Catalysis Letters Vol. 91, Nos. 3–4, December 2003 (© 2003)

Catalytic properties of molybdenum carbide, nitride and phosphide: a theoretical study

Ping Liu and José A. Rodriguez*

Department of Chemistry, Brookhaven National Laboratory, Bldg. 555, Upton, NY 11973, USA

Received 28 August 2003; accepted 30 October 2003

The control and optimization of the catalytic properties of nonexpensive early transition metals is an important issue in the chemical industry. Density functional theory was employed to study the relative stability and chemical activities of molybdenum carbides, nitrides and phosphides. The results show that molybdenum phosphides display the *highest reactivity* toward CO and sulfur adsorption as compared to molybdenum carbides and nitrides. Considering the better catalysts, those that combine high stability and a reasonable chemical activity, we observe that the catalytic potential of these systems should increase following the sequence: $\mathrm{Mo} < \mathrm{MoC} \approx \mathrm{MoN} < \mathrm{MoP}$. An electronic analysis is included to understand the better performance of molybdenum phosphide.

KEY WORDS: molybdenum; molybdenum carbide; molybdenum nitride; molybdenum phosphide; catalytic property; carbon monoxide; hydrodesulfurization.

1. Introduction

The removal of sulfur-containing compounds by hydrodesulfurization (HDS) is an extremely important reaction in petroleum refineries and has received considerable attention over the last decades. In recent years, new legislations require a very low content of sulfur in the oil-derived products, and new catalysts have been developed for deep HDS processes. Many of these catalysts are Mo-based compounds. It has been indicated that the molybdenum carbides [1,2] and nitrides [3,4] exhibit high activity in many reactions including Fischer–Tropsch [5], ammonia synthesis [6] and HDS, and have the potential to replace the commercial sulfided molybdenum catalysts [7,8]. A series of experimental studies show that the molybdenum phosphides display a substantial improvement for HDS as compared to the sulfided molybdenum catalysts [9–14]. For a further development of HDS catalysts, it is very important to fundamentally understand the good catalytic performance of the molybdenum carbides, nitrides and phosphides. To do that, in general one has to consider electronic and geometric factors.

The remarkable activities of molybdenum carbides, nitrides and phosphides have been attributed to a distinct electronic structure induced by the presence of carbon, nitrogen or phosphorus (a "ligand effect") on one hand. On the other hand, the carbon, nitrogen or phosphorus atoms limit the number of metal sites that can be exposed on a surface (a "ensemble effect"). For the carbides and nitrides, several studies have been devoted to understand the phenomena responsible for their catalytic properties [15–19]. After increasing the C/Mo or N/Mo ratio, the molybdenum carbides or nitrides become more stable with the activity of molybdenum decreasing due to a big electron transfer from molybdenum to carbon or nitrogen (ligand effect). The better performance was observed for systems like Mo_2C [15] or Mo_2N [18]. For the phosphides, not much is known in this respect. The fundamental studies on molybdenum phosphides are limited to the geometric and electronic properties of the bulk systems (pure or supported on oxides) [9,20]. So far, no systematic study examining the reactivity of well-defined surfaces of molybdenum carbide, nitride and phosphide has been published.

With recent improvements, density functional theory (DFT) is capable of providing qualitative and, in many cases, quantitative insights into surface science and catalysis [21]. In the present study, a set of DFT calculations were carried out to understand the different effect of carbon, nitrogen or phosphorus on the stability and activity of molybdenum. The systems we study here include δ-MoC(001), γ-MoC(001), δ-MoN(001), MoP(001) and Mo(001). γ-MoC(001), δ-MoN(001) and MoP(001) all have a hexagonal structure with the same C,N,P/Mo ratio. In addition, by considering the Mo-terminated surfaces, all the systems have the same surface composition as Mo(001). It makes them the perfect candidates for a fundamental study of the ligand effect of carbon, nitrogen or phosphorus on the chemical activities of carbide, nitride or phosphide systems.

