

UNEXPECTED SINTERING OF SMALL SUPPORTED Ni₂P UNDER REAL FEED CONDITIONS

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X-ray Diffraction (EXRD). XRD patterns were recorded on a PANalytical X'Pert Pro instrument in reflection mode with Cu KR radiation ($\lambda = 1.54178 \text{ \AA}$). The accelerating voltage was set at 45 kV with 40 mA current. The diffractometer was equipped with X'Celerator detector. Scan rates were typically $0.06^\circ \text{ s}^{-1}$ (continuous scan, step size 0.0167° , time per step 35 s). Scans at 1.0° to 75.0° typically take 10 minutes. Antiscatter slit, receiving slit, and divergent slit were all fixed to be $1/2''$.

Transmission Electron Microscope (TEM). The catalyst powder was prepared for characterization in the TEM by crushing it into small pieces ($<100 \text{ nm}$ thick) using an agate mortar and pestle. The fines were dusted onto a 200 mesh, holey-carbon-coated, copper TEM grid. The grid was examined in the bright field (BF) TEM imaging mode of a Philips CM200F electron microscope that was operated at an accelerating voltage of 200 kV. Digital images were collected from randomly selected areas using a Gatan CCD camera and Digital Micrograph v. 2.5.4 software. Metal particles were visually identified in the images, and the diameters of more than 250 of these features were measured “by hand” using the “line” tool in Digital Micrograph. The particle diameter measurement data was stored in the Digital Micrograph Results file and then transferred into KaleidaGraph v.3.0 software in order to generate a particle size distribution (PSD) histogram and the statistical data. A surface-volume-averaged diameter, $D_{(sv)}$, was also calculated using the following equation:

$$D_{sv} = (N_i D_i^3) / (N_i D_i^2)$$

where N represents the number of particles of a given measured diameter and D is the diameter that is measured from the digital TEM image.

Calculation of RVA (and conversion).

$$\text{Conversion\%} = (\text{Feed N or S} - \text{Product N or S}) / \text{Feed N or S} * 100$$

$$\text{RVA (for N we assume 1.0 reaction order)} = \text{Feed N} * \text{EXP}((\text{LN}(\text{Product N of experimental catalyst/Feed N})) / \text{Product N of reference catalyst})$$

$$\text{RVA (for S we assume 1.3 reaction order)} = ((\text{Product S of experimental catalyst})^{-0.3/-0.3} - (\text{Feed N})^{-0.3/-0.3}) / ((\text{Product S of reference catalyst})^{-0.3/-0.3} - (\text{Feed N})^{-0.3/-0.3})$$

Detailed run conditions – vacuum gas oil.

A three phase fixed bed reactor operating in an upflow mode was used to measure HDS activities on a real feed (2013 Antwerp vacuum gas oil). Pressure was maintained at 1200 psi and temperature at 360°C. K 's were calculated using 1.3 order kinetics. Sulfur in the feed measured around 1.7% and nitrogen around

1500 ppm. Three reactors are heated in a common sand bath. Temperature was controlled with a single multi-step programmable controller which allows for multiple temperature ramps during pretreatment. The reactors are approximately 0.28" ID and are approximately three feet long. Typical catalyst bed height is approximately 7". Each reactor has a dedicated Brooks for individual hydrogen control. Liquid feeds are delivered using two types of pumps.

For catalyst sulfidation, three HPLC type pumps are used to deliver diesel feed that has been spiked with 7.5 wt% dimethyl disulfide. Since it is not always known in advance what the required activation process should be, the most conservative activation procedure (2 day sulfidation at 360C, 600 psig, flow rate is at 8 ml/h). However, no evidence currently exists linking the longer activation process to higher catalyst activity. Product analysis was done on an Antek Total S and N analyzer. The run last for a week and day one activity was the same as day 7.

Detailed run conditions – straight run diesel.

