_2 catalysts, exhibiting a characteristic ν_{CO} absorbance at 2083 cm^{-1} that indicates that the magnitude of δ is likely closer to 0 than to 1. Treatment of the Ni_2P/SiO_2 catalysts with a 3.03 mol % H_2S/H_2 mixture shifts the ν_{CO} absorbance to 2093 cm^{-1}.

To be an effective probe molecule, CO must specifically interact with the surface sites on Ni_2P/SiO_2 catalysts where thiophene HDS occurs.[19−21] However, we observed four different ν_{CO} absorbances for the adsorption of CO on reduced and sulfided Ni_2P/SiO_2 catalysts with the following assignments: (1) CO terminally bonded to *cus* $Ni^{\delta+}$ ($0 < \delta < 1$) sites (2083−2093 cm^{-1}); (2) CO adsorption on $Ni^{\delta+}$ ($0 < \delta < 1$) bridge sites (1914 cm^{-1}); (3) CO terminally bonded to P ($\sim$2200 cm^{-1}) as P=C=O species; and (4) formation of $Ni(CO)_4$ (2056 cm^{-1}). We concluded that CO should be used cautiously for titrating sites on Ni_2P/SiO_2 catalysts. In this paper, we present IR spectroscopic data for the adsorption of thiophene on reduced and sulfided Ni_2P/SiO_2 catalysts. For comparison purposes, we carried out parallel IR spectroscopic studies of thiophene on reduced and sulfided Ni/SiO_2 catalysts. Finally, to determine if IR spectroscopic investigation of the adsorption of CO on sulfided and reduced Ni_2P/SiO_2 catalysts can be used to qualitatively characterize the active sites on which thiophene HDS occurs, we also used IR spectroscopy to study the coadsorption of CO and thiophene on reduced Ni_2P/SiO_2 catalysts.

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Experimental Methods

Catalyst Preparation. *Ni₂P/SiO₂.* A 20 wt % Ni$_2$P/SiO$_2$ catalyst was prepared following a procedure described in detail elsewhere.[15] Briefly, 4.90 g of nickel nitrate (Ni(NO$_3$)$_2$·6H$_2$O) was dissolved in approximately 10 mL of deionized water. The solution was impregnated onto 5.0 g of calcined silica (SiO$_2$, Cab-O-Sil, M-7D grade, 200 m^2/g) and dried at 373 K. The impregnated silica was calcined at 773 K for 2 h. After calcination, the sample was impregnated with 1.55 g of ammonium dihydrogen phosphate (NH$_4$H$_2$PO$_4$) and dried at 373 K overnight. The oxidic precursor was reduced via temperature-programmed reduction (TPR) in flowing H$_2$ (150 sccm) from 298 to 923 K (1 K/min). The freshly prepared Ni$_2$P/SiO$_2$ catalyst was then cooled to room temperature in flowing H$_2$, flushed with flowing He (60 sccm) for 15 min, and then passivated in a flow of 1.0 mol % O$_2$/He (30 sccm) for 2 h to yield silica-supported Ni$_2$P. Samples of the *passivated* Ni$_2$P/SiO$_2$ catalyst were transferred through air to a flow reactor or a UHV system where they were reduced or sulfided as described later.

Ni/SiO₂ and Sulfided Ni/SiO₂. For comparison purposes, an oxidic precursor (NiO/SiO$_2$) of reduced and sulfided Ni/SiO$_2$ catalysts was prepared with a Ni loading similar to that of the 20 wt % Ni$_2$P/SiO$_2$ catalyst. Specifically, 4.90 g of nickel nitrate was dissolved in approximately 10 mL of deionized water and impregnated onto 5.0 g of silica. The impregnated silica was dried at 373 K and calcined at 773 K for 3 h. Samples of the NiO/SiO$_2$ precursor were transferred through air to a flow reactor or a UHV system where they were reduced or sulfided as described later.

Thiophene HDS Activity Measurements. Thiophene HDS activity measurements were carried out with an atmospheric pressure flow reactor that has been described in detail elsewhere.[22] Activity measurements were carried out at a reaction temperature of 643 K, using a reactor feed consisting of a 3.2 mol % thiophene/H$_2$ mixture. Prior to the measurement of thiophene HDS activities, samples of the NiO/SiO$_2$ precursor or of the Ni$_2$P/SiO$_2$ catalyst were subjected to either reduction or sulfidation pretreatments. All catalysts were subjected to a degas in He (60 sccm) at room temperature for 30 min. For a reduction pretreatment, the degassed catalyst was reduced by heating from room temperature to 650 K (5.9 K/min) in 60 sccm H$_2$ and holding at 650 K for 2 h. For a sulfidation pretreatment, the degassed catalyst was sulfided by heating from room temperature to 650 K (5.9 K/min) in a 60 sccm flow of 3.0 mol % H$_2$S/H$_2$ and holding at 650 K for 2 h. Following each pretreatment, the temperature was adjusted to the reaction temperature of 643 K and the flow was switched to the 3.2 mol % thiophene/H$_2$ reactor feed (50 sccm). The reaction was carried out for over 100 h, with automated sampling of the gas effluent occurring at 1-h intervals. Thiophene HDS activities (nmol of thiophene/g of catalyst/s) were calculated from the total product peak areas determined from the chromatogram after 100 h of reaction time.

Infrared Spectroscopy Measurements. The IR spectroscopic experiments were conducted in an ion pumped (110 L/s) ultrahigh vacuum (UHV) chamber that has a base pressure of ∼5 × 10^{-9} Torr. This chamber is equipped with a Mattson RS-1 FTIR spectrometer outfitted with a narrow-band MCT detector and a Leybold-Inficon Quadrex 200 quadrupole mass spectrometer for residual gas analysis. The FTIR spectrometer and the mass spectrometer are interfaced to a personal computer for data acquisition and treatment. The chamber also contains a high-pressure cell that can be isolated from the UHV chamber. This system has been described in detail elsewhere.[23]

The catalyst under study was mounted in the UHV system following a procedure described previously.[23] Briefly, 5.0−15.0 mg of the desired catalyst was pressed at 10 000 psi into a nickel metal mesh (50 × 50 mesh size, 0.002 in. wire diameter); the area of the pressed samples was 0.80 cm^2. A chromel−alumel thermocouple was spot-welded to the nickel mesh to monitor the temperature of the sample. This assembly was then mounted onto a sample holder equipped with resistive heating and liquid-nitrogen cooling.

Following mounting in the UHV system, the catalyst samples were evacuated to 10^{-3} Torr over a period of ∼30 min. Unless otherwise stated, the catalysts were then either reduced or sulfided in situ. Specifically, the catalysts were reduced in flowing H$_2$ (60 sccm) at 650 K for 1 h or sulfided in 100 Torr of a 3.03 mol % H$_2$S/H$_2$ mixture at 625 K for 15 min. To remove loosely bound species from the surface of both the reduced and sulfided catalysts, the high-pressure cell was then evacuated to ∼1 × 10^{-7} Torr prior to annealing the sample at 650 K for 1 min.

Transmission FTIR spectra were acquired in the 4000−1000 cm^{-1} range by collecting 128 scans at 4-cm^{-1} resolution. The sample spectrum was ratioed against a background spectrum acquired by using a blank nickel mesh mounted in the sample holder. Depending upon the experiment, the background spectrum was acquired either in UHV, in 5.0 Torr of CO, or in 5.0 Torr of thiophene. All IR spectra were prepared by subtracting the IR spectrum obtained prior to dosing from the IR spectrum acquired after dosing. The IR spectra presented in this study have been reproduced without any smoothing treatment.

Thiophene Adsorption at Low Temperature. Following pretreatment, a reduced/sulfided catalyst sample (or pure silica) was cooled to 150 K at a pressure of ∼1 × 10^{-8} Torr and a background IR spectrum was acquired. Following acquisition of the pre-dose IR spectrum, the sample was heated to 190 K, and then the sample was exposed to 0.100 Torr of thiophene for 40 min. The thiophene used in this study (Aldrich Chemical Co., 99+% purity) was purified according to the procedure of Spies and Angelici[24] and by repeated freeze−pump−thaw cycles. Following the thiophene exposure, the high-pressure cell was evacuated to UHV pressures and the sample was cooled to 150 K. An IR spectrum was then collected at a temperature of 150 K. The sample was subsequently annealed at 175 K for 1 min in UHV. After the sample was cooled to 150 K, another IR spectrum was collected. The sample was then annealed to higher temperatures in 25-K increments and an IR spectrum was collected at 150 K after each anneal cycle until all of the adsorbed thiophene had either desorbed or undergone reaction.

Thiophene and Thiophene/H₂ Exposures at Elevated Temperatures. Following pretreatment, samples of a sulfided Ni/SiO$_2$ catalyst and of a reduced Ni$_2$P/SiO$_2$ catalyst were cooled to room temperature in UHV and an IR spectrum was acquired. The catalyst was then heated to 300 K, exposed to either 5.0 Torr of thiophene or a 3.2 mol % thiophene/H$_2$ gas mixture (P_{Th} = 5.0 Torr; P_{H_2} = 151.25 Torr) at 300 K and an IR spectrum was acquired. While in the presence of the desired vapor, the reduced Ni$_2$P/SiO$_2$ (or sulfided Ni/SiO$_2$) catalyst was annealed from 300 K to increasing temperatures in 25-K increments for 1 min. After each anneal, the reduced Ni$_2$P/SiO$_2$ (or sulfided Ni/SiO$_2$) catalyst was cooled to 300 K in the presence of the thiophene or the thiophene/H$_2$ gas mixture prior to collecting an IR spectrum.
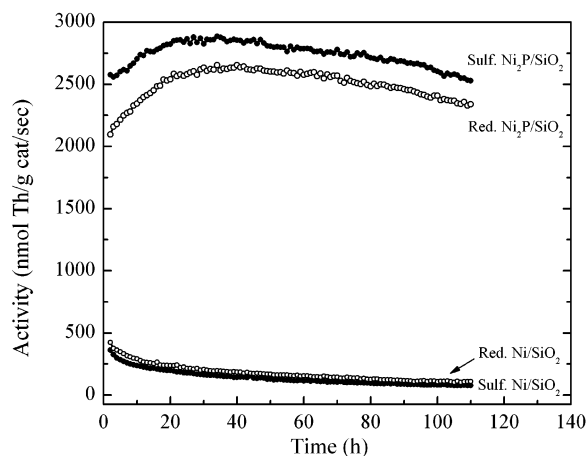
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Figure 1. Thiophene HDS activity data for reduced and sulfided Ni/SiO_2 and Ni_2P/SiO_2 catalysts.