As in most of the fundamental studies on transition metal compounds [15–18,22], small adsorbates, atomic

---

[*] To whom correspondence should be addressed.
E-mail: rodrigez@bnl.gov

1011-372X/03/1200–0247/0

sulfur (S) and carbon monoxide (CO), were used here to test the reactivities of the metal carbides, nitrides and phosphides. CO is a typical probe molecule for adsorption reactions [16,17], and adsorbed sulfur is important because of the essential role of these molybdenum compounds in HDS processes [1–4,9–14].

2. Theoretical method

Our calculations use the DMol^3 code [23,24], which allows the description of both molecular systems and periodic surfaces. The calculations were based on a spin-restricted DFT with a basis set of double numerical plus d functions (comparable to a Gaussian 6–31G* basis set) and a local basis cutoff of 5.5 Å. The generalized gradient approximation (GGA), with the revised version of the Perdew-Burke-Ernzerhof (RPBE) functional was used here [28]. The extensive studies using the RPBE functional [28] show absolute errors in adsorption energy of ~0.2 eV. It has been shown previously that calculations using DMol^3 with the RPBE functional can reproduce well experimental results and are reasonably consistent with other theoretical calculations [15,25–27]. For instance, the first bond dissociation energy of a $Mo(CO)_6$ molecule, i.e. $Mo(CO)_6 \rightarrow Mo(CO)_5 + CO$, calculated with DMol^3 (1.63 eV) is in good agreement with the experimental value (1.73 eV) [29]. In addition, the difference in the CO adsorption energy on Mo(110) between DMol^3 [26] and CASTEP [30] or DACAPO [31] is only less than 0.1 eV, while less than 0.2 eV is found for sulfur adsorption on Mo(110) [26,30]. Thus, we have a lot of confidence when describing the CO and sulfur adsorption on molybdenum sites using DMol^3.

The adsorption of sulfur and CO was investigated on the γ-MoC(001), δ-MoN(001), MoP(001) and Mo(001) surfaces (see figure 1). In the present study, all the possible adsorption sites were considered for both adsorbates. To model the surfaces, we followed the supercell approach with four-layer slabs and a 11 Å vacuum between the slabs (figure 1). Enough K-points (16) have been selected for the surfaces [15,25–27]. When more K-points (25) were employed, the energy difference was less than 0.1 eV. The adsorbate coverage was one-fourth of a monolayer (ML). At this low coverage, lateral interactions between the adsorbed species should be weak, and the adsorption energy should reflect interactions with the surface. In the calculations, the top three layers of the surfaces and the adsorbates were allowed to relax in all dimensions, while only the bottom layer was kept fixed at the calculated bulk lattice positions. In test calculations for sulfur on four- and five-layer slabs of MoC(001), we found essentially the same adsorption energy by relaxing three of four layers and three of five layers. The calculated adsorption energy is defined as

$$E_{\text{ads}} = E(\text{adsorbate/substrate}) - E(\text{substrate}) - E(\text{adsorbate}) \qquad (1)$$

In addition, for each optimized structure, a Mulliken population analysis was carried out to estimate the partial charge on each atom and examine *qualitative trends* in charge redistribution.

3. Results and discussion

3.1. Geometry optimization and stability

In this section, we present our predictions for the geometries and stability of γ-MoC, δ-MoN and MoP. As shown in figure 1, the γ-MoC phase, the δ-MoN phase and MoP adopt hexagonal crystal structures with the space group being $P_{63/mmc}$, P_{63mc} and $P_{\bar{6}m2}$, respectively. The calculated equilibrium lattice constants are listed in table 1 and compared with experimental measurements [33–35]. In general, the agreement is very good.