All reactors was placed in a down flow mode. After the charged reactors were pressure-tested with N2, and with H2 at 600 psig. Then with H2 flowing at 2.14 l/hr at 25C, it is evenly distributed among 16 reactors to reach reactor pressure 6.9 bar. Then temperature was raised to 100oC. At 100oC, the pressure was maintained at 100 psig, H-2 flow was set to minimum, and the sulfiding feed (7.5 wt% of dimethyl disulfide dissolved in a diesel feed) flowing at 8 ml/h (2.667 LHSV with a pump flow rate target of 1.067 cc/min over 16 channels) was passed over each catalyst for 4 hours. Then, with the sulfiding feed continuing, 24 l/hr H2 (48sccm per each reactor) was added to each reactor, and the pressure raised to 41.4bar. The temperature was then increased to 225oC over 4 hours. The reactor was held isothermal at 225oC for 12 hours. Following the isothermal hold, the temperature was raised to 335oC over a period of 4.5 hours and held isothermal for 16 hours. The ramp rate and final hold temperature were varied up to 1hr to accommodate operator's schedule at the time. These steps completed the sulfiding of the catalyst. Five conditions were run in a total of 6 weeks. NiP activity was stably bad from day 1!

Process Detail:

Variable	1	2	3	4	5 (activity check)
Pressure (psig)	600	600	300	450	600
Temperature (°C)	335	335	335	335	335
Feed (15-108704)	Billings HU6A	Billings HU6A	Billings HU6A	Billings HU6A	Billings HU6A
LHSV (1/hr)	0.5	1.0	0.5	0.5	0.5
TGR (SCF/bbl)	1000	1000	1000	1000	1000
TG composition	100% H2	100% H2	100% H2	100% H2	100% H2

Feed Detail:

	<i>Baytown Straight run diesel</i>	<i>Antwerp Vacuum gas oil</i>
Feed Sulfur, wt%	1.22	1.8
Nitrogen (ppm)	168	1266
API Gravity	33.86	22.1
Distillation		
10%	406.6	636
30%	505.9	705
50%	566.9	823
70%	616.7	898
90%	680.9	994
95%	707.0	1035

Supporting figures cited in the main manuscript.

