

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

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The surface chemistry of CO on reduced and sulfided  $\text{Ni}_2\text{P}/\text{SiO}_2$  catalysts has been investigated with infrared (IR) spectroscopy. There are four different  $\nu_{\text{CO}}$  absorbances observed for adsorbed CO on reduced and sulfided  $\text{Ni}_2\text{P}/\text{SiO}_2$  catalysts with the following assignments: (1) CO terminally bonded to *cus*  $\text{Ni}^{\delta+}$  ( $0 < \delta < 1$ ) sites ( $2083\text{--}2093\text{ cm}^{-1}$ ); (2) CO adsorbed on  $\text{Ni}^{\delta+}$  ( $0 < \delta < 1$ ) bridge sites ( $1914\text{ cm}^{-1}$ ); (3) CO terminally bonded to P ( $\sim 2200\text{ cm}^{-1}$ ); and (4) formation of  $\text{Ni}(\text{CO})_4$  ( $2056\text{ cm}^{-1}$ ). At 298 K, CO terminally bonded to *cus*  $\text{Ni}^{\delta+}$  ( $0 < \delta < 1$ ) sites on reduced  $\text{Ni}_2\text{P}/\text{SiO}_2$  catalysts exhibited a characteristic  $\nu_{\text{CO}}$  absorbance at  $2083\text{ cm}^{-1}$ , while treatment of  $\text{Ni}_2\text{P}/\text{SiO}_2$  catalysts with a 3.03 mol %  $\text{H}_2\text{S}/\text{H}_2$  mixture shifts this  $\nu_{\text{CO}}$  absorbance to  $2093\text{ cm}^{-1}$ . The enthalpy of adsorption ( $\Delta H_{\text{ads}}$ ) of CO on the  $\text{Ni}_2\text{P}/\text{SiO}_2$  catalysts was estimated by using a van't Hoff plot:  $\Delta H_{\text{ads}} = -31.4 \pm 1.5$  and  $-30.5 \pm 1.5\text{ kJ/mol}$  for reduced and sulfided  $\text{Ni}_2\text{P}/\text{SiO}_2$  catalysts, respectively. The IR spectroscopic data for the adsorption of CO on reduced and sulfided  $\text{Ni}_2\text{P}/\text{SiO}_2$  and  $\text{Ni}/\text{SiO}_2$  catalysts correlate well with the trend of hydrodesulfurization (HDS) activity of catalysts. Specifically, we observe a higher site density and higher  $\Delta H_{\text{ads}}$  for CO adsorption on the  $\text{Ni}_2\text{P}/\text{SiO}_2$  catalysts compared to both reduced and sulfided  $\text{Ni}/\text{SiO}_2$  catalysts. The IR spectroscopic and HDS catalytic results are consistent with the formation of a surface phosphosulfide phase (i.e.  $\text{NiP}_x\text{S}_y$ ) on the  $\text{Ni}_2\text{P}/\text{SiO}_2$  catalysts under sulfiding conditions.

## 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 high activity hydrodesulfurization (HDS) catalysts. A new class of materials, the transition metal phosphides (e.g.  $\text{MoP}$ ,<sup>1–3</sup>  $\text{WP}$ ,<sup>4,5</sup> and  $\text{Ni}_2\text{P}$ <sup>6–12</sup>), has shown high HDS activity. Of these catalysts, silica-supported  $\text{Ni}_2\text{P}$  demonstrated the highest HDS activity and has been reported to have a higher activity, under conditions similar to those used in industry, than commercial  $\text{Ni-Mo}/\text{Al}_2\text{O}_3$  and  $\text{Co-Mo}/\text{Al}_2\text{O}_3$  catalysts for the HDS of a model feed containing quinoline (2000 ppm N), dibenzothiophene (3000 ppm S), tetralin (20 wt %), and tetradecane (balance).<sup>6</sup> Therefore,  $\text{Ni}_2\text{P}/\text{SiO}_2$  may have promise as a future hydroprocessing catalyst.

In a previous study, we described the HDS catalytic properties of  $\text{Ni}_2\text{P}/\text{SiO}_2$  catalysts with a wide range of loadings, and compared them with sulfided  $\text{Ni}/\text{SiO}_2$ ,  $\text{Mo}/\text{SiO}_2$ , and  $\text{Ni-Mo}/\text{SiO}_2$  ( $\text{Ni}/\text{Mo} = 0.5$ ) catalysts.<sup>8</sup> Briefly, we observed that the thiophene HDS activity, after 100 h on-stream, of a 30 wt %  $\text{Ni}_2\text{P}/\text{SiO}_2$  catalyst was approximately 15 and 3 times more active than sulfided  $\text{Mo}/\text{SiO}_2$  and  $\text{Ni-Mo}/\text{SiO}_2$  catalysts, respectively. In addition, silica-supported  $\text{Ni}_2\text{P}$  catalysts showed excellent stability under HDS conditions. The HDS activities of the catalysts correlated with their  $\text{O}_2$  chemisorption capacities and it was concluded that the high HDS activity of  $\text{Ni}_2\text{P}/\text{SiO}_2$  catalysts can be traced to both a high site density and a high turnover frequency (TOF). X-ray photoelectron spectroscopic (XPS) measurements yielded a surface composition of  $\text{Ni}_{2.2}\text{P}_{1.0}$  and indicated the transfer of some electron density from Ni to

P in both unsupported and silica-supported  $\text{Ni}_2\text{P}$ . As a result, the phosphorus bears a partial negative charge,  $\delta^-$ , and Ni bears a partial positive charge,  $\delta^+$ , where  $0 < \delta \leq 2$ .<sup>8</sup> Solid-state NMR spectroscopic data indicate that  $\text{Ni}_2\text{P}$  has metallic properties.<sup>13</sup> However, the role that these properties play in the high HDS activity of  $\text{Ni}_2\text{P}/\text{SiO}_2$  catalysts is not well understood. In addition, the chemical properties of the surface sites of  $\text{Ni}_2\text{P}/\text{SiO}_2$  catalysts and the effects of pretreatment (reduction, sulfidation) need to be elucidated. Furthermore, since CO is often used to estimate active site densities of catalysts, it is important to probe the chemistry of adsorbed CO on  $\text{Ni}_2\text{P}/\text{SiO}_2$  catalysts.

Infrared (IR) spectroscopy of adsorbed probe molecules (e.g. CO, NO, and pyridine ( $\text{C}_5\text{H}_5\text{N}$ )) on various catalytic surfaces is one of the most widely employed methods for the determination of concentration, nature, and acidity of catalytic active sites.<sup>14–18</sup> CO is typically chosen as the probe molecule since its small molecular size enables it to probe all available catalytic sites, it is generally unreactive, and its C–O stretching frequency is well characterized for CO adsorption on most metal and metal oxide surfaces.<sup>15,16,19–23</sup> We, therefore, have chosen to perform an IR spectroscopic investigation of CO adsorption on  $\text{Ni}_2\text{P}/\text{SiO}_2$  catalysts to characterize the sites available on these catalysts for the HDS of thiophene.

## Experimental Methods

**Catalyst Preparation.**  $\text{Ni}_2\text{P}/\text{SiO}_2$ . A 20 wt %  $\text{Ni}_2\text{P}/\text{SiO}_2$  catalyst was prepared following a procedure described in detail elsewhere.<sup>8</sup> Briefly, 4.90 g of nickel nitrate was dissolved in approximately 10 mL of deionized water. The solution was impregnated onto 5.0 g of calcined silica ( $\text{SiO}_2$ , Cab-O-Sil, M-7D, 200  $\text{m}^2/\text{g}$ ) and dried at 373 K. The impregnated silica was calcined at 773 K for 2 h. After calcination, the sample

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was impregnated with 1.55 g of ammonium dihydrogen phosphate (NH<sub>4</sub>H<sub>2</sub>PO<sub>4</sub>) and dried at 373 K overnight. The oxidic precursor was reduced via temperature programmed reduction (TPR) in flowing H<sub>2</sub> (150 sccm) from 298 to 923 K (1 K/min). The sample was then cooled to room temperature in the flowing H<sub>2</sub>, flushed with flowing He (60 sccm) for 15 min, and then passivated in a flow of 1.0 mol % O<sub>2</sub>/He (30 sccm) for 2 h to yield silica-supported Ni<sub>2</sub>P. The *passivated* Ni<sub>2</sub>P/SiO<sub>2</sub> catalysts were transferred through air to the flow reactor or the UHV system where they were reduced or sulfided as described later.

**Ni/SiO<sub>2</sub> and Sulfided Ni/SiO<sub>2</sub>.** For comparison purposes, an oxidic precursor (NiO/SiO<sub>2</sub>) of reduced and sulfided Ni/SiO<sub>2</sub> catalysts was prepared with a Ni loading similar to that of the 20 wt % Ni<sub>2</sub>P/SiO<sub>2</sub> 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. The NiO/SiO<sub>2</sub> precursors were transferred through air to the flow reactor or the 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.<sup>24</sup> Activity measurements were carried out at a reaction temperature of 643 K, using a reactor feed consisting of a 3.2 mol % thiophene/H<sub>2</sub> mixture. Prior to the measurement of thiophene HDS activities, the Ni/SiO<sub>2</sub> and Ni<sub>2</sub>P/SiO<sub>2</sub> catalysts 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<sub>2</sub> 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<sub>2</sub>S/H<sub>2</sub> 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<sub>2</sub> 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  $\sim 5 \times 10^{-9}$  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.<sup>25</sup>

The catalyst under study was mounted in the UHV system following the procedures described previously.<sup>25</sup> Briefly, 5.0–15.0 mg of the desired catalyst was pressed at 10 000 psi into a nickel metal mesh (50  $\times$  50 mesh size, 0.002 in. wire diameter); the area of the pressed samples was 0.80 cm<sup>2</sup>. 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  $\sim 30$  min. Unless otherwise stated, the catalysts were then either reduced or sulfided in situ. Specifically, the catalysts were reduced in flowing H<sub>2</sub> (60 sccm) at 650 K for 1 h or sulfided in 100 Torr of a 3.03 mol % H<sub>2</sub>S/H<sub>2</sub> mixture at 625 K for 15 min. To remove weakly bonded species from the surface of both the reduced and sulfided catalysts, the high-pressure cell was then evacuated to  $\sim 1 \times 10^{-7}$  Torr prior to annealing the sample at 650 K for 1 min.

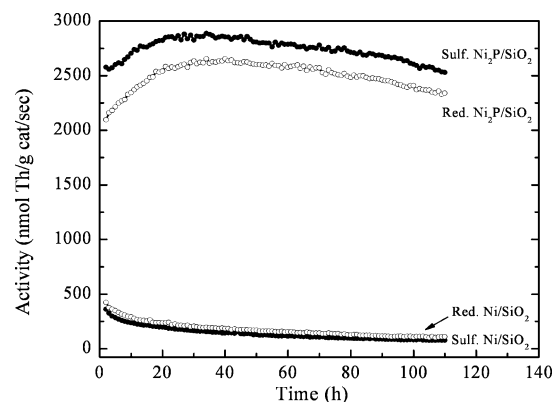
Transmission FTIR spectra were acquired in the 4000–1000-cm<sup>-1</sup> range by collecting 128 scans at 4-cm<sup>-1</sup> resolution. The sample spectrum was ratioed against a background spectrum acquired by using a blank nickel mesh mounted in the sample holder. Depending upon the experiment, the background spectrum was acquired in UHV, in 5.0 Torr CO, or in 5.0 Torr 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.

**Adsorbed CO in the Presence of 5.0 Torr of CO at 298 K.** Following pretreatment, the reduced/sulfided sample was cooled to room temperature at a pressure of  $\sim 1 \times 10^{-8}$  Torr and a background IR spectrum was acquired. An IR spectrum of adsorbed CO was then collected at 298 K while the catalyst sample was in the presence of 5.0 Torr of CO.