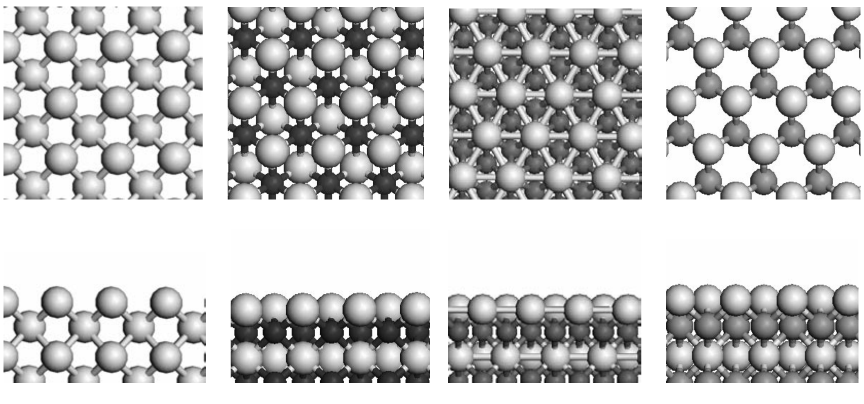
Mo(001) γ-MoC(001) δ-MoN(001) MoP(001)

Figure 1. Configurations of Mo(001) and Mo-terminated bulk γ-MoC(001), δ-MoN(001) and MoP(001) surfaces. Up: top view, down: side view. Light gray balls represent Mo atoms. Black, dark gray and gray balls stand for C, N and P atoms, respectively.

Table 1
Equilibrium lattice constants of the bulk molybdenum compounds calculated using DFT

	$a = b$ (Å)	c (Å)
γ-MoC	3.046 (3.010[a])	14.793 (14.610[a])
δ-MoN	5.751 (5.740[b])	5.657 (5.740[b])
MoP	3.235 (3.223[c])	3.165 (3.191[c])

Note: Values in parentheses are from experiments [33–35].
[a] [33].
[b] [34].
[c] [35].

We now look at the geometries of Mo-terminated γ-MoC(001), δ-MoN(001) and MoP(001) surfaces (figure 1), which to our best knowledge have not been reported so far. A Mo(001) surface was also considered for comparison. As shown in figure 1, the surface sites of all the surfaces are occupied with molybdenum atoms, but the Mo–Mo distances vary from one system to another. The molybdenum layers of Mo(001) are separated when saturated with 50% carbon, nitrogen or phosphide (i.e. 1 : 1 compounds) and form structures in which layers of molybdenum and carbon, molybdenum and nitrogen or molybdenum and phosphorus alternate. Table 2 lists the calculated parameters for each system after optimization. For Mo(001), the molybdenum atoms in the surface strongly interact with molybdenum atoms in the subsurface (2.646 Å), but are much more weakly bonded to other neighbors in the surface due to a separation of 3.165 Å. By 50% carbon or phosphorus saturation, the molybdenum atoms in the γ-MoC(001) and MoP(001) surfaces are isolated from each other by distances of 3.046 and 3.235 Å, respectively, while strong interactions between the surface molybdenum atoms and carbon or phosphorus atoms underneath are observed with bond lengths of 2.118 and 2.379 Å, respectively. The δ-MoN(001) surface is somewhat different. In this system, the molybdenum atoms bond strongly not only with nitrogen atoms in the subsurface (bond length, 2.132 Å) but also with other molybdenum atoms in the surface (bond length, 2.875 Å). The surfaces in figure 1 are ideal for a fundamental study of the ligand effect of carbon, nitrogen and phosphorus on the chemical activities of molybdenum in carbide, nitride and phosphide compounds.

The DFT calculations show a big electron transfer from molybdenum to the nonmetal component in MoC or MoN (see the calculated Mulliken charges in table 2). The direction of charge transfer (metal → C or N) found in the present slab calculations is consistent with previous theoretical studies and measurements of near edge X-ray adsorption spectroscopy for the bulk carbides [16,17]. In contrast, as in studies for bulk MoP [9], our calculations indicate that the charge for both molybdenum in the surface and phosphorus in the subsurface is very small in absolute value. As listed in table 2, the charge on molybdenum in the surface of MoP(001) is 0.045 e, while it is 0.558 e for molybdenum in γ-MoC(001) and 0.438 e for molybdenum in δ-MoN(001). The charge of phosphorus in the subsurface of MoP(001) is only -0.077 e, while carbon and nitrogen in the subsurface of MoC(001) and MoN(001) are negatively charged by -1.079 e and -0.910 e respectively. It is known that a 3p-group element (phosphorus, in this case) should not be as strong as a 2p-group element (carbon and nitrogen in this case) as an electron acceptor [36]. Therefore, the bonds in MoP are less ionic than those in MoC and MoN as seen in our DFT calculations. In addition, we also notice that the molybdenum atoms on the surface of MoP(001) and Mo(001) are both weakly charged (table 2). It implies a similar activity of MoP(001) and Mo(001) as we will see in the following section.

