Molybdenum Phosphide as an *o*-Propylaniline Hydrodenitrogenation Catalyst: A First Principles Study

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Abstract: MoP has been shown experimentally to be an active catalyst in the hydrodenitrogenation of *o*-propylaniline. We investigate the structure and the energetics of the *o*-propylaniline adsorption on the Mo-terminated MoP(001) surface. Detailed information on the structure of the free MoP(001) surface and on the structure and adsorption energy of *o*-propylaniline on MoP(001) is obtained by using density functional theory. The transition state, reaction path, and the energy barrier are reported for one of the branches of the HDN reaction network that leads to the formation of propylbenzene by hydrogenolysis of the C–N bond.

Keywords: adsorption · catalysis · density functional calculations · hydrodenitrogenation

Transition-metal phosphides have a wide range of interesting chemical and physical properties: they are hard, wear resistant, stable at elevated temperatures, and have relatively high thermal and electrical conductivities.[1] Molybdenum phosphide, MoP, is a promising catalyst in both unsupported and supported form for such processes as hydrodenitrogenation (HDN) and hydrodesulfurization (HDS).[1–6] MoP exhibits the highest intrinsic activity in the HDN process of *o*-propylaniline out of a number of related transition-metal phosphides, with product selectivities similar to those of sulfidic catalysts.[2] Furthermore, it has been predicted recently that MoP should have a higher potential as a catalyst than Mo, MoC, or MoN.[5]

The microscopic information on the mechanism of the MoP catalytic action cannot be inferred from the available experimental studies. Thus quantum-mechanical modeling offers the most reliable route to understanding the catalytic activity of the MoP surface. The crystal chemistry and the nature of bonding in bulk molybdenum phosphides has been studied recently by using quantum-mechanical calculations based on density functional theory (DFT), a plane wave basis set, and pseudopotentials.[7] The results of that work show that the structure of the bulk MoP is accurately reproduced in the simulations, with the errors of −0.2 % and −0.5 % for the *a* and *c* lattice parameters, respectively. MoP crystallizes in the tungsten carbide type structure, space group $P\bar{6}2m$, so that each molybdenum atom is trigonal-prismatically surrounded by six phosphorus atoms, and vice versa. The high value of the calculated bulk modulus of MoP, 218 GPa,[7] is consistent with the experimentally observed high hardness of MoP. The Mulliken bond population for the Mo–P bond in MoP is not exceptionally high when compared to that of other molybdenum phosphides, so the low compressibility of MoP was ascribed to the spatial arrangement of Mo–P bonds rather than to extreme bond strength.[7]

Recently the bulk and surface structure of MoP have been investigated theoretically in connection with the chemical activity toward CO and sulfur adsorption.[5] These particular adsorbates were chosen as model probe systems, with the expectation that the qualitative trends obtained for a family of Mo-terminated surfaces would be applicable to more complex adsorbates. The present study is aimed at elucidating the catalytic processes on the MoP(001) surface for realistic HDN reactions: namely, for one of the important branches of the HDN reaction network for *o*-propylaniline. *o*-Propylaniline is a relatively simple test molecule that has sufficient structural complexity to be a representative N-containing aromatic compound.[2]

Computational Details

The quantum-mechanical calculations described here are based on density functional theory and the PBE version of the generalized gradient ap-

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DOI: 10.1002/chem.200400510

proximation.[8] Ultrasoft pseudopotentials were used with a maximum cutoff energy of the plane waves of 320 eV. The pseudopotentials were generated by using the PBE exchange-correlation functional in the atomic calculations. The Monkhorst–Pack sampling of the Brillouin zone was used with the distances between the grid points of about 0.05 $Å^{-1}$.[9] This spacing corresponds to 48 k-points in the irreducible part of the Brillouin zone for bulk MoP calculations, and to 2 k-points for the MoP surface studies.