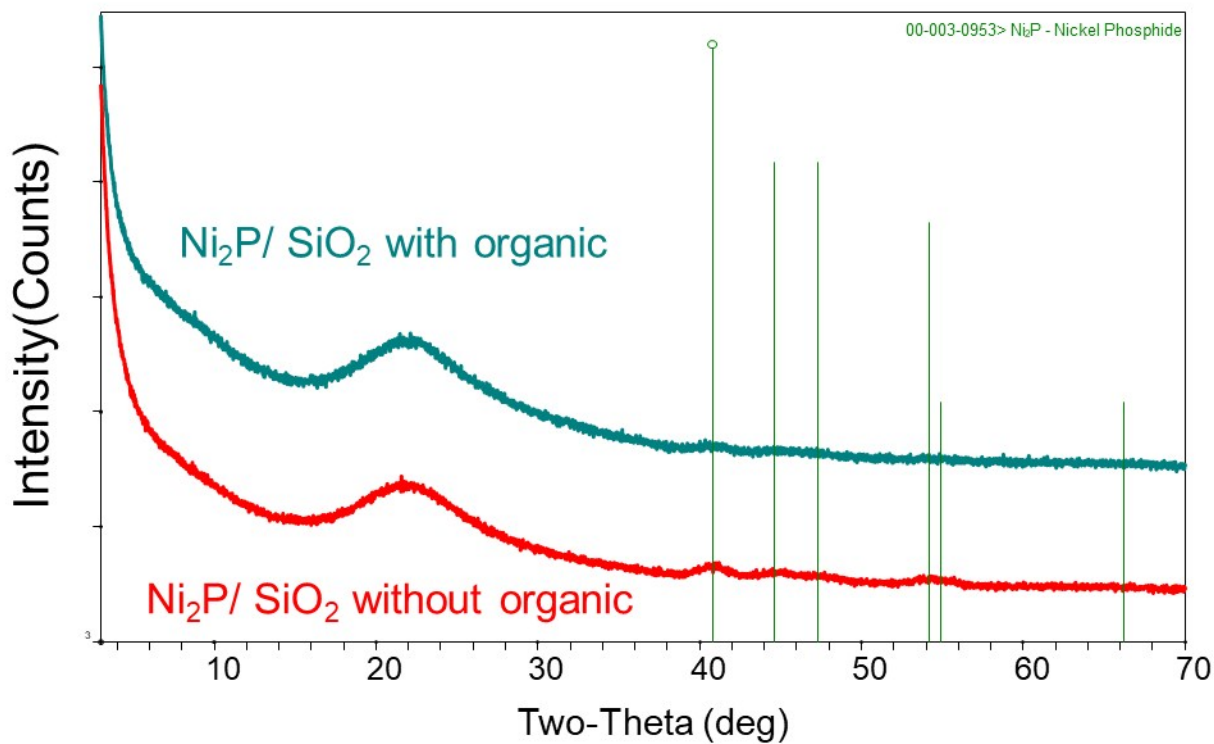


Figure S1: XRD of small nickel phosphide after 500 °C H₂ with (green, top) or without organic (red, bottom), proving organic addition improves Ni₂P dispersion.

