

# Carbon Monoxide Adsorption on Molybdenum Phosphides: Fourier Transform Infrared Spectroscopic and Density Functional Theory Studies

Zhaochi Feng,<sup>†</sup> Changhai Liang,<sup>\*,†</sup> Weicheng Wu,<sup>†</sup> Zili Wu,<sup>†</sup> R. A. van Santen,<sup>‡</sup> and Can Li<sup>\*,†</sup>

State Key Laboratory of Catalysis, Dalian Institute of Chemical Physics, Chinese Academy of Sciences, P.O. Box 110, Dalian 116023, China, and Schuit Institute of Catalysis, Eindhoven University of Technology, Eindhoven, The Netherlands

Received: May 16, 2003; In Final Form: October 17, 2003

Molybdenum phosphide (MoP) and supported molybdenum phosphide (MoP/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub>) have been prepared by the temperature-programmed reduction method. The surface sites of the MoP/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> catalyst were characterized by carbon monoxide (CO) adsorption with in situ Fourier transform infrared (FT-IR) spectroscopy. A characteristic IR band at 2037 cm<sup>-1</sup> was observed on the MoP/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> that was reduced at 973 K. This band is attributed to linearly adsorbed CO on Mo atoms of the MoP surface and is similar to IR bands at 2040–2060 cm<sup>-1</sup>, which correspond to CO that has been adsorbed on some noble metals, such as platinum, palladium, and rhodium. Density functional calculations of the structure of molybdenum phosphides, as well as CO chemisorption on the MoP(001) surface, have also been studied on periodic surface models, using the generalized gradient approximation (GGA) for the exchange-correlation functional. The results show that the chemisorption of CO on MoP occurred mainly on top of molybdenum, because the bonding of CO requires a localized minimum potential energy. The adsorption energy obtained is  $\Delta H_{\text{ads}} \approx -2.18$  eV, and the vibrational frequency of CO is 2047 cm<sup>-1</sup>, which is in good agreement with the IR result of CO chemisorption on MoP/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub>.

## 1. Introduction

Transition-metal nitrides and carbides have attracted much attention because they show catalytic properties that resemble group VIII metals in many hydrogen-involved reactions. In particular, they have potential applications in both hydrodenitrogenation (HDN) and hydrodesulfurization (HDS) processes.<sup>1–6</sup> Recently, transition-metal phosphides have also been found to possess excellent catalytic properties for HDS<sup>7</sup> and HDN reactions.<sup>8–10</sup> It was found that molybdenum phosphides were intrinsically the most active catalysts in hydroprocessing reactions among a series of catalysts.<sup>11–14</sup> However, although many investigations have been conducted on catalytic reactivities, very little work has been done toward the fundamental understanding of the surface-active sites of molybdenum phosphides, and several questions concerning the nature of the surface-active sites on transition-metal phosphide catalysts still remain.

Infrared (IR) spectroscopy is a powerful technique for the characterization of surface-active sites. Using IR spectroscopy combined with the adsorption of probe molecules, it is possible to study the surface sites of supported molybdenum phosphides, judging from the fact that transmittance IR spectroscopy has been successfully used to study reduced and passivated Mo<sub>2</sub>N/Al<sub>2</sub>O<sub>3</sub> and Mo<sub>2</sub>C/Al<sub>2</sub>O<sub>3</sub> catalysts.<sup>6</sup> Very recently, we developed an in situ IR spectroscopy method to study fresh Mo<sub>2</sub>N/Al<sub>2</sub>O<sub>3</sub> and Mo<sub>2</sub>C/Al<sub>2</sub>O<sub>3</sub> catalysts,<sup>15,16</sup> and we have observed different properties in surface sites, when compared with the reduced and passivated catalysts. In this paper, we report, for the first

time, on the IR spectra of CO that has been adsorbed on MoP/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> catalysts.