The Mo-terminated MoP(001) surface was studied in the slab geometry using the supercell approach. A (4×4) surface cell with 16 atoms in each atomic layer was used. This cell size is sufficiently big to eliminate spurious interactions between periodic images of the adsorbates. Six atomic layers were included in the calculations, with the bottom two layers being fixed at the theoretical bulk lattice positions. The width of the vacuum layer was about 11 Å, so that the overall thickness of the supercell was 19 Å.

Geometry optimization with the fixed lattice parameters was performed until the remaining forces on the atoms were less than 0.01 eV $Å^{-1}$. Transition-state calculations for the HDN reaction of *o*-propylaniline on MoP(001) and in the gas phase were carried out by using a generalized synchronous transit method.[10] Starting from reactants and products, the synchronous transit methods interpolate a reaction pathway to find a transition state. The transition state search comprises the definition of the reaction pathway based on the structures of the reactants and products, the linear maximization procedure (LST) along this pathway which brackets the transition state, the energy minimization of the LST structure in directions conjugate to the reaction pathway, quadratic interpolation (QST) based on the reactants, products, and the minimized LST structure, amd conjugate gradient minimization of the QST structure. The QST cycle can be repeated until convergence is achieved. The modification of the conventional LST/QST procedures for the periodic boundary conditions includes the summation over all periodic images of the atoms, and thus requires a modification in the object function that defines the reaction pathway.[10]

Mulliken population analysis was performed to evaluate atomic charges and bond populations and thus to examine the nature of chemical bonding in the systems studied. We used a population analysis scheme implemented for a plane wave basis set by Segall et al.,[11] which is based on a formalism suggested by Sanchez-Portal et al.[12] All calculations were carried out using the CASTEP[13] program, versions 4.2[14] and 3.0.[15]

Results and Discussion

Bulk MoP and clean MoP(001) surface: In this section we present the calculated structural properties of the bulk MoP and of the ideal Mo-terminated MoP(001) surface, and compare them to the available experimental and theoretical data.

The calculated geometry of the bulk MoP is described in Table 1. The present results are in marginally better agreement with experiment than the previous CASTEP calculations performed with similar settings.[7] The differences with respect to the DMol^3 calculations[5] are due to 1) different exchange-correlation functional (we use PBE, whereas Liu and Rodriguez[5] used RPBE), and 2) different DFT implementation (numerical basis set in DMol^3, plane wave basis in CASTEP). The results presented in Table 1 confirm that the DFT accuracy for this system is sufficient for reliable structural investigations: regardless of the actual DFT implementation, the cell parameters agree with experiment to better than 2%, and the calculated MoP bond length is within 0.5% of the experimental value.

Table 1. Structural parameters of MoP. The space group is $P\bar{6}2m$ and there is $Z=1$ formula unit per unit cell. Mo atom is at the origin (000), P atom is at (2/3 1/3 1/2). Deviations from experimental values are given in parentheses.

	a [Å]	*c* [Å]	*c*/*a*	Mo−P [Å]
exp. [17]	3.223	3.191	0.9901	2.451
DMol^3 [5]	3.235	3.165	0.9784	2.448
	(0.4%)	(−0.8%)	(−1.2%)	(−0.1%)
CASTEP [6]	3.286	3.146	0.9574	2.464
	(1.9%)	(−1.4%)	(−3.3%)	(0.5%)
CASTEP [7]	3.218	3.176	0.9869	2.444
	(−0.2%)	(−0.5%)	(−0.3%)	(−0.3%)
CASTEP (present)	3.229	3.184	0.9859	2.452
	(0.2%)	(−0.2%)	(−0.4%)	(0%)