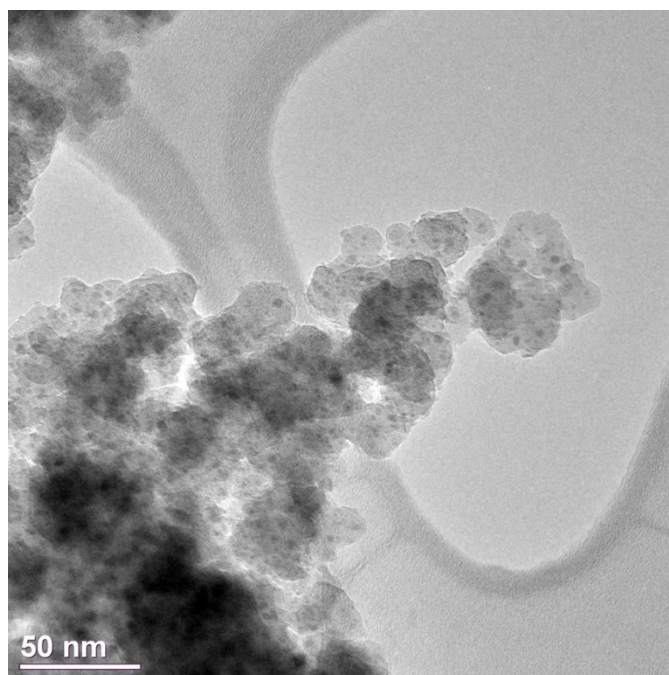


Figure S2: TEM of nickel phosphide after 500 °C H₂ reduction with no organic

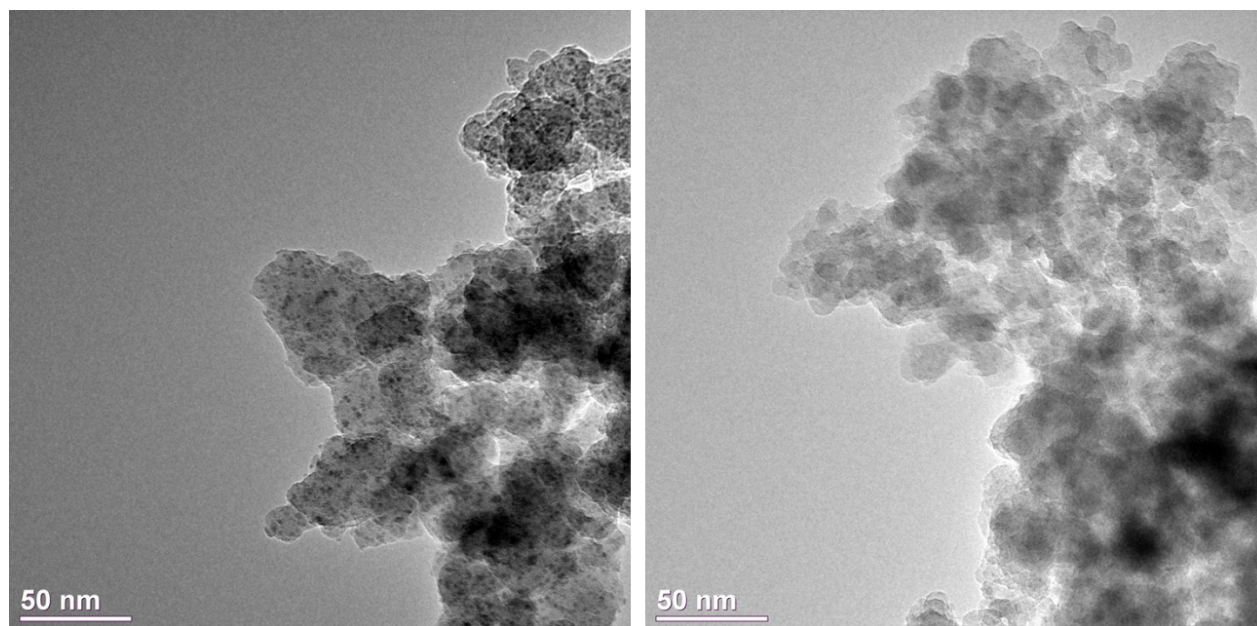


Figure S3: TEM of small nickel phosphide after 500 °C H₂ reduction in the presence of organic. 30% area has small particles vs. 70% area is absence of any noticeable particles within our resolution, indicating with organic the particles are made even smaller.

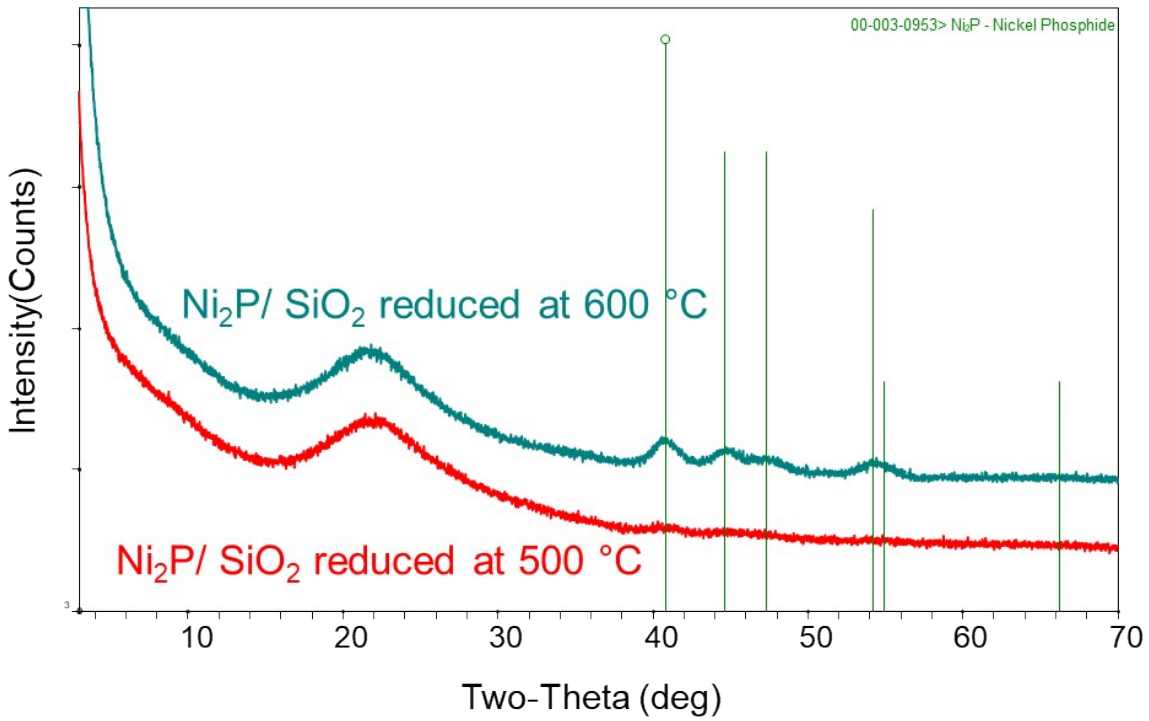


Figure S4: XRD of small nickel phosphide after H₂ reduction at different temperature, indicating 600 °C induced some sintering of the Ni₂P crystallites. The TEM is in Figure 1.