CO and Thiophene Coadsorption at Low Temperature. Two different coadsorption experiments were performed. In the first, a sample of a reduced Ni_2P/SiO_2 catalyst was exposed to 5.0 Torr of CO at 150 K, evacuated to UHV, heated to 190 K, and then exposed to 0.100 Torr of thiophene for 40 min. The high-pressure cell was then evacuated to UHV, and the sample re-cooled to 150 K. IR spectra were obtained for the reduced Ni_2P/SiO_2 catalyst at different steps in the coadsorption experiment: (1) in the presence of 5.0 Torr of CO at 150 K, (2) after being evacuated to UHV at 150 K, (3) after heating to 190 K, (4) after dosing with thiophene and evacuating to UHV at 190 K, and (5) after re-cooling to 150 K. This enabled us to monitor changes in intensity and peak position of the ν_{CO} absorbances as well as the appearance of vibrational bands associated with adsorbed thiophene.

In the second experiment, a sample of a reduced Ni_2P/SiO_2 catalyst was exposed to 0.100 Torr of thiophene for 40 min at 190 K, evacuated to UHV, cooled to 150 K, exposed to 5.0 Torr of CO, and then evacuated to UHV. IR spectra were acquired for the reduced Ni_2P/SiO_2 catalyst at different stages of this coadsorption experiment: (1) after dosing with thiophene and cooling to 150 K in UHV, (2) in the presence of 5.0 Torr of CO at 150 K, and (3) after evacuating to UHV at 150 K. These spectra were collected to monitor changes in the intensity and frequency of the vibrational bands associated with adsorbed thiophene and the appearance of ν_{CO} absorbance features.

Results

Thiophene HDS activity data as a function of time on-stream for reduced and sulfided Ni/SiO_2 and Ni_2P/SiO_2 catalysts are shown in Figure 1. As reported previously,[15] Ni_2P/SiO_2 catalysts have high thiophene HDS activities when pretreated by reduction or sulfidation at 650 K. The HDS activities of the Ni_2P/SiO_2 catalysts reached a maximum after 25−40 h on-stream and then declined gradually thereafter. After 100 h on-stream, the sulfided Ni_2P/SiO_2 catalyst was ∼10% more active than the reduced Ni_2P/SiO_2 catalyst. As shown in Figure 1, the reduced and sulfided Ni/SiO_2 catalysts had very low HDS activities which decreased monotonically as a function of time on-stream. The HDS activities of the Ni/SiO_2 catalysts were significantly more sensitive to the pretreatment utilized than was observed for the Ni_2P/SiO_2 catalysts. After 100 h on-stream, the reduced Ni/SiO_2 catalyst was ∼30% more active than the sulfided Ni/SiO_2 catalyst. The effect of P on the HDS activities of silica-supported Ni catalysts is dramatic; the reduced Ni_2P/SiO_2 catalyst was observed to be ∼21 times more active than the reduced Ni/
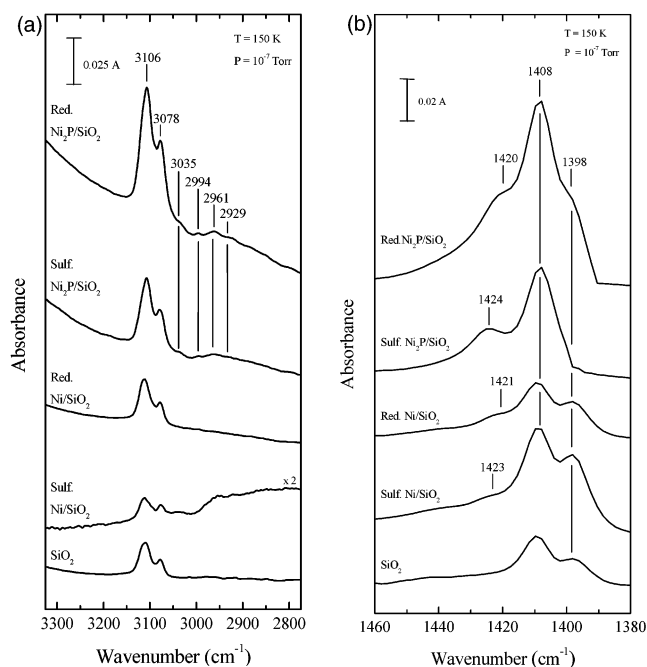

Figure 2. Infrared spectra in the (a) ν_{CH} and (b) $\nu_{(C=C)sym}$ regions for thiophene adsorbed on SiO_2 and on reduced and sulfided Ni/SiO_2 and Ni_2P/SiO_2 catalysts. The IR spectra were acquired in UHV following dosing at 190 K and then cooling to 150 K.

SiO_2 catalyst after 100 h, while the sulfided Ni_2P/SiO_2 catalyst was observed to be ∼30 times more active than the sulfided Ni/SiO_2 catalyst after 100 h.

Infrared Spectroscopy Measurements of Thiophene Adsorption at Low Temperature. Shown in Figure 2 are the IR spectra collected for reduced and sulfided Ni/SiO_2 and Ni_2P/SiO_2 catalysts (and pure silica) exposed to 0.100 Torr for 40 min at 190 K and then cooled to 150 K in UHV. After IR spectra were collected at 150 K, the thiophene dosed catalysts were annealed at increasing temperatures (in 25-K increments) for 1 min. Infrared spectra were collected at 150 K after each anneal cycle. Thiophene adsorbs molecularly on Ni/SiO_2 catalysts dosed at 190 K, as indicated by the presence of aromatic ν_{CH} absorbances at 3078 and 3106 cm^{-1} and the absence of aliphatic ν_{CH} absorbances in the 2800−3000-cm^{-1} region. It has been shown previously that the $\nu_{(C=C)sym}$ absorbance of thiophene is sensitive to the bonding mode of adsorbed thiophene on catalyst surfaces.[25−28] For pure silica, the $\nu_{(C=C)sym}$ absorbance located at 1398 cm^{-1} is assigned to thiophene bonded via its sulfur atom to hydroxyl groups ($C_4H_4S\cdots H-O-Si$) of SiO_2 based on analogy with thiophene adsorbed on pure γ-Al_2O_3.[25] The $\nu_{(C=C)sym}$ absorbance at 1408 cm^{-1} is assigned to a high coverage thiophene species whose adsorption site has not been determined.[25] For thiophene adsorbed on the reduced Ni/SiO_2 catalyst, a weak $\nu_{(C=C)sym}$ absorbance is apparent at ∼1421 cm^{-1} (Figure 2b). On the basis of analogy to the vibrational spectra of thiophene coordinated in organometallic complexes[28] as well as adsorbed on sulfided Mo/Al_2O_3[26,27] and Rh/Al_2O_3[27] catalysts, this absorbance is assigned to thiophene adsorbed via its sulfur atom ($\eta^1(S)$) to coordinately unsaturated (cus) Ni sites. This $\nu_{(C=C)sym}$ absorbance is observed at ∼1423 cm^{-1} for thiophene adsorbed on a sulfided Ni/SiO_2 catalyst.

Infrared spectra collected after annealing the reduced and sulfided Ni/SiO_2 catalysts (and pure silica) to 250 K are shown in Figure 3. No thiophene remains adsorbed on the silica support, but there is evidence for thiophene reaction on the reduced Ni/SiO_2 catalyst after annealing to 250 K. Weak ν_{CH}
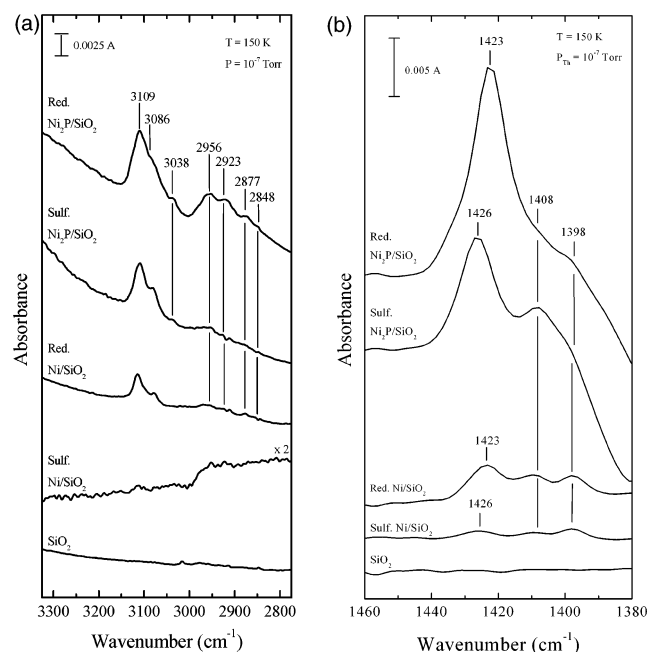
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Figure 3. Infrared spectra in the (a) ν_{CH} and (b) $\nu_{(C=C)sym}$ regions for thiophene adsorbed on SiO_2 and on reduced and sulfided Ni/SiO_2 and Ni_2P/SiO_2 catalysts. The IR spectra were acquired in UHV following dosing at 190 K, annealing to 250 K for 1 min, and then cooling to 150 K.

absorbances observed in the 2800–3000-cm^{-1} region for the thiophene-dosed, reduced Ni/SiO_2 catalyst indicate the formation of C_4 hydrocarbons as well as possibly the production of smaller hydrocarbon fragments (Figure 3a).[27,29–32] This is not surprising since thiophene decomposition and the formation of adsorbed C_4 hydrocarbon species has been reported to occur on the Ni(111) and Ni(100) single-crystal surfaces at low temperatures.[33–38] Huntley et al.[33] reported that C–S bond scission of adsorbed thiophene on the Ni(111) single-crystal surface was complete by 150 K. The formation of adsorbed hydrocarbons on the Ni(111) surface, due to the decomposition of adsorbed thiophene, was observed in high-resolution electron energy loss spectra (HREELS) collected after annealing the thiophene-dosed crystal at 250 K for 1 min.[33] Similarly, IR spectroscopic investigation by others of the adsorption of thiophene on silica-supported Ni catalysts indicates that hydrocarbon fragments formed on these catalysts upon thiophene adsorption at 300 K.[39,40] As discussed later, however, we believe that a significant fraction of the observed reactivity in these earlier studies of thiophene adsorption on SiO_2 and Ni/SiO_2 catalysts may be associated with thiol impurities in the thiophene used. While we detected a small amount of thiophene reaction after annealing to 250 K, most of the adsorbed thiophene did not react on the reduced Ni/SiO_2 catalyst, as indicated by the strong aromatic ν_{CH} absorbances at 3078 and 3106 cm^{-1} (Figure 3a), the $\nu_{(C=C)sym}$ absorbance at 1423 cm^{-1} (Figure 3b), and the ν_{ring} absorbance at 1604 cm^{-1} (not shown), which are associated with molecular thiophene adsorbed on the catalyst. The increased intensity of the $\nu_{(C=C)sym}$ absorbance at 1423 cm^{-1} relative to the $\nu_{(C=C)sym}$ absorbances at 1398 and 1408 cm^{-1} is expected since very little thiophene remains adsorbed to the SiO_2 support after annealing to 250 K (Figure 3b). This observation confirms that the $\nu_{(C=C)sym}$ absorbance at 1423 cm^{-1} is associated with thiophene adsorbed on the Ni sites of the reduced Ni/SiO_2 catalyst. Annealing to temperatures greater than 300 K resulted in the complete reaction and/or desorption of molecular thiophene.