The ionic component of the chemical bonding is small in bulk MoP, in contrast with other Mo compounds (MoC, MoN, MoS2) in which charge transfer is significant.[5,6] The Mulliken charges on Mo and P atoms have been quoted as 0.09 *e* and −0.09 *e*, respectively,[6] and the creation of the Mo-terminated surface reduces these charges to 0.045 and −0.077 *e*.[5] The present calculation gives −0.20 *e* and 0.20 *e* for Mo and P, respectively. These values are higher than the previously reported ones and also of the opposite sign. We have also calculated Mulliken charges for bulk δ-MoN, one of the compounds studied by Liu and Rodriguez,[5] and obtained 0.63 *e* on Mo and −0.63 *e* on N, confirming the donor nature of Mo in MoN in agreement with the earlier results. Thus our results for MoP imply that this compound is qualitatively different from molybdenum carbide and nitride in that the direction of the charge transfer becomes reversed, not just that the amplitude of the transfer diminishes. According to our results, phosphorus in MoP is a weak donor rather than a weak acceptor. This qualitative difference is clearly important for the understanding of the surface chemistry and catalytic activity of MoP.

The Mulliken bond population in bulk MoP was previously reported as 0.38 *e*,[7] whereas the present results give 0.32 *e*. The differences of this order of magnitude are indicative of the qualitative nature of the Mulliken population analysis, and given that LDA-based pseudopotentials were used in the earlier study, the agreement is actually very reasonable.

The structure of the Mo-terminated MoP(001) surface is illustrated in Figure 1. The two layers of Mo and P atoms were kept fixed during geometry optimization to imitate the bulk-like geometry at the bottom of the slab, while the other four layers were allowed to relax. The quantitative characteristics of the relaxed structure are given in Table 2. The main feature is a very strong inward relaxation of the top layer, the interlayer distance becomes 1.39 Å compared to the ideal bulk distance of 1.59 Å. The relaxation pattern is oscillatory, which suggests that a large number of layers might be required to model the MoP(001) surface. The previous theoretical study of this surface employed four atomic layers[5] compared to six layers used here. The Mo−P bond length between the surface and subsurface layers was then found to be 2.8% shorter than the bulk bond length, whereas the present results predict a twice stronger effect, a 5.2% bond shortening (Table 2). It is likely that the difference is due to the insufficient number of layers used in the earlier work, furthermore, Liu and Rodriguez[5] fixed only one