Theoretical studies have found wide applications in catalysis, such as use in systems of metal, metal oxides, and zeolite catalysts. Recently, the density functional theory (DFT) and local approximation (LDA) methods have become widely accepted schemes for the study of the electronic ground states of solids, surfaces, and molecules. Marlo and Milman<sup>17</sup> studied the bulk and the surface properties of titanium nitride (TiN), using different exchange-correlation functionals. They found that sites for CO adsorption existed on top of the Ti atoms and had a chemisorption energy of  $-2.88$  eV.<sup>17</sup> Frapper et al. also reported on CO adsorption on the  $\gamma$ -Mo<sub>2</sub>N(100) surface of molybdenum nitride using DFT calculation, which can explain our experimental observation of N=C=O species.<sup>15,18</sup>

In the IR spectra of CO adsorption on MoP/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> catalysts obtained in this work, the adsorbed CO gives a characteristic IR band at 2037 cm<sup>-1</sup>, which corresponds to linearly adsorbed CO species on the Mo sites. DFT calculations substantiated that these IR spectra represent linearly adsorbed CO on molybdenum phosphide (MoP).

## 2. Experiment and Methodology

MoP/Al<sub>2</sub>O<sub>3</sub> catalysts with different molybdenum loadings were prepared by the incipient wetness impregnation of  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> supports with an aqueous molybdenum phosphate precursor, followed by temperature-programmed reduction in flowing hydrogen.<sup>12</sup> After the reduction, the sample was passivated in 1% O<sub>2</sub>/N<sub>2</sub> before being exposed to air. For high loadings of the MoP/Al<sub>2</sub>O<sub>3</sub> catalysts, X-ray diffraction (XRD) shows that a MoP phase is formed, whereas no diffraction peaks due to the MoP phase were observed for loadings of <20 wt %, probably

\* Authors to whom correspondence should be addressed. E-mail: chliang@dicp.ac.cn, canli@dicp.ac.cn (homepage: <http://www.canli.dicp.ac.cn>).

<sup>†</sup> Dalian Institute of Chemical Physics.

<sup>‡</sup> Eindhoven University of Technology.

because of the good dispersion of MoP, as well as the interaction between MoP and the support. X-ray photoelectron spectroscopy (XPS) data shows that there were some oxygen species on the passivated MoP/Al<sub>2</sub>O<sub>3</sub> surface after exposure to air (not shown here).

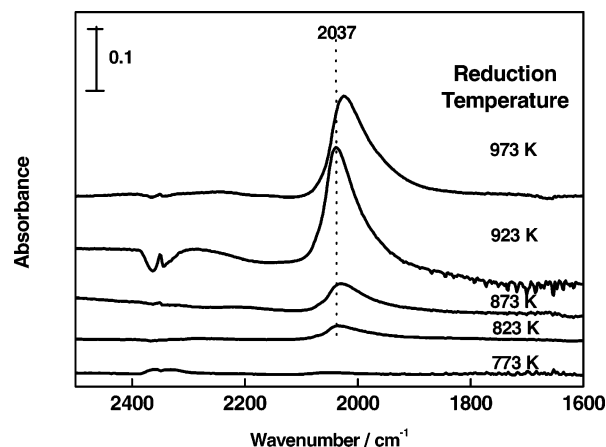
The passivated MoP/Al<sub>2</sub>O<sub>3</sub> sample (10 wt % molybdenum) was pressed into a self-supporting wafer that had an areal mass of  $\sim 15$  mg/cm<sup>2</sup>. The wafer was placed in a quartz IR cell that was equipped with CaF<sub>2</sub> windows, and then the wafer was reduced in flowing hydrogen at different temperatures for 2 h. Subsequently, the cell was cooled to room temperature, evacuated to  $10^{-5}$  Torr, and then exposed to 10 Torr of CO for IR studies. IR spectra were collected at room temperature on a Fourier transform infrared (FT-IR) spectrometer (Nicolet model Impact 410), with a resolution of 4 cm<sup>-1</sup>.

The density functional calculations reported here were performed with the Vienna ab initio simulations program (VASP)<sup>19</sup> within the framework of the generalized gradient approximation (GGA) of Perdew and Wang.<sup>20</sup> This method uses periodic boundary conditions and applies a plane-wave basis and fully optimized nonlocal Vanderbilt-type ultrasoft pseudo-potentials.