We observed no evidence of thiophene reactivity on sulfided Ni/SiO_2 catalysts exposed to thiophene at 190 K (Figure 2). The observed thiophene vibrations are identical with those assigned, in the previous paragraph, for thiophene adsorption on a reduced Ni/SiO_2 catalyst at 190 K. The IR spectrum has been multiplied by two since only a small amount of thiophene adsorbed on Ni sites due to site blocking by adsorbed sulfur and because the sulfided Ni/SiO_2 catalysts were highly absorbing, so very little transmitted light reached the detector. Annealing the sulfided Ni/SiO_2 catalyst to 250 K (Figure 3) resulted in desorption of most of the thiophene, since we do not observe discernible aromatic ν_{CH} absorbances and only very weak $\nu_{(C=C)sym}$ absorbances. It is interesting to note that the weak $\nu_{(C=C)sym}$ absorbance is shifted to 1426 cm^{-1} from its value of 1423 cm^{-1} for the reduced Ni/SiO_2 catalyst.

The adsorption and reactivity of thiophene on reduced and sulfided Ni_2P/SiO_2 catalysts are significantly different from those observed on the reduced and sulfided Ni/SiO_2 catalysts. Most of the thiophene adsorbs molecularly on the reduced Ni_2P/SiO_2 catalyst at 190 K, as indicated by the aromatic ν_{CH} absorbances 3078 and 3106 cm^{-1} (Figure 2a). Relative to the Ni/SiO_2 catalysts, the coverage of adsorbed thiophene on cus Ni sites is higher as indicated by the strong $\nu_{(C=C)sym}$ absorbance at ∼1420 cm^{-1} (Figure 2b). On the basis of CO adsorption studies, we reported previously that Ni sites of reduced (and sulfided) Ni_2P/SiO_2 catalysts bear a partial positive charge ($\delta+$, $0 < \delta < 1$), with the magnitude of δ closer to 0 than to 1.[17] Even at an adsorption temperature of 190 K, additional ν_{CH} absorbances are observed, with the most intense features centered at 2929, 2961, 2994, and 3035 cm^{-1} (Figure 2a). New absorbances are present at 1477, 1571, and 1614 cm^{-1} (not shown), the latter two of which are assigned to $\nu_{C=C}$ modes of adsorbed hydrocarbon species. These vibrations are similar to those observed after thiophene adsorption on a sulfided Rh/Al_2O_3 catalyst at 300 K,[27] which were assigned to adsorbed 1,3-butadiene and a mixture of butadiene-derived, adsorbed hydrocarbon fragments based upon comparison with IR spectra of 1,3-butadiene adsorption on Rh/Al_2O_3 catalysts.[27,29] Similar absorbances have also been observed for adsorbed 1,3-butadiene on $Mo_2N/\gamma-Al_2O_3$ catalysts.[32] Clearly, cleavage of the C–S bonds has occurred in some of the adsorbed thiophene on the Ni_2P/SiO_2 catalysts upon adsorption at 190 K in UHV. Annealing the thiophene-dosed, reduced Ni_2P/SiO_2 catalyst to 250 K results in a red shift in the ν_{CH} absorbances with frequencies less than 3000 cm^{-1} (Figure 3). In addition, there is a significant increase in the intensity of the ν_{CH} absorbances at 3038 cm^{-1} and below 3000 cm^{-1}, with the predominant contributions in the latter region located at 2848, 2877, 2923, and 2956 cm^{-1}. Additional absorbances are located at 1457, 1471, 1593, and 1614 cm^{-1}, with the latter two assigned to $\nu_{C=C}$ modes of adsorbed hydrocarbon species. On the basis of literature reports for 1-butene and 2-butene adsorption on metal single crystal surfaces and supported catalysts, these absorbances are tentatively assigned to a mixture of hydrocarbon species, with the primary one being an adsorbed C_4H_7 fragment containing a double bond.[27,29–32,41] All of the molecularly adsorbed thiophene reacts on or desorbs from the reduced Ni_2P/SiO_2 catalyst after annealing to temperatures ≥350 K.

The reactivity of thiophene on sulfided Ni_2P/SiO_2 catalysts is very similar to that for reduced Ni_2P/SiO_2 catalysts. Specifically, most of the thiophene adsorbs molecularly on sulfided Ni_2P/SiO_2 catalysts at 190 K (Figure 2). Similar to the reduced Ni_2P/SiO_2 catalyst, the $\nu_{(C=C)sym}$ absorbance associated with thiophene η^1(S)-coordinated to Ni sites is more intense than

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that for the Ni/SiO$_2$ catalysts, indicating a higher site density on the sulfided Ni$_2$P/SiO$_2$ catalyst. Interestingly, the $\nu_{(C=C)sym}$ absorbance on both the sulfided Ni/SiO$_2$ and Ni$_2$P/SiO$_2$ catalysts is slightly shifted to higher frequency (1423−1424 cm^{-1}) compared to the position of this same absorbance on reduced Ni/SiO$_2$ and Ni$_2$P/SiO$_2$ catalysts (1420−1421 cm^{-1}). This small shift may reflect the withdrawal of electron density from cus Ni sites by sulfur incorporated into or adsorbed onto the sulfided catalysts. It has been concluded elsewhere that electron donation from a lone pair on the sulfur atom of thiophene to a metal site upon adsorption leads to a slight strengthening of C=C bonds of the coordinated thiophene;[28] this electron donation may be greater on the sulfided catalysts than on the reduced catalysts.

A small amount of C−S bond cleavage was observed upon thiophene adsorption on a sulfided Ni$_2$P/SiO$_2$ catalyst at 190 K, as indicated by absorbance features in the ν_{CH} and $\nu_{C=C}$ regions of the IR spectrum collected following cooling to 150 K. Consistent with the IR spectra for a reduced Ni$_2$P/SiO$_2$ catalyst dosed similarly, these vibrations are indicative of the formation of 1,3-butadiene and/or butadiene-derived, adsorbed hydrocarbon species on the surface. Annealing the thiophene-dosed, sulfided Ni$_2$P/SiO$_2$ catalyst to 250 K results in the desorption of some molecularly adsorbed thiophene as well as increases in the extent of thiophene reaction. In the $\nu_{(C=C)sym}$ region (Figure 3b), the absorbance associated with thiophene η^1(S)-coordinated to Ni sites (1426 cm^{-1}) is quite prominent and is clearly shifted to a higher frequency than was observed for the reduced Ni$_2$P/SiO$_2$ catalyst (1423 cm^{-1}). In the ν_{CH} region (Figure 3a), the predominant absorbance features are located at similar frequencies as observed for the reduced Ni$_2$P/SiO$_2$ catalyst treated in the same manner, but they have substantially lower intensities. These results indicate that under the conditions of this experiment, sulfur incorporated into and/or adsorbed onto the catalyst hinders thiophene reaction relative to the reduced Ni$_2$P/SiO$_2$ catalyst. All of the molecularly adsorbed thiophene reacts or desorbs from the reduced Ni$_2$P/SiO$_2$ catalyst after annealing to temperatures ≥325 K.

Infrared Spectroscopy of Thiophene Adsorption at High Temperature. To gain a better understanding of thiophene reactivity on Ni$_2$P/SiO$_2$ catalysts, the adsorption of thiophene on reduced Ni$_2$P/SiO$_2$ (and sulfided Ni/SiO$_2$) catalysts at 300 K in the presence of 5.0 Torr of thiophene vapor or a 3.2 mol % thiophene/H$_2$ gas mixture (P_{Th} = 5.0 Torr; P_{H_2} = 151.25 Torr) was investigated. While in the presence of the desired vapor, reduced Ni$_2$P/SiO$_2$ (and sulfided Ni/SiO$_2$) catalysts were annealed from 300 to 650 K, in 25 K increments. After each anneal cycle, the reduced Ni$_2$P/SiO$_2$ (and sulfided Ni/SiO$_2$) catalysts were cooled to 300 K in the presence of the gas or gas mixture prior to collecting an IR spectrum. While the signal-to-noise ratio was poor, some thiophene adsorption was observed on Ni sites of the sulfided Ni/SiO$_2$ catalyst at 300 K, but there was no evidence for reaction of thiophene on this catalyst upon annealing to temperatures as high as 650 K (IR spectra not shown).

Shown in Figure 4 are IR spectra for selected anneal temperatures in the range 300−650 K for the reduced Ni$_2$P/SiO$_2$ catalysts exposed to 5.0 Torr of thiophene. Focusing first on the IR spectrum of the reduced Ni$_2$P/SiO$_2$ catalyst exposed to 5.0 Torr of thiophene at 300 K, most of the thiophene adsorbs molecularly as indicated by the aromatic ν_{CH} absorbances at 3077 and 3111 cm^{-1}. The $\nu_{(C=C)sym}$ absorbance at 1420 cm^{-1} indicates that the molecularly adsorbed thiophene is η^1(S)-coordinated to Ni sites of the reduced Ni$_2$P/SiO$_2$ catalyst at 300 K. A substantial amount of thiophene reacts on the reduced Ni$_2$P/
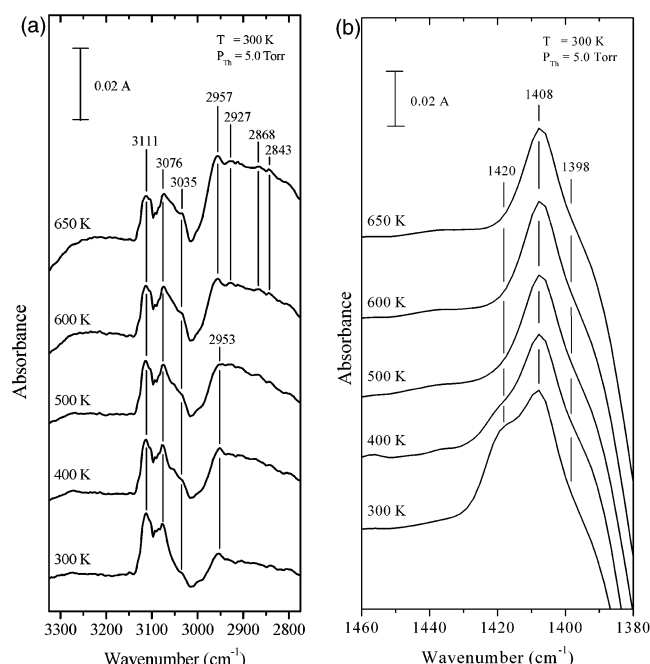

Figure 4. Infrared spectra in the (a) ν_{CH} and (b) $\nu_{(C=C)sym}$ regions for a reduced Ni$_2$P/SiO$_2$ catalyst exposed to thiophene (P_{Th} = 5.0 Torr). The catalyst sample was annealed to the indicated temperatures for 1 min in the presence of the thiophene vapor and the IR spectra were acquired following cooling to room temperature.