**Adsorbed CO as a Function of Pretreatment Temperature.** The following reduction/sulfidation process was repeated in 50 K increments between 400 and 650 K. The desired catalyst (not pretreated) was heated to 400 K in either 100 Torr of H<sub>2</sub> or in 100 Torr of a 3.03 mol % H<sub>2</sub>S/H<sub>2</sub> mixture for 15 min followed by cooling to room temperature. The high-pressure cell was then evacuated to  $\sim 1 \times 10^{-7}$  Torr prior to annealing the sample at 400 K for 1 min. Following pretreatment, the reduced/sulfided sample was cooled to room temperature at a pressure of  $\sim 1 \times 10^{-8}$  Torr and a background IR spectrum was acquired. An IR spectrum of adsorbed CO was then collected at 298 K while the catalyst sample was in the presence of 5.0 Torr of CO.

**Adsorbed CO at Low Temperature.** Following pretreatment, the reduced/sulfided catalyst sample was cooled to 150 K at a pressure of  $\sim 1 \times 10^{-8}$  Torr and a background IR spectrum was acquired. An IR spectrum of adsorbed CO was then collected at 150 K while the catalyst sample was in the presence of 5.0 Torr of CO. The high-pressure cell was then evacuated to UHV pressures prior to collecting another IR spectrum. The sample was then annealed (in UHV) at 175 K for 1 min. 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 collected at 150 K after each anneal cycle until all of the adsorbed CO had desorbed from the surface of the catalyst under study.

**Determination of  $\Delta H_{ads}$  for CO.** Following pretreatment, the reduced/sulfided catalyst was cooled to room temperature at a pressure of  $\sim 1 \times 10^{-8}$  Torr and a background IR spectrum was acquired. An IR spectrum of adsorbed CO was then collected at 298 K while the catalyst sample was in the presence of 5.0 Torr of CO. While maintaining a background pressure of 5.0 Torr of CO, the sample was then heated to 325 K and allowed to equilibrate for 1 min, and an IR spectrum was collected at 325 K. This procedure was repeated while heating to higher temperatures in 25 K increments until no CO remained adsorbed on the surface.



**Figure 1.** Thiophene HDS activity data for reduced and sulfided Ni/SiO<sub>2</sub> and Ni<sub>2</sub>P/SiO<sub>2</sub> catalysts.

**TABLE 1: IR Spectral and HDS Activity Results**

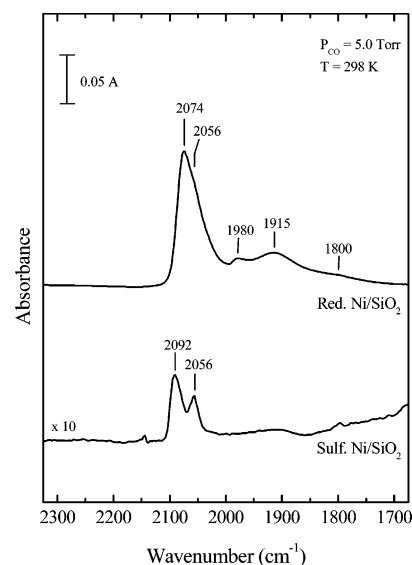
catalyst	$\nu_{\text{CO}}$ (cm <sup>-1</sup> ) <sup>a</sup>	relative CO site densities <sup>d,b</sup>	$\Delta H_{\text{ads}}(\text{CO})$ (kJ/mol) <sup>c</sup>	thiophene HDS activities <sup>d,e</sup>
reduced Ni/SiO <sub>2</sub>	2074	0.87	-23.7 ± 1.4	112.6
sulfided Ni/SiO <sub>2</sub>	2092	0.04	-18.9 ± 1.0	86.9
reduced Ni <sub>2</sub> P/SiO <sub>2</sub>	2083	3.41	-31.4 ± 1.5	2370.7
sulfided Ni <sub>2</sub> P/SiO <sub>2</sub>	2093	1.38	-30.5 ± 1.5	2591.6

<sup>a</sup> For CO adsorbed on Ni atop sites only at 298 K. <sup>b</sup> Integrated absorbance/mg of catalyst. <sup>c</sup> For CO adsorption on Ni atop and bridge sites. <sup>d</sup> nmol of thiophene/g of catalyst/s. <sup>e</sup> Activities after 100 h on-stream.

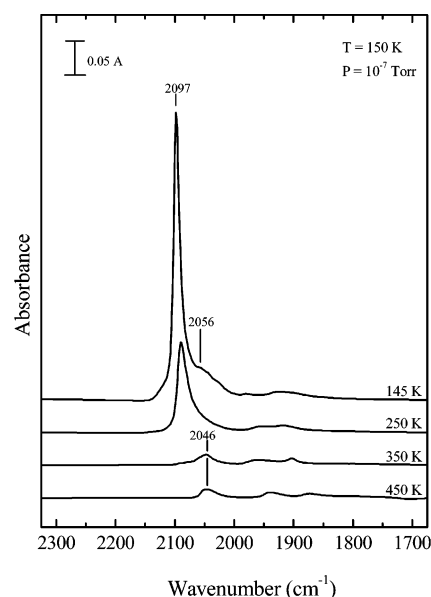
## Results

**Thiophene HDS Activity Measurements.** Thiophene HDS activity data as a function of time on-stream for reduced and sulfided Ni/SiO<sub>2</sub> and Ni<sub>2</sub>P/SiO<sub>2</sub> catalysts are shown in Figure 1. The HDS activities of the catalysts after 100 h on-stream are listed in Table 1. As reported previously,<sup>8</sup> Ni<sub>2</sub>P/SiO<sub>2</sub> catalysts have high thiophene HDS activities when pretreated by reduction or sulfidation at 650 K. The HDS activities of the Ni<sub>2</sub>P/SiO<sub>2</sub> catalysts reached a maximum after 25–40 h on-stream and then declined gradually thereafter. After 100 h on-stream, the sulfided Ni<sub>2</sub>P/SiO<sub>2</sub> catalyst was ~10% more active than the reduced Ni<sub>2</sub>P/SiO<sub>2</sub> catalyst. As shown in Figure 1, the reduced and sulfided Ni/SiO<sub>2</sub> catalysts have very low HDS activities which decrease monotonically as a function of time on-stream. The HDS activities of the Ni/SiO<sub>2</sub> catalysts are significantly more sensitive to the pretreatment utilized than was observed for the Ni<sub>2</sub>P/SiO<sub>2</sub> catalysts. After 100 h on-stream, the reduced Ni/SiO<sub>2</sub> catalyst is ~30% more active than the sulfided Ni/SiO<sub>2</sub> catalyst. The effect of P on the HDS activities of the catalysts is dramatic; the reduced Ni<sub>2</sub>P/SiO<sub>2</sub> catalyst is ~21 times more active than the reduced Ni/SiO<sub>2</sub> catalyst after 100 h while the sulfided Ni<sub>2</sub>P/SiO<sub>2</sub> catalyst is ~30 times more active than the sulfided Ni/SiO<sub>2</sub> catalyst after 100 h.

**Infrared Spectroscopy Measurements of Adsorbed CO on Ni/SiO<sub>2</sub> Catalysts at 298 K.** To facilitate comparison with Ni<sub>2</sub>P/SiO<sub>2</sub> catalysts, IR spectra for CO adsorbed on reduced and sulfided Ni/SiO<sub>2</sub> catalysts in the presence of 5.0 Torr of CO at 298 K were obtained and these are shown in Figure 2. The peak position of the intense  $\nu_{\text{CO}}$  absorbance for the reduced Ni/SiO<sub>2</sub> catalyst, 2074 cm<sup>-1</sup>, is slightly above the range given for a single, terminally bonded CO molecule on Ni<sup>0</sup> sites (2040–2070 cm<sup>-1</sup>),<sup>26–29</sup> but is within the range reported for multiple coordination of CO to a single Ni<sup>0</sup> site (2065–2090 cm<sup>-1</sup>).<sup>26,28,29</sup> The observed upward shift in frequency for the  $\nu_{\text{CO}}$  absorbance compared to that expected for CO terminally bonded on Ni<sup>0</sup>



**Figure 2.** IR spectra of adsorbed CO on reduced and sulfided Ni/SiO<sub>2</sub> catalysts ( $P_{\text{CO}} = 5.0$  Torr;  $T = 298$  K).



**Figure 3.** IR spectra of adsorbed CO on reduced Ni/SiO<sub>2</sub> catalysts as a function of anneal temperature. The catalyst was initially exposed to 5.0 Torr of CO at 145 K and then evacuated to UHV. The IR spectra were acquired after annealing to the given temperatures for 1 min in UHV and cooling to 150 K.

sites is a result of dipole–dipole coupling between neighboring CO molecules. Evidence for this assignment comes from another experiment, the results of which are shown in Figure 3. Briefly, in this experiment, a reduced 20 wt % Ni/SiO<sub>2</sub> catalyst was exposed to 5.0 Torr of CO at 145 K. The catalyst sample was then evacuated to UHV pressures, and an IR spectrum was acquired. Following the acquisition of this IR spectrum, the sample was annealed to 175 K and higher in 25 K increments. The peak position for the  $\nu_{\text{CO}}$  absorbance for CO linearly bonded to Ni<sup>0</sup> atoms shifted from 2097 cm<sup>-1</sup> at 145 K to 2048 cm<sup>-1</sup> at 450 K as the peak intensity decreased, indicating a decrease in the concentration of CO adsorbed on the Ni/SiO<sub>2</sub> catalyst.

The two weak  $\nu_{\text{CO}}$  absorbances at 1980 and 1915 cm<sup>-1</sup> in the IR spectrum for the reduced Ni/SiO<sub>2</sub> catalyst are due to the adsorption of CO on Ni<sup>0</sup> bridge sites. The observation of CO adsorbed on two types of Ni<sup>0</sup> bridge sites suggests that there are two different crystalline planes available for CO adsorption.

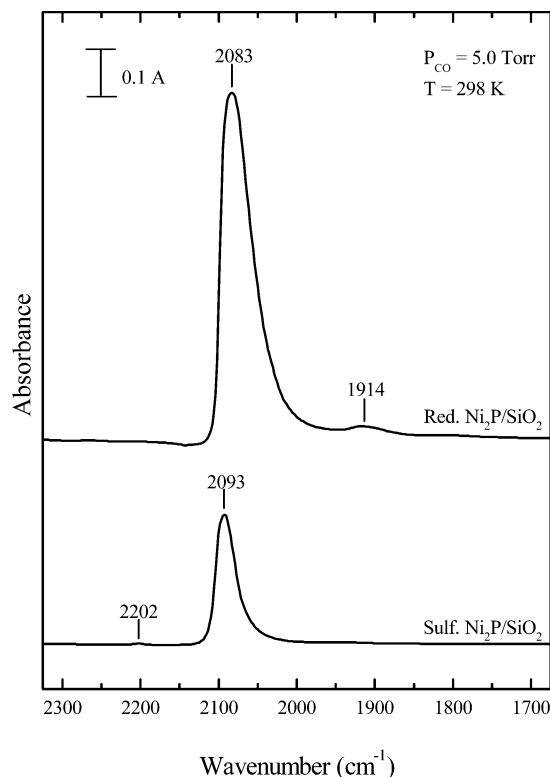


On the basis of the results for CO adsorption on the well-defined Ni(111), Ni(110), and Ni(100) surfaces reported by others,<sup>30–32</sup> we have assigned the  $\nu_{\text{CO}}$  absorbance at 1980 cm<sup>-1</sup> to CO adsorbed on Ni<sup>0</sup> bridge sites of the Ni(110) crystalline plane and the absorbance at 1915 cm<sup>-1</sup> to CO adsorbed on Ni<sup>0</sup> bridge sites of the Ni(111) crystalline plane. The observed  $\nu_{\text{CO}}$  absorbance at 1980 cm<sup>-1</sup> is slightly higher than the frequencies reported in the literature for the adsorption of CO on Ni<sup>0</sup> bridge sites of reduced Ni/SiO<sub>2</sub> catalysts (1810–1960 cm<sup>-1</sup>).<sup>30–32</sup> A very weak  $\nu_{\text{CO}}$  absorbance is also observed at 1800 cm<sup>-1</sup>. This absorbance feature is assigned to either a second type of CO adsorption on the Ni bridge sites of the Ni(111) crystalline plane or to CO adsorption on a 4-fold Ni bridge site located in the Ni(110) crystalline plane.<sup>30–32</sup>