An important parameter to consider is the relative stability of a catalytic surface. To describe the surface stability, we use the formation energy, E_f. E_f can be expressed as

$$E_\mathrm{f} = E[\mathrm{Mo}X(001)] - E(\mathrm{Mo}) - E(X) \qquad (2)$$

where "E" is the total energy of the corresponding composition in bulk. "X" represents carbon, nitrogen and phosphorus, respectively. In order to compare the systems with different compositions, E_f is normalized by the number of atoms in the supercell (4-layer slab with a

Table 2
Optimized parameters for the clean surfaces using DFT

	$d(\mathrm{Mo_{surf}} - \mathrm{Mo_{surf}})$ (Å)	$d(\mathrm{Mo_{surf}} - \mathrm{X_{sub}})$ (Å)	$q_{\mathrm{Mo_{surf}}}$ (e)	$q_{\mathrm{X_{sub}}}$ (e)
γ-MoC(001)	3.046	2.118	0.558	-1.079
δ-MoN(001)	2.875	2.132	0.438	-0.910
MoP(001)	3.235	2.379	0.045	-0.077
Mo(001)	3.165	2.646	0.040	-0.051

Note: "d" and "q" represent the bond length and Mulliken charge, respectively; $\mathrm{Mo_{surf}}$ and $\mathrm{X_{sub}}$ stand for a molybdenum atom in the surface and an atom "X" in the subsurface, respectively; "X" corresponds to carbon in the case of γ-MoC(001), nitrogen in the case of δ-MoN(001), phosphorus in the case of MoP(001) and molybdenum in the case of Mo(001).

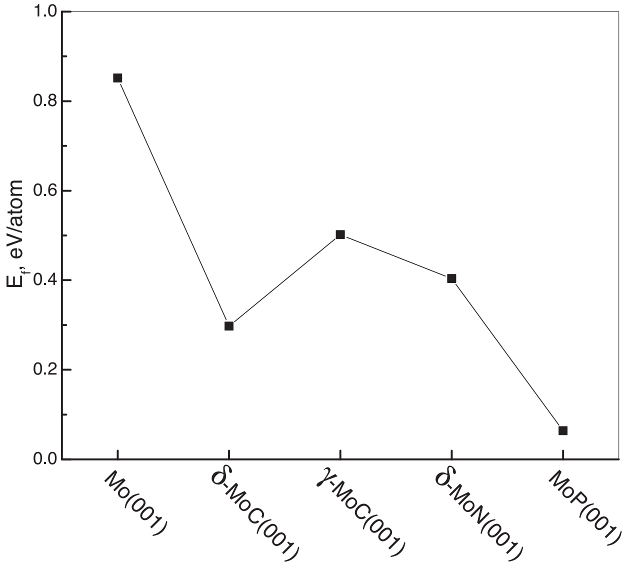

Figure 2. Calculated formation energy (E_f, equation 2) of Mo(001), δ, γ-MoC(001), δ-MoN(001) and MoP(001) surfaces. E_f is normalized by the number of Mo and X (C, N or P) atoms.

2 × 2 unit cell) including both molybdenum and X atoms. Here, we note that the surface formation energy in figure 2 is relative to bulk molybdenum, diamond, P-black and N_2 gas. The difference of the heat of formation between the graphite and diamond phases of carbon is less than 0.02 eV [37]. Therefore, it does not make much difference whether the formation energy is taken with respect to diamond or graphite. For phosphorus, P-black is more stable than P-red by ~0.4 eV [37]. Thus, P-black was considered.