MoP crystallizes with a tungsten carbide (WC)-type structure, in which each Mo atom is trigonalprismatically coordinated by six P atoms.<sup>13</sup> The MoP (001) plane consists of a five-layer slab, in which the first three layers are allowed to relax and take the values that give a minimum total energy, whereas the two bottom layers are fixed in their bulk positions. To model the catalytic activity of MoP, CO chemisorption on the relaxed (001) surface of the MoP is calculated by the pseudo-potential density functional calculation on periodic systems. The CO molecules are placed on the top layer, followed by an empty region whose thickness is equivalent to 14 layers. The Methfessel–Paxton smearing is  $\sigma = 0.2$  eV. The cutoff energy for the plane wave expansion of the eigenstates can be set at 400 eV. A spin-restricted approach is used for all surface models to consider the polarization effect. Brillouin zone integration is performed on a grid of  $15 \times 15 \times 1$  Monkhorst–Pack special *k*-points (225 *k*-points). The number of *k*-points was considered to have converged when the atomic positions changed by  $<0.01$  Å in structural optimization.

The  $\nu_{\text{CO}}$  and  $\nu_{\text{Mo-CO}}$  stretching frequencies were calculated from the potential-energy surface (PES), which consisted of eight points for displacements  $[-0.1, +0.25]$  Å from the equilibrium bond lengths, with a step of 0.05 Å. This wide range ensured a reasonable description of the first vibrational excited state and any possible anharmonic contributions. The PES for the adsorbed CO was obtained by fixing the center of mass of the CO molecule at its coordinated equilibrium position. The PES for the Mo–CO chemisorbate bond was obtained by altering the Mo–C distance, while fixing the CO bond at its coordinated equilibrium values. These procedures effectively decoupled the CO stretching from the Mo–CO vibration, because it has a considerably (5-fold to 10-fold) low frequency.<sup>21,22</sup>

The harmonic frequencies were calculated using the polynomials up to the fifth order on a grid. For comparison, the calculated free CO harmonic frequency and the experimental vibrational frequency are also presented. The distance of free CO variation was calculated using the same procedure that was used to determine the VASP optimized equilibrium distance (1.146 Å) to get the PES. A comparison between the calculated vibrational frequency for the free CO molecule (2096 cm<sup>-1</sup>) and the experimental value (2143 cm<sup>-1</sup>) gave an indication of



**Figure 1.** FT-IR spectra of adsorbed CO on MoP/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> reduced at different temperatures.

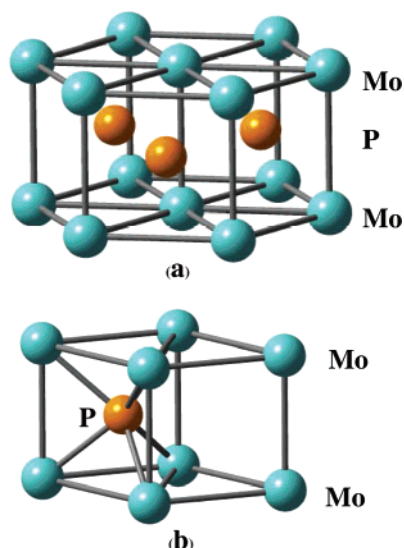
the accuracy of the method that was used.<sup>23</sup> A deviation of 3% was found for the DFT, molecular, and other periodic calculations.<sup>18,24</sup> This deviation of 3% in vibrational calculations was mainly caused by the VASP periodic method.

### 3. Results and Discussion

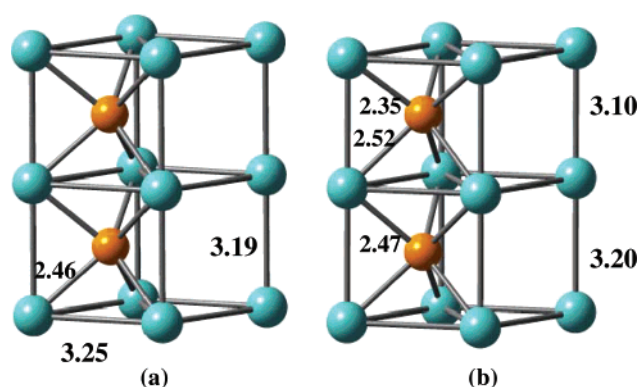
**3.1. IR Spectra of CO Adsorbed on MoP/Al<sub>2</sub>O<sub>3</sub>.** Figure 1 presents the IR spectra of CO adsorbed on MoP/Al<sub>2</sub>O<sub>3</sub> that has been reduced at different temperatures. No IR band for adsorbed CO can be observed on the sample that was reduced at  $<773$  K. A weak band at 2037 cm<sup>-1</sup> appears at a reduction temperature of 823 K. This band continues to increase in intensity as the reduction temperature increases, which indicates that more surface sites for CO adsorption are generated (because of the formation of MoP), and the maximum intensity is attained at a temperature of 923 K. The band at 2037 cm<sup>-1</sup> shifts slightly downward to 2023 cm<sup>-1</sup> and decreases in intensity when the sample was reduced at 973 K. According to the contour of the IR spectra and the preparation process, the reduced MoP/Al<sub>2</sub>O<sub>3</sub> at 923 K can be regarded as a fresh molybdenum phosphide supported on alumina.