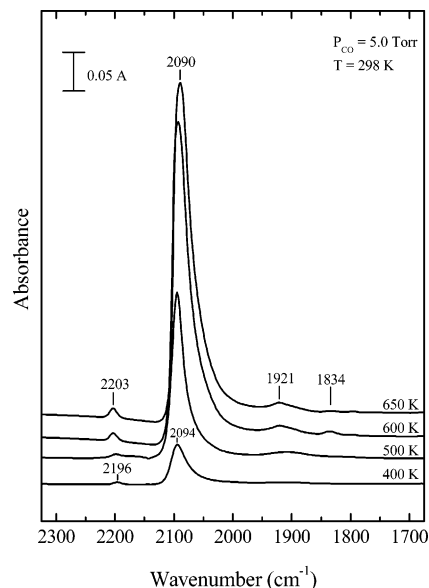
For the sulfided Ni/SiO<sub>2</sub> catalysts (Figure 2), the frequency of the  $\nu_{\text{CO}}$  absorbance for CO terminally bonded to Ni sites shifts from 2074 to 2092 cm<sup>-1</sup>, and no  $\nu_{\text{CO}}$  absorbance associated with adsorption of CO on bridge-bonding sites is observed. In addition, there is a significant decrease in the intensity of the  $\nu_{\text{CO}}$  absorbance assigned to CO terminally bonded to Ni sites, indicating a decrease in the number of these sites available for CO adsorption. Comparing the frequency of this  $\nu_{\text{CO}}$  absorbance to the frequency observed for terminally bonded CO on Ni/SiO<sub>2</sub> (2040–2070 cm<sup>-1</sup>),<sup>26–29</sup> Ni/Al<sub>2</sub>O<sub>3</sub> (2085–2090 cm<sup>-1</sup>),<sup>33,34</sup> Ni<sup>+</sup>/SiO<sub>2</sub> (2145 cm<sup>-1</sup>),<sup>35</sup> Ni<sup>+</sup>/Al<sub>2</sub>O<sub>3</sub> (2137–2155 cm<sup>-1</sup>),<sup>33</sup> and Ni<sup>2+</sup>/SiO<sub>2</sub> (2190–2217 cm<sup>-1</sup>),<sup>35,36</sup> we observe that the magnitude of the positive charge ( $\delta$ ) on the Ni in the sulfided Ni/SiO<sub>2</sub> catalyst is between 0 and 1, and is presumably closer to zero than to 1.

For the sulfided Ni/SiO<sub>2</sub> catalyst, a second  $\nu_{\text{CO}}$  absorbance is observed at 2056 cm<sup>-1</sup>; a shoulder at this position is apparent in the IR spectrum for adsorbed CO on the reduced Ni/SiO<sub>2</sub> catalyst. The position of this absorbance is similar to those reported for a nickel tetracarbonyl (Ni(CO)<sub>4</sub>)—surface vibration on SiO<sub>2</sub>,<sup>33</sup> suggesting that some of the CO reacts on the surface of the reduced and sulfided Ni/SiO<sub>2</sub> catalysts, producing adsorbed Ni(CO)<sub>4</sub>. Other experimental results collected in our laboratory confirm the assignment of this absorbance to a vibration of adsorbed Ni(CO)<sub>4</sub>. In the previously described low-temperature CO experiment for the Ni/SiO<sub>2</sub> catalyst, this absorbance is more pronounced due to the blue shift of the  $\nu_{\text{CO}}$  absorbance corresponding to terminally bonded CO on metallic Ni atoms (see Figure 3). In addition, the  $\nu_{\text{CO}}$  absorbance at 2056 cm<sup>-1</sup> does not shift for the sulfided Ni/SiO<sub>2</sub> catalyst. Since we do not observe a shift in the frequency of this  $\nu_{\text{CO}}$  absorbance upon sulfidation of the catalyst under study, we can rule out the possibility that the shoulder is due to CO terminally bonded to Ni atoms within a different crystalline plane. We, therefore, assign the absorbance at 2056 cm<sup>-1</sup> on both the reduced and sulfided Ni/SiO<sub>2</sub> catalysts to a vibration of adsorbed Ni(CO)<sub>4</sub>.

**Infrared Spectroscopy Measurements of Adsorbed CO on Ni<sub>2</sub>P/SiO<sub>2</sub> Catalysts at 298 K.** The IR spectra for CO adsorbed on reduced and sulfided Ni<sub>2</sub>P/SiO<sub>2</sub> catalysts, shown in Figure 4, are dramatically different from the IR spectra collected after adsorption of CO on reduced and sulfided Ni/SiO<sub>2</sub> catalysts (Figure 2). First, the adsorption of CO on Ni bridge sites is strongly suppressed, as indicated by the attenuation of the previously observed  $\nu_{\text{CO}}$  absorbances between 1844 and 1980 cm<sup>-1</sup>. The formation of Ni(CO)<sub>4</sub> is also suppressed on reduced and sulfided Ni<sub>2</sub>P/SiO<sub>2</sub> catalysts, i.e., the  $\nu_{\text{CO}}$  absorbance at 2056 cm<sup>-1</sup> is less intense on these catalysts. A new, very weak,  $\nu_{\text{CO}}$  absorbance feature is observed at 2202 cm<sup>-1</sup> for the sulfided Ni<sub>2</sub>P/SiO<sub>2</sub> catalyst; the assignment of this absorbance feature will be discussed in the following section. Finally, the frequency



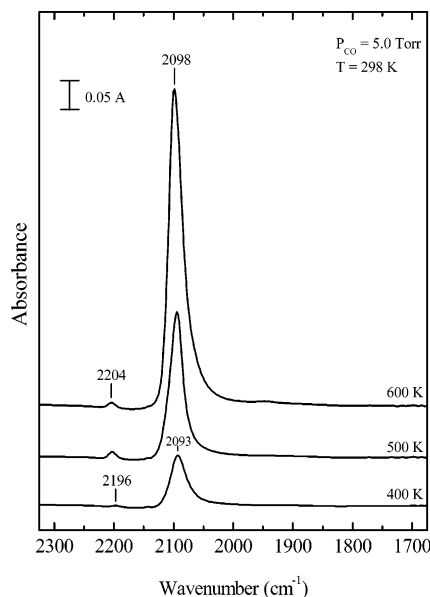
**Figure 4.** IR spectra of adsorbed CO on reduced and sulfided Ni<sub>2</sub>P/SiO<sub>2</sub> catalysts ( $P_{\text{CO}} = 5.0$  Torr;  $T = 298$  K).



**Figure 5.** IR spectra of adsorbed CO on Ni<sub>2</sub>P/SiO<sub>2</sub> catalysts as a function of reduction temperature ( $P_{\text{CO}} = 5$  Torr;  $T = 298$  K).

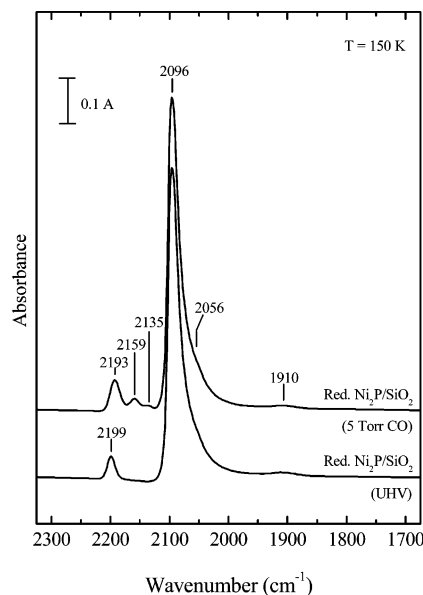
of the  $\nu_{\text{CO}}$  absorbance has shifted from 2074 cm<sup>-1</sup> for the reduced Ni/SiO<sub>2</sub> catalyst to 2083 cm<sup>-1</sup> for the reduced Ni<sub>2</sub>P/SiO<sub>2</sub> catalyst; essentially no shift is observed for the sulfided catalysts.

**Infrared Spectroscopy Measurements of Adsorbed CO as a Function of Pretreatment Temperature.** We have studied the effect of pretreatment temperature on the adsorption of CO on Ni<sub>2</sub>P/SiO<sub>2</sub> catalysts. Figures 5 and 6 display the IR spectra obtained for CO adsorption on Ni<sub>2</sub>P/SiO<sub>2</sub> catalysts as a function of the reduction and sulfidation temperatures, respectively. While IR spectra were collected at 50 K intervals between 400 and 650 K (400–600 K for the sulfidation experiment), we have



**Figure 6.** IR spectra of adsorbed CO on  $\text{Ni}_2\text{P}/\text{SiO}_2$  catalysts as a function of sulfidation temperature ( $P_{\text{CO}} = 5$  Torr;  $T = 298$  K).

only reproduced the spectra collected after reducing (sulfiding) the sample for 15 min at 400, 500, 600, and 650 K (400, 500, and 600 K for sulfiding). From the spectra shown in Figure 5, we observe a shift to lower frequencies of the intense  $\nu_{\text{CO}}$  absorbance (2094 to 2090  $\text{cm}^{-1}$ ) and a simultaneous increase in the intensity of the  $\nu_{\text{CO}}$  absorbance with increasing reduction temperature. The frequency of the  $\nu_{\text{CO}}$  absorbance after reducing the  $\text{Ni}_2\text{P}/\text{SiO}_2$  catalyst in 100 Torr of  $\text{H}_2$  at 650 K for 15 min (2090  $\text{cm}^{-1}$ ) is higher than the frequency of the  $\nu_{\text{CO}}$  absorbance obtained for the  $\text{Ni}_2\text{P}/\text{SiO}_2$  catalyst reduced in flowing  $\text{H}_2$  (60 sccm) at 650 K for 1 h (2083  $\text{cm}^{-1}$ ). This higher frequency indicates that under the conditions of this experiment (100 Torr of  $\text{H}_2$ , static), the thin oxide layer at the surface of the silica-supported  $\text{Ni}_2\text{P}$  particles is not completely reduced. In addition to the intense  $\nu_{\text{CO}}$  absorbance (2090–2094  $\text{cm}^{-1}$ ), we observe a weak  $\nu_{\text{CO}}$  absorbance at 2196  $\text{cm}^{-1}$  in the IR spectrum collected after reducing a  $\text{Ni}_2\text{P}/\text{SiO}_2$  catalyst in 100 Torr of  $\text{H}_2$  at 400 K. Based on analogy to CO adsorption on  $\gamma\text{-Mo}_2\text{N}$  and  $\text{Mo}_2\text{N}/\text{Al}_2\text{O}_3$  catalysts<sup>37–40</sup> and other experimental results discussed later in this paper, we assign the  $\nu_{\text{CO}}$  absorbance at 2196  $\text{cm}^{-1}$  to the formation of surface-bonded  $\text{P}=\text{C}=\text{O}$  species. A search of the literature revealed the existence of a class of compounds called phosphaketenes ( $\text{R}-\text{P}=\text{C}=\text{O}$ ), which contain the  $\text{P}=\text{C}=\text{O}$  functional group.<sup>41</sup> Normal coordinate analysis has been carried out for  $\text{H}-\text{P}=\text{C}=\text{O}$ , yielding an antisymmetric stretching frequency for the  $\text{P}=\text{C}=\text{O}$  group of 2164–2195  $\text{cm}^{-1}$ ,<sup>42</sup> in good agreement with the range of 2193–2204  $\text{cm}^{-1}$  we observed for surface-bonded  $\text{P}=\text{C}=\text{O}$  species on  $\text{Ni}_2\text{P}/\text{SiO}_2$  catalysts. Returning to Figure 5, the intensity of the  $\text{P}=\text{C}=\text{O}$  absorbance increases with increasing reduction temperatures, and the frequency of this absorbance feature shifts to higher wavenumbers and is centered at 2203  $\text{cm}^{-1}$  following reduction of the  $\text{Ni}_2\text{P}/\text{SiO}_2$  catalyst in 100 Torr of  $\text{H}_2$  at 650 K for 15 min. It is interesting that the formation of  $\text{P}=\text{C}=\text{O}$  species is not consistently observed for  $\text{Ni}_2\text{P}/\text{SiO}_2$  catalysts reduced at 650 K for 1 h in flowing  $\text{H}_2$  and then exposed to 5.0 Torr of CO at 298 K. It may be that under these more severe reduction conditions, some surface P that would otherwise form  $\text{P}=\text{C}=\text{O}$  species is hydrogenated and volatilized as  $\text{PH}_3$ . CO adsorption on Ni bridge sites (1834 and 1921  $\text{cm}^{-1}$ ) and the formation of a  $\text{Ni}(\text{CO})_4$  species, as indicated by the formation of a shoulder

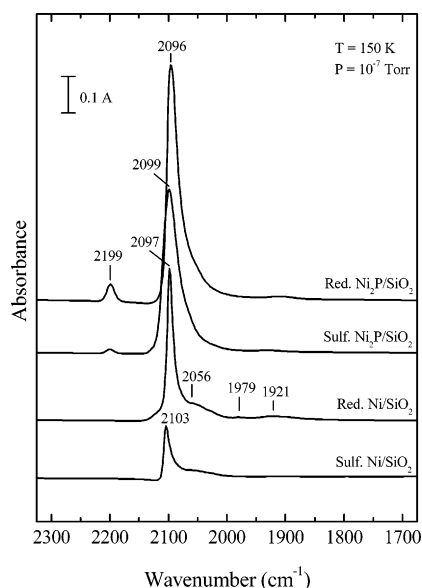


**Figure 7.** IR spectra of adsorbed CO on reduced  $\text{Ni}_2\text{P}/\text{SiO}_2$  catalysts in the presence of 5.0 Torr of CO and after evacuating to UHV pressures ( $T = 150$  K).

at 2056  $\text{cm}^{-1}$ , also become more prominent with increasing reduction temperatures.