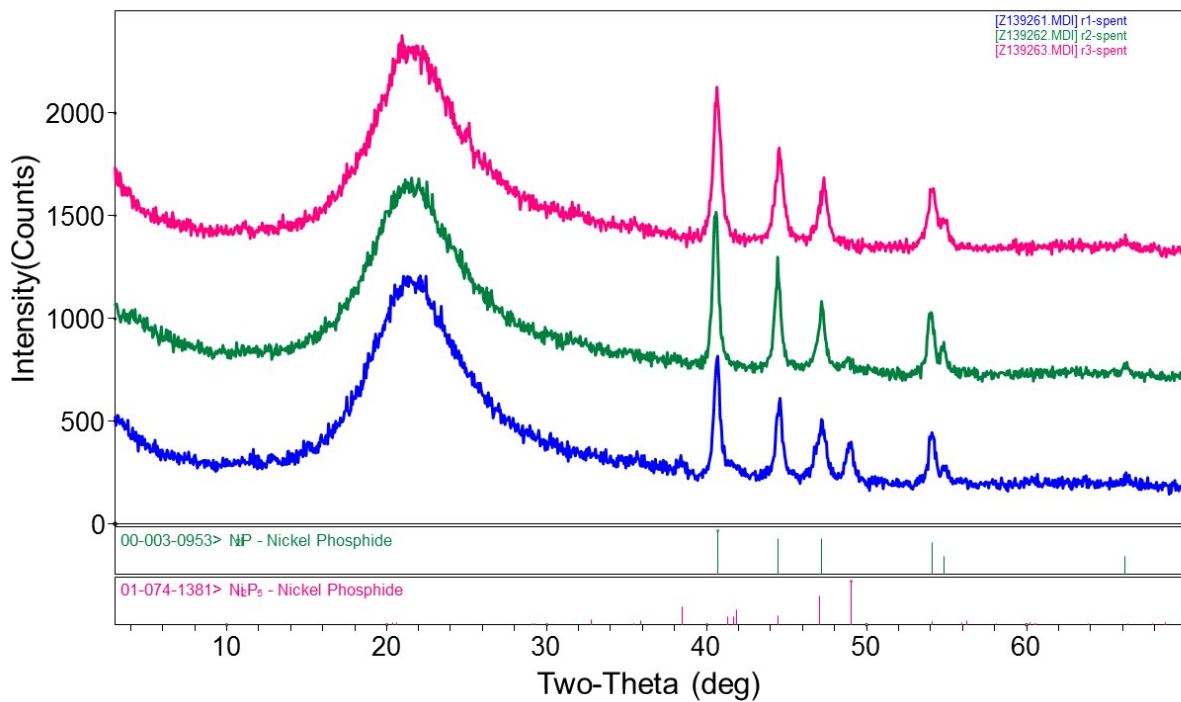


Figure S5: XRD for the three samples after reactor indicating severe sintering (pink-500 °C, green 600 °C, blue with organic precursor no reduction in place), all of which show

similarly low activity with relative volume activity (RVA) <0.01. Control is using commercial catalyst in this pressure region.

