Supporting Information

Nitrate and Nitroarene Hydrogenations Catalyzed by Alkaline-Earth Nickel Phosphide Clathrates

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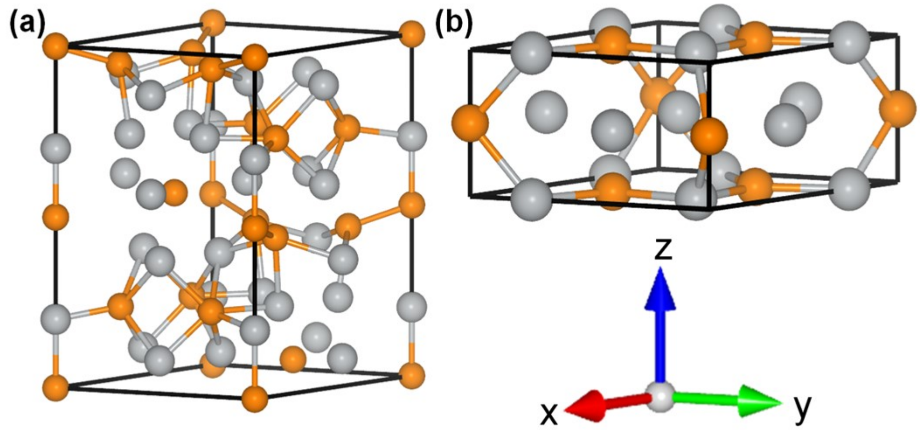


Figure S1. Unit cells of crystalline Ni_5P_4 (a) and Ni_2P (b). (Ni in gray, P in orange)