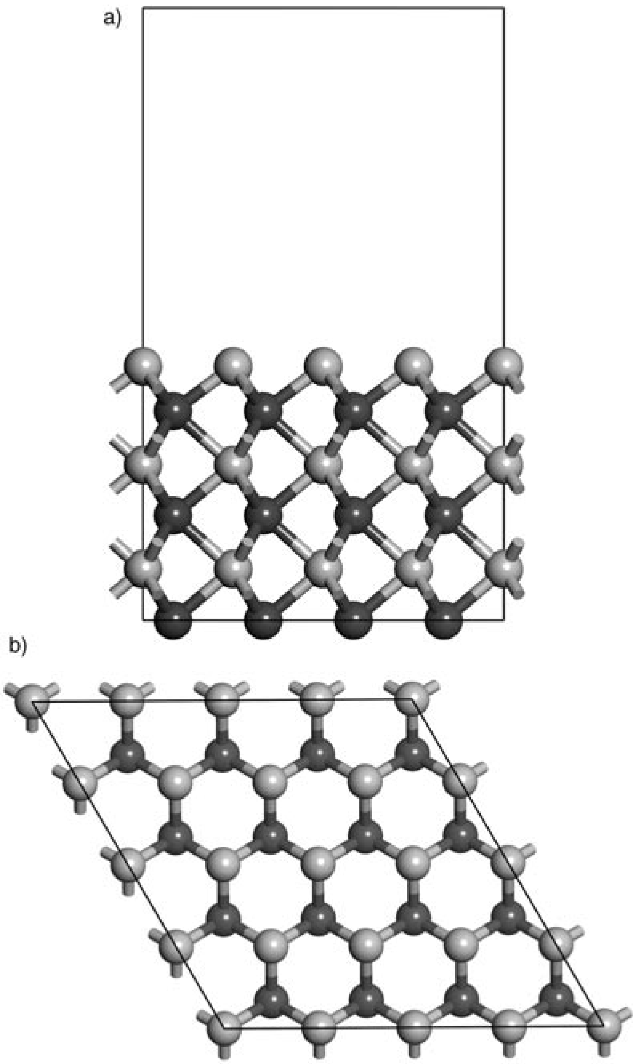

Figure 1. The structure of the Mo-terminated MoP(001) surface: top view (a) and side view (b) of the simulation supercell. Mo: light gray spheres; P: dark gray spheres.

Table 2. The structure and Mulliken populations of the clean MoP(001) surface.[a]

Layer	$\Delta d/d_0$ [%]	Mo–P [Å]	$\Delta b/b_0$ [%]	BP [e]	q [e]
Mo (top)					−0.18 (−0.18)
	−12.8 (−11.3)	2.325 (2.337)	−5.2 (−4.7)	0.37 (0.38)	
P					0.23 (0.24)
	5.1 (6.6)	2.504 (2.522)	2.1 (2.9)	0.31 (0.28)	
Mo					−0.12 (−0.19)
	−1.5 (−1.4)	2.436 (2.438)	−0.6 (−0.6)	0.39 (0.52)	
P					0.15
	2.9	2.481	1.2	0.29	
Mo					−0.18
	0	2.452	0	0.51	
P (bottom)					0.11

[a] $\Delta d/d_0$ is the relative change of the interlayer spacing, $\Delta b/b_0$ is the relative change of the Mo–P bond length with respect to the bulk value, BP is the Mulliken population for the Mo–P bond, q is the Mulliken charge. Values in parentheses refer to the calculation with four atomic layers (the bottom layer fixed).

bottom layer so that the slab did not have bulk-like geometry in any of its layers.

The charge transfer between Mo and P atoms is clearly affected by the presence of free surfaces. However, the effect is stronger on the P-terminated surface that does not present any interest for the present study. The Mulliken charges on P atoms in the bottom layer of the slab are two times smaller than those observed in the bulk. This change is accompanied by the strengthening of the Mo–P bonds between the two bottom layers as witnessed by the increase in bond populations relative to the bulk value of 0.38 e (see Table 2). Mulliken charges on the atoms in the surface and subsurface layers of the Mo-terminated surface are close to their bulk values. Previous study showed stronger relative changes, with the Mulliken charge on Mo atoms decreasing from 0.09 e in the bulk to 0.045 e on the surface.[5] This change is, however, small on the absolute scale and is of the same order of magnitude as found here.

We carried out convergence tests to verify that the number of MoP layers we used is sufficient: the MoP(001) relaxation has been repeated for a slab with only four atomic layers, the bottom layer of P atoms being fixed. This geometry is the same as has been used by Liu and Rodriguez.[5] Table 2 shows that the bond lengths change by no more than 0.02 Å when going from four to six layer slab, so the structure we used is converged with respect to the number of atomic layers. The main differences in the local electronic structure between the six-layer and four-layer calculations are in the subsurface Mo layer. It is safe to assume that the details of the structure and charge distribution at that depth are unimportant for the description of adsorption of atoms and small molecules on MoP(001), and thus the four-layer slab is sufficient for the study of CO and S adsorption.[5] The interactions with big organic molecules studied here do cause long-range changes in the geometry and in the local electronic structure, thus we believe that the six-layer slab is necessary to investigate HDN reactions.