The sulfidation temperature also strongly influences the adsorption of CO on  $\text{Ni}_2\text{P}/\text{SiO}_2$  catalysts, as indicated by the IR spectra shown in Figure 6. While the intensity of the  $\nu_{\text{CO}}$  absorbance also increases with increasing reduction temperature, we do not observe a similar decrease in the frequency of this absorbance. There does appear to be a slight increase in the frequency of the  $\nu_{\text{CO}}$  absorbance (2093  $\text{cm}^{-1}$  to 2098  $\text{cm}^{-1}$ ) after sulfiding the sample at 600 K for 15 min. However, this shift is not observed for all IR spectra collected after sulfiding the sample at temperatures  $\geq 600$  K for 15 min, and appears to depend on the intensity of the  $\nu_{\text{CO}}$  absorbance. This implies that the shift likely results from the dipole coupling of neighboring CO molecules. A weak  $\nu_{\text{CO}}$  absorbance at 2196  $\text{cm}^{-1}$  due to the formation of  $\text{P}=\text{C}=\text{O}$  species is observed in the IR spectrum collected after sulfiding a  $\text{Ni}_2\text{P}/\text{SiO}_2$  catalyst in 100 Torr of a 3.03 mol %  $\text{H}_2\text{S}/\text{H}_2$  gas mixture at 400 K. With increasing sulfidation temperatures, the intensity of the  $\text{P}=\text{C}=\text{O}$  absorbance increases as the frequency of this absorbance feature shifts to higher wavenumbers, and is centered at 2204  $\text{cm}^{-1}$  following sulfidation of the  $\text{Ni}_2\text{P}/\text{SiO}_2$  catalyst in 100 Torr of a 3.03 mol %  $\text{H}_2\text{S}/\text{H}_2$  gas mixture at 600 K for 15 min. Unlike CO adsorption on the reduced  $\text{Ni}_2\text{P}/\text{SiO}_2$  catalysts, we observe an insignificant amount of CO adsorption on Ni bridge sites and very little formation of  $\text{Ni}(\text{CO})_4$  species on the sulfided  $\text{Ni}_2\text{P}/\text{SiO}_2$  catalysts, even at the higher sulfidation temperatures. This result is expected since the combination of surface P and adsorbed S blocks the available sites for CO adsorption on Ni bridge sites and the formation of  $\text{Ni}(\text{CO})_4$  species.

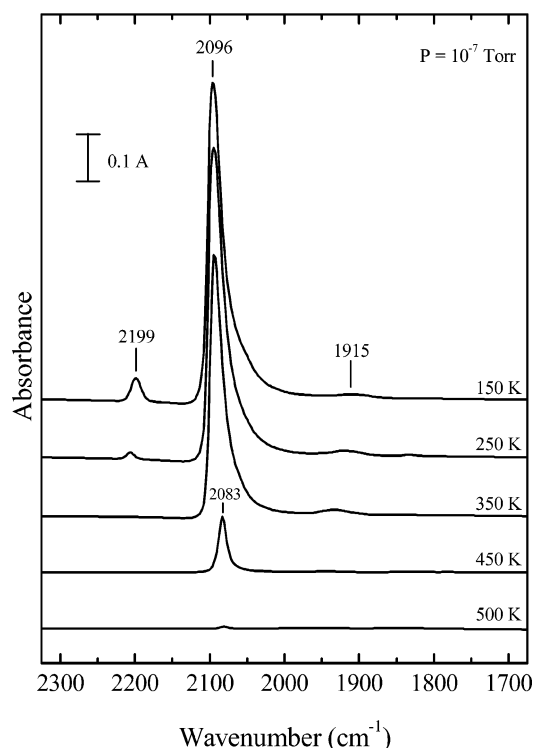
**Infrared Spectroscopy Measurements of Adsorbed CO at Low Temperature.** To more fully characterize the adsorption sites on the catalysts, reduced and sulfided  $\text{Ni}/\text{SiO}_2$  and  $\text{Ni}_2\text{P}/\text{SiO}_2$  catalysts were exposed to 5.0 Torr of CO at 150 K. The IR spectra obtained for the reduced  $\text{Ni}_2\text{P}/\text{SiO}_2$  catalyst in both the presence of 5.0 Torr of CO and after evacuating to UHV conditions are shown in Figure 7. In the presence of 5.0 Torr of CO, an intense  $\nu_{\text{CO}}$  absorbance is observed at 2096  $\text{cm}^{-1}$ , indicating that CO is terminally bonded to the  $\text{Ni}_2\text{P}/\text{SiO}_2$  surface. The frequency is significantly higher than that observed for the



**Figure 8.** IR spectra of adsorbed CO on reduced and sulfided Ni/SiO<sub>2</sub> and Ni<sub>2</sub>P/SiO<sub>2</sub> catalysts ( $T = 150$  K). IR spectra were obtained after exposing the catalysts to 5.0 Torr of CO followed by evacuation to UHV.

adsorption of CO on a Ni<sub>2</sub>P/SiO<sub>2</sub> catalyst at room temperature in the presence of 5.0 Torr of CO (2083 cm<sup>-1</sup>). This observed shift in frequency is most likely a result of dipole coupling between neighboring CO molecules. A  $\nu_{\text{CO}}$  absorbance at 2193 cm<sup>-1</sup> due to the formation of P=C=O species on the reduced Ni<sub>2</sub>P/SiO<sub>2</sub> catalyst is also observed. Furthermore,  $\nu_{\text{CO}}$  absorbances at 2056 and 1910 cm<sup>-1</sup> indicate a small amount of Ni-(CO)<sub>4</sub> formation and CO adsorption on Ni bridge sites, respectively. The additional  $\nu_{\text{CO}}$  absorbances at 2159 and 2135 cm<sup>-1</sup> are assigned to CO adsorption on the silica support.<sup>43</sup> This assignment has been confirmed by IR spectroscopic data for CO adsorption on SiO<sub>2</sub> in our laboratory also. Evacuating the high-pressure cell to UHV conditions does not cause a significant change in the intensity and peak position for the  $\nu_{\text{CO}}$  absorbance assigned to CO linearly bonded to Ni sites on the Ni<sub>2</sub>P/SiO<sub>2</sub> catalyst. This result indicates that CO is strongly adsorbed to Ni sites on the silica-supported Ni<sub>2</sub>P particles. On the other hand, the peak position for  $\nu_{\text{CO}}$  absorbance assigned to a P=C=O species shifts from 2193 to 2199 cm<sup>-1</sup> when the high-pressure cell is evacuated to UHV pressures.

Likewise, CO was observed to strongly adsorb to Ni sites on reduced and sulfided Ni/SiO<sub>2</sub>, and sulfided Ni<sub>2</sub>P/SiO<sub>2</sub> catalysts at 150 K, as indicated by an undetectable difference in the intensity and peak position for the  $\nu_{\text{CO}}$  absorbance assigned to CO linearly bonded to Ni sites in the IR spectra obtained in the presence of 5.0 Torr of CO and under UHV conditions. Figure 8 compares the IR spectra for the reduced and sulfided Ni/SiO<sub>2</sub> and Ni<sub>2</sub>P/SiO<sub>2</sub> catalysts after exposure to 5.0 Torr of CO and evacuating the high-pressure cell to UHV pressures. In this figure, the  $\nu_{\text{CO}}$  absorbances for terminally bonded CO are shifted to higher wavenumbers (compared to the frequency obtained for CO adsorption at 298 K) due to dipole coupling between neighboring CO molecules. The relative peak intensities and peak positions of the  $\nu_{\text{CO}}$  absorbances on the reduced and sulfided Ni/SiO<sub>2</sub> and Ni<sub>2</sub>P/SiO<sub>2</sub> catalysts at 150 K are generally similar to the relative intensities and peak positions of the  $\nu_{\text{CO}}$  absorbances observed on these catalysts at 298 K. The main differences are that the frequency for the  $\nu_{\text{CO}}$  absorbance for CO adsorbed on reduced Ni<sub>2</sub>P/SiO<sub>2</sub> and Ni/SiO<sub>2</sub> catalysts are very similar (2096 and 2097 cm<sup>-1</sup>, respectively), and that we

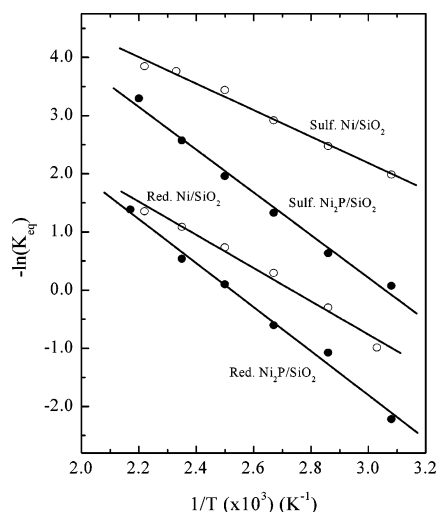


**Figure 9.** IR spectra of adsorbed CO on reduced Ni<sub>2</sub>P/SiO<sub>2</sub> catalysts as a function of anneal temperature. The catalyst was initially exposed to 5.0 Torr of CO at 145 K and then evacuated to UHV. The IR spectra were acquired after annealing to the given temperatures for 1 min in UHV and cooling to 150 K.

now observe a significant difference between the sulfided Ni<sub>2</sub>P/SiO<sub>2</sub> and Ni/SiO<sub>2</sub> catalysts (2099 and 2103 cm<sup>-1</sup>, respectively).

Adsorption of CO on the reduced and sulfided Ni<sub>2</sub>P/SiO<sub>2</sub> catalysts at 150 K results in an additional absorbance feature at 2200 cm<sup>-1</sup> that is not observed for CO adsorption on reduced and sulfided Ni/SiO<sub>2</sub> catalysts. This result confirms that this absorbance feature is unique to the reduced and sulfided Ni<sub>2</sub>P/SiO<sub>2</sub> catalysts. Since the main difference between the reduced and sulfided Ni<sub>2</sub>P/SiO<sub>2</sub> and Ni/SiO<sub>2</sub> catalysts is the presence of P in the former, we conclude that the  $\nu_{\text{CO}}$  absorbance at 2200 cm<sup>-1</sup> is due to an interaction between P and CO. On the basis of analogy to CO adsorption on  $\gamma$ -Mo<sub>2</sub>N and Mo<sub>2</sub>N/Al<sub>2</sub>O<sub>3</sub> catalysts,<sup>37–40</sup> we assign the  $\nu_{\text{CO}}$  absorbance at 2200 cm<sup>-1</sup> to the formation of P=C=O species.