SiO$_2$ catalyst at 300 K, producing a mixture of adsorbed hydrocarbon species that could not be definitively assigned. Several of the ν_{CH} absorbances (e.g., 2953 and 3035 cm^{-1}) are similar to those observed for reduced and sulfided Ni$_2$P/SiO$_2$ catalysts exposed to 0.100 Torr of thiophene for 40 min at 190 K followed by cooling to 150 K (see Figure 2), suggesting the formation of adsorbed 1,3-butadiene and butadiene-derived, adsorbed hydrocarbon species on the surface. Annealing the reduced Ni$_2$P/SiO$_2$ catalyst in the presence of 5.0 Torr of thiophene to temperatures between 300 and 650 K further increased the extent of reaction. For anneal temperatures of 500 K and higher, most of the adsorbed thiophene has reacted on the catalyst surface as indicated by the prominent ν_{CH} absorbances at 2843, 2868, 2927, 2957, and 3035 cm^{-1}, and the absence of spectral intensity at 1420 cm^{-1}. The ν_{CH} absorbances which remain at 3076 and 3111 cm^{-1} as well as the $\nu_{(C=C)sym}$ absorbances at 1398 and 1408 cm^{-1} are most likely associated with molecular thiophene that readsorbs on the silica support upon cooling to 300 K. The peak positions and intensities for the ν_{CH} absorbances at 3035 cm^{-1} and below 3000 cm^{-1} observed in the IR spectrum associated with the 650 K anneal are quite similar to those observed in UHV following a 250 K anneal (Figure 3a). Again, we conclude that the predominant species on the reduced Ni$_2$P/SiO$_2$ catalyst are adsorbed 1,3-butadiene and butadiene-derived, adsorbed hydrocarbon species. In contrast to the substantial thiophene reactivity observed for the reduced Ni$_2$P/SiO$_2$ catalyst in the temperature range 300−650 K, no reactivity was observed for thiophene on sulfided Ni/SiO$_2$ and Mo/Al$_2$O$_3$[27] catalysts, or on a freshly prepared Mo$_2$NAl$_2$O$_3$ catalyst.[42] Similar thiophene reactivity was observed for a sulfided Rh/Al$_2$O$_3$ catalyst[27] in the range 300−650 K as was observed in the current study for the reduced Ni$_2$P/SiO$_2$ catalyst; an IR spectrum acquired following thiophene adsorption on a sulfided Rh/Al$_2$O$_3$ catalyst at 300 K is remarkably similar to the 300 K spectrum shown in Figure 4. For the sulfided Rh/Al$_2$O$_3$ catalyst, the ν_{CH} absorbances at 3035 cm^{-1} and below 3000 cm^{-1} show essentially the same relative intensities and
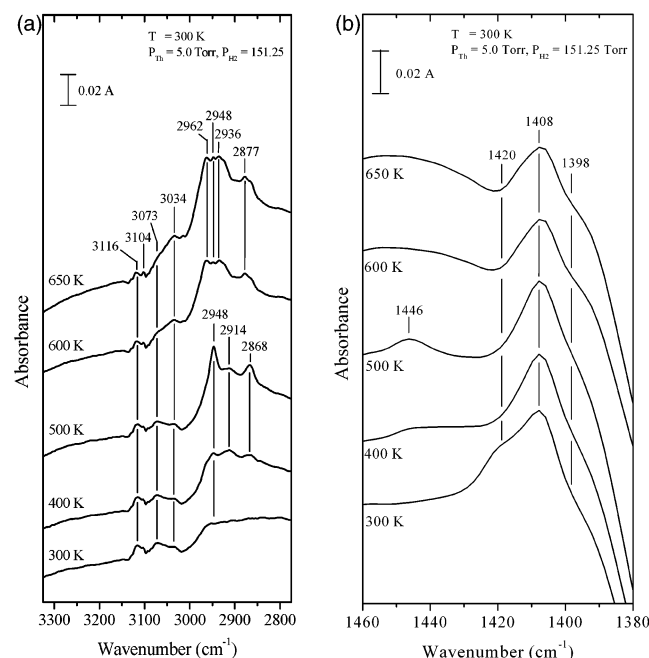
Figure 5. Infrared spectra in the (a) ν_{CH} and (b) $\nu_{(C=C)sym}$ regions for a reduced Ni_2P/SiO_2 catalyst exposed to thiophene ($P_{Th} = 5.0$ Torr, $P_{H_2} = 151.25$ Torr). The catalyst sample was annealed to the indicated temperatures for 1 min in the presence of the thiophene/H_2 mixture and the IR spectra were acquired following cooling to room temperature.

Figure 6. Infrared spectra in the (a) ν_{CH} and ν_{CO} regions and in the (b) $\nu_{(C=C)sym}$ region for reduced Ni_2P/SiO_2 catalysts exposed to CO, CO and then thiophene, or thiophene.

peak positions as those for the reduced Ni_2P/SiO_2 catalyst, indicating that the adsorbed species formed are similar and that these materials have similar reactivities toward thiophene. It is not surprising, therefore, that Ni_2P/SiO_2 and sulfided Rh/Al_2O_3 catalysts exhibit similar activities for thiophene HDS in flow reactor studies as discussed earlier.

The presence of hydrogen gas in addition to thiophene vapor ($P_{Th} = 5.0$ Torr; $P_{H_2} = 151.25$ Torr) enhances the reactivity of reduced Ni_2P/SiO_2 catalysts toward thiophene at 300 K. Unfortunately, a poor signal-to-noise ratio made it difficult to interpret the IR spectra (not shown) for a sulfided Ni/SiO_2 catalyst exposed to a thiophene/H_2 mixture. However, the thiophene coverage appears to be quite low under these conditions, and there was no evidence for thiophene reaction within the sensitivity limit of the spectrometer upon annealing above 300 K. As shown in Figure 5a, when a reduced Ni_2P/SiO_2 catalyst was placed in a thiophene/H_2 gas mixture at 300 K, the ν_{CH} absorbances with frequencies <3000 cm^{-1} became more intense than the ν_{CH} absorbances with frequencies >3000 cm^{-1}. However, the $\nu_{(C=C)sym}$ absorbance at 1420 cm^{-1} (Figure 5b) remains relatively intense indicating that a substantial amount of thiophene remains molecularly adsorbed to Ni sites. Annealing the reduced Ni_2P/SiO_2 catalyst to 500 K in the presence of the thiophene/H_2 gas mixture results in elimination of the $\nu_{(C=C)sym}$ absorbance at 1420 cm^{-1}, indicating that the remaining molecularly adsorbed thiophene on Ni sites has reacted. Annealing the catalyst to 500 K results in significant increases in the ν_{CH} absorbances located at 2868 and 2948 cm^{-1} relative to the others in this region, and a new absorbance at 1446 cm^{-1} becomes apparent, which is tentatively assigned to a bending vibration [$\delta(=CH_2)$].[27] The reduced Ni_2P/SiO_2 catalyst is considerably more active toward thiophene decomposition at 500 K than was a sulfided Mo/Al_2O_3 catalyst heated to 500 K in a thiophene/H_2 mixture, and shows a reactivity quite similar to that of a sulfided Rh/Al_2O_3 catalyst.[27] The predominant hydrocarbon species on the reduced Ni_2P/SiO_2 catalyst is most likely a saturated hydrocarbon fragment, since the ν_{CH}

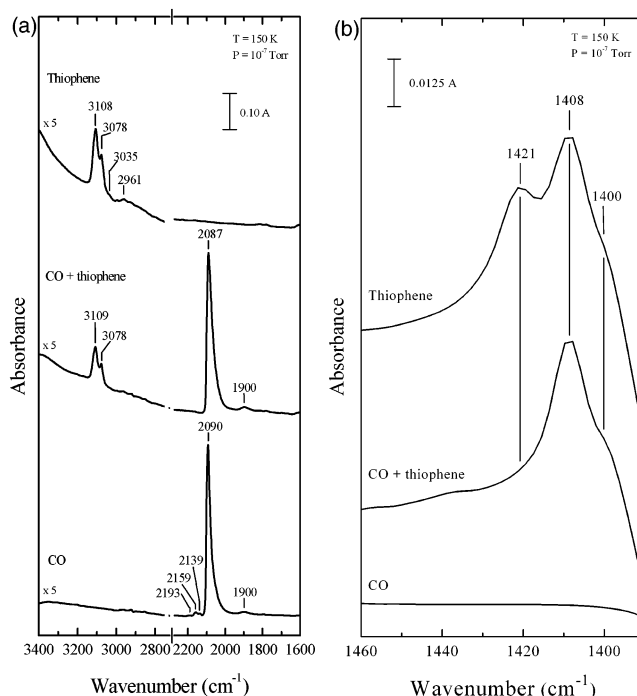absorbances located at 2868 [$\nu_s(CH_3)$] and 2948 cm^{-1} [$\nu_{as}(CH_3)$] are the most intense in the ν_{CH} region.[27] After annealing the reduced Ni_2P/SiO_2 catalyst to 650 K in the presence of the thiophene/H_2 gas mixture, the IR spectrum becomes more complex with the most intense ν_{CH} absorbances observed at 2877, 2933, 2948, and 2962 cm^{-1}. The most intense absorbances elsewhere in the spectrum are centered at ~1452, 1610, 1654, and 1672 cm^{-1}. The complexity of the IR spectrum is probably the result of a mixture of adsorbed hydrocarbon fragments, both unsaturated and saturated, present on the surface of the reduced Ni_2P/SiO_2 catalyst.

