Initial Stages in the Formation of Nickel Phosphides

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ABSTRACT: Metal phosphides have emerged as a new powerful class of materials that can be employed as heterogeneous catalysts in transformations mainly to generate new energy vectors and the valorization of renewables. Synthetic protocols based on wet techniques are available and are based on the decomposition of the organic layer decorating the nanoparticles. For nickel, the phosphine of choice is trioctylphosphine, and this leads to the formation of NiP_x materials. However, the temperature at which the decomposition starts has been found to depend on the quality of the nickel surface. Density functional theory, DFT, holds the key to analyze the initial steps of the formation of these phosphide materials. We have found how clean nickel surfaces, either (111) or (100), readily breaks the ligand P–C bonds. This triggers the process that leads to the replacement of a surface nickel atom by P and concomitantly forms a Ni adatom on the surface surrounded by two methyl groups, thus starting the formation of the NiP_x phase. The whole process requires low energies, in agreement with the low temperature found in the experiments, 150 °C. In contrast, if the surface is oxidized, the reaction does not proceed at low temperatures and oxygen vacancies need to be created first to start the P–C bond breaking on the Ni-clean patches. Our results show that the cleaner the surface is, the milder the reactions are required for the NiP_x formation, and thus they pave the way for gentler synthetic protocols that can improve the control of these materials.

INTRODUCTION

Metal phosphides are attracting a large amount of attention, as they have appealing properties in different areas of physics and chemistry.¹ The applications extend from optics^{2,3} to magnets^{4,5} and for energy storage.^{6,7} Among these applications, one of the fastest growing areas is the use of metal phosphides as catalysts. Initially, they were used in hydrotreatment and selective hydrogenations,^{8–10} but nowadays, energy vector generation is the blooming area.^{11–13} Particularly, growing attention has been put in the hydrogen evolution reaction (HER) of the Ni_2P and CoP compositions,^{14–23} but also on the H_2 production from BH_3NH_3 .^{24,25} These properties appear as a consequence of the modifications in the ensemble, and the electronic structure of these materials.²⁶ Thus, the P atoms in the lattice can be seen as embedded lattice poisons. In some cases, these materials present an almost continuum phase diagram with different P contents^{27,28} and thus some stability issues can be foreseen. The nature of the particular Ni–P phase is highly relevant in the catalytic performance; for instance, different performances are found for the HER reaction on Ni_2P , Ni_{12}P_5 , and Ni_5P_4 ,²¹ and thus, a strict control on the synthetic procedures that lead to the formation of the active phase is required.

Very recently, colloidal protocols to produce these materials have been generalized. The synthetic routes are based on the formation of nanoparticles decorated by phosphine ligands that evolve toward the formation of the phosphides by thermal

treatment. For instance, the tri-*n*-octylphosphine, TOP, is employed both to decorate the nanoparticles and to control their size and as the source for P. The reaction then is performed at medium temperatures of about 250 °C and pressures close to the normal, ambient pressure^{29,30} and can generate phosphides for a wide variety of reactive metals. For Ni, two phases, Ni_2P and Ni_{12}P_5 , can be prepared by changing the conditions.^{31,32} The decomposition of the phosphide precursor depends on the metal, and for Ni, the starting temperature for decomposition was reported to be 210 °C,³³ while the complete decomposition and crystallization of the phosphide occurs at 230 °C.³⁴ In a deep XPS study, Salmeron et al.³⁵ were able to describe more precisely how the wet synthesis of the Ni-based phosphide proceeds. In summary, when a Ni metal foil is clean, the surface can be decorated with TOP ligands that limit the growth of the nanoparticles. Upon heating to 150 °C, the phosphines start degrading, and as a consequence, the P appears. However, this process is slightly more complex. Particularly, when the synthesis starts from nanoparticles, the decomposition of the organic fragment leads to the formation of a C-containing Ni core and the outermost surface is mostly NiP with Ni_2P and Ni_5P_4 stoichiometries.