Ni₂P crystallizes in the P-62m tetragonal space group with a=b=5.859Å, c=3.382Å with the atomic positions of Ni and P listed in Table S1. The 3D structure of ball-stick model with polyhedral are listed in Figure S6. In the polyhedral only model, it can be seen more clearly that there are two types of Ni. One is in four coordination of P and the other is in five coordination of P. In the tetrahedral arrays, two of the four corner P are then shared with another three tetrahedra and the remaining two are sharing with another six tetrahedra making the whole structure Ni rich. The five coordinated Ni form an array in between the tetrahedral arrays as in Figure S6. We also plot the same structure in ball and stick presentation with or without P in Figure S7, which helps to understand how the presence of P distorts the close packing of Ni.

Ni₁₂P₅ on the other hand crystallizes in the I4/m tetragonal space group with a=b=8.646Å, c=5.07Å. Its coordinates and 3D polyhedral structures are show below in Table S2 and Figure S8 respectively. Here there is only one type of Ni and they are all in tetrahedral coordination, connected through the edges. Each corner P is then connected to eight other tetrahedral. In this structure, most of Ni appear to pack in simple cubic structure with some P in the cubic center. Ni atoms are further connected through some Ni and P junctions leaving P rich channels. It can be view better in the ball and stick model as shown in Figure S9.

TABLE S1. Ni₂P ATOMIC POSITIONS

#	ID	S.F.	Site	Fill	x	y	z	Biso
1	Ni 1	Ni	3	1	0.2575	0	0	0.5
2	Ni 2	Ni	3	1	0.5957	0	1/2	0.5
3	P 1	P	2	1	1/3	2/3	0	0.5
4	P 2	P	1	1	0	0	1/2	0.5

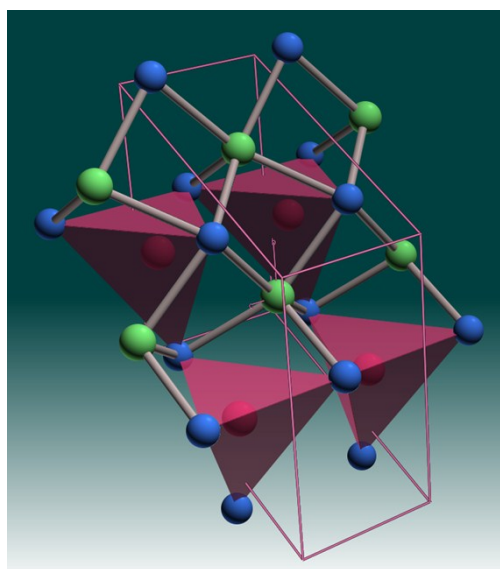
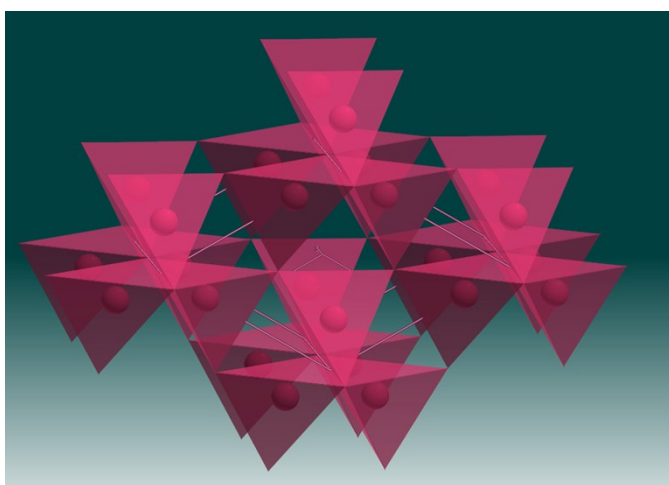


FIGURE S6: 3D STRUCTURE OF Ni₂P IN POLYHEDRAL PRESENTATIONS (Ni: RED OR GREEN; P: BLUE; NiP₄: PINK IN 4 COORDINATION; NiP₅: GREEN IN 5 COORDINATION)