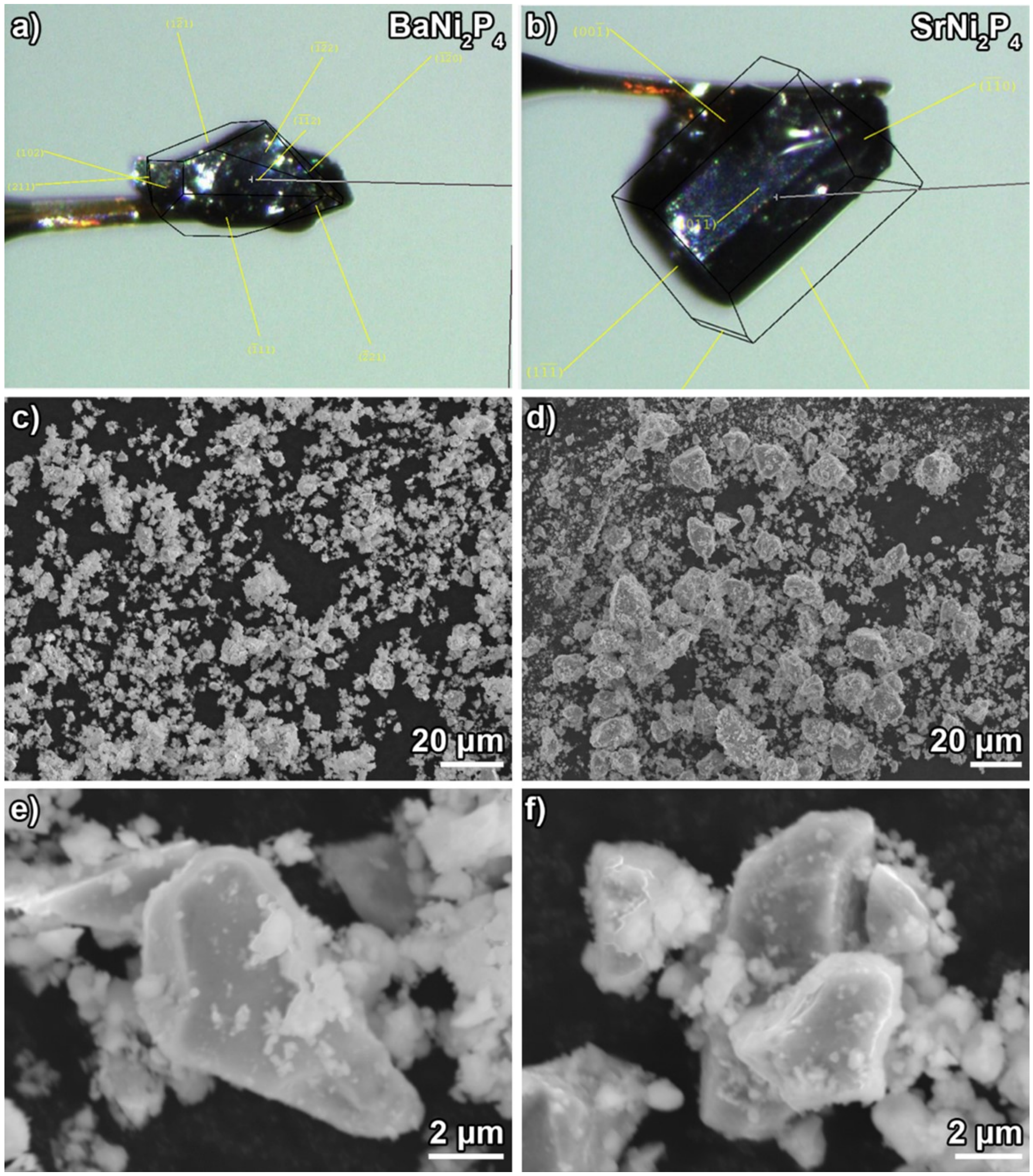


Figure S2. Optical and SEM images of (a, c, e) $BaNi_2P_4$ and (b, d, f) $SrNi_2P_4$ before (a and b on top) and after 2 h hand-grinding (middle and bottom c through f).

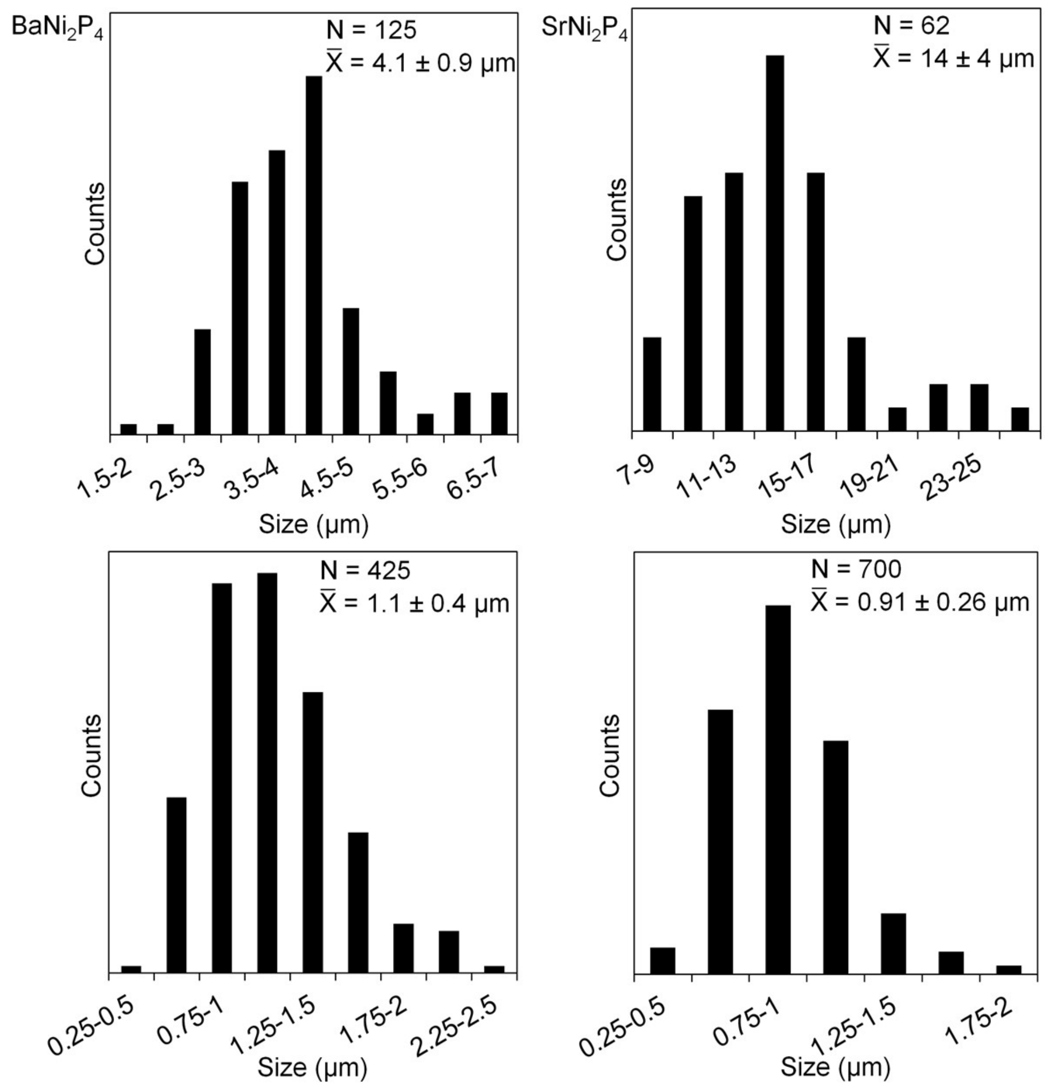


Figure S3. Histograms of large (top) and small (bottom) particle size distributions for $BaNi_2P_4$ (left) and $SrNi_2P_4$ (right) after 2 h hand-grinding.