***o*-Propylaniline on MoP(001) surface:** The bonding of *o*-propylaniline to MoP was investigated by using the same approach as in the study of the clean MoP(001) surface. The two bottom layers of the slab were kept fixed at their bulk positions, while the rest of the slab and the molecule were allowed to relax. The 4×4 surface mesh (96 substrate atoms) was used to provide supercells that were sufficiently big to eliminate unphysical interactions between the periodic images of the adsorbates. The resultant structure is shown in Figure 2. The aromatic ring of the adsorbate is oriented so as to match the hexagonal lattice of the substrate. The center of the ring is positioned on top of the subsurface P atom (hollow site). This configuration allows three strong Mo–C bonds between the carbon atoms of the aromatic ring and the top substrate layer to be formed. The C–N bond of *o*-propylaniline is oriented along the Mo–P bond in the top view, so that nitrogen

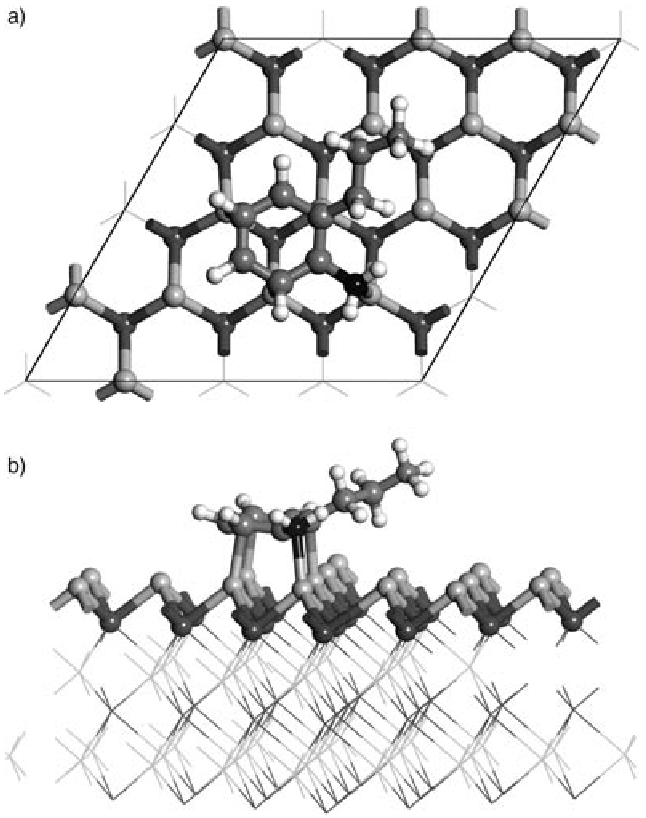

Figure 2. The structure of *o*-propylaniline adsorbed on the Mo-terminated MoP(001) surface: top view (a) and perspective view (b). Mo: light gray spheres; P: dark gray speheres; N: black sphere; C: large gray spheres; H: small white spheres. Only the two top layers of the MoP surface are shown in ball-and-stick mode, the rest of the slab is shown in the line mode.

atom is in perfect registry to create another bond to a Mo atom of the substrate.

The Mo–C bonds formed during adsorption are 2.24(1) Å long, which is very similar to the geometry found in molybdenum carbides. The typical Mo–C bond lengths in a variety of MoC and Mo_2C modifications are 2.1–2.2 Å, the tungsten carbide type modification of MoC which is isostructural to MoP has a Mo–C bond length of 2.19 Å.[16] The Mo–N bond length is 2.26 Å, again in good agreement with the values observed in bulk MoN compounds, from 2.08 to 2.25 Å. The main change in the structure of the molecule due to the molecule–surface interaction is the bending of the hydrocarbon chain: *o*-propylaniline is not flat in its adsorbed configuration, while all carbon atoms lie exactly in a plane in the gas phase geometry. The hydrocarbon chain points away from the surface at an angle of nearly 30° after adsorption (Figure 2). Other structural changes are less pronounced: the bonds in the aromatic ring are lengthened by about 2%, from 1.40–1.42 to 1.43–1.46 Å, so as to allow for the optimal Mo–C bond lengths. Similarly the C–N bond becomes 1.45 Å instead of 1.40 Å. All other bond lengths in *o*-propylaniline are essentially the same as in the gas phase.