To verify that CO is strongly adsorbed on the reduced and sulfided Ni<sub>2</sub>P/SiO<sub>2</sub> and Ni/SiO<sub>2</sub> catalysts, the catalysts exposed to 5.0 Torr of CO at 150 K were annealed to sequentially higher temperatures (at intervals of 25 K) in UHV for 1 min. Shown in Figure 9 are the IR spectra collected after initial exposure of the Ni<sub>2</sub>P/SiO<sub>2</sub> sample to UHV (150 K) and annealing at 250, 350, 450, and 500 K. In general, we observe a decrease in both the intensity and vibrational frequency of the  $\nu_{\text{CO}}$  absorbance assigned to CO linearly bonded to Ni and P sites with increasing anneal temperature. The decrease in the vibrational frequency as the intensity of the  $\nu_{\text{CO}}$  absorbance decreases confirms that the shift in the C–O vibrational frequency from 2083 cm<sup>-1</sup> when CO was adsorbed at 298 K to 2096 cm<sup>-1</sup> when CO was adsorbed at 150 K is due to an increase in the dipole coupling between neighboring CO molecules. CO is not completely removed from the atop Ni sites on reduced Ni<sub>2</sub>P/SiO<sub>2</sub> catalysts until after annealing the sample to temperatures  $\geq 500$  K. For the  $\nu_{\text{CO}}$  absorbance assigned to P=C=O species on reduced Ni<sub>2</sub>P/SiO<sub>2</sub> catalysts, we observe that its vibrational frequency



**Figure 10.** Determination of  $\Delta H_{\text{ads}}$  for CO adsorption on reduced and sulfided Ni/SiO<sub>2</sub> and Ni<sub>2</sub>P/SiO<sub>2</sub> catalysts.

increases from 2199 to 2208 cm<sup>-1</sup> and its intensity decreases with increasing anneal temperatures. The  $\nu_{\text{CO}}$  absorbance assigned to the P=C=O species is no longer observed in the IR spectra after annealing reduced Ni<sub>2</sub>P/SiO<sub>2</sub> catalysts to temperatures  $\geq 300$  K.

Annealing a CO-dosed sulfided Ni<sub>2</sub>P/SiO<sub>2</sub> catalyst to higher temperatures in UHV results in similar IR spectroscopic changes. First, decreases in intensity and vibrational frequency of the  $\nu_{\text{CO}}$  absorbance assigned to linearly bonded CO with increasing anneal temperature were observed for the sulfided Ni<sub>2</sub>P/SiO<sub>2</sub> catalyst. In addition, the  $\nu_{\text{CO}}$  absorbance assigned to linearly bonded CO splits into two  $\nu_{\text{CO}}$  absorbances, centered at 2095 and 2086 cm<sup>-1</sup> after annealing a sulfided Ni<sub>2</sub>P/SiO<sub>2</sub> catalyst at temperatures  $\geq 275$  K. This result is presumably due to the presence of two different atop Ni sites, perhaps sites with and without adsorbed sulfur, now present on the sulfided Ni<sub>2</sub>P/SiO<sub>2</sub> catalyst. The intensity of the  $\nu_{\text{CO}}$  absorbance assigned to the P=C=O species on the sulfided Ni<sub>2</sub>P/SiO<sub>2</sub> catalyst also decreases with increasing anneal temperature. As the intensity of the  $\nu_{\text{CO}}$  absorbance assigned to the P=C=O species on the sulfided Ni<sub>2</sub>P/SiO<sub>2</sub> catalyst decreases, the vibrational frequency of this absorbance feature slowly increases to 2208 cm<sup>-1</sup>. CO was completely removed from atop Ni and terminally bonded P sites on sulfided Ni<sub>2</sub>P/SiO<sub>2</sub> catalysts after annealing the catalyst to temperatures  $\geq 400$  and 250 K, respectively. A similar decrease in intensity and vibrational frequency of the  $\nu_{\text{CO}}$  absorbance assigned to linearly bonded CO with increasing anneal temperature was observed for sulfided Ni/SiO<sub>2</sub> catalysts. CO was completely removed from the sulfided Ni/SiO<sub>2</sub> catalyst by annealing the sample to temperatures  $\geq 325$  K.

While the intensity and vibrational frequency of the  $\nu_{\text{CO}}$  absorbance assigned to CO linearly bonded to the Ni sites on reduced Ni/SiO<sub>2</sub> catalysts also decrease with increasing anneal temperature, the changes in the IR spectra of adsorbed CO on this catalyst are more complex (Figure 3). Specifically, with increasing anneal temperature, peak intensities of the bridge-bonded CO species decrease more slowly than for terminally bonded CO. The peak positions of the  $\nu_{\text{CO}}$  absorbances for the bridge-bonded CO species do not shift with increasing anneal temperature. While the linearly bonded CO species is completely removed after annealing the reduced Ni/SiO<sub>2</sub> catalyst to temperatures  $\geq 375$  K, the bridge-bonded CO species are not completely removed until after the reduced Ni/SiO<sub>2</sub> catalyst has been annealed to temperatures  $\geq 525$  K.

**Determination of the Enthalpy of Adsorption ( $\Delta H_{\text{ads}}$ ) for CO.** On the basis of the anneal temperature required to completely removed the linearly bonded CO species from the reduced and sulfided Ni/SiO<sub>2</sub> and Ni<sub>2</sub>P/SiO<sub>2</sub> catalysts, we concluded that CO is more strongly bound to the Ni<sub>2</sub>P/SiO<sub>2</sub> catalysts than to the Ni/SiO<sub>2</sub> catalysts. For each type of catalyst, the reduced catalyst has a higher enthalpy of adsorption than its sulfided counterpart. To assign a numerical value for the enthalpy of adsorption for CO ( $\Delta H_{\text{ads}}(\text{CO})$ ) on the reduced and sulfided Ni/SiO<sub>2</sub> and Ni<sub>2</sub>P/SiO<sub>2</sub> catalysts, IR spectra were collected of the catalyst under study in the presence of 5.0 Torr of CO at substrate temperatures between 300 and 450 K in intervals of  $\sim 25$  K. Then, using the method described by Ballinger and Yates,<sup>19</sup> a van't Hoff plot (Figure 10) was constructed for the equilibrium between adsorbed CO on the catalyst and gas-phase CO ( $P_{\text{CO}} = 5.0$  Torr).



This process has the following expression for the equilibrium constant

$$K_{\text{eq}} = \frac{\theta_{\text{CO}}}{P_{\text{CO}}(1 - \theta_{\text{CO}})}$$

where  $\theta_{\text{CO}}$  is the fractional coverage of CO, which was determined from the absorbance ratio  $A_{\text{CO}}/A_{\text{CO}}(300 \text{ K})$ .  $A_{\text{CO}}(300 \text{ K})$  is the integrated intensity of the  $\nu_{\text{CO}}$  absorbance (1994–2133 cm<sup>-1</sup>) acquired at 300 K; only slight changes are observed in the integrated absorbance in this region below 300 K, so saturation coverage is assumed under the conditions of the experiment.  $A_{\text{CO}}$  is the integrated intensity of the  $\nu_{\text{CO}}$  absorbance acquired at 25 K intervals in the range 325–450 K. An estimate for the enthalpy of adsorption ( $\Delta H_{\text{ads}}$ ) is obtained from the slope of a plot of negative  $\ln(K_{\text{eq}})$  versus  $1/T$  (Figure 10) and the values obtained for the reduced and sulfided Ni/SiO<sub>2</sub> and Ni<sub>2</sub>P/SiO<sub>2</sub> catalysts are listed in Table 1. These results agree well with the qualitative enthalpy of adsorption order we obtained from our anneal experiments: sulfided Ni/SiO<sub>2</sub> < reduced Ni/SiO<sub>2</sub> < sulfided Ni<sub>2</sub>P/SiO<sub>2</sub> < reduced Ni<sub>2</sub>P/SiO<sub>2</sub>.

## Discussion

Ni<sub>2</sub>P/SiO<sub>2</sub> catalysts have shown high stability and activity under HDS conditions.<sup>6–12</sup> As shown in Figure 1 and Table 1, reduced and sulfided Ni<sub>2</sub>P/SiO<sub>2</sub> catalysts have HDS activities over 20 times higher than those of reduced and sulfided Ni/SiO<sub>2</sub> catalysts. These catalytic results show that *passivated* Ni<sub>2</sub>P/SiO<sub>2</sub> catalysts subjected to reduction or sulfidation pretreatments have high HDS activities and provide evidence that these pretreatments do not convert the supported Ni<sub>2</sub>P particles to metallic Ni or Ni sulfides, the species present on reduced and sulfided Ni/SiO<sub>2</sub> catalysts.

The high thiophene HDS activity of Ni<sub>2</sub>P/SiO<sub>2</sub> catalysts has been reported to be due to both a high site density and a high turnover frequency.<sup>8</sup> Since IR spectroscopy of adsorbed molecules (e.g. CO, NO, and pyridine (C<sub>5</sub>H<sub>5</sub>N)) on catalytic surfaces is one of the most widely used methods for characterizing active sites, we have used this method to characterize the sites available for thiophene HDS on Ni<sub>2</sub>P/SiO<sub>2</sub> catalysts. Specifically, we have studied the adsorption of CO on the surfaces of Ni<sub>2</sub>P/SiO<sub>2</sub> catalysts to gain insight about the nature of the active sites for thiophene HDS on these catalysts, and to probe the effects of reduction and sulfidation pretreatments on the properties of *passivated* Ni<sub>2</sub>P/SiO<sub>2</sub> 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<sub>2</sub>O<sub>3</sub><sup>44</sup> and Rh/Al<sub>2</sub>O<sub>3</sub><sup>44</sup>), carbides (e.g. Mo<sub>2</sub>C/Al<sub>2</sub>O<sub>3</sub><sup>45–47</sup>), nitrides (e.g. Mo<sub>2</sub>N/Al<sub>2</sub>O<sub>3</sub><sup>45–47</sup>), and phosphides (e.g. MoP/SiO<sub>2</sub><sup>3</sup>). We, therefore, desired to characterize the adsorption sites for CO on Ni<sub>2</sub>P/SiO<sub>2</sub> catalysts using IR spectroscopy.