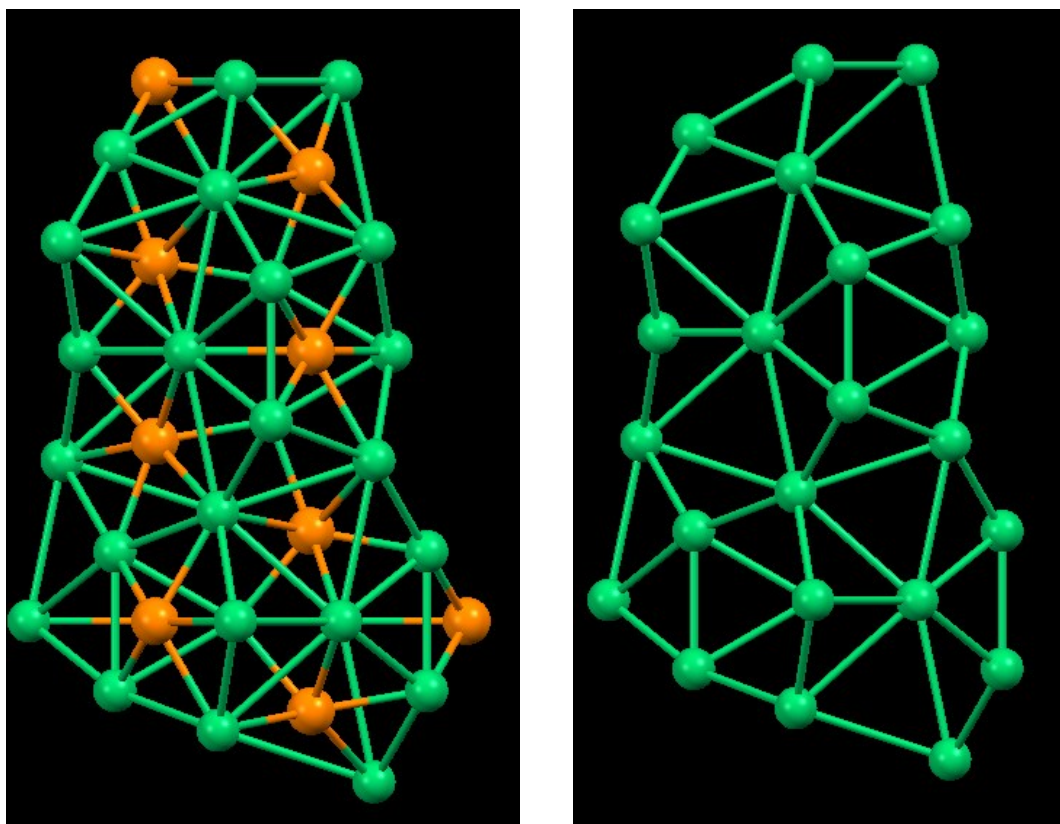


FIGURE S7: 3D STRUCTURE OF Ni₂P IN BALL AND STICK PRESENTATIONS (Ni: GREEN; P: ORANGE) ALONG C AXIS.

TABLE S2. Ni₁₂P₅ ATOMIC POSITIONS

#	ID	S.F.	Site	Fill	x	y	z	Biso
1	Ni1	Ni	16	1	0.1166	0.1812	0.249	0.5
2	Ni2	Ni	8	1	0.3655	0.0609	0	0.5
3	P 1	P	8	1	0.1939	0.4132	0	0.5
4	P 2	P	2	1	0	0	0	0.5