Infrared Spectroscopy Measurements of Coadsorbed CO and Thiophene. In two sets of experiments, thiophene and CO were coadsorbed on a reduced Ni_2P/SiO_2 catalyst to gain further insight into the nature of the adsorption sites on this catalyst and the competition between CO and thiophene for these sites. The surface chemistry of CO adsorbed alone on Ni_2P/SiO_2 catalysts has been reported previously.[17] In one coadsorption experiment, a reduced Ni_2P/SiO_2 catalyst was exposed to 5.0 Torr of CO (at 150 K) prior to dosing 0.100 Torr of thiophene for 40 min at 190 K. Shown in Figure 6 are the IR spectra collected after exposure of the catalyst to CO, and after subsequent dosing with thiophene. For comparison purposes, the IR spectrum for a reduced Ni_2P/SiO_2 catalyst dosed with 0.100 Torr of thiophene for 40 min at 190 K and then cooled to 150 K is also shown. The IR spectrum for the reduced Ni_2P/SiO_2 catalyst exposed to only CO displays a strong ν_{CO} absorbance at 2093 cm^{-1} and as well as weak ν_{CO} absorbances at 1900, 2139, 2159, and ~2193 cm^{-1}. The peaks at 1900 and 2093 cm^{-1} are assigned to CO adsorbed on bridge and atop $Ni^{\delta+}$ sites, respectively, while the peaks at 2139 and 2159 cm^{-1} are assigned to CO adsorbed on the silica support.[17] The weak absorbance at ~2193 cm^{-1}, reported recently for the first time,[17] is assigned to CO adsorbed on P sites of Ni_2P/SiO_2 catalysts as P=C=O species. The intensity of the ~2193 cm^{-1} absorbance feature has been shown to vary substantially depending upon the pretreatment and CO adsorption conditions.[17] After exposure
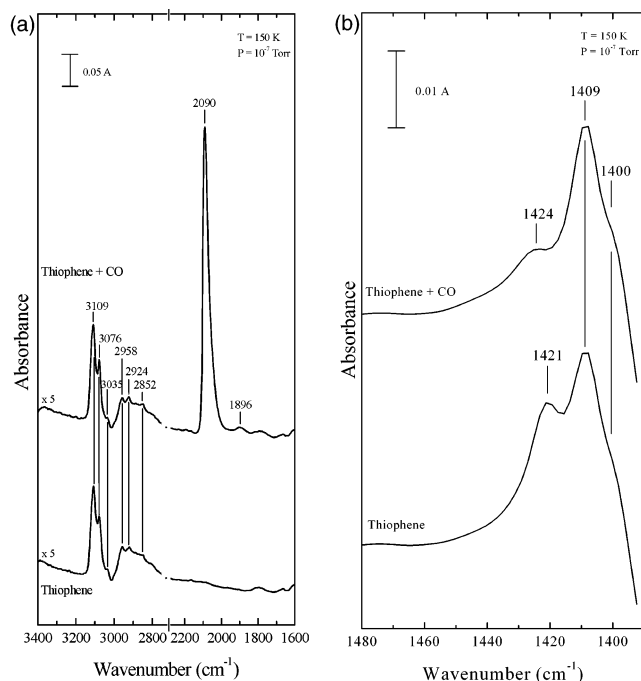
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Figure 7. Infrared spectra in the (a) ν_{CH} and ν_{CO} regions and in the (b) $\nu_{(C=C)sym}$ region for reduced Ni_2P/SiO_2 catalysts exposed to thiophene or thiophene then CO.

of the reduced Ni_2P/SiO_2 catalyst to thiophene at 190 K and subsequent cooling to 150 K, the ν_{CO} absorbance at 2090 cm^{-1} broadens and shifts slightly to 2087 cm^{-1}, while the absorbances at 2139, 2159, and ~2193 cm^{-1} disappear. In the ν_{CH} region (Figure 6a), peaks are observed at 3078 and 3109 cm^{-1}, but it is not possible to discern absorbance features above the background in the range 2800–3000 cm^{-1}. In the $\nu_{(C=C)sym}$ region (Figure 6b), peaks are observed at 1398 and 1408 cm^{-1}. The absence of a peak at 1421 cm^{-1} indicates that preadsorbed CO blocks thiophene adsorption on Ni sites of the reduced Ni_2P/SiO_2 catalyst, and that thiophene is presumably adsorbed only on uncovered areas of the silica support. Consistent with this observation, there is no evidence in the 2800–3000-cm^{-1} region for thiophene decomposition, which occurs on Ni sites of the supported Ni_2P particles.

In another coadsorption experiment, a reduced Ni_2P/SiO_2 catalyst was dosed with 0.100 Torr of thiophene for 40 min at 190 K prior to exposing the catalyst to 5.0 Torr of CO at 150 K. The IR spectra collected after dosing with thiophene and cooling to 150 K and after subsequent dosing with CO are shown in Figure 7. Similar to Figure 2, absorbance features associated with adsorbed thiophene and its reaction products are clearly observed on the Ni_2P/SiO_2 catalyst prior to exposure to 5.0 Torr of CO (Figure 7a). Exposing the thiophene-dosed sample to 5.0 Torr of CO at 150 K results in the displacement of some of the adsorbed thiophene by CO, as indicated by a decrease in the $\nu_{(C=C)sym}$ absorbance at 1421 cm^{-1}, which is associated with thiophene molecularly adsorbed on Ni sites of reduced Ni_2P/SiO_2 catalysts (Figure 7b). In addition, the $\nu_{(C=C)sym}$ absorbance shifts to ~1424 cm^{-1} after exposing the thiophene-dosed, reduced Ni_2P/SiO_2 catalyst to CO. While CO displaced some of the thiophene molecularly adsorbed to $Ni^{\delta+}$ sites, it was apparently unable to displace the adsorbed hydrocarbon fragments produced by the decomposition of thiophene at 190 K. Hydrocarbon fragments produced by thiophene decomposition have previously been observed to be strongly bonded to the surfaces of sulfided Mo/Al_2O_3 and Rh/Al_2O_3 catalysts.[27] While CO does displace some thiophene from

Ni sites, the strong intensity of the ν_{CO} absorbance at 2090 cm^{-1} suggests that CO is accessible to additional Ni sites on reduced Ni_2P/SiO_2 catalysts on which thiophene is unable to adsorb when dosed alone.

Discussion

Ni_2P/SiO_2 catalysts have recently been shown to have high activity and stability for thiophene HDS under atmospheric pressure conditions[14,15,17] and for dibenzothiophene HDS under more industrially relevant conditions.[8,11–13,16] As shown in Figure 1, the incorporation of P into silica-supported Ni catalysts has a substantial effect on the thiophene HDS activity of the catalysts, with the trend of activity increasing in the following order: sulfided Ni/SiO_2 < reduced Ni/SiO_2 ≪ reduced Ni_2P/SiO_2 < sulfided Ni_2P/SiO_2.

The high thiophene HDS activity of Ni_2P/SiO_2 catalysts has been reported to be due to both a high site density and a high turnover frequency.[15] To gain insight into the high HDS activity of silica-supported Ni_2P, we undertook the current investigation of the adsorption and reactions of thiophene on Ni_2P/SiO_2 (and Ni/SiO_2) catalysts. Since probe molecules (e.g., CO, NO, and O_2) are commonly used to measure active site densities on HDS catalysts, we also investigated the relationship between the adsorption sites for CO and thiophene on Ni_2P/SiO_2 catalysts. CO has been shown to be a good probe molecule for the titration of the active sites for thiophene HDS on a number of catalytic materials, including sulfides (e.g., sulfided Mo/Al_2O_3),[43] carbides (e.g., Mo_2C/Al_2O_3),[22,43,44] nitrides (e.g., Mo_2N/Al_2O_3),[22,43,44] and phosphides (e.g., MoP/SiO_2).[6] As described elsewhere, we observed four different ν_{CO} absorbances for the adsorption of CO on silica-supported Ni_2P particles.[17] Since CO titrates more than one type of site, we concluded that it should be used cautiously to estimate site densities on Ni_2P/SiO_2 catalysts. The coadsorption experiments allowed us to further access whether CO is a suitable probe molecule for characterizing the active sites for thiophene HDS on Ni_2P/SiO_2 catalysts.

Thiophene Adsorption and Reactivity on Ni/SiO₂ Catalysts at Low Temperatures. So that the effect of incorporating P into silica-supported Ni catalysts on the surface chemistry of thiophene could be assessed, adsorption studies were carried out on Ni/SiO_2 catalysts as well as on Ni_2P/SiO_2 catalysts. While others have used IR spectroscopy to investigate thiophene adsorption on Ni/SiO_2 catalysts at room temperature and above,[39,40] to our knowledge this is the first IR spectroscopy study of thiophene adsorption and reactivity on reduced and sulfided Ni/SiO_2 catalysts below 298 K. When interpreting the results of thiophene adsorption experiments on Ni/SiO_2 (and Ni_2P/SiO_2) catalysts, the interactions of thiophene with the silica support must also be examined. Different results have been reported in two vibrational spectroscopic studies of thiophene adsorption on pure silica.[40,45] In one case, only molecular adsorption of thiophene on silica was observed at room temperature,[45] while in the second case significant ν_{CH} absorbances were observed in the 2800–3000-cm^{-1} range (in addition to those for molecularly adsorbed thiophene above 3000 cm^{-1}) following exposure of pure silica to thiophene vapor at room temperature.[40] The authors of the second study concluded that some thiophene decomposes on silica upon adsorption at 300 K. We observed no evidence for the decomposition of thiophene on pure silica either when dosed with thiophene at 190 K in UHV and annealed to higher temperatures (Figures 2 and 3) or when pure silica is exposed to 5.0 Torr of thiophene at 300 K and annealed to higher temperatures (not shown). As described previously,[25] we have found it necessary to rigorously purify

commercially available thiophene to remove trace butanethiol impurities that were observed to preferentially adsorb on γ-Al$_2$O$_3$ upon exposure of this material to commercially available thiophene (Aldrich, 99+%). We believe butanethiol impurities may be responsible for the ν_{CH} absorbances observed in the 2800−3000=cm^{-1} range in the earlier study of thiophene adsorption on pure silica.[40] These impurities may also explain some of the reactivity attributed to thiophene in earlier studies of thiophene adsorption on reduced Ni/SiO$_2$ catalysts.[39,40]

Our IR spectroscopic results indicate that thiophene adsorbs molecularly on reduced and sulfided Ni/SiO$_2$ catalysts when dosed at 190 K. The absorbance features at 1421−1423 cm^{-1} are consistent with thiophene η^1(S)-coordinated to cus Ni sites of the Ni/SiO$_2$ catalysts, similar to what was concluded previously for thiophene adsorbed on sulfided Mo/Al$_2$O$_3$ and Rh/Al$_2$O$_3$ catalysts.[26,27] There is no evidence for reaction of thiophene on sulfided Ni/SiO$_2$ catalysts in UHV; thiophene desorbs molecularly from this catalyst by ∼250 K. This observation is consistent with those reported by others for thiophene adsorption on a sulfided Ni(111) single crystal, for which molecular desorption was observed by 315 K.[36] The onset of reactivity for adsorbed thiophene on a reduced Ni/SiO$_2$ catalyst was observed when the catalyst was annealed at 250 K. On the basis of the observed ν_{CH} absorbances at ∼3035 and below 3000 cm^{-1}, we conclude that some thiophene reacted to form C$_4$ hydrocarbons and/or other thiophene decomposition products. However, most of the adsorbed thiophene remained molecularly intact, as indicated by the intensity of ν_{CH} absorbances at 3106 and 3078 cm^{-1}, which are associated with adsorbed thiophene. Desorption of molecularly adsorbed thiophene from a reduced Ni/SiO$_2$ catalyst was complete by 350 K. While not observed directly by vibrational spectroscopy, thiophene has been reported to undergo C−S bond cleavage on Ni(111) and Ni(100) single-crystal surfaces at temperatures as low as 90−150 K.[33−38] It is not obvious why higher reactivity toward thiophene is observed for the Ni(111) and Ni(100) single-crystal surfaces than is observed here for reduced Ni/SiO$_2$ catalysts.