Many IR studies of surface sites of supported molybdenum-based catalysts that use CO as the probe molecule have been reported in the literature.<sup>6,15,16,25–30</sup> These studies can be used as references for the assignment of the IR bands of adsorbed CO on MoP. Generally speaking, linear carbonyl species coordinated to Mo <sup>$\delta+$</sup>  ( $3 < \delta < 5$ ) sites exhibit  $\nu_{\text{MoC-O}}$  frequencies higher than those of free CO molecules (2143 cm<sup>-1</sup>).<sup>6,15,16,26,28</sup> In contrast, those held by Mo <sup>$\delta+$</sup>  ( $0 < \delta < 3$ ) sites exhibit  $\nu_{\text{MoC-O}}$  frequencies of  $<2143$  cm<sup>-1</sup>.<sup>25</sup> A band at 2070–2050 cm<sup>-1</sup> can be assigned to adsorbed CO on Mo<sup>2+</sup>.<sup>6,15,16,28,30</sup> Therefore, the IR band at 2037 cm<sup>-1</sup> can be safely assigned to the linearly adsorbed CO on the surface Mo atoms of the MoP/Al<sub>2</sub>O<sub>3</sub> catalyst, which may likely be positively charged, i.e., Mo <sup>$\delta+$</sup>  ( $0 < \delta < 2$ ). To our knowledge, this is the first time an IR spectrum has been recorded for CO adsorbed on the surface sites of MoP.

**3.2. Calculation of Bulk MoP and Clean MoP Surfaces.** MoP has a simple hexagonal structure. The structure and the primitive cell of MoP are described in Figure 2. The calculated equilibrium lattice parameters are  $a = 3.251$  Å and  $c = 3.193$  Å, with  $15 \times 15 \times 15$  Monkhorst–Pack *k*-points, which corresponds to a distance of 1.63 Å between the (001) layers. The calculated Mo–P distance is equal to 2.46 Å. These lattice parameters are in good agreement with the experimental values of  $a = 3.22$  Å and  $c = 3.19$  Å (see Table 1).



**Figure 2.** (a) Simple hexagonal structure and (b) the primitive cell of MoP.



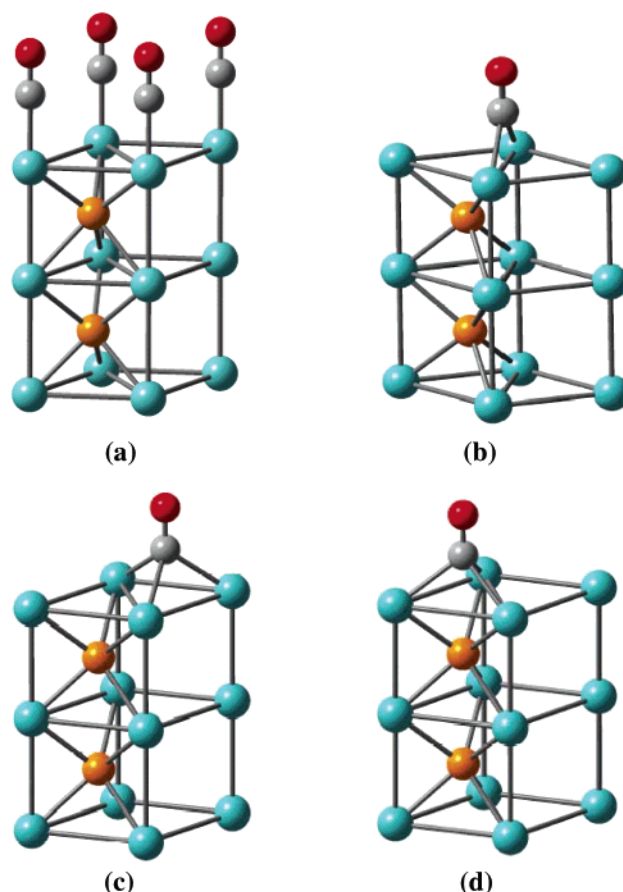
**Figure 3.** (a) MoP(001)–(1 × 1) surface model. (b) Relaxed MoP(001)–(1 × 1) surface in the side view. The first three layers are relaxed, and the two bottom layers are fixed.