The substrate structure changes locally around the adsorption site, the Mo–P bonds between the top two layers change by 2–3% relative to the structure observed for the clean surface. The effect of the adsorbate is relatively long-ranged: the bonds between the second and the third layer are modified by about 1%, and between the third and the fourth layer by about 0.5%. The fourth layer already preserves the geometry of the clean surface, which shows that the width of the slab we use is sufficient to describe adsorption on the MoP(001) surface. The geometry and electronic structure of the substrate is practically unaffected two coordination spheres away from the adsorbate. Mo atoms in the corners of the cell shown in the top view of Figure 2 have the same local coordination and the same Mulliken charges as on the clean surface. Mo atoms involved in the newly created bonds to carbon and nitrogen atoms act as donors, so that their Mulliken charges change from $-0.18\,e$ to $0.06\,e$ (Mo–N bond) and to $0.28–0.32\,e$ (three Mo–C bonds). The C–C aromatic bonds as well as the C–N bond in the molecule are weakened during adsorption, since they are extended relative to the gas phase structure in order to create strong bonds with the substrate. However, all other bonds: C–H, N–H and C–C bonds in the hydrocarbon tail - are strengthened after adsorption even though their length is unchanged. This conclusion is based on the Mulliken bond population increase by about 0.1 *e*.

The energy of adsorption is determined as the difference between the total energy of the adsorbed complex and the sum of the energies of the clean surface and of *o*-propylaniline in the gas phase. The energy of *o*-propylaniline was obtained from the calculation with exactly the same simulation supercell and the same settings as in the calculations for the MoP surface. The calculated adsorption energy of −3.32 eV corresponds to fairly strong adsorption.[5]

Propylbenzene on MoP(001) surface: The HDN reaction network of *o*-propylaniline results in a number of different products.[2] One of the products, propylbenzene, forms through C–N bond hydrogenolysis. There is a more complex reaction pathway that involves hydrogenation of the aromatic ring system. The final products of this multistage reaction are butylcyclopentane, propylcyclohexane, and propylcyclohexene. The goal of this work is to show the feasibility of the DFT investigations of complex reactions on catalytic surfaces rather than to carry out a full study of the HDN reaction network. Thus we concentrate on just one branch of the network, the single-step reaction that produces propylbenzene.

Geometry and energetics of the propylbenzene adsorption are relevant to the understanding of the reaction mechanism and of the details of the MoP catalytic activity. The adsorption geometry for propylbenzene on the MoP(001) surface is very similar to that of *o*-propylaniline (Figure 3). The aromatic ring is positioned on the hollow site, with three strong Mo–C bonds. The adsorption energy is found to be −2.68 eV. It seems likely that the adsorption energy of *o*-propylaniline is higher because of one extra bond (Mo–N) between the molecule and the substrate. This implies that propylbenzene will desorb easier than *o*-propylaniline, so that the reaction products can be efficiently removed from the catalytic surface.

C–N bond hydrogenolysis: *o*-propylaniline to propylbenzene: The energy barrier for the hydrogenolysis reaction