The reactivity of thiophene on reduced and sulfided Ni/SiO$_2$ catalysts can be compared with that observed for sulfided Cu/Al$_2$O$_3$, Mo/Al$_2$O$_3$, and Rh/Al$_2$O$_3$ catalysts.[26,27] Thiophene adsorbed molecularly on sulfided Cu/Al$_2$O$_3$, Mo/Al$_2$O$_3$, and Rh/Al$_2$O$_3$ catalysts at 190 K. Upon annealing of the thiophene-dosed, sulfided Cu/Al$_2$O$_3$, Mo/Al$_2$O$_3$, and Rh/Al$_2$O$_3$ catalysts to increasing temperatures in UHV, only a gradual decrease in intensity of the ν_{CH} absorbances associated with adsorbed thiophene was observed. Examination of the $\nu_{(C=C)sym}$ region revealed that essentially no thiophene adsorbed to Cu sites of the sulfided Cu/Al$_2$O$_3$ catalyst at 190 K. On the other hand, the $\nu_{(C=C)sym}$ absorbance at ∼1430 cm^{-1}, which is associated with thiophene adsorbed on cus Mo and Rh sites, was observed for adsorbed thiophene on sulfided Mo/Al$_2$O$_3$ and Rh/Al$_2$O$_3$ catalysts until annealing to ∼350 K. In the current study, a weak $\nu_{(C=C)sym}$ absorbance is apparent at ∼1424 cm^{-1} following dosing of a sulfided Ni/SiO$_2$ catalyst with thiophene at 190 K, indicating the presence of a small amount of thiophene adsorbed to cus Ni sites. However, thiophene is only weakly adsorbed on the sulfided Ni/SiO$_2$ catalyst, as indicated by the nearly complete desorption of thiophene upon annealing this catalyst to ∼250 K. Therefore, we conclude that thiophene has a somewhat stronger interaction with sulfided Ni/SiO$_2$ catalysts than with a sulfided Cu/Al$_2$O$_3$ catalyst, but the sulfided Ni/SiO$_2$ catalyst adsorbs thiophene more weakly than do sulfided Mo/Al$_2$O$_3$ and Rh/Al$_2$O$_3$ catalysts. On the basis of these IR spectroscopic observations, therefore, we can establish the

following trend for the strength of thiophene adsorption on the transition metal sulfide catalysts investigated: sulfided Cu/Al$_2$O$_3$ < sulfided Ni/SiO$_2$ < sulfided Mo/Al$_2$O$_3$ < sulfided Rh/Al$_2$O$_3$. This trend is in good qualitative agreement with the trend of HDS activities measured in our laboratory for these same transition metal sulfide catalysts,[17,27] as well as the trends measured by others for unsupported and supported transition metal sulfides.[46−50]

Thiophene Adsorption and Reactivity on Ni$_2$P/SiO$_2$ Catalysts at Low Temperatures. The high HDS activity of Ni$_2$P/SiO$_2$ catalysts is reflected in the surface chemistry of thiophene adsorbed on the surfaces of these catalysts at low temperatures. Thiophene is more strongly adsorbed and more reactive on reduced and sulfided Ni$_2$P/SiO$_2$ catalysts than on reduced and sulfided Ni/SiO$_2$ catalysts (Figures 2 and 3). For catalysts that were dosed with thiophene at 190 K and then cooled to 150 K, the IR spectra in the $\nu_{(C=C)sym}$ region show significant absorbances at 1420−1424 cm^{-1}. The relatively high intensity of this absorbance feature, which is assigned to thiophene adsorbed in an η^1(S) geometry to Ni sites, indicates that there is a substantially higher site density on the reduced and sulfided Ni$_2$P/SiO$_2$ catalysts than on the reduced and sulfided Ni/SiO$_2$ catalysts (Figure 2b). It has been shown previously that the intensity of this $\nu_{(C=C)sym}$ absorbance (for catalysts dosed similarly) correlated qualitatively with the thiophene HDS activities of sulfided Cu/Al$_2$O$_3$, Mo/Al$_2$O$_3$, and Rh/Al$_2$O$_3$ catalysts.[27] Upon annealing thiophene dosed, reduced, and sulfided Ni/SiO$_2$ and Ni$_2$P/SiO$_2$ catalysts to 250 K in UHV, the relative differences in the amount of thiophene adsorbed to Ni sites becomes dramatically apparent. As indicated by the $\nu_{(C=C)sym}$ absorbance at 1423−1426 cm^{-1}, very little thiophene is adsorbed to Ni sites of the reduced and sulfided Ni/SiO$_2$ catalysts, while substantially more thiophene remains adsorbed to the supported Ni$_2$P particles. These results indicate that the reduced and sulfided Ni$_2$P/SiO$_2$ catalysts not only have high site densities for adsorbed thiophene, but also that thiophene is more strongly adsorbed to the Ni sites of reduced and sulfided Ni$_2$P/SiO$_2$ catalysts than to Ni sites of reduced and sulfided Ni/SiO$_2$ catalysts. As described previously in a study of CO adsorption on reduced and sulfided Ni/SiO$_2$ and Ni$_2$P/SiO$_2$ catalysts, incorporation of P into the Ni catalysts to give supported Ni$_2$P particles increases the dispersion of Ni on the silica support.[17] Furthermore, P withdraws electron density from Ni in the supported Ni$_2$P particles so that the Ni sites bear a partial positive charge (Ni$^{\delta+}$, 0 < δ < 1). IR spectroscopic and XPS measurements,[15,17] as well as density functional calculations,[14] indicate that the magnitude of δ is small, but the slight electron withdrawal from Ni may increase somewhat the acidity of the Ni sites on Ni$_2$P/SiO$_2$ catalysts relative to Ni/SiO$_2$ catalysts. Together, the increased dispersion and acidity of the Ni sites on the Ni$_2$P/SiO$_2$ catalysts likely explains the higher coverage and stronger adsorption observed for thiophene on reduced Ni$_2$P/SiO$_2$ catalysts than on reduced Ni/SiO$_2$ catalysts. It is also possible that thiophene η^1(S)-coordinated to Ni sites of Ni$_2$P/SiO$_2$ catalysts also interacts directly with surface P atoms, increasing the strength of thiophene adsorption on these catalysts. Rodriguez and co-workers[51] recently reported that surface C atoms in a TiC(001) single crystal surface participate directly in the adsorption and reactions of SO$_2$ on this surface.

Sulfidation of Ni$_2$P/SiO$_2$ catalysts lowers somewhat the amount of thiophene adsorbed on Ni sites relative to Ni$_2$P/SiO$_2$ catalysts subjected to a reduction pretreatment, as indicated by the intensity of the $\nu_{(C=C)sym}$ absorbance (Figures 2b and 3b). As is evident in Figure 3b, however, a far greater loss of

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$\nu_{(C=C)sym}$ spectral intensity at 1423−1426 cm^{-1} occurs for Ni/SiO$_2$ catalysts upon sulfidation. For the Ni/SiO$_2$ catalysts, it is clear that a sulfidation pretreatment leads to a substantial decrease in Ni sites available for thiophene adsorption due to site blocking either by adsorbed S on Ni particles or by S incorporated into a nickel sulfide phase (e.g. Ni$_3$S$_2$). For the Ni$_2$P/SiO$_2$ catalyst, two possible explanations for the relatively smaller decrease of the thiophene adsorption capacity (relative to the Ni/SiO$_2$ catalysts) as a result of a sulfidation pretreatment are that the surfaces of the Ni$_2$P particles are resistant to significant sulfur adsorption or sulfidation, or that a surface phosphosulfide (NiP$_x$S$_y$) phase is formed. Resistance to sulfur uptake by Ni$_2$P particles would preserve sites that might otherwise be blocked by sulfur. A dispersed or defected phosphosulfide phase at the surface of Ni$_2$P particles could have a structure quite different from that of sulfided Ni, one that exposes a high density of sites for thiophene adsorption. X-ray diffraction study of a 20 wt % Ni$_2$P/SiO$_2$ catalyst subjected to H$_2$S/H$_2$ pretreatments at temperatures as high as 1023 K showed no evidence for bulk sulfidation of the supported Ni$_2$P particles.[15] Infrared spectroscopy measurements of adsorbed CO on reduced and sulfided Ni$_2$P/SiO$_2$ catalysts revealed a shift of the ν_{CO} absorbance assigned to CO adsorbed on atop Ni sites from 2083 cm^{-1} for the reduced catalyst to 2093 cm^{-1} for the sulfided catalyst.[17] It was concluded that this shift is due to the withdrawal of electron density from Ni sites by adsorbed sulfur on the sulfided Ni$_2$P/SiO$_2$ catalyst. Further supporting this conclusion, the relative CO site density for Ni$_2$P/SiO$_2$ catalysts as measured by IR spectroscopy decreased substantially upon sulfidation, indicating that adsorbed sulfur blocked CO adsorption in Ni sites. On the other hand, O$_2$ chemisorption capacities for a reduced 20 wt % Ni$_2$P/SiO$_2$ catalyst (123.9 μmol/g)[15] and a sulfided 20 wt % Ni$_2$P/SiO$_2$ catalyst (125.7 μmol/g)[52] were determined to be identical within the error of the measurements. It is important to note that for the O$_2$ chemisorption measurement, the sulfided Ni$_2$P/SiO$_2$ catalyst was reduced in flowing H$_2$ following sulfidation but this was not the case for the IR spectroscopy measurement of adsorbed CO. It may be, therefore, that a significant amount of the S incorporated into Ni$_2$P/SiO$_2$ catalysts upon sulfidation is labile to hydrogenation and removal as H$_2$S, regenerating Ni sites. Extended X-ray adsorption fine structure (EXAFS) measurements conducted by Oyama et al.[16] indicate incorporation of S into Ni$_2$P/SiO$_2$ catalysts tested under HDS conditions. The EXAFS measurements revealed the formation of Ni−S linkages at the surface of the supported Ni$_2$P particles, leading the authors to conclude that the active surface of a Ni$_2$P/SiO$_2$ catalyst was probably a NiP$_x$S$_y$ phase. It may be that the sulfur in the Ni−S linkages of a surface NiP$_x$S$_y$ phase is more labile to hydrogenation and removal as H$_2$S than is surface S in a sulfided Ni/SiO$_2$ catalyst. This could explain the substantially higher thiophene adsorption capacity of sulfided Ni$_2$P/SiO$_2$ catalysts relative to sulfided Ni/SiO$_2$ catalysts, and be an important factor in determining the high HDS activity of Ni$_2$P/SiO$_2$ catalysts.