**TABLE 1. Lattice Constants  $a$  and  $c$  for Simple Hexagonal Molybdenum Phosphides, as Compared to Experimental Values from Oyama et al.<sup>14</sup>**

lattice constant	Value (Å)	
	calculated	experimental
$a$	3.251	3.22
$c$	3.193	3.19

The Mo-terminated surface is very important for the catalytic activity, because the reaction occurs mainly on the Mo sites, as known from experimental observation. In the calculation, the Mo-terminated MoP(001)–(1 × 1) surface with a slab of five layers of MoP is built, which gives five atoms per cell, and the Mo atoms are in the first layer, thus forming the outer Mo layer. The first three layers are relaxed layers and take values that give a minimum total energy, whereas the two bottom layers are fixed in their bulk positions. The vacuum spacing between two repeated slabs is set to 23.6 Å.

In contrast to bulk MoP, the calculated in-plane Mo–Mo and P–P distances do not change. However, the out-of-plane distances vary considerably, as shown in Figure 3, from 3.21 Å to 3.10 Å for the Mo–Mo distance, from 2.46 Å to 2.52 Å for the Mo–P distance, and from 3.21 Å to 3.28 Å for the P–P distance. The surface formation energy of a clean and unrelaxed surface is 0.168 eV. The main structural modification for the MoP relaxation might be reflected by the changes in the Mo–P–Mo bond.



**Figure 4.** Four local coordinates modes of CO molecule on clean MoP(001)–(1 × 1) surface: (a) on-top Mo, (b) bridge, (c) fcc site, and (d) hcp hollow site.

For comparison, the P-terminated MoP(001)–(1 × 1) surface with a slab that has five layers of molybdenum phosphides is also built, which is very similar to the Mo-terminated surface model. In this P-terminated surface, the P atoms are in the first layer, just as the outer Mo layer does. The first three layers are also relaxed, and the two bottom layers are fixed in their bulk positions. The vacuum spacing between two repeated slabs is also set to 23.6 Å. In comparison with the Mo-terminated surface, the relaxation result of the P-terminated surface shows that the first and third layers, i.e., the P atom layers, move toward the surface direction a distance of  $\sim 0.01$  Å from the original bulk position, and the distance of the two P layers is almost unchanged. However, the second layer, i.e., the Mo layer, moves toward the surface direction a distance of 0.04 Å from the original bulk position.

**3.3. Calculation of CO Adsorption on a Clean MoP(001) Surface.** The calculated CO adsorption on the Mo-terminated surface leads to the identification of four minima on the PES. The four calculated local bonding modes of CO adsorption—namely, on-top, bridge, face-centered cubic (fcc), and hexagonal close-packed (hcp) sites, are shown in Figure 4.

The CO adsorption energy on the surface,  $E_{\text{ads}}$ , is given by

$$E_{\text{ads}} = \frac{E_{\text{tot}} - E_{\text{s}} - nE_{\text{CO}}}{n}$$

where  $E_{\text{tot}}$  is the total energy of the CO covered slab (which depends on the CO coverage and surface strain),  $E_{\text{CO}}$  is the energy of a free CO molecule ( $E_{\text{CO}} = -14.725$  eV), and  $n$  is the number of CO molecules in a supercell. For monolayer coverage,  $n = 1$  and  $E_{\text{s}}$  is the energy of the MoP slab without