Care shall be taken also, as Ni is relatively easy to oxidize. When starting by oxidized nanostructures, the phosphine decomposition starts only at 250 °C. The process is schematically represented in Figure 1. Density functional

Figure 1. Required conditions for the formation of the NiP phase from Ni. The different color codes show the dominating phases all throughout the manuscript (metallic Ni gray, oxidized green, phosphide orange). Adapted from Carenco et al.³⁵

theory simulations have been extensively used to analyze the chemical properties of materials including phosphides. However, DFT is less often applied in the study of wet chemistry and synthetic protocols, although we have shown the potentiality of the approach in a wide series of systems.^{36–39} For instance, we have analyzed the role of surfactants when driving the structure of nanoparticles, controlling the catalytic properties therein.^{40–46} However, in all of the cases considered so far, the surfactants kept their entity under reaction conditions and the surface was poorly reactive. In the present work, we aim at investigating the evolution of the ligand on a relatively active surface as well as its decomposition and integration in the lattice as the first step in the formation of the phosphide phase.

COMPUTATIONAL DETAILS

The initial steps for the formation of phosphide under wet synthesis conditions were investigated by density functional theory, DFT, applied to slabs representing different nickel phases. The calculations were performed with the VASP⁴⁷ code, and the functional of choice was PBE.⁴⁸ Inner electrons were replaced by PAW,⁴⁹ and the valence electrons were expanded in plane waves with a cutoff energy of 450 eV. The pure Ni(111) and (100) surfaces were described by a four-layer slab in a $p(3 \times 3)$ supercell with spin polarization; see Figure 2. The NiO structure was constructed similarly: the slab contained four layers, and the U parameter was set to 5.4 eV following previous computational studies.^{50,51} The k -point were sampled by a Γ -centered $4 \times 4 \times 1$ Monkhorst–Pack⁵² grid. The adsorbates were only placed in one side of the slabs and interleaved by at least 14 Å. Dipole correction along the z direction has been considered,⁵³ and vdW interaction have been employed via the DFT-D3 method developed by Grimme et al.⁵⁴ The large phosphines used in the experimental synthetic protocol were replaced by small surrogates $P(CH_3)_3$. Transition states were located with the climbing image version of the

Figure 2. Top views of the models employed for the Ni(111) and (100) surfaces and for the oxide phase NiO(100) and the labels for the corresponding surface atoms. Gray Ni, red O, and fading O the position where the vacancy is formed.

nudged elastic band method.⁵⁵ All of the structures can be retrieved from our ioChem-BD repository.⁵⁶

RESULTS

Four model systems have been used to characterize the fosfine decomposition and initial steps of the formation of the phosphide phase. As the trioctylphosphine (TOP) employed in the experiments is very large, instead a surrogate compound trimethylphosphine $P(CH_3)_3$ (TMP) has been used as reacting phosphine. The replacement would have an effect provided that the packing or stabilization contributions with respect to the solvent were investigated, but for the purpose of analyzing the decomposition, the effect is minor, as the interactions are local in nature. Phosphine decomposition in the model systems has been summarized in Figure 3. The first model corresponds to a

Figure 3. Reaction energy profile for the decomposition of $P(CH_3)_3$ on Ni(111) and Ni(100) (gray-orange) and NiO(100), both on the clean and oxygen-depleted surface (green continuous and dashed, respectively). The insets represent the most relevant structures along the reaction coordinates. Gray spheres stand for Ni, red for O, orange for P, black for C, and H are white.

pure Ni(111) surface that represents the clean surface model (dark gray); this is complemented by using the second lowest energy surface Ni(100) as the second model for which the reaction has also been inspected (gray). A third model represents a completely oxidized nickel system shown by the NiO(100) surface (green); this is the lowest energy surface for the oxide. The fourth model corresponds to a NiO(100) surface where an oxygen vacancy site has been created (green dashed), as oxides can lose oxygen atoms and they create