For the systems under study here, the calculated heats of formation for the bulk compounds were negative (exothermic process), but positive values (endothermic process) were obtained for the formation of the surface. Thus, a small value of E_f in figure 2 corresponds to a relatively high stability. According to the results in figure 2, the Mo(001) surface becomes more energetically stable by forming the carbides, nitrides and phosphides. The MoP(001) surface is the most stable system of all. The stability of δ-MoN(001) and γ-MoC(001) is substantially lower than that of MoP(001). Here we note that δ-MoC(001) with a NaCl cubic structure is more stable than γ-MoC(001) and δ-MoN(001) with a hexagonal structure [15,16], but still not as stable as MoP(001).

3.2. Chemical activities

In the present study, the Co molecule and atomic sulfur were used to probe the chemical activities of the γ-MoC(001), δ-MoN(001) and MoP(001) surfaces. Atop, bridge and hollow adsorption sites were considered. To our best knowledge, similar comparative studies with well-defined surfaces have not been published so far. The interaction of Co with clean molybdenum single crystal surfaces has been well-documented [38]. The CO molecule bonds strongly to Mo(100) at 100 K. By raising the temperature to only 170 K, it decomposes to carbon and oxygen adatoms. Our calculations show that the CO species prefers to adsorb on the molybdenum atop sites. It is tilted and molecularly adsorbed in the surface at extremely low temperatures as observed in experiments [32,39]. A strong interaction between CO and the Mo(001) surface is predicted (−2.3 eV, table 3). It leads to dissociation with a very low barrier (~0.2 eV) [40], which can be overcome by thermal activation at low temperature. Atomic sulfur favors the hcp hollow site of the Mo(001) surface. The sulfur adsorption energy is much stronger than that of CO (−7.02 eV, table 3).

Table 3
Calculated energy for CO and sulfur adsorption on the molybdenum compounds using DFT

	E_{ads}^{CO} (eV)	E_{ads}^{S} (eV)
γ-MoC(001)	−1.75	−6.41
δ-MoN(001)	−1.74	−6.25
MoP(001)	−1.98	−6.71
Mo(001)	−2.30	−7.02

Similar to the case of pure molybdenum, the preferred adsorption sites on molybdenum compounds (γ-MoC(001), δ-MoN(001) and MoP(001)) are molybdenum atop site for CO adsorption (with tilting of the molecule) and hcp hollow for atomic sulfur adsorption. Thus, there is a direct interaction between carbon, nitrogen or phosphorus atoms underneath and the sulfur adatoms, although it is much weaker than the S–Mo interactions. The calculated adsorption energies for CO and sulfur are shown in figure 3 and table 3. One

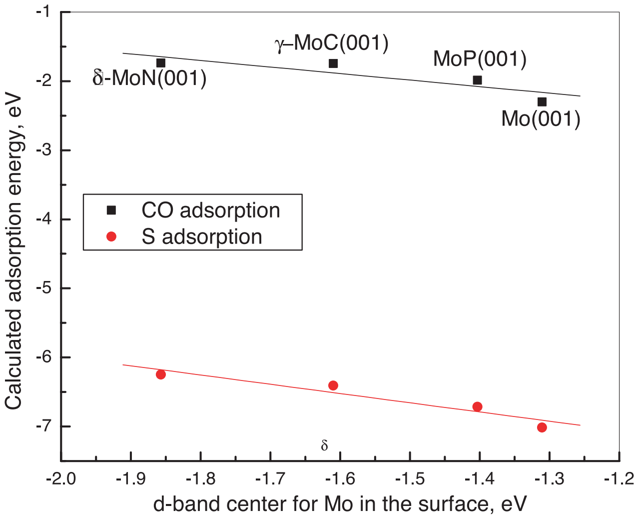

Figure 3. Calculated adsorption energy of CO (■) and S (●) as a function of the d-band center for Mo in clean surfaces of Mo(001), γ-MoC(001), δ-MoN(001) and MoP(001). Here, the d-band centers are relative to the Fermi energy.