**TABLE 2. Adsorption Energy ( $E_{\text{ads}}$ ), Optimized Geometry, and Harmonic Vibrational Frequency for CO, as a Function of the Chemisorption Sites on a Clean Mo-Terminated MoP(001)–(1 × 1) Surface**

parameter	Value			
	top	bridge	fcc	hcp
$E_{\text{ads}}$ (eV)	−2.180	−1.752	−1.740	−1.727
$d_{\text{Mo-C}}$ (Å)	2.05	2.26	2.34	2.29
$Z_{\text{s-c}}$ <sup>a</sup> (Å)	2.05	1.57	1.39	1.32
$d_{\text{C-O}}$ (Å)	1.16	1.18	1.19	1.20
$\nu_{\text{CO}}$ (cm <sup>−1</sup> )	2047	1877	1814	1761
$\nu_{\text{M-CO}}$ (cm <sup>−1</sup> )	427	346	269	165
$\nu_{\text{CO exp.}}$ (cm <sup>−1</sup> )	2037			

<sup>a</sup>  $Z_{\text{s-c}}$  is the distance between the C atom and the (001) surface.

CO on it. The definition of the CO adsorption energy  $E_{\text{ads}}$  includes the lateral interactions between the molecules.

The calculated adsorption energies, optimized geometries, and the vibrational frequencies of adsorbed CO on the four different local bonding sites are shown in Table 2. The most energetically favorable sites for CO chemisorption are the on-top sites of Mo. The CO molecule is connected to one Mo atom ( $\text{Mo-C} = 2.05$  Å;  $\text{C-O} = 1.16$  Å) with an adsorption energy of  $E_{\text{ads}} = -2.180$  eV. The CO frequency on an on-top site is calculated to be 2047 cm<sup>−1</sup>, and the Mo–CO frequency on an on-top site is 427 cm<sup>−1</sup>. The adsorption energies of CO on the bridge, fcc, and hcp hollow sites are −1.752, −1.740, and −1.727 eV, respectively. The adsorption energies of the CO on these three sites are much less than that on the on-top site: the differences are in the range of 0.428–0.425 eV. From this point of view, CO adsorption on the MoP surface should occur mainly on the on-top sites. Table 2 shows that the CO frequency on a bridge site is calculated to be 1877 cm<sup>−1</sup> and the Mo–CO frequency is 346 cm<sup>−1</sup>, whereas the CO adsorption frequency on a fcc site is calculated to be 1814 cm<sup>−1</sup> and the Mo–CO frequency is 269 cm<sup>−1</sup>, and the CO adsorption frequency on a hcp site is 1761 cm<sup>−1</sup> and the Mo–CO frequency is 165 cm<sup>−1</sup>. Moreover, the calculated C–O distances are 1.16, 1.18, 1.19, and 1.20 Å for CO adsorption on the on-top, bridge, fcc, and hcp surface sites, respectively. The changes in adsorption energies of CO on the surface agree with the changes in CO vibrational frequencies and the C–O distances. These changes seem to be disagreeable with the M–C distances, in which the calculated Mo–C distances are 2.05, 2.26, 2.34, and 2.29 Å for CO adsorption on the on-top, bridge, fcc, and hcp surface sites, respectively. The reason is that two Mo atoms are interacting with the CO in the bridge site, whereas three Mo atoms are interacting in the fcc and hcp sites. Under these situations, the distance between the C and the surface ( $Z_{\text{s-c}}$ ) should be considered. The  $Z_{\text{s-c}}$  distances are 2.05, 1.57, 1.39, and 1.32 Å for CO adsorption on the atop, bridge, fcc, and hcp surface sites, respectively. The changes in adsorption energies, C–O distances, and CO vibrational frequencies agreed well with the distance between the C atoms and the surface. The calculated vibrational frequencies of Mo–CO are 427, 346, 269, and 165 cm<sup>−1</sup> for CO adsorption on the on-top, bridge, fcc, and hcp surface sites, respectively. The change in vibrational frequencies of Mo–CO also corresponds with the adsorption energies, C–O distances, CO vibrational frequencies, and the  $Z_{\text{s-c}}$  distance for the four different adsorption sites.

The four local bonding modes of CO adsorption on the P-terminated surface (on-top, bridge, fcc, and hcp sites), and the calculated adsorption energies, optimized geometries, and the vibrational frequencies of CO adsorption on the four different local bonding sites are shown in Table 3.