Table 1. Magnetic Moments, μ_B , for the Most Relevant Ni Atoms during the Formation of the Phosphide Phase^a

Ni(111)	1	2	3	4	5	6	7	8	9	total
IS-1	0.60	0.65	0.66	0.46	0.32	0.61	0.64	0.61	0.63	5.18
TS1	0.40	0.63	0.65	0.41	0.31	0.62	0.62	0.28	0.63	4.55
IS-2	0.52	0.49	0.67	0.53	0.29	0.67	0.54	0.32	0.66	4.69
TS-2	0.53	0.57	0.67	0.30	0.34	0.65	0.52	0.38	0.69	4.65
IS-3	0.48	0.59	0.67	0.23	0.46	0.50	0.21	0.32	0.55	4.01
TS-3	0.30	0.52	0.66	0.30	0.08	0.60	0.62	0.34	0.54	3.96
FS	0.29	0.44	0.66	0.15	0.04	0.58	0.63	0.36	0.30	3.45
Ni(100)	1	2	3	4	5	6	7	8	9	total
IS-1	0.72	0.69	0.72	0.69	0.30	0.70	0.72	0.34	0.66	5.54
TS1	0.70	0.62	0.71	0.70	0.26	0.70	0.70	0.68	0.72	5.79
IS-2	0.72	0.43	0.73	0.68	0.14	0.68	0.0.68	0.27	-0.68	5.02
TS-2	0.71	0.47	0.71	0.43	0.21	0.66	0.49	0.34	0.67	4.69
IS-3	0.67	0.44	0.72	0.34	0.03	0.55	0.35	0.34	0.70	4.14
TS-3	0.66	0.39	0.64	0.30	0.02	0.43	0.26	0.33	0.68	3.71
FS	0.67	0.43	0.71	0.33	0.16	0.33	0.31	0.30	0.64	3.88
NiO(100)	1	2	3	4	5	6	7	8	total	
IS-1	-1.75	-1.79	1.79	1.80	-1.80	-1.80	1.80	1.80	0.05	
TS-1	-1.68	-1.79	1.79	1.79	-1.78	-1.80	1.80	1.80	0.13	
FS-1	-1.55	-1.79	1.80	1.80	-1.77	-1.80	1.79	1.79	0.27	
NiO(100)-v	1	2	3	4	5	6	7	8	total	
IS-1	-1.67	-1.80	1.79	1.80	-1.71	-1.80	1.66	1.66	-0.07	
TS-1	-1.69	-1.80	1.79	1.80	-1.74	-1.80	1.26	1.66	-0.52	
FS-1	-1.73	-1.80	1.79	1.78	-1.76	-1.80	1.72	0.95	-0.85	

^aThe atoms are numbered as in [Figure 2](#).**Table 2. Bader Charges, in $|e^-|$, for the Surface Ni Atoms during the Formation of the Phosphide Phase^a**