As mentioned earlier, the $\nu_{(C=C)sym}$ absorbance of adsorbed thiophene on both the sulfided Ni/SiO$_2$ and Ni$_2$P/SiO$_2$ catalysts is slightly shifted to higher frequency (1423−1424 cm^{-1}) compared to its position on reduced Ni/SiO$_2$ and Ni$_2$P/SiO$_2$ catalysts (1420−1421 cm^{-1}). This small shift may reflect the withdrawal of electron density from cus Ni sites by sulfur incorporated into or adsorbed onto the sulfided catalysts. It has been concluded elsewhere that electron donation from a lone pair on the sulfur atom of thiophene to a metal site upon adsorption leads to a slight strengthening of C=C bonds of the

coordinated thiophene;[28] this electron donation may be greater on the sulfided Ni/SiO$_2$ and Ni$_2$P/SiO$_2$ catalysts than on the reduced catalysts, reflecting a slightly higher acidity of the Ni sites on the sulfided catalysts. As discussed elsewhere in this article, however, this similar shift of the $\nu_{(C=C)sym}$ absorbance of adsorbed thiophene upon sulfidation of Ni/SiO$_2$ and Ni$_2$P/SiO$_2$ catalysts is not reflected in similar effects on the HDS activities of the catalysts. The HDS activity of a Ni$_2$P/SiO$_2$ catalyst was observed to increase when pretreated by sulfidation (relative to a reduction pretreatment), while the HDS activity of a Ni/SiO$_2$ catalyst decreased as a result of a sulfidation pretreatment.

The ν_{CH} absorbances at ∼3035 and ≤3000 cm^{-1} in the IR spectra collected at 150 K following exposure of reduced and sulfided Ni$_2$P/SiO$_2$ catalysts to thiophene at 190 K indicate that C−S bond scission has occurred in some adsorbed thiophene on the catalysts even at 190 K (Figure 2). The extent of thiophene reactivity on the reduced and sulfided Ni$_2$P/SiO$_2$ catalysts increased when the thiophene-dosed catalysts were annealed at 250 K, the temperature at which thiophene decomposition is first apparent on a reduced Ni/SiO$_2$ catalyst. Desorption of molecular thiophene from reduced and sulfided Ni$_2$P/SiO$_2$ catalysts is complete by 350 and 325 K, respectively, which is close to the temperature of 350 K observed for complete desorption of thiophene from sulfided Mo/Al$_2$O$_3$ and Rh/Al$_2$O$_3$ catalysts in UHV conditions.[27] However, there is an important difference, in that thiophene decomposition is observed on reduced and sulfided Ni$_2$P/SiO$_2$ catalysts in UHV while this pathway is not observed for thiophene adsorbed on sulfided Mo/Al$_2$O$_3$ and Rh/Al$_2$O$_3$ catalysts dosed with thiophene at 190 K and annealed to increasing temperatures in UHV.[27] Reaction of thiophene was observed for a sulfided Rh/Al$_2$O$_3$ catalyst upon exposure to 5.0 Torr of thiophene at 300 K, and for a sulfided Mo/Al$_2$O$_3$ catalyst only after exposure to a thiophene/H$_2$ mixture at 500 K. On the basis of these observations and the trend developed above for the strength of thiophene adsorption on the transition metal sulfide catalysts, we can establish the following trend of increasing thiophene interaction (i.e., strength of adsorption/onset of decomposition) in UHV conditions: sulfided Cu/Al$_2$O$_3$ < sulfided Ni/SiO$_2$ < sulfided Mo/Al$_2$O$_3$ < sulfided Rh/Al$_2$O$_3$ < sulfided Ni$_2$P/SiO$_2$. This qualitative trend of thiophene interaction can be compared with thiophene HDS activities measured for these catalysts (nmol of thiophene/g of catalyst/s): sulfided Cu/Al$_2$O$_3$ (13) < sulfided Ni/SiO$_2$ (180) < sulfided Mo/Al$_2$O$_3$ (427) < sulfided Rh/Al$_2$O$_3$ (2133) < sulfided Ni$_2$P/SiO$_2$ (2865).[15,27] The HDS activities were measured at 643 K and are compared based upon the activities after 24 h on-stream and are normalized on the basis of catalyst mass. If the catalyst activities are instead normalized on the basis of sites as titrated by CO (or O$_2$ in the case of the Ni-based catalysts) chemisorption to give turnover frequencies, then the trend changes slightly (s^{-1}): sulfided Cu/Al$_2$O$_3$ (0.0019) < sulfided Ni/SiO$_2$ (0.0025) < sulfided Mo/Al$_2$O$_3$ (0.0092) < sulfided Ni$_2$P/SiO$_2$ (0.0230) < sulfided Rh/Al$_2$O$_3$ (0.0288).[15,27]

As indicated by the trends in HDS activities and turnover frequencies discussed in the preceding paragraph, Ni$_2$P/SiO$_2$ is a highly active HDS catalyst and this is reflected in the reactivity of thiophene on reduced and sulfided Ni$_2$P/SiO$_2$ catalysts compared to reduced and sulfided Ni/SiO$_2$ catalysts (Figures 2 and 3). The ν_{CH} absorbances at ∼3035 and ≤3000 cm^{-1} in the IR spectra collected at 150 K following exposure of the catalysts to thiophene at 190 K indicate that significant C−S bond scission has occurred on the reduced and sulfided Ni$_2$P/SiO$_2$ catalysts at 190 K (Figure 2). The ν_{CH} absorbances at ≤3000

cm^{-1} are indicative of the formation of adsorbed C$_4$ hydrocarbon species resulting from breaking the C$-$S bonds in thiophene. While it is possible that only one of the C$-$S bonds is broken to produce an adsorbed thiolate species, we expect that this species would be highly reactive on the Ni$_2$P/SiO$_2$ catalysts even at 190 K and would rapidly undergo subsequent cleavage of the second C$-$S bond to give an adsorbed C$_4$ hydrocarbon and sulfur on the catalyst surface. The ν_{CH} absorbances observed at ~3035 and below 3000 cm^{-1} as well as other absorbances at 1614, 1571, and 1477 cm^{-1} for reduced and sulfided Ni$_2$P/SiO$_2$ catalysts dosed with thiophene at 190 K (Figure 2) are similar to those observed for a sulfided Rh/Al$_2$O$_3$ catalyst exposed to thiophene at 300 K. These vibrations were assigned to adsorbed 1,3-butadiene and butadiene-derived, adsorbed hydrocarbon fragments on the sulfided Rh/Al$_2$O$_3$ catalyst.[27,29] As noted earlier, similar vibrations have also been observed on Mo$_2$N/γ-Al$_2$O$_3$ catalysts and were assigned to molecularly adsorbed 1,3-butadiene.[32] These results suggest that cleavage of the C$-$S bonds in thiophene on the Ni$_2$P/SiO$_2$ catalysts at 190 K results in the formation of an adsorbed 1,3-butadiene-like species.

The extent of thiophene reactivity on reduced and sulfided Ni$_2$P/SiO$_2$ catalysts increased when thiophene-dosed, reduced, and sulfided Ni$_2$P/SiO$_2$ catalysts were annealed to higher temperatures, as shown in Figure 3 for a 250 K anneal. For the reduced and sulfided Ni/SiO$_2$ catalysts, thiophene was relatively weakly adsorbed and unreactive, although a small amount of thiophene decomposition is apparent after the 250 K anneal for the reduced Ni/SiO$_2$ catalyst. On the basis of the peak intensity of ν_{CH} absorbances $\leq$3000 cm^{-1} in the IR spectra following annealing the thiophene-dosed catalysts at 250 K, the following trend of thiophene reactivity can be determined: sulfided Ni/SiO$_2$ < reduced Ni/SiO$_2$ < sulfided Ni$_2$P/SiO$_2$ < reduced Ni$_2$P/SiO$_2$. This trend is similar to that observed for the enthalpies of adsorption of CO on the Ni/SiO$_2$ and Ni$_2$P/SiO$_2$ catalysts.[17] Each of the thiophene-dosed, reduced, and sulfided Ni/SiO$_2$ and Ni$_2$P/SiO$_2$ catalysts was annealed until all of the thiophene had either desorbed or reacted on the surface. This required annealing the catalyst samples to 250, 300, 325, and 350 K for the sulfided Ni/SiO$_2$, reduced Ni/SiO$_2$, sulfided Ni$_2$P/SiO$_2$, and reduced Ni$_2$P/SiO$_2$ catalysts, respectively. On the basis of the absorbances in the ν_{CH} region of the IR spectra (Figure 3) and comparison of the IR spectra for thiophene adsorbed on sulfided Mo/Al$_2$O$_3$ and Rh/Al$_2$O$_3$ catalysts,[26,27] we conclude that the primary adsorbed hydrocarbon species on the thiophene-dosed, reduced, and sulfided Ni$_2$P/SiO$_2$ catalysts following annealing to 250 K is a C$_4$H$_7$ hydrocarbon fragment. Upon further annealing, this adsorbed hydrocarbon fragment presumably undergoes further reaction, either dehydrogenation to give 1,3-butadiene or hydrogenation to give butenes and butane.

Thiophene Adsorption and Reactivity at High Temperatures. Not surprisingly, a reduced Ni$_2$P/SiO$_2$ catalyst exhibits even higher reactivity when exposed to thiophene or a thiophene/H$_2$ mixture at 300 K and above (Figures 4 and 5) than was observed at low temperatures. The ν_{CH} absorbance features below 3000 cm^{-1} for a reduced Ni$_2$P/SiO$_2$ catalyst exposed to a static pressure of thiophene vapor (P_{Th} = 5.0 Torr) at 300 K are more intense (relative to those for molecularly adsorbed thiophene) than those for a reduced Ni$_2$P/SiO$_2$ catalyst exposed to thiophene at 190 K. While difficult to assign definitively, the peak positions for absorbance features at 3035 cm^{-1} and below 3000 cm^{-1} are similar in the low- and high-temperature spectra, indicating that they are likely associated with adsorbed 1,3-butadiene or butadiene-derived, adsorbed hydrocarbon fragments in both cases. Upon annealing the reduced Ni$_2$P/SiO$_2$

catalyst to higher temperatures (300$-$650 K) in the thiophene vapor, the extent of thiophene reaction increased substantially. These observations are in contrast to those reported previously from our laboratory for sulfided Mo/Al$_2$O$_3$[26,27] and Rh/Al$_2$O$_3$[27] catalysts, as well as with our observations for a sulfided Ni/SiO$_2$ catalyst in this study (not shown). For each of these catalysts, there was no evidence of thiophene decomposition when the catalysts were annealed to temperatures of 650 K and above in 5.0$-$9.5 Torr of thiophene vapor. No reactivity toward thiophene was also observed for a Mo$_2$N/Al$_2$O$_3$ catalyst when it was heated as high as 673 K in 5.0 Torr of thiophene.[42] Clearly, the active sites on a reduced Ni$_2$P/SiO$_2$ catalyst are significantly more reactive toward thiophene in the absence of gas-phase hydrogen than are those on the sulfided Ni/SiO$_2$, Mo/Al$_2$O$_3$, and Rh/Al$_2$O$_3$ catalysts and on the Mo$_2$N/Al$_2$O$_3$ catalyst. We do not have an explanation for these observations at this time, but it may involve differences in the availability of hydrogen for cleavage of the C$-$S bonds of thiophene. Prior to thiophene exposure, the reduced Ni$_2$P/SiO$_2$ catalyst was degassed at 650 K, so it is unlikely that much adsorbed hydrogen is available on the surface at the outset. More likely, hydrogen becomes available for hydrogenolysis of C$-$S bonds via decomposition of some thiophene on the surface or via an intramolecular desulfurization mechanism similar to that proposed by Kolboe.[53] On the basis of our IR spectroscopic observations, we do not see evidence for formation of a highly unsaturated C$_4$ species (e.g., adsorbed diacetylene) on the reduced Ni$_2$P/SiO$_2$ catalyst that would be expected for an intramolecular desulfurization mechanism. As a result, we conclude that the high reactivity of reduced Ni$_2$P/SiO$_2$ catalysts toward thiophene in the absence of gaseous hydrogen is due to the ability of the phosphide catalyst to decompose some thiophene to give adsorbed H (as well as C and S species) on the surface. This adsorbed H subsequently participates in C$-$S bond cleavage of the remaining adsorbed thiophene to give adsorbed C$_4$ species on the reduced Ni$_2$P/SiO$_2$ catalysts, as observed in the IR spectra associated with annealing the catalysts in the 300$-$650 K range.