can clearly see that the activity of molybdenum toward CO and sulfur adsorption degrades by forming molybdenum carbides, nitrides or phosphides. The deactivation of the MoP(001) surface is the smallest. In contrast, the γ-MoC(001) and δ-MoN(001) surfaces are more inert. To understand this, only a ligand effect or electronic effect should be considered since all the surfaces are Mo-terminated. Thus, the deactivation of Mo by electronic effects increases in the sequence: MoP $<$ MoC $\approx$ MoN. We note that the situation should be more complicated for a real catalyst. The surface sites could be a mixture of molybdenum and carbon, nitrogen or phosphorus [2,9,16]. Then, ensemble effects should also be considered and could induce a large reduction in the adsorption with respect to molybdenum. In any case, under similar structural configurations, we expect that molybdenum atoms bonded to phosphorus will be more chemically active than those bonded to carbon or nitrogen.

It is well known that variations in adsorption energy for a transition or noble metal (molybdenum in this case) under different chemical environments can be related to the changes in the metal electronic structure (ligand effect) [21,31,40]. To a first approximation, the interaction energy between an adsorbate and a transition metal should depend on the coupling of the adsorbate orbitals to the metal d-bands and, thus, depends on the position of the center of the d-band [21,31,40]. (Of course coupling to the metal s,p states also can contribute to the chemisorption bond [17b].) The general rule is that, the stronger the interaction with the ligand (carbon, nitrogen, phosphorus), the broader and lower-lying the d-band, therefore the weaker the binding with the adsorbates (CO, S) [21,31,40]. As shown in figure 3, our calculations for CO and sulfur adsorption on the Mo-terminated surfaces obey this rule well by displaying a nearly linear relationship between the position of the molybdenum d-band center and the adsorption energy.

For γ-MoC(001), there is a strong coupling between molybdenum d and Carbon s,p orbitals accompanied by a big electron transfer (table 2), which leads to a broadening of the molybdenum d orbitals. Thus, we observe a downward shift of the d-band center of molybdenum atoms in the surface of γ-MoC(001) (by 0.30 eV) and a weaker adsorption energy (by 0.55 eV for CO, 0.61 eV for sulfur) as compared with the case of Mo(001) (figure 3). Similar phenomena are also seen for δ-MoN(001). Here, the downshift of the molybdenum d-band center increases to 0.55 eV (figure 3). It may be ascribed to a broader molybdenum d-band, since the d orbitals of the molybdenum atoms in the δ-MoN(001) surface not only couple with s,p orbitals of the nitrogen atoms underneath but also with other molybdenum atoms in the surface (see figure 1). In contrast, for MoP(001) there is a very small electron transfer (table 2) and the downshift of the molybdenum d-band center is only 0.09 eV relative to the case of Mo(001) (figure 3). Thus, the calculations show that the MoP(001) surface exhibits much higher activity toward the CO and sulfur adsorption than the γ-MoC(001) and δ-MoN(001) surfaces. The adsorption energies of CO and sulfur on a MoP(001) surface are only $\sim$0.3 eV weaker than those on a Mo(001) surface.

3.3. *Catalytic potential*

In this section, we take a step further to evaluate the possible performance of the *Mo-based compounds* by considering good catalysts, those that combine high stability and a reasonable or moderate chemical activity [21,31,40]. High stability is necessary to prevent degradation of the catalytic materials in an aggressive chemical environment. Early transition metals like molybdenum are inexpensive materials, but their surface stability seems not high enough and easily transform into oxides, carbides, nitrides, etc. The formation of these compounds leads to a gain of stability, but there is a drop in the chemical activity of the early transition metal. According to the Sabatier's principle [42,43], early transition metals bond adsorbates too strongly to be efficient catalysts. Thus, the reduction in chemical activity induced by the formation of phosphides, carbides and nitrides can be beneficial if it is not excessively large (i.e. a phenomenon equivalent to a drop from the top to the bottom in a volcano plot) [42,43]. Following Sabatier's ideas, figure 3 implies that MoP and MoC should be better catalysts than molybdenum. In addition, one must also consider the relative stability of these compounds since they may degrade overtime in a reactive chemical environment. We think that both high stability and a moderate activity are necessary for the molybdenum compounds to become good catalysts. The values in figure 2 indicate that MoP should be the catalyst less susceptible to degradation. When the results of figures 2 and 3 are put together, one finds that the catalytic potential of these materials increases in the following order: Mo $<$ MoC, MoN $<$ MoP. Consistent with existing experimental data [9–14], our DFT calculations predict that the molybdenum phosphide should exhibit a better catalytic behavior than the carbide and nitride.