Ni(111)	1	2	3	4	5	6	7	8	9	total	P
IS-1	−0.03	−0.04	−0.05	−0.01	−0.04	−0.05	−0.03	−0.03	−0.03	−0.31	1.19
TS1	0.09	−0.02	−0.06	0.00	0.01	−0.06	−0.02	−0.04	−0.03	−0.13	0.86
IS-2	0.11	0.09	−0.05	0.00	−0.03	−0.03	0.10	−0.03	0.00	0.16	0.75
TS-2	0.11	0.08	−0.04	−0.07	0.11	−0.03	0.12	−0.01	0.02	0.29	0.48
IS-3	0.08	0.09	−0.02	−0.10	0.17	0.11	0.11	−0.02	0.11	0.53	0.40
TS-3	0.17	0.03	−0.03	−0.08	0.23	−0.05	0.04	−0.05	0.15	0.41	0.41
FS	0.15	0.06	−0.04	0.12	0.29	−0.04	0.02	0.00	0.15	0.71	−0.09
Ni(100)	1	2	3	4	5	6	7	8	9	total	P
IS-1	−0.09	−0.05	−0.01	−0.03	−0.06	−0.04	0.00	0.01	0.06	−0.21	1.32
TS1	0.00	−0.02	0.02	−0.02	0.09	−0.07	−0.04	0.00	−0.03	−0.07	0.99
IS-2	−0.03	0.13	−0.04	0.02	0.14	0.03	−0.04	−0.05	−0.04	0.12	0.84
TS-2	−0.04	0.12	0.01	0.04	0.25	−0.06	0.02	0.02	−0.02	0.34	0.48
IS-3	0.01	0.09	0.03	−0.01	0.34	0.11	−0.02	0.03	−0.05	0.53	0.31
TS-3	−0.03	0.09	0.04	−0.04	0.31	0.09	0.16	−0.02	0.01	0.61	0.02
FS	0.04	0.16	0.02	0.05	0.29	0.15	0.12	0.06	0.03	0.92	−0.22
NiO(100)	1	2	3	4	5	6	7	8		total	P
IS-1	1.12	1.21	1.24	1.24	1.21	1.22	1.24	1.23		9.71	1.34
TS-1	1.09	1.19	1.23	1.24	1.21	1.22	1.24	1.24		9.66	0.85
FS-1	0.83	1.20	1.18	1.18	1.18	1.16	1.18	1.23		9.14	0.60
NiO(100)-v	1	2	3	4	5	6	7	8		total	P
IS-1	0.87	1.21	1.23	1.23	0.95	1.23	0.93	0.93		8.58	1.27
TS-1	0.98	1.23	1.25	1.19	1.06	1.21	0.91	1.04		8.87	0.81
FS-1	1.07	1.22	1.20	1.22	1.08	1.16	1.09	0.63		8.67	0.86

^aThe atoms are numbered as in [Figure 2](#).

vacancies that present completely different properties when increasing the temperature.⁵⁷ The magnetic moments and Bader charges⁵⁸ of the surface Ni atoms and P are presented in [Tables 1 and 2](#).

The phosphines adsorb on the most stable surface termination of Ni(111) by -2.14 eV, with the P atom directly

in contact with one Ni and effectively quenching the magnetic moment of the Ni atom to which it is directly adsorbed due to the donor nature of the lone pair from the P atom. From this starting point, the phosphine can break; see [Figure 3](#). The first P-C breaking shows a rather small barrier of about 0.99 eV and results in a configuration where the methyl group migrates to

Figure 4. Transition state structures (TS-3) leading to the formation of the phosphide with the most relevant distances for the first Ni replacement by P (left (111) surface, right (100) surface). The origin of the stabilization of adatoms by the methyl groups is highlighted. Gray spheres stand for Ni, orange for P, black for C, and white for H. The atoms are numbered as in Figure 2.