In the presence of a thiophene/H$_2$ mixture (P_{Th} = 5.0 Torr; P_{H_2} = 151.25 Torr), substantially higher reactivity is observed for thiophene on reduced Ni$_2$P/SiO$_2$ catalysts than in the presence of thiophene alone. Even at 300 K, the ν_{CH} absorbances associated with adsorbed hydrocarbon species are more intense than those for molecularly adsorbed thiophene for a reduced Ni$_2$P/SiO$_2$ catalyst exposed to the thiophene/H$_2$ mixture. The intensities of the ν_{CH} absorbances below 3000 cm^{-1}, particularly those at 2868 [ν_s(CH$_3$)] and 2948 cm^{-1} [ν_{as}(CH$_3$)], grow substantially upon annealing to 400$-$500 K, indicating facile hydrogenation of unsaturated hydrocarbon fragments adsorbed on the reduced Ni$_2$P/SiO$_2$ catalyst to give predominantly saturated hydrocarbon species on the catalyst surface. As was observed for a reduced Ni$_2$P/SiO$_2$ catalyst annealed in 5.0 Torr of thiophene alone, these IR spectroscopic results are remarkably similar to what was observed previously on a sulfided Rh/Al$_2$O$_3$ catalyst.[27] In contrast, within the signal-to-noise limitations of the measurements, no reactivity was observed for a sulfided Ni/SiO$_2$ catalyst annealed in a thiophene/H$_2$ mixture. Clearly, the incorporation of P into Ni catalysts to give supported Ni$_2$P particles has a profound influence on the reactivity of the catalysts toward thiophene relative to S incorporation into a sulfided Ni/SiO$_2$ catalyst to give a sulfided Ni phase on the support. Similar annealing experiments in a thiophene/H$_2$ mixture have also been reported for sulfided Mo/Al$_2$O$_3$[26,27] and freshly prepared Mo$_2$N/Al$_2$O$_3$ catalysts,[42] and substantial dif-

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ferences are apparent in the IR spectra acquired following each anneal. For the sulfided Mo/Al$_2$O$_3$ catalyst,[26] ν_{CH} absorbances below 3000 cm^{-1} became apparent only after annealing to 600 K, while for the Mo$_2$N/Al$_2$O$_3$ catalysts similar absorbance features were first observed after annealing to 373 K.[42] Consistent with our observations for the Ni catalysts, the main group element incorporated into the Mo-based catalysts (i.e., N or S) significantly affects the reactivity of these catalysts toward thiophene. For both the Ni- and Mo-based catalysts, the incorporated main group element modifies both the electronic and structural properties of the metal, so it is not surprising that the catalytic properties are also significantly altered.

In addition to the effects on thiophene adsorption and reactivity described above, differences are observed in the adsorption of CO on Ni$_2$P/SiO$_2$ and Mo$_2$N/Al$_2$O$_3$ catalysts relative to the sulfided metal catalysts. While risking oversimplification, it can be summarized that sulfur withdraws electron density from metal sites and lowers the amount of CO adsorbed on sulfided Ni/SiO$_2$ and Mo/Al$_2$O$_3$ catalysts by blocking sites.[17,54,55] The effect of P and N in Ni$_2$P/SiO$_2$ and Mo$_2$N/Al$_2$O$_3$ catalysts, respectively, is more complicated.[17,56−58] In each case, the main group element appears to withdraw a small amount of electron density from the metal sites, but surface P and N atoms also serve as adsorption sites for CO in the form of surface-bonded P=C=O and N=C=O species, respectively. These observations suggest that surface P and N atoms may also participate directly in the adsorption and reactions of thiophene on Ni$_2$P/SiO$_2$ and Mo$_2$N/Al$_2$O$_3$ catalysts, respectively, enhancing the HDS properties of the catalysts. Finally, the effect of P on the HDS activities of the Ni-based catalysts is more significant than that of N in the Mo-based catalysts. As discussed earlier, Ni$_2$P/SiO$_2$ catalysts are 20−30 times more active than Ni/SiO$_2$ catalysts, while we reported previously that Mo$_2$N/ Al$_2$O$_3$ catalysts were only about 20% more active than sulfided Mo/Al$_2$O$_3$ catalysts.[43] In the case of the Mo$_2$N/Al$_2$O$_3$ catalysts, IR spectroscopic measurements showed that a thin sulfided Mo layer formed on the surface of the Mo$_2$N particles.[22,44] While these sites were identical with those on sulfided Mo/Al$_2$O$_3$ catalysts, the sulfided Mo layer on the Mo$_2$N/Al$_2$O$_3$ catalysts possessed a higher site density, which explains the higher HDS activity of these catalysts. For the Ni-based catalysts, the Ni$_2$P/ SiO$_2$ catalysts are more resistant to sulfidation. Experimental evidence points to the formation of a surface NiP$_x$S$_y$ phase,[8,11,16,17] which the results presented in the current study indicate is much more reactive toward thiophene than is sulfided Ni.

Coadsorption of CO and Thiophene on Ni$_2$P/SiO$_2$ Catalysts. Preadsorbed CO strongly suppresses thiophene adsorption on the available Ni sites of a reduced Ni$_2$P/SiO$_2$ catalyst as indicated by the absence of the symmetric $\nu_{(C=C)sym}$ absorbance at 1424 cm^{-1} (Figure 6). In addition, a negligible amount of the preadsorbed CO was removed by thiophene adsorption nor did CO desorb for the Ni$_2$P/SiO$_2$ catalyst upon evacuation to UHV and heating from 150 to 190 K. Furthermore, CO was observed to displace preadsorbed thiophene (Figure 7). These results clearly indicate that CO and thiophene compete for the available Ni sites on the reduced Ni$_2$P/SiO$_2$ catalysts. Since CO adsorbs to the same sites as thiophene on the Ni$_2$P particles, IR spectroscopic studies of CO adsorption on Ni$_2$P/SiO$_2$ yield qualitative information concerning the type and reactivity of the available sites on which thiophene HDS occurs on reduced and sulfided Ni$_2$P/SiO$_2$ catalysts. However, CO must be used cautiously as a probe molecule for determining active site density since CO titrates more than one type of site on Ni$_2$P/ SiO$_2$ catalysts under the conditions typically used for chemi-

sorption capacity measurements. This conclusion is based on the following observations: (1) we observe the formation of Ni(CO)$_4$ on reduced and sulfided Ni$_2$P/SiO$_2$ catalysts;[17] (2) CO adsorbs on the bridge sites of reduced Ni$_2$P/SiO$_2$ catalysts; and (3) CO also reacts with the surface P atoms of Ni$_2$P/SiO$_2$ catalysts. These sites were detected in our IR spectroscopic data even when the reduced and sulfided Ni$_2$P/SiO$_2$ catalysts were exposed to 5.0 Torr of CO at temperatures as high as 298 K. CO chemisorption measurements are typically conducted at 273 or 298 K. On the basis of our IR spectroscopic results for the adsorption of 5.0 Torr of CO on our reduced and sulfided Ni$_2$P/ SiO$_2$ catalysts, we conclude that CO chemisorption measurements would titrate sites in addition to those active for thiophene HDS. Thus, CO chemisorption measurements would overestimate the number of available active sites for thiophene HDS on reduced and sulfided Ni$_2$P/SiO$_2$ catalysts.

Conclusion

We have investigated the surface chemistry of thiophene and coadsorbed CO and thiophene on reduced and sulfided Ni$_2$P/ SiO$_2$ catalysts using infrared (IR) spectroscopy. Thiophene is very reactive on Ni$_2$P/SiO$_2$ catalysts; even at 190 K, cleavage of the C−S bonds occurred, forming 1,3-butadiene-like species on the surface. Annealing this thiophene-dosed surface to 250 K resulted in the formation of more saturated hydrocarbon species (e.g., C$_4$H$_7$) on the catalyst surface. In the presence of H$_2$ and elevated temperatures, the reactivity of thiophene on Ni$_2$P/SiO$_2$ catalysts increased substantially. The IR spectroscopic data for the adsorption and reactivity of CO and thiophene on reduced and sulfided Ni/SiO$_2$ and Ni$_2$P/SiO$_2$ catalysts correlate well with the trend of HDS activity of the catalysts. Specifically, Ni$_2$P/SiO$_2$ catalysts are more reactive toward thiophene than reduced and sulfided Ni/SiO$_2$ catalysts in UHV. Comparing the thiophene reactivity of reduced and sulfided Ni$_2$P/SiO$_2$ and Ni/SiO$_2$ catalysts to the thiophene reactivity reported for sulfided Cu/Al$_2$O$_3$, Mo/Al$_2$O$_3$, and Rh/Al$_2$O$_3$ catalysts, we concluded the following thiophene reactivity order for the HDS catalysts: sulfided Cu/Al$_2$O$_3$ < sulfided Ni/SiO$_2$ < reduced Ni/SiO$_2$ < sulfided Mo/Al$_2$O$_3$ < sulfided Rh/Al$_2$O$_3$ < sulfided Ni$_2$P/SiO$_2$ < reduced Ni$_2$P/SiO$_2$. From this ranking, we conclude that sulfided and reduced Ni$_2$P/SiO$_2$ catalysts exhibit the highest thiophene reactivity of the different catalysts under UHV conditions. Above room temperature, the reactivity of thiophene on Ni$_2$P/SiO$_2$ catalysts is similar to that observed previously for sulfided Rh/Al$_2$O$_3$ catalysts. Coadsorption experiments indicate that CO and thiophene compete for the same sites on the Ni$_2$P/SiO$_2$ catalysts, as preadsorbed CO blocked the adsorption of thiophene. Therefore, IR spectroscopic studies of the adsorption of CO on sulfided and reduced Ni$_2$P/SiO$_2$ catalysts can be used to qualitatively characterize the active sites on which thiophene HDS occurs. However, since CO would titrate sites other than those involved in the HDS of thiophene, it should be used cautiously as a probe molecule for determining active site density.

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