**CO Adsorption Sites.** Four distinct  $\nu_{\text{CO}}$  absorbance features were observed in the IR spectra of adsorbed CO on reduced Ni<sub>2</sub>P/SiO<sub>2</sub> catalysts due to (1) CO adsorption on atop Ni sites, (2) CO adsorption on Ni bridge sites, (3) formation of adsorbed Ni(CO)<sub>4</sub>, and (4) formation of surface-bonded P=C=O species. At 298 K, CO adsorbed linearly to the Ni atoms of reduced Ni<sub>2</sub>P/SiO<sub>2</sub> with a characteristic  $\nu_{\text{CO}}$  absorbance at 2083 cm<sup>-1</sup>. This frequency is midway between the vibrational frequencies for the  $\nu_{\text{CO}}$  absorbances observed on reduced Ni/SiO<sub>2</sub> (2074 cm<sup>-1</sup>) and sulfided Ni/SiO<sub>2</sub> (2092 cm<sup>-1</sup>) catalysts. Sulfidation of Ni/SiO<sub>2</sub> catalysts has been previously reported to cause similar changes in the adsorption of CO as observed here for phosphide formation. Specifically, CO only adsorbed on the Ni atop sites of sulfided Ni/SiO<sub>2</sub> and Ni/Al<sub>2</sub>O<sub>3</sub> catalysts.<sup>27,29,33,48</sup> The frequency for the  $\nu_{\text{CO}}$  absorbance on these sulfided catalysts shifted to higher frequencies when compared to the frequency of the  $\nu_{\text{CO}}$  absorbance for adsorbed CO on reduced Ni/SiO<sub>2</sub> catalysts. In the current study, a shift from 2074 to 2092 cm<sup>-1</sup> was observed for a Ni/SiO<sub>2</sub> catalyst as a result of sulfidation. This shift is attributed to the electron-withdrawing nature of sulfur, either adsorbed on Ni particles or incorporated into a nickel sulfide phase (e.g. Ni<sub>3</sub>S<sub>2</sub>). Sulfur withdraws electron density from the Ni atoms, weakening the interaction between CO and Ni. For the phosphide catalysts, therefore, we conclude that the shift in frequency of the intense  $\nu_{\text{CO}}$  absorbance from 2074 cm<sup>-1</sup> for reduced Ni/SiO<sub>2</sub> to 2083 cm<sup>-1</sup> for Ni<sub>2</sub>P/SiO<sub>2</sub> is due to the fact that the P atoms are withdrawing electron density from the Ni atoms, giving the Ni atoms a partial positive charge (Ni<sup>δ+</sup>) and the P atoms a partial negative charge (P<sup>δ-</sup>). This result is in agreement with XPS results reported previously.<sup>8</sup> Clearly, P does not withdraw as much electron density from the Ni atoms as S does; otherwise, the shift in the  $\nu_{\text{CO}}$  absorbance would have been larger for the Ni<sub>2</sub>P/SiO<sub>2</sub> catalysts. This result is not unexpected since P (EN: 2.1) has a lower electronegativity (EN) than does S (EN: 2.5).<sup>49</sup> Therefore, because P withdraws less electron density than S, the magnitude of  $\delta$  for Ni<sup>δ+</sup> species in Ni<sub>2</sub>P/SiO<sub>2</sub> catalysts should be smaller than the magnitude of  $\delta$  observed for Ni<sup>δ+</sup> in sulfided Ni/SiO<sub>2</sub> catalysts. On the basis of the frequencies for the  $\nu_{\text{CO}}$  absorbance reported in the literature for terminally bonded CO on Ni/SiO<sub>2</sub> (2040–2070 cm<sup>-1</sup>),<sup>26–29</sup> Ni<sup>1+</sup>/SiO<sub>2</sub> (2145 cm<sup>-1</sup>),<sup>35</sup> and Ni<sup>2+</sup>/SiO<sub>2</sub> (2190–2217 cm<sup>-1</sup>)<sup>35,36</sup> catalysts, we conclude that the magnitude of the charge ( $\delta$ ) on the Ni<sup>δ+</sup> species in Ni<sub>2</sub>P/SiO<sub>2</sub> catalysts is between 0 and 1. Since the observed vibrational frequency for the  $\nu_{\text{CO}}$  absorbance (2083 cm<sup>-1</sup>) for CO adsorbed on Ni<sub>2</sub>P/SiO<sub>2</sub> is closer to the range reported for Ni/SiO<sub>2</sub> catalysts than that given for Ni<sup>1+</sup>/SiO<sub>2</sub>, the magnitude of the charge ( $\delta$ ) on the Ni<sup>δ+</sup> species in the Ni<sub>2</sub>P/SiO<sub>2</sub> catalyst is presumably closer to 0 than to 1. This conclusion is in agreement with the magnitude of the positive charge on the Ni in bulk Ni<sub>2</sub>P of 0.06 calculated by Rodriguez et al.,<sup>7</sup> using density functional theory (DFT).

Besides withdrawing electron density from Ni, the P in Ni<sub>2</sub>P/SiO<sub>2</sub> catalysts plays a similar role, in most, but not all respects, to that observed for S in the sulfided Ni/SiO<sub>2</sub> catalysts. For example, P hinders CO adsorption on Ni bridge sites. However, a weak  $\nu_{\text{CO}}$  absorbance at 1914 cm<sup>-1</sup> was observed on the CO-dosed, reduced Ni<sub>2</sub>P/SiO<sub>2</sub> catalysts (Figure 4), which is char-

acteristic of CO adsorption on Ni bridge sites. Comparing the frequency of this  $\nu_{\text{CO}}$  absorbance to the frequency observed for bridge-bonded CO on Ni(111) crystalline planes (1815–1920 cm<sup>-1</sup>) and on Ni<sup>1+</sup>/Al<sub>2</sub>O<sub>3</sub> catalysts (1920 cm<sup>-1</sup>), we conclude that the magnitude of the positive charge ( $\delta$ ) on Ni<sup>δ+</sup> in the bridge sites is between 0 and 1, and is presumably closer to zero than to 1. When a Ni<sub>2</sub>P/SiO<sub>2</sub> catalyst was reduced at 600 and 650 K in the presence of 100 Torr of H<sub>2</sub> for 15 min, we observed an additional  $\nu_{\text{CO}}$  absorbance at 1834 cm<sup>-1</sup> that is assigned to CO adsorption on a stronger 2-fold Ni<sup>δ+</sup> bridge site.<sup>30–32</sup> The frequencies of these  $\nu_{\text{CO}}$  absorbances are very similar to those reported in the literature for CO adsorption on the Ni bridge sites of reduced Ni/SiO<sub>2</sub> catalysts.<sup>30–32</sup> With the exception of the absence of the 1980-cm<sup>-1</sup> feature and the presence of a  $\nu_{\text{CO}}$  absorbance at 1834 cm<sup>-1</sup> for CO adsorption on reduced Ni<sub>2</sub>P/SiO<sub>2</sub> catalysts, these  $\nu_{\text{CO}}$  absorbances are also similar to those that we observed for CO adsorption on our reduced Ni/SiO<sub>2</sub> catalysts. The most striking difference between CO adsorption on the Ni bridge sites of reduced Ni<sub>2</sub>P/SiO<sub>2</sub> and Ni/SiO<sub>2</sub> catalysts, when comparing the IR spectra shown in Figures 2 and 4, is that the intensity of the  $\nu_{\text{CO}}$  absorbances associated with CO adsorption on Ni bridge sites was greater for reduced Ni/SiO<sub>2</sub> catalysts than it is for reduced Ni<sub>2</sub>P/SiO<sub>2</sub> catalysts. From this observation, we conclude that the surface P in reduced Ni<sub>2</sub>P/SiO<sub>2</sub> catalysts hinders CO adsorption on the Ni<sup>δ+</sup> bridge sites. This result is not surprising; P and S have approximately the same atomic size (0.11 and 0.10 nm, respectively<sup>49</sup>). Therefore, we would expect each P atom to occupy approximately the same amount of space that an adsorbed S atom does. Surface P and S species would occupy previously available Ni sites and hinder CO adsorption on more than one Ni atom. Indeed, adsorbed S on sulfided Ni/SiO<sub>2</sub> catalysts has been reported to hinder CO adsorption on the Ni bridge sites.<sup>27,29,33,48</sup> We observe a similar blocking of CO adsorption on the Ni bridge sites of our sulfided Ni/SiO<sub>2</sub> catalysts (Figure 2).

The surface P in the reduced Ni<sub>2</sub>P/SiO<sub>2</sub> catalysts also hinders the formation of Ni(CO)<sub>4</sub>, as indicated by a reduction in the intensity of the  $\nu_{\text{CO}}$  absorbance at 2056 cm<sup>-1</sup> compared to that observed on the reduced Ni/SiO<sub>2</sub> catalysts (compare Figures 2 and 4). Adsorbed S on the sulfided Ni/SiO<sub>2</sub> catalyst also inhibited the formation of Ni(CO)<sub>4</sub> (Figure 2). The decreased amount of Ni(CO)<sub>4</sub> on sulfided Ni/SiO<sub>2</sub> catalysts is clearly a result of a reduction in the number of available Ni sites for CO adsorption. This is indicated by the fact that the ratio of the intensity of the  $\nu_{\text{CO}}$  absorbance for Ni(CO)<sub>4</sub> with respect to the intensity of the  $\nu_{\text{CO}}$  absorbance for the adsorption of CO on Ni atop sites is approximately the same for reduced and sulfided Ni/SiO<sub>2</sub> catalysts (Figure 2). However, this ratio is less for the reduced Ni<sub>2</sub>P/SiO<sub>2</sub> catalysts than the ratio observed for the reduced and sulfided Ni/SiO<sub>2</sub> catalysts (compare Figures 2 and 4). This result may indicate that surface P influences the energetics for the formation of Ni(CO)<sub>4</sub> in addition to reducing the number of available Ni sites for CO adsorption.

While the P atoms hinder both CO adsorption on bridging Ni sites and the formation of Ni(CO)<sub>4</sub>, the P species also provide sites for the adsorption of CO, as indicated by the  $\nu_{\text{CO}}$  absorbance at 2193–2204 cm<sup>-1</sup>. In this respect, the behavior of surface P in Ni<sub>2</sub>P/SiO<sub>2</sub> catalysts is distinctly different from that of S in sulfided Ni/SiO<sub>2</sub> catalysts. To our knowledge, there have been no reports in the literature of surface S participating directly in bonding with CO. Others have reported observing  $\nu_{\text{CO}}$  absorbances at ~2195 cm<sup>-1</sup> associated with CO adsorption on 3-fold Ni<sup>2+</sup> sites for P-free Ni/SiO<sub>2</sub> and Ni<sup>2+</sup>/SiO<sub>2</sub> cata-



lysts.<sup>28,36</sup> We did not observe this  $\nu_{\text{CO}}$  absorbance on our reduced and sulfided Ni/SiO<sub>2</sub> catalysts. Even when the Ni/SiO<sub>2</sub> catalysts were not fully reduced, we did not observe a  $\nu_{\text{CO}}$  absorbance at  $\sim 2193\text{ cm}^{-1}$ . On the partially reduced catalysts, there likely would have been Ni<sup>2+</sup> sites, within the NiO domains, available for CO adsorption. Therefore, we conclude that the absorbance feature at  $2193\text{--}2204\text{ cm}^{-1}$  is unique to the reduced and sulfided Ni<sub>2</sub>P/SiO<sub>2</sub> catalysts and that this  $\nu_{\text{CO}}$  absorbance is due to an interaction between P and CO. On the basis of analogy to CO adsorption on Mo<sub>2</sub>N/Al<sub>2</sub>O<sub>3</sub> catalysts for which surface-bonded N=C=O species were observed,<sup>37–40</sup> we have assigned the  $\nu_{\text{CO}}$  absorbance at  $2200\text{ cm}^{-1}$  to the formation of surface-bonded P=C=O species. To our knowledge, this is the first observation of a P=C=O species on a catalyst surface; compounds known as phosphaketenes (R–P=C=O) have been reported.<sup>41</sup> The antisymmetric stretch of the P=C=O group has been predicted to be at  $2164\text{--}2195\text{ cm}^{-1}$  based upon a normal coordinate analysis of H–P=C=O,<sup>42</sup> which is consistent with the frequency range of  $2193\text{--}2204\text{ cm}^{-1}$  for the  $\nu_{\text{CO}}$  absorbance we assign to surface-bonded P=C=O species. The similarity between the chemistry observed for the P=C=O species and that of surface-bonded N=C=O species reported by others provides additional evidence for its existence. Yang et al.<sup>38–40</sup> observed a strong absorbance at  $2200\text{ cm}^{-1}$  following exposure of Mo<sub>2</sub>N/Al<sub>2</sub>O<sub>3</sub> catalysts to CO. On the basis of the vibrational frequencies of coordinated isocyanate ion (N=C=O<sup>–</sup>), these authors concluded that CO reacted with surface active N atoms to form coordinated N=C=O species. Frapper et al.<sup>37</sup> subsequently used DFT calculations to examine the formation of adsorbed N=C=O on the  $\gamma$ -Mo<sub>2</sub>N(100) surface and concluded that this species is formed via an Eley-Rideal type mechanism in which gas-phase CO reacts with an adsorbed N atom that is coordinated to four Mo atoms. The absorbance feature observed at  $2200\text{ cm}^{-1}$  for CO adsorbed on Mo<sub>2</sub>N/Al<sub>2</sub>O<sub>3</sub> catalysts is assigned to the antisymmetric vibration of coordinated N=C=O, in good agreement with the vibrational frequency of  $2206\text{ cm}^{-1}$  calculated in the DFT studies.<sup>37</sup> We conclude, therefore, that the absorbance feature observed at  $2193\text{--}2204\text{ cm}^{-1}$  for CO adsorption on Ni<sub>2</sub>P/SiO<sub>2</sub> catalysts is due to the antisymmetric vibration of a coordinated P=C=O species on the catalyst surface. Ab initio studies of H–P=C=O indicate that the bonding can be rationalized in terms of the interactions of PH and CO fragments, with CO donating electron density from the lone pair on carbon and phosphorus back-donating electron density from a p orbital lone pair.<sup>42</sup> This description of the bonding is similar to that for CO bonded to a coordinately unsaturated metal site, except that the back-donation of electron density from the metal occurs from a filled d orbital. Our results suggest, therefore, that surface P atoms in Ni<sub>2</sub>P/SiO<sub>2</sub> catalysts may participate directly in bonding with other molecules, including sulfur-containing species (e.g. thiophene, H<sub>2</sub>S) which adsorb via donation of electron density from S to the surface site.