the surface and the remaining $P(CH_3)_2$ fragment changes from a top to a bridge-like configuration to satisfy the valence of P. The overall reaction is slightly exothermic. This finding agrees with the experimental observations on Ni nanoparticles or organometallic compounds with phosphine ligands for which bond cleavage was observed at temperatures about 100 °C.^{59,60} The elimination of the second methyl group requires a slightly larger energy barrier of 1.07 eV. In that case, the overall thermodynamic cost for this step is endothermic by 0.51 eV. In this configuration, one of the Ni atoms from the surface is already displaced out of the equilibrium position, by 0.16 Å, and thus points toward the formation of an adatom.⁶¹ The dimethyl coordinated phosphine is then reactive enough to start penetration into the lattice. The final step leads to the bond breaking of the third P–C bond and the full replacement of one of the Ni atoms from the surface by the P, thus becoming the seed of the nickel phosphide formation. The reaction is uphill by 1 eV, and the activation barrier is 1.09 eV. In the final structure, one of the methyl groups sits on the Ni surface and the total magnetic moment is reduced due to the Ni–C bond formation, from the starting value of 5.18 μ_B for the surface layer down to 4.69, then 4.01 after one and two methyl cleaves, and 3.45 μ_B for the final structure. In parallel, the initial positive charge of P, about 1.2 e^- , gets reduced down to the final state where it is slightly negatively charged, -0.1 , while the metal surface changes from slightly negative to positive 0.7 e^- . In the final configuration, detailed in Figure 4, the adatom is coordinated to the two methyl groups (distances 2.13 and 1.96 Å and the Ni atom is extracted from the plane by 2.40 Å). The energy cost of forming the adatom (roughly $2/3$ of the cohesive energy) is counterbalanced by the increasing interaction with the methyl fragments and PCH_3 , which also moves toward a fcc-like configuration on the surface to saturate as many bonds as possible. The overall energy profile starting from the adsorbed phosphine is 1.37 eV uphill with the largest barrier being 1.47 eV, which agrees very well with the temperature of 150 °C reported in the experiments needed to see the initial spectroscopic features corresponding to the formation of the nickel phosphide phase. Further adsorption of the phosphine on the adatom is much less exothermic, around 0.7 eV. Therefore, scavenging atoms from another area of the clean surface would be more favorable than reacting on the formed adatom.

Alternatively, the second most stable surface (100) has been set as the initial state. The coverage considered for the phosphine is the same as that in the previous case. Initially, the phosphine adsorbs to a single Ni atom on the surface, and the binding energy is slightly larger than that for the (111) surface,

-2.36 eV. The reaction proceeds in the same manner as described for the (111) surface, with the barriers for the different P–CH₃ cleavages being 0.74, 0.75, and 0.74 eV. The overall process is more exothermic than that on (111), and the barriers are smaller, since the coordination number of the (100) surface is smaller than that of the (111), which allows larger reorganizations at a lower energy cost. The magnetic moments behave similarly to the (111) case, as from an initial magnetization of 5.54 μ_B , the value decreases to 5.02, 4.14, and 3.88 μ_B during the different cleavages. The corresponding charges for P are positive by 1.3 e^- in the starting configuration and -0.2 e^- in the final state, while the surface goes from slightly negative, -0.2 , to 0.9 e^- in the surface layer. Again, as for the (111) surfaces, the last step ends with the replacement of the surface Ni by a P atom and the formation of the adatom stabilized by the two methyl groups. The last transition states where the replacement occurs are represented in Figure 4, and show that the Ni atom is less displaced upward in the (100) surface because the surface is less compact than the (111).

On the nickel oxide, TMP adsorption is very exothermic, -3.16 eV, and takes place on top of the Ni cations. The dissociation could only occur heterolytically, as the activation in many oxides,⁶² and ends up forming a cationic CH_3^+ fragment that is attached to a lattice oxygen and the negatively charged $P(CH_3)_2$ still bonded to the cation. Although the phosphine adsorption is very exothermic, the dissociation is very endothermic, about 2.24 eV. This is due to two fundamental terms: (i) the C–O bond formation is not very effective and (ii) the phosphine cannot coordinate properly to two cations on the surface, as they are far apart in the structure. In the initial structure, the P is positively charged, 1.3 e^- , and this charge is reduced along the reaction path to 0.6 e^- , which is compensated by the charge variation in one of the Ni atoms that also reduces its magnetization. The consequence is that the fully oxidized NiO surface is inert with respect to phosphines and then an alternative mechanism needs to be identified. As oxides are known to lose oxygen when the temperature is raised, we included a model showing a surface oxygen vacancy. In the case of NiO, the vacancy formation requires 2.32 eV. On the model system close to a surface oxygen vacancy, the adsorption of the basic $P(CH_3)_3$ is less favorable than Ni or NiO. The first step in the demethylation is now endothermic by 2.10 eV, and the barrier is 2.35 eV. Therefore, the process is also unlikely on this surface under the reaction conditions described in the experiments. The interpretation of the results is thus clear: the NiO surface can trap the surfactant but would require extensive reduction with the formation of Ni patches