4. Conclusions

The control and optimization of the catalytic properties of nonexpensive early transition metals is an important issue in the chemical industry. We have investigated the effects of carbon, nitrogen and phosphorus on the stability and chemical reactivity of the molybdenum sites in carbides, nitrides and phosphides. By employing DFT-GGA slab calculations on Mo-terminated γ-MoC(001), δ-MoN(001) and MoP(001) surfaces, we find that the catalytic potential (combining high stability and moderate chemical reactivity) increases following the sequence: Mo $<$ MoC $\approx$ MoN $<$ MoP. As compared with carbides and nitrides, the better performance of the molybdenum phosphide may be ascribed to the weaker ligand effect of phosphorus atoms on the molybdenum atoms (very small Mo $\rightarrow$ P electron transfer, almost no downward shift in the molybdenum 4d states). The trends in our calculations agree with recent experiments [9–14], which show that metal phosphides are very good catalysts for several important reactions.

Acknowledgments

The authors would like to thank Xianqin Wang, Jingguang Chen and Mark Bussell for very useful conversations about the catalytic properties of metal phosphides and carbides. This research was carried out at Brookhaven National Laboratory under contract DE-AC02-98CH10886 with the US Department of Energy, Division of Chemical Sciences.

Reference

[1] J. Rodriguez, J. Dvorak and T. Jirsak, J. Phys. Chem. B 104 (2000) 11515.
[2] S.T. Oyama, Catal. Today 15 (1992) 179.
[3] D.J. Sajkowski and S.T. Oyama, Appl. Catal. A: Gen. 134 (1996) 339.
[4] M. Nagai, Y. Goto, H. Ishii and S. Omi, Appl. Catal. A: Gen. 192 (2000) 189.
[5] E.B. Yeh, L.H. Schwartz and J.B. Butt, J. Catal. 91 (1985) 241.
[6] R. Kijima and K. Aika, Appl. Catal. A: Gen. 219 (2001) 141.
[7] G.A. Somorjai, *Introduction to Surface Chemistry and Catalysis* (Wiley-Interscience, New York, 1994).
[8] H. Topsøe, B.S. Clausen and F. Massoth, *Catalysis Science and technology in Hydrotreating catalysis* (Springer, Berlin, 1996).
[9] J.A. Rodriguez, J. Kim, J.C. Hansen, S.J. Sawhill and M.E. Bussell, J. Phys. Chem. B 107 (2003), 6276.
[10] S.T. Oyama, P. Clark, V.L.S. Teixeira da Silva, E.J. Lede and F.G. Requejo, J. Phys. Chem. B 105 (2001) 4961.
[11] P. Clark and S.T. Oyama, J. Catal. 218 (2003) 78.
[12] P. Clark, X. Wang, P. Deck and S.T. Oyama, J. Catal. 210 (2002) 116.
[13] D.C. Phillips, S.J. Sawhill, R. Self and M.E. Bussell, J. Catal. 207 (2002) 266.
[14] S.T. Oyama, J. Catal. 216 (2003) 343.
[15] (a) P. Liu and J.A. Rodriguez, J. Phys. Chem. B (2003), submitted. (b) P. Liu, J.A. Rodriguez and J.T. Muckerman, J. Am. Chem. Soc. (2003), submitted.