The formation of P=C=O species was observed on Ni<sub>2</sub>P/SiO<sub>2</sub> catalysts treated in a static pressure (100 Torr) of H<sub>2</sub> or of a 3.03 mol % H<sub>2</sub>S/H<sub>2</sub> mixture at 400 K prior to CO exposure at 298 K. Increasing the pretreatment temperature resulted in an increase in frequency and peak intensity of this  $\nu_{\text{CO}}$  absorbance. This result is expected since the thin oxide layer on *passivated* Ni<sub>2</sub>P/SiO<sub>2</sub> catalysts would hinder CO adsorption on surface P atoms. XPS spectra of a *passivated* Ni<sub>2</sub>P/SiO<sub>2</sub> catalyst reported previously revealed the majority of the surface P to have a +5 oxidation state, presumably associated with phosphate-like species.<sup>8</sup> Pretreatment of *passivated* Ni<sub>2</sub>P/SiO<sub>2</sub>

catalysts in H<sub>2</sub> or H<sub>2</sub>S/H<sub>2</sub> results in the reduction of this passive oxide layer, permitting CO adsorption on the surface P atoms; higher pretreatment temperatures are generally more effective in reducing passivating layers. Similarly, Yang et al.<sup>38–40</sup> only observed the formation of N=C=O species on freshly nitrated Mo<sub>2</sub>N/Al<sub>2</sub>O<sub>3</sub> catalysts. The formation of P=C=O species was not observed on Ni<sub>2</sub>P/SiO<sub>2</sub> catalysts reduced in flowing H<sub>2</sub> (60 sccm) at 650 K for 1 h prior to CO exposure at 298 K. Adsorption of CO at 150 K on Ni<sub>2</sub>P/SiO<sub>2</sub> catalysts reduced in flowing H<sub>2</sub> (60 sccm) at 650 K for 1 h, however, did result in formation of P=C=O species. These results may indicate a reduction in the number of available P atoms for CO under more severe reduction conditions. Treatment of freshly nitrated Mo<sub>2</sub>N/Al<sub>2</sub>O<sub>3</sub> catalysts with hydrogen also resulted in a reduction in the band intensity of the  $\nu_{\text{CO}}$  absorbance associated with N=C=O species due to removal of some surface active nitrogen atoms.<sup>38–40</sup> It appears, therefore, that under the more severe reduction conditions obtained in the flowing H<sub>2</sub> at 650 K for 1 h, a small amount of surface P that would otherwise adsorb CO to form P=C=O species was hydrogenated and volatilized as PH<sub>3</sub>. Oyama and co-workers<sup>11,12</sup> have observed the loss of excess P as PH<sub>3</sub> during the TPR synthesis of Ni<sub>2</sub>P/SiO<sub>2</sub> catalysts in flowing H<sub>2</sub>, but only above 700 K. The loss of P from the surface of *passivated* Ni<sub>2</sub>P/SiO<sub>2</sub> catalysts reduced in flowing H<sub>2</sub> at 650 K must be small as a Ni<sub>2</sub>P/SiO<sub>2</sub> catalyst reduced under these conditions was observed to be over 20 times more active than a reduced Ni/SiO<sub>2</sub> catalyst (see Figure 1 and Table 1). Significant loss of surface P would be expected to result in the formation of metallic Ni at the surface of a Ni<sub>2</sub>P/SiO<sub>2</sub> catalyst, but the HDS results do not indicate this to be the case. Finally, we observe that the P=C=O species formed on Ni<sub>2</sub>P/SiO<sub>2</sub> catalysts to be stable upon evacuation. Indeed this species was not completely removed until annealing the reduced and sulfided Ni<sub>2</sub>P/SiO<sub>2</sub> catalysts to temperatures above 300 and 250 K, respectively. The N=C=O species formed on freshly nitrated Mo<sub>2</sub>N/Al<sub>2</sub>O<sub>3</sub> catalysts was likewise quite stable.<sup>37–40</sup>

#### Influence of Pretreatment Conditions on CO Adsorption.

As indicated in Figures 4–6, the intensity and frequency of the  $\nu_{\text{CO}}$  absorbances for CO adsorption on Ni<sub>2</sub>P/SiO<sub>2</sub> catalysts depended on the pretreatment conditions (reduction/sulfidation, temperature, and time). The  $\nu_{\text{CO}}$  absorbances for CO adsorption on reduced Ni<sub>2</sub>P/SiO<sub>2</sub> catalysts have been described in detail in the previous section. Sulfidation of the Ni<sub>2</sub>P/SiO<sub>2</sub> catalyst resulted in a shift of the vibrational frequency of the  $\nu_{\text{CO}}$  absorbance assigned to CO adsorption on Ni atop sites from  $2083$  to  $2093\text{ cm}^{-1}$  (see Figure 4). In addition, the intensity of this absorbance feature decreased, indicating that sulfidation of the Ni<sub>2</sub>P/SiO<sub>2</sub> catalysts decreased the number of CO adsorption sites. Sulfidation of the Ni<sub>2</sub>P/SiO<sub>2</sub> catalysts also further hindered the adsorption of CO on Ni bridge sites and the formation of Ni(CO)<sub>4</sub>. From Figures 4 and 6, we observe that a negligible amount of CO adsorbed on Ni bridge sites, and very little, if any, Ni(CO)<sub>4</sub> formed on a sulfided Ni<sub>2</sub>P/SiO<sub>2</sub> catalyst. The frequency of the  $\nu_{\text{CO}}$  absorbance associated with the formation of surface-bonded P=C=O species was not influenced by sulfidation of the Ni<sub>2</sub>P/SiO<sub>2</sub> catalyst. The intensity of this feature did, however, decrease when the Ni<sub>2</sub>P/SiO<sub>2</sub> catalyst was sulfided.

The observed frequency shifted from  $2083$  to  $2093\text{ cm}^{-1}$  for the  $\nu_{\text{CO}}$  absorbance assigned to CO adsorption on Ni atop sites when the Ni<sub>2</sub>P/SiO<sub>2</sub> catalyst was sulfided. This indicates that adsorbed sulfur withdraws additional electron density from the surface Ni species in the Ni<sub>2</sub>P/SiO<sub>2</sub> catalysts. Interestingly, XRD measurements reported previously indicate that the bulk structure

of silica-supported Ni<sub>2</sub>P did not change after sulfidation of a 20 wt % Ni<sub>2</sub>P/SiO<sub>2</sub> catalyst at temperatures as high as 1023 K.<sup>8</sup> However, as shown in Figure 1, the HDS activity of a *passivated* Ni<sub>2</sub>P/SiO<sub>2</sub> catalyst was enhanced (relative to a reduced catalyst) by pretreating it in a 3.0 mol % H<sub>2</sub>S/H<sub>2</sub> mixture at 650 K. Our IR spectroscopic results clearly indicate that S adsorbs to the surfaces of Ni<sub>2</sub>P/SiO<sub>2</sub> catalysts, blocking some of the sites available for CO adsorption (see Table 1 and Figure 4) and withdrawing electron density from Ni sites. This result corroborates the elemental analysis and extended X-ray adsorption fine structure (EXAFS) measurements conducted by Oyama et al.<sup>6,9,12</sup> that indicate incorporation of S into Ni<sub>2</sub>P/SiO<sub>2</sub> catalysts. EXAFS measurements of catalysts tested under HDS conditions revealed the formation of Ni–S linkages at the surface of the supported Ni<sub>2</sub>P particles, leading the authors to conclude that the active surface of a Ni<sub>2</sub>P/SiO<sub>2</sub> catalyst was probably a phosphosulfide phase (i.e. NiP<sub>x</sub>S<sub>y</sub>). The fact that a *passivated* Ni<sub>2</sub>P/SiO<sub>2</sub> catalyst subjected to a sulfidation pretreatment had a higher thiophene HDS activity than a sample of the same catalyst subjected to a reduction pretreatment (see Figure 1) suggests that the controlled formation of a surface phosphosulfide phase is beneficial to the catalytic properties of Ni<sub>2</sub>P.

Interestingly, the observed frequency for the  $\nu_{\text{CO}}$  absorbance for CO adsorbed on Ni atop sites of a sulfided Ni<sub>2</sub>P/SiO<sub>2</sub> catalyst (2093 cm<sup>-1</sup>) was similar to that observed for CO adsorbed on these sites on a sulfided Ni/SiO<sub>2</sub> catalyst (2092 cm<sup>-1</sup>). This result may indicate that the oxidation state of Ni in the sulfided Ni<sub>2</sub>P/SiO<sub>2</sub> catalyst was similar to the oxidation state in the sulfided Ni catalyst. However, this result may also be due to mere coincidence, which can be understood as follows. The sulfided Ni<sub>2</sub>P/SiO<sub>2</sub> catalyst has more sites available for CO adsorption than does the sulfided Ni/SiO<sub>2</sub> catalyst (Table 1). As a result, the CO molecules adsorbed on the sulfided Ni<sub>2</sub>P/SiO<sub>2</sub> catalyst are likely closer together than those on the sulfided Ni/SiO<sub>2</sub> catalyst, and therefore, would experience increased dipole-coupling. This dipole-coupling would shift the  $\nu_{\text{CO}}$  absorbance to higher wavenumbers. Therefore the shift in the  $\nu_{\text{CO}}$  absorbance that we observe after sulfiding the Ni<sub>2</sub>P/SiO<sub>2</sub> catalyst may have two components: (1) additional electron density withdrawn from the Ni sites and (2) additional dipole coupling between neighboring CO molecules. What is clear, however, is that there are significantly more sites on a sulfided Ni<sub>2</sub>P/SiO<sub>2</sub> catalyst than on a sulfided Ni/SiO<sub>2</sub> catalyst and that this is a critical factor responsible for the substantially higher HDS activity of Ni<sub>2</sub>P/SiO<sub>2</sub> catalysts. While the EXAFS results of Oyama and co-workers<sup>6,9,12</sup> indicate that Ni–S linkages are formed on Ni<sub>2</sub>P/SiO<sub>2</sub> catalysts exposed to sulfiding conditions, P atoms may also serve as sites for the adsorption and bonding of S-containing species. As described earlier, surface P atoms adsorb CO to give P=C=O species on reduced and sulfided Ni<sub>2</sub>P/SiO<sub>2</sub> catalysts, indicating that P atoms can participate in surface bonding. Rodriguez et al.<sup>50</sup> recently reported that surface C sites in a TiC(001) single crystal surface participate directly in the adsorption and reactions of SO<sub>2</sub> on this surface. It is possible, therefore, that surface P atoms in Ni<sub>2</sub>P/SiO<sub>2</sub> catalysts participate in bonding to sulfur in the formation of a surface NiP<sub>x</sub>S<sub>y</sub> phase or via the adsorption of sulfur-containing species (e.g. thiophene, H<sub>2</sub>S). These interactions may play a role in explaining the high HDS activity observed for Ni<sub>2</sub>P/SiO<sub>2</sub> catalysts.