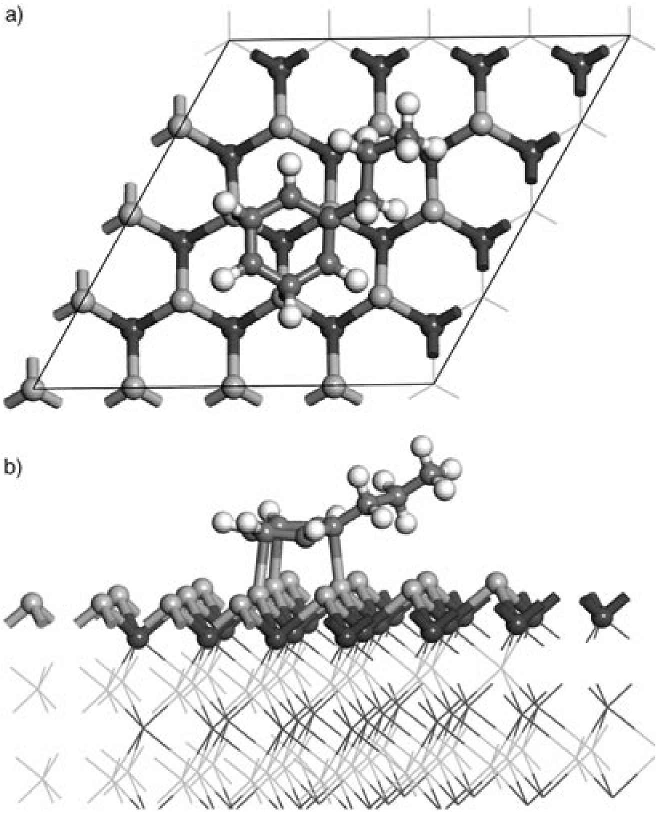

Figure 3. The structure of propylbenzene adsorbed on the Mo-terminated MoP(001) surface: top view (a) and perspective view (b).

was evaluated for both gas phase *o*-propylaniline and for the molecule adsorbed on the MoP(001) surface. The algorithm we used combines linear and quadratic synchronous transit method with conjugate gradient refinements.[10] The first step of the calculation is to define the reactants and products. In both cases the reactants included *o*-propylaniline, either in its gas phase or as an adsorbate, and an H_2 molecule at about 3 Å from the nitrogen atom. The products of the reaction include propylbenzene and ammonia molecules at a separation of 2–3 Å. These are either free molecules for the gas-phase calculations, or two adsorbed molecules for the reaction on the MoP surface.

The reaction on the MoP surface is exothermic with an energy release of 1.18 eV. The transition state corresponds to the broken C–N bond with the NH_2 group attached to the surface Mo atom. The Mo–N bond in this configuration is 2.14 Å long, shorter than for either *o*-propylaniline (2.26 Å) or ammonia (2.29 Å) adsorption. The H_2 molecule in the transition state configuration is located roughly halfway between the carbon and nitrogen atoms of the already broken C–N bond, and the H–H bond length is about 4% longer than in the reactant configuration. The energy barrier for the reaction is 0.97 eV from the reactants and 2.16 eV from the products.

The energy effect of the reaction is 50% smaller in the gas phase, only 0.61 eV. The structure of the transition state is qualitatively the same as on the MoP surface, except that the H–H bond in the H_2 molecule is already broken. The H–H distance in the transition-state geometry is 1.0 Å as opposed to 0.8 Å in the presence of MoP surface. The main difference though can be seen from the comparison of the energy barriers. The energy barrier from reactants in the gas phase is 5.61 eV (6.26 eV from products), significantly higher than in the presence of the MoP catalyst. The special feature of the reaction on the MoP surface seems to be that the Mo–N bond does not get broken during the reaction, the NH_2 group pivots around this bond to tilt away from *o*-propylaniline molecule and to acquire an additional H atom from the incoming H_2 molecule. The full analysis of the reaction process should further include the calculation of the surface diffusion properties for ammonia on the MoP surface which would be required to fully separate the products of the reaction, this is however beyond the scope of the present study.

The large reduction of the reaction barrier on MoP surface is thus assigned to the C–N bond weakening as a result of the creation of new bonds to the substrate, especially of the Mo–N bond. The discovery that the reaction can take place with the Mo–N bond intact implies that the weakening of the C–N bond affects not only the equilibrium structure of adsorbed *o*-propylaniline, but also the complete pathway for C–N bond hydrogenolysis.