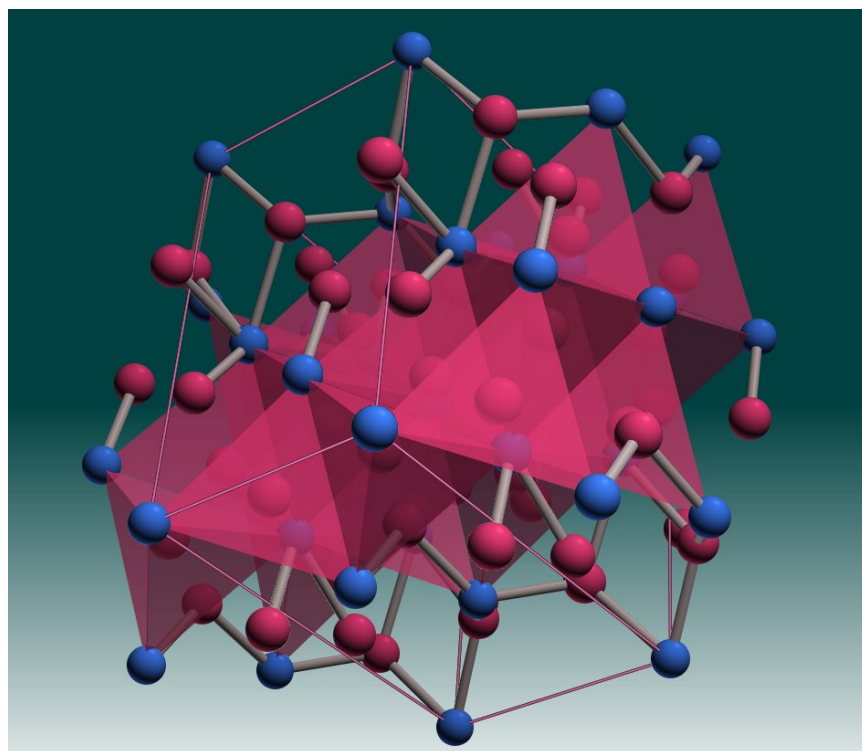


FIGURE S8: 3D STRUCTURE OF Ni₁₂P₅ IN POLYHEDRAL PRESENTATIONS (Ni: RED; P: BLUE)

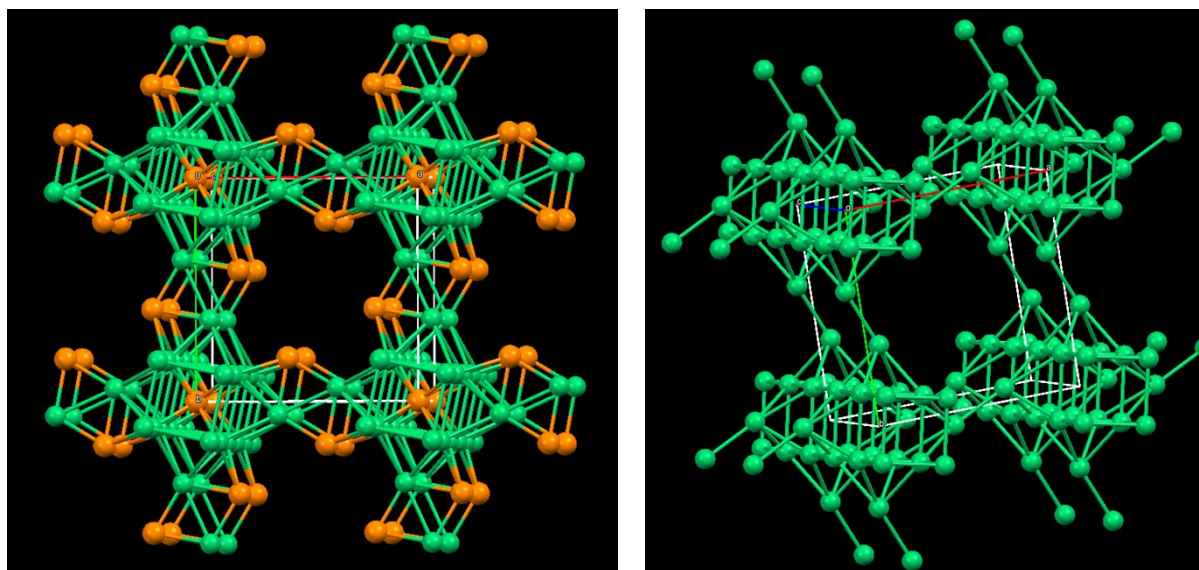


FIGURE S9: 3D STRUCTURE OF Ni₁₂P₅ IN BALL AND STICK PRESENTATIONS (Ni: GREEN; P: ORANGE) ALONG C AXIS.