The temperature and duration of the reduction/sulfidation pretreatment also influenced the observed frequency and intensity of the  $\nu_{\text{CO}}$  absorbances for *passivated* Ni<sub>2</sub>P/SiO<sub>2</sub>

catalysts. For example, the frequency of the  $\nu_{\text{CO}}$  absorbance associated with CO adsorption on the Ni atop sites of a reduced Ni<sub>2</sub>P/SiO<sub>2</sub> catalyst decreased from 2094 to 2083 cm<sup>-1</sup> with increasing reduction temperature and time. Higher temperatures and longer exposure times during reduction of the Ni<sub>2</sub>P/SiO<sub>2</sub> catalyst are clearly needed to reduce the passivation layer, and thus expose the adsorption sites on Ni<sub>2</sub>P/SiO<sub>2</sub> catalysts. Correspondingly, the intensity of the  $\nu_{\text{CO}}$  absorbance increased with increasing reduction temperature and time. A similar dependence on the frequency and intensity of the  $\nu_{\text{CO}}$  absorbance for CO adsorbed on Ni atop sites was observed for reduced Ni/SiO<sub>2</sub> catalysts. For the Ni<sub>2</sub>P/SiO<sub>2</sub> catalyst, the frequency and intensity of the  $\nu_{\text{CO}}$  absorbance associated with the formation of surface-bonded P=C=O species also depended on the reduction conditions. Both the frequency and intensity of this  $\nu_{\text{CO}}$  absorbance were observed to increase with increasing reduction temperatures when a Ni<sub>2</sub>P/SiO<sub>2</sub> catalyst was treated in a static pressure of H<sub>2</sub> (100 Torr). Alternatively, for Ni<sub>2</sub>P/SiO<sub>2</sub> catalysts reduced in flowing H<sub>2</sub> (60 sccm) at 650 K for 1 h, we did not observe a  $\nu_{\text{CO}}$  absorbance associated with the formation of P=C=O species when the catalyst was exposed to 5.0 Torr of CO at 298 K. On the other hand, we observed a weak  $\nu_{\text{CO}}$  absorbance associated with P=C=O species on Ni<sub>2</sub>P/SiO<sub>2</sub> catalysts reduced in flowing H<sub>2</sub> (60 sccm) at 650 K for 1 h after exposing the catalysts to 5.0 Torr of CO at 150 K. It may be that under these more severe reduction conditions, some surface P that would otherwise form P=C=O species is hydrogenated and volatilized as PH<sub>3</sub>. In the case of the  $\nu_{\text{CO}}$  absorbances associated with CO adsorbed on Ni bridge sites and the formation of Ni(CO)<sub>4</sub>, only the intensity of these absorbances depended on the reduction temperature. In both cases, the intensity of the  $\nu_{\text{CO}}$  absorbance increased with reduction temperature. The reduction temperature also influenced the number of  $\nu_{\text{CO}}$  absorbances for CO adsorbed on Ni bridge sites in reduced Ni<sub>2</sub>P/SiO<sub>2</sub> catalysts.

The sulfidation behavior of the Ni<sub>2</sub>P/SiO<sub>2</sub> catalyst as a function of the pretreatment temperature was similar to that for reduction, particularly for CO adsorbed on Ni atop sites. As the sulfidation temperature was increased in the range 400–600 K, the intensity of the  $\nu_{\text{CO}}$  absorbance for CO adsorbed to Ni atop sites increased to approximately the same extent as observed for reduction (see Figures 5 and 6). This observation is not surprising as X-ray diffraction studies in our laboratory showed that the oxidic precursor of a silica-supported Ni<sub>2</sub>P catalyst could be successfully reduced to Ni<sub>2</sub>P/SiO<sub>2</sub> by treatment of the precursor with a 3.03 mol % H<sub>2</sub>S/H<sub>2</sub> mixture at 723 K.<sup>8</sup> Presumably, the thin oxide layer present on the surface of the 20 wt % Ni<sub>2</sub>P/SiO<sub>2</sub> catalyst used in the current study could be reduced in H<sub>2</sub>S/H<sub>2</sub> by using milder conditions, as indicated by the IR spectroscopic measurements. Different from the reduction pretreatments, however, the H<sub>2</sub>S/H<sub>2</sub> treatments at 400–600 K suppressed the formation of Ni bridging sites on the Ni<sub>2</sub>P/SiO<sub>2</sub> catalyst, indicating that such treatments result in the adsorption of S on the surface of the Ni<sub>2</sub>P particles as discussed earlier. As observed for the Ni atop sites, the evolution of P sites with pretreatment temperature was similar for reduced and sulfided Ni<sub>2</sub>P/SiO<sub>2</sub> catalysts. While S adsorption blocked the adsorption of bridge-bonded CO species, there was no evidence for blocking of sites for P=C=O formation by sulfur.

**CO Adsorption Strength and Site Density Analysis.** Ni<sub>2</sub>P/SiO<sub>2</sub> catalysts have been shown to be dramatically more catalytically active than sulfided Ni/SiO<sub>2</sub> catalysts toward the HDS of thiophene (see Figure 1). In previous characterization studies, the high HDS activity of Ni<sub>2</sub>P/SiO<sub>2</sub> catalysts was traced

to both a high site density and a high turnover frequency.<sup>8</sup> Our IR spectroscopic results confirm that Ni<sub>2</sub>P/SiO<sub>2</sub> catalysts have a higher site density when compared to both reduced and sulfided Ni/SiO<sub>2</sub> catalysts, as indicated in Table 1. In this table, we report the integrated peak area for terminally bonded CO per mg of sample for reduced and sulfided Ni/SiO<sub>2</sub> and Ni<sub>2</sub>P/SiO<sub>2</sub> catalysts. Assuming similar extinction coefficients for terminally bonded CO on the different catalysts, these values provide a relative measure of the site densities for CO adsorption. Interestingly, although the added P hindered the adsorption of CO on the bridging Ni sites of Ni<sub>2</sub>P/SiO<sub>2</sub> catalysts, it also increased the total amount of CO adsorbed. These observations may indicate that the P species in Ni<sub>2</sub>P/SiO<sub>2</sub> catalysts increase the dispersion of Ni on the silica support. Meanwhile, sulfidation of the Ni/SiO<sub>2</sub> and Ni<sub>2</sub>P/SiO<sub>2</sub> catalysts resulted in a decrease in CO adsorption.

The interaction of CO was much stronger with the Ni<sub>2</sub>P/SiO<sub>2</sub> catalysts than with the Ni/SiO<sub>2</sub> catalysts. We observed that CO was not completely removed from the reduced Ni<sub>2</sub>P/SiO<sub>2</sub>, sulfided Ni<sub>2</sub>P/SiO<sub>2</sub>, reduced Ni/SiO<sub>2</sub> (linear species only), and sulfided Ni/SiO<sub>2</sub> catalysts until after annealing to temperatures above 500 (see Figure 9), 400, 375, and 325 K, respectively. The enthalpies of adsorption for CO on these catalysts (see Figure 10 and Table 1) are consistent with these observations. While these adsorption enthalpies should be considered estimates as discussed earlier, we conclude that the interaction of CO with the reduced Ni<sub>2</sub>P/SiO<sub>2</sub> catalyst is stronger than that for reduced and sulfided Ni/SiO<sub>2</sub> catalysts, and is only slightly weakened by sulfidation of the Ni<sub>2</sub>P/SiO<sub>2</sub> catalyst.

Comparing the enthalpies of adsorption and the relative site densities for CO on the catalysts (see Table 1), smaller changes were measured for the Ni<sub>2</sub>P/SiO<sub>2</sub> catalysts subjected to reduction and sulfidation pretreatments relative to the Ni/SiO<sub>2</sub> catalysts pretreated similarly. The CO site densities decrease for both the Ni/SiO<sub>2</sub> and Ni<sub>2</sub>P/SiO<sub>2</sub> catalysts upon sulfidation, but the decrease is far greater for the Ni/SiO<sub>2</sub> catalyst. Likewise, the enthalpies of adsorption decrease for the catalysts upon sulfidation, but the decrease is substantially larger for P-free catalysts. These results clearly suggest that the CO adsorption properties of the Ni<sub>2</sub>P/SiO<sub>2</sub> catalysts are less sensitive to sulfidation than for the Ni/SiO<sub>2</sub> catalysts. Possible explanations for these observations are that the P in the supported Ni<sub>2</sub>P particles decreases the extent of sulfur adsorption relative to the P-free catalysts or that a surface NiP<sub>x</sub>S<sub>y</sub> phase is formed on the Ni<sub>2</sub>P particles that retains a relatively high CO site density and enthalpy of adsorption.

From the results of coadsorption experiments to be described elsewhere,<sup>51</sup> CO and thiophene were observed to compete for the same sites on Ni<sub>2</sub>P/SiO<sub>2</sub> catalysts. In particular, CO preadsorption on a 20 wt % Ni<sub>2</sub>P/SiO<sub>2</sub> catalyst effectively blocked thiophene adsorption on Ni sites. This observation suggests that CO is a good choice for measuring site densities on Ni<sub>2</sub>P/SiO<sub>2</sub> catalysts. However, the results of the current study suggest that CO should be used cautiously for this purpose. As indicated by the IR spectra of adsorbed CO on reduced Ni<sub>2</sub>P/SiO<sub>2</sub> catalysts (see Figures 4–9), CO adsorbs in at least four distinct forms on silica-supported Ni<sub>2</sub>P catalysts: CO on atop and bridging Ni<sup>δ+</sup> sites, Ni(CO)<sub>4</sub> species, and P sites (P=C=O). It is likely that these different types of sites are not equally active for HDS. The formation of adsorbed Ni(CO)<sub>4</sub> species on Ni<sub>2</sub>P/SiO<sub>2</sub> catalysts may explain why we have obtained inconsistent results for CO chemisorption capacity measurements for these catalysts.<sup>52</sup> Nevertheless, CO can be used to characterize the nature of the sites on reduced and sulfided Ni<sub>2</sub>P/

SiO<sub>2</sub> catalysts. From this IR spectroscopic study of CO adsorption on reduced and sulfided Ni<sub>2</sub>P/SiO<sub>2</sub> catalysts, we conclude that the active site for thiophene HDS is most likely a Ni<sup>δ+</sup> atop site, where the magnitude of the positive charge (δ) in the reduced and sulfided Ni<sub>2</sub>P/SiO<sub>2</sub> catalysts is between 0 and 1. Furthermore, by comparing integrated peak intensities for the ν<sub>CO</sub> absorbance associated with terminally bonded CO, we observe that reduced and sulfided Ni<sub>2</sub>P/SiO<sub>2</sub> catalysts have a higher active site density than reduced and sulfided Ni/SiO<sub>2</sub> catalysts. The Ni<sup>δ+</sup> atop sites may be associated with a surface NiP<sub>x</sub>S<sub>y</sub> phase and the participation of surface P sites in the bonding of S-containing species cannot be ruled out.

## Conclusion

We have investigated the surface chemistry of CO on reduced and sulfided Ni<sub>2</sub>P/SiO<sub>2</sub> catalysts using infrared (IR) spectroscopy. Four different ν<sub>CO</sub> absorbances were observed for the adsorption of CO on reduced and sulfided Ni<sub>2</sub>P/SiO<sub>2</sub> catalysts with the following assignments: (1) CO terminally bonded to *cus* Ni<sup>δ+</sup> (0 < δ < 1) sites; (2) CO bridge-bonded on two Ni sites; (3) CO terminally bonded to P in the form of P=C=O species; and (4) formation of Ni(CO)<sub>4</sub>. The frequency of the ν<sub>CO</sub> absorbances observed for the adsorption of CO on Ni atop sites depends on the pretreatment conditions (reduction/sulfidation, temperature, duration) and the temperature of the catalyst during CO exposure. For example, CO adsorbed on *cus* Ni<sup>δ+</sup> (0 < δ < 1) sites on reduced Ni<sub>2</sub>P/SiO<sub>2</sub> catalysts at 298 K exhibited a characteristic ν<sub>CO</sub> absorbance at 2083 cm<sup>-1</sup>. Treatment of the Ni<sub>2</sub>P/SiO<sub>2</sub> catalysts with a 3.03 mol % H<sub>2</sub>S/H<sub>2</sub> mixture shifts the ν<sub>CO</sub> absorbance to 2093 cm<sup>-1</sup>. The enthalpy of adsorption (Δ*H*<sub>ads</sub>) of CO on the Ni<sub>2</sub>P/SiO<sub>2</sub> catalysts was estimated by using a van't Hoff plot; Δ*H*<sub>ads</sub> is -31.4 ± 1.5 and -30.5 ± 1.5 kJ/mol for reduced and sulfided Ni<sub>2</sub>P/SiO<sub>2</sub> catalysts, respectively. The IR spectroscopic data for the adsorption of CO on Ni<sub>2</sub>P/SiO<sub>2</sub>, Ni/SiO<sub>2</sub>, and sulfided Ni/SiO<sub>2</sub> catalysts correlate well with the trend of HDS activity of these catalysts. Specifically, we observe a higher site density and higher Δ*H*<sub>ads</sub> for CO adsorption on the Ni<sub>2</sub>P/SiO<sub>2</sub> catalysts compared to both the reduced and sulfided Ni/SiO<sub>2</sub> catalysts. The IR spectroscopic and HDS catalytic results are consistent with the formation of a surface phosphosulfide phase (i.e. NiP<sub>x</sub>S<sub>y</sub>) under sulfiding conditions and surface P atoms may participate in bonding with S-containing species.

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