Summary and Discussion

The results of the DFT study presented herein provide an atomistic picture of the adsorption of *o*-propylaniline on the Mo-terminated MoP(001) surface as well as the insight into the catalytic activity of MoP for the HDN reaction. The energetics of the C–N bond hydrogenolysis which results in the propylbenzene formation is obtained, and the insight into the likely reaction pathway is provided. The comparison of the reaction in gas phase and on the MoP surface explains the catalytic effect of MoP as being due to the C–N bond weakening. The charge transfer from the substrate to *o*-propylaniline is important in the reorganization of the bond strengths of the adsorbate. The high activity of MoP compared to other Mo compounds[5] is related to the fact that Mo atoms in the top layer of the clean MoP(001) surface act as weak acceptors and have excessive charge. The top layer of MoC(001) or MoN(001) surfaces is depleted of electron charge, since Mo acts as a donor in those compounds.

The C–C aromatic bonds are also weakened in the adsorbed state, which should explain catalytic activity of MoP for the branches of the HDN reaction that involve hydrogenation of the aromatic ring as the first step.[2] We are hopeful that the suggested approach can be further used to investigate the full HDN reaction network for *o*-propylaniline on MoP.

Acknowledgements

B. W. would like to thank the Deutsche Forschungsgemeinschaft for funding through grant Wi1232/12.

[1] C. Stinner, R. Prins, T. Weber, *J. Catal.* **2000**, *191*, 438–444.

[2] C. Stinner, R. Prins, T. Weber, *J. Catal.* **2001**, *202*, 187–194.

[3] S. T. Oyama, P. Clark, V. L. S. T. da Silva, E. J. Lede, F. Requejo, *J. Phys. Chem. B* **2001**, *105*, 4961–4966.

[4] D. C. Phillips, S. J. Sawhill, R. Self, M. E. Bussell, *J. Catal.* **2002**, *207*, 266–273.

[5] P. Liu, J. A. Rodriguez, *Catal. Lett.* **2003**, *91*, 247–252.

[6] J. A. Rodriguez, J.-Y. Kim, J. C. Hanson, S. J. Sawhill, M. E. Bussell, *J. Phys. Chem. B* **2003**, *107*, 6276–6285.

[7] B. Winkler, K. Knorr, M. Hytha, V. Milman, V. Soto, M. Avalos, *J. Phys. Chem. Solids* **2003**, *64*, 405–411.

[8] J. P. Perdew, K. Burke, M. Ernzerhof, *Phys. Rev. Lett.* **1996**, *77*, 3865–3868.

[9] H. J. Monkhorst, J. D. Pack, *Phys. Rev. B* **1976**, *13*, 5188–5192.

[10] N. Govind, M. Petersen, G. Fitzgerald, D. King-Smith, J. Andzelm, *J. Phys. Chem. Solids* **2003**, *64*, 405–411.

[11] M. D. Segall, R. Shah, C. J. Pickard, M. C. Payne, *Phys. Rev. B* **1996**, *54*, 16317–16320.

[12] D. Sanchez-Portal, E. Artacho, J. M. Soler, *J. Phys. Condens. Matter* **1996**, *8*, 3859–3880.

[13] Accelrys, San Diego, CA “CASTEP User Guide”, **1998**.

[14] V. Milman, B. Winkler, J. A. White, C. J. Pickard, M. C. Payne, E. V. Akhmatskaya, R. H. Nobes, *Int. J. Quantum Chem.* **2000**, *77*, 895–910.

[15] M. D. Segall, P. J. D. Lindan, M. J. Probert, C. J. Pickard, P. J. Hasnip, S. J. Clark, M. C. Payne, *J. Phys. Condens. Matter* **2002**, *14*, 2717–2744.

[16] J. Schuster, E. Rudy, H. Nowotny, *Monatsh. Chem.* **1976**, *107*, 1167–1176.

[17] S. Rundqvist, T. Lundström, *Acta Chem. Scand. A* **1963**, *17*, 37–46.

Received: May 24, 2004
Revised: September 14, 2004