**TABLE 3. Adsorption Energy ( $E_{\text{ads}}$ ), Optimized Geometry, and Harmonic Vibrational Frequencies for CO, as a Function of the Chemisorption Sites on a Clean P-Terminated MoP(001)–(1 × 1) Surface**

parameter	Value			
	top	bridge	fcc	hcp
$E_{\text{ads}}$ (eV)	0.007	−0.103	−0.214	−0.004
$d_{\text{P-C}}$ (Å)	1.70	2.17	2.39	2.99
$Z_{\text{s-c}}$ (Å)	1.70	1.44	1.48	2.33
$d_{\text{C-O}}$ (Å)	1.18	1.17	1.17	1.15
$\nu_{\text{CO}}$ (cm <sup>−1</sup> )	1960	1897	1943	2088
$\nu_{\text{M-CO}}$ (cm <sup>−1</sup> )	522	199	184	

<sup>a</sup>  $Z_{\text{s-c}}$  is the distance between the C atom and the (001) surface.

For the CO adsorption on the on-top sites of the P atoms, the adsorption energy is  $E_{\text{ads}} = 0.007$  eV, and the CO molecule is connected to one P atom, with a P–C distance of 1.70 Å, whereas the C–O distance is 1.18 Å. The calculated CO frequency on an on-top site is 1960 cm<sup>−1</sup>, and the P–CO frequency on an on-top site is 522 cm<sup>−1</sup>. According to the calculated results, the CO  $E_{\text{ads}}$  value indicates a slightly endothermic reaction.

For CO adsorption on the other three sites, i.e., the bridge, fcc, and hcp sites, the CO  $E_{\text{ads}}$  values on the P-terminated surface are −0.103, −0.214, and −0.004 eV, respectively, the distances of the CO molecule connected to one P atom (P–C) are 2.17, 2.39, and 2.99 Å, respectively, and the distances of the C atom to the P surface are 1.44, 1.48, and 2.33 Å, respectively. The C–O distances for CO adsorption on the bridge, fcc, and hcp sites are 1.17, 1.17, and 1.15 Å, respectively. The calculated CO frequencies on the bridge, fcc, and hcp sites are 1897, 1943, and 2088 cm<sup>−1</sup>, respectively. The P–CO vibrational frequencies are 199 and 184 cm<sup>−1</sup> for the CO adsorption on the respective bridge and fcc sites of the P-terminated surface. The P–CO vibrational frequency of CO adsorption on the hcp site cannot be calculated in the present situation, because of the poor interaction of CO on the hcp sites. The CO adsorption energy (−0.004 eV) and vibrational frequency (2088 cm<sup>−1</sup>) show that there is almost no adsorption of CO on the hcp sites of the P-terminated surface, so that the CO vibrational frequency of 2088 cm<sup>−1</sup> for the CO adsorption on the hcp sites of the P-terminated surface is very similar to the calculated free CO vibrational frequency (2096 cm<sup>−1</sup>). Table 3 clearly shows that weak CO adsorptions exist on the P-terminated surface, or even a slightly endothermic reaction exists. These observations can explain why the vibrational frequencies of CO adsorption on the four adsorption sites of the P-terminated surface cannot be measured in experiments.

Compared with Table 3, the CO adsorption energies on the Mo-terminated surface in Table 2 are greater than those on the P-terminated surface. The most energetically favorable sites for CO chemisorption are the on-top sites on the Mo-terminated surface. Consequently, the Mo-terminated surface is catalytically active, whereas the P-terminated surface has no catalytic activity at all.

Table 2 and Figure 1 show that the binding energy reaches its lowest value along the top PES ( $Z_{\text{s-c}} \approx 2.05$  Å) when a CO molecule adsorbs on the on-top site of the MoP surface. When the CO molecule moves to the surface further, to reach the lowest energies of the other three local adsorption sites, the processes are endothermic. In this way, a CO molecule prefers the on-top sites to the bridge, fcc, and hcp sites, because these three latter sites are 0.43–0.45 eV higher than the on-top site in energy. This is the reason only CO that has been adsorbed on on-top sites is observed in the IR spectra.