[16] J.G. Chen, Chem. Rev. 96 (1996) 1477 and reference therein.
[17] (a) J.G. Chen, J. Eng and S.P. Kelty, Catal. Today 43 (1998) 147. (b) R. Hoffmann, *Solids and Surfaces: A Chemist's View of Bonding in Extended Structures* (VCH, New York, 1988)
[18] G. Frapper, M. Pélissier and J. Hafner, J. Phys. Chem. B 104 (2000) 11972.
[19] E. Furimsky, Appl. Catal. A: Gen. 240 (2003) 1 and references therein.
[20] B. Winkler, K. Knorr, M. Hytha, V. Milman, V. Soto and M. Avalos, J. Phys. Chem. Solids 64 (2003) 405.
[21] J. Greeley, J.K. Nørskov and M. Mavrikakis, Annu. Rev. Phys. Chem. 53 (2002) 319.
[22] T.P. St. Clair, S.T. Oyama and D.F. Cox, Surf. Sci. 511 (2002) 294.
[23] B. Delley, J. Chem. Phys. 92 (1990) 508.
[24] B. Delley, J. Chem. Phys. 113 (2000) 7756.
[25] J.A. Rodriguez, P. Liu, J. Dvorak, T. Jirsak, J. Gomes, Y. Takahashi and K. Nakamura, Surf. Sci. 543 (2003) L675.
[26] P. Liu and J.A. Rodriguez, J. Chem. Phys. (2003), in press.
[27] P. Liu, J.A. Rodriguez, H. Hou and J.T. Muckerman, J. Chem. Phys. 118 (2003) 7737.
[28] B. Hammer, L.B. Hansen and J.K. Nørskov, Phys. Rev. B 59 (1999) 7413.
[29] K.E. Lewis, S.M. Golden and G.P. Smith, J. Am. Chem. Soc. 106 (1984) 3095.
[30] P. Liu, J.A. Rodriguez, J.T. Muckerman and J. Hrbek, Phys. Rev. B 67 (2003) 155416.
[31] B. Hammer and J.K. Nørskov, Adv. Catal. 45 (2000) 71.
[32] P.J. Feibelman, B. Hammer, J.K. Nørskov, F. Wagner, M. Scheffler, R. Stumpf, R. Watwe and J. Dumesic, J. Phys. Chem. B 105 (2001) 4018.
[33] H. Nowotny, E. Parthe, R. Kieffer and F. Benesovsky, Monatshefte fuer Chem. 85 (1954) 255.
[34] A. Bezinge, K. Yvon, J. Muller, W. Lengauer and P. Ettmayer, Solid State Commun. 63 (1987) 141.
[35] S. Harris and R.R. Chianelli, J. Catal. 202 (2001) 187.
[36] http://www.webelements.com/
[37] J.A. Dean, *Lange's Handbook of Chemistry* (McGraw-Hill Inc., 1979).
[38] (a) T.E. Felter and P.J. Estrup, Surf. Sci. 76 (1978) 464. (b) E.I. Ko and R.J. Madix, Surf. Sci. 100 (1980) L505.
[39] (a) A.J. Jaworowski, M. Smedh, M. Borg, A. Sandell, A. Beulter, S.L. Sorensen, E. Lundgren and N.J. Anderson, Surf. Sci. 492 (2001) 185. (b) J.W. He, W.K. Kuhn and D.W. Goodman, Surf. Sci. 262 (1992) 351.
[40] J.K. Nørskov, T. Bligaard, A. Logadottir, S. Bahn, L.B. Hansen, M. Bollinger, H. Bengaard, B. Hammer, Z. Sljivancanin, M. Mavrikakis, Y. Xu, S. Dahl and C.J.H. Jacobsen, J. Catal. 209 (2002) 275.
[41] B. Hammer and J.K. Nørskov, *Chemisorption and Reactivity on Supported Clusters and Thin Films* (Kluwer Academic Publishes, Netherland, 1997).
[42] P. Sabatier, Ber. Dtsch. Chem. Ges. 44 (1911) 2001.
[43] M. Boudart and G. Djéga-Mariadassou, *Kinetics of Heterogeneous Catalytic Reactions* (Princeton University Press, New York, 1984).