before the reaction occurs. In summary, our results are compatible with the 250 °C temperature needed to start the phosphine decomposition effectively on the Ni-only patches of the surface of the oxides that are already oxygen depleted. As we have indicated in the [Introduction](#), our calculations only represent the very first stages of the formation of the NiP phase. The methyl groups on the surface could decompose further following the paths that have been already described in the literature.⁶³

DISCUSSION

For the metal Ni(111) and (100) surfaces, the barriers for all of the steps follow two Brønsted–Evans–Polanyi⁶⁴ relationships (see [Figure 5](#)); this indicates the local nature of the bond that

Figure 5. Brønsted–Evans–Polanyi (BEP) relationship between the activation energy for each of the P–C steps as a function of the reaction energy for each particular step on the Ni(111) and Ni(100) surfaces. The numbers correspond to the transition state structures identified in [Figure 3](#). Notice that NiO(100) surface would not follow the same BEP, as the bond-breaking transition state corresponds to a heterolytic path.

drives the formation of the adatom and the phosphide structure. The reason for the lower values found for Ni(100) can be traced back to the more open nature of the surface that allows lower energy processes and is slightly more flexible. Therefore, this would allow one to couple the present results to the coordination dependence rules to expand the thermodynamic and kinetic requirements to finite size nanoparticles and low coordinated sites.⁶⁵ However, it shall be noticed that the low barriers found for all of the steps imply that the activation can easily occur even in the denser packed surfaces; thus, no important size contributions are expected.

The present replacement mechanism is related to several other observations in the literature. For instance, in homogeneous catalysis, the reductive cleavage of P–C bonds and the concomitant formation of phosphido species is extensively reported in the literature for low-valent metal complexes.⁶⁶ The formation of adatoms in reactive environments has been identified in other contexts, like the adsorption of S-containing thiols on gold,⁶⁷ or under reaction conditions by reaction–deposition–elimination cycles⁶⁸ or the identification of organometallic-like compounds as intermediates on surface C–C couplings.⁶¹

CONCLUSIONS

Density functional theory simulations have been employed to unravel the initial states of the decomposition of ligands based on phosphines to form metal phosphides. We have found that the reaction is slightly endothermic on the bare Ni(111) and (100) surfaces, but it proceeds smoothly with relatively small energy barriers. The values obtained are compatible with the

temperatures at which the experiments are carried out. In addition, the reaction paths encompass the extraction of Ni atoms from the surface and their replacement by the reactive P from the ligand. However, nickel reacts easily with oxygen; therefore, many surfaces are better described as oxides. On Ni oxides the phosphidation reaction is very endothermic and thus cannot proceed. Even when they are partially oxygen depleted, oxide surfaces are not reactive enough to allow the decomposition of the phosphine. Therefore, the reaction can only proceed by increasing the overall temperature and will take place on the Ni patches of the surface. The number of potential simultaneous paths leading to full decomposition and phosphide formation calls for an integrated effort where detailed characterization with *in situ* techniques can be coupled to density functional theory models to fully describe the reaction mechanisms involved. The present results open a new path toward the rational understanding of synthetic protocols and pave the way for establishing new, more suitable ligands that can allow milder reaction conditions and thus more control on the synthesis.

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Notes

The authors declare no competing financial interest.

Data-set collection of computational results, including all the structures, are available in: <http://dx.doi.org/10.19061/iochem-bd-1-42>.

ACKNOWLEDGMENTS

The authors thank MINECO CTQ2015-68770-R project for financial support. The authors gratefully acknowledge the generous computing time and assistance provided by the Barcelona Supercomputing Center and the Spanish Supercomputing Network.

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