Many studies of CO adsorption on transition metals have been made recently. Eichler and Hafner studied the molecular adsorption of CO on Pd(100), and they showed that different adsorption energies resulted for CO adsorption on different planes.<sup>31</sup> They calculated the adsorption energies of CO on the Pd(100) surface, which was evaluated to be  $-1.44$  eV on an on-top site,  $-1.97$  eV on a bridge site, and  $-1.74$  eV on a hollow site.<sup>31</sup> The height of the C atom above the surface was  $1.88$  Å for CO on the on-top site,  $1.44$  Å for CO on the bridge site, and  $1.04$  Å for CO on the hollow site. The corresponding CO vibrational frequencies were 2063, 1887, and  $1828\text{ cm}^{-1}$ , respectively. They made use of the CO steering effect to explain the fact that CO molecules could adsorb on the on-top, bridge, and hollow sites, although the bridge and hollow sites are more energetically favorable than the on-top sites. They also studied the adsorption of CO on the (100) surface of rhodium and obtained similar results.<sup>32</sup> Furthermore, they found that the adsorption energies of CO on the Pd(100) surface was  $-1.92$  eV on an on-top site,  $-2.13$  eV on a bridge site, and  $-1.98$  eV on a hollow site. Their results confirmed that adsorption on the bridge sites is always energetically more favorable than those on either the on-top or hollow sites. Marlo and Milman observed that the adsorption of CO on the titanium nitride (TiN) gave a chemisorption energy of  $-2.88$  eV.<sup>17</sup> Frapper et al. studied the electronic surface properties of  $\gamma\text{-Mo}_2\text{N}(100)$ , as well as the CO chemisorption on periodic surface models, using the generalized gradient approximation (GGA) for the exchange-correlation functional. They demonstrated theoretically, for the first time by DFT calculation, the CO adsorption on the  $\gamma\text{-Mo}_2\text{N}(100)$  surface and obtained an adsorption energy of  $-1.43$  eV and a vibrational frequency of  $1994\text{ cm}^{-1}$ .<sup>18</sup> Their results illustrated the well-known platinum-like catalytic properties of the nitride molybdenum.

Our calculations also demonstrated certain rhodium- or palladium-like properties of the molybdenum phosphide. However, we have found that CO adsorption on the Mo-terminated surface is different from that on the  $\gamma\text{-Mo}_2\text{N}(100)$ , Pd(100), and Rh(100) surfaces. The height of the C atom above the surface is  $2.05$  Å for CO on the on-top site,  $1.57$  Å on the bridge site,  $1.39$  Å on the fcc site, and  $1.32$  Å on the hcp site. The corresponding CO adsorption energies are  $-2.180$ ,  $-1.752$ ,  $-1.740$ , and  $-1.727$  eV, respectively. Thus, the adsorption on the on-top sites is always energetically more favorable. From this point of view, it is clear that only the vibrational frequency for the CO adsorbed on the on-top sites of the MoP surface can be measured in the IR spectra.

#### 4. Conclusion

Catalysts of molybdenum phosphide supported on alumina ( $\text{MoP}/\gamma\text{-Al}_2\text{O}_3$ ) were successfully prepared and characterized by CO adsorption, using in situ Fourier transform infrared (FT-IR) spectroscopy. CO that has been adsorbed on the surface of  $\text{MoP}/\text{Al}_2\text{O}_3$  has a characteristic band at  $\sim 2037\text{ cm}^{-1}$ , because of the linearly adsorbed CO on  $\text{Mo}^{\delta+}(0 < \delta < 2)$  sites. Density functional calculations of the structure of molybdenum phosphide (MoP) and the CO chemisorption on the Mo-terminated and P-terminated  $\text{MoP}(001)$  surfaces were also studied. The calculated chemisorption sites for CO on the Mo-terminated MoP surface are on-top sites of Mo, with an adsorption energy of  $\Delta H_{\text{ads}} \approx -2.18$  eV. For CO chemisorption on the on-top metallic sites, the calculated vibrational frequency for adsorbed CO is  $2047\text{ cm}^{-1}$ , which agrees with the experimental results.

The adsorption energy of CO on the on-top sites is greater than the other three sites calculated (in the range of  $-1.727$  to  $-1.752$  eV). In contrast with the calculated Mo-terminated surface, only very weak CO adsorptions or even slightly endothermic reactions on the P-terminated surface were found to exist. These observations can explain why the vibrational frequencies of CO adsorption on the four types of adsorption sites of the P-terminated surface do not exist in experiments.

**Acknowledgment.** This study was financially supported by the Holland-China Project, the State Key Project for Basic Research and Development of China (Grant No. G2000048003), and the Natural Science Foundation of China (Grant No. 20333060).

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