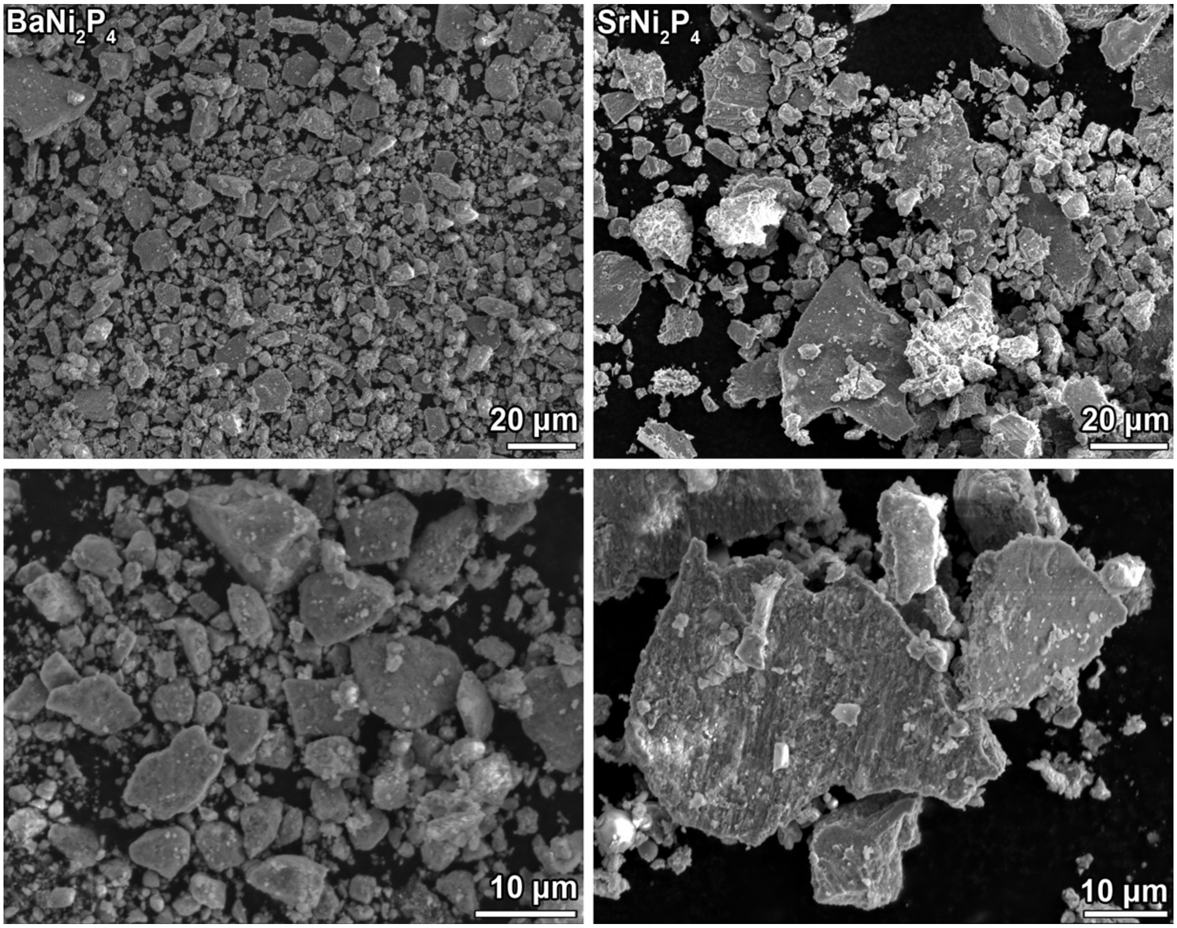


Figure S4. Representative SEM images of $BaNi_2P_4$ (left) and of $SrNi_2P_4$ (right) after 2 h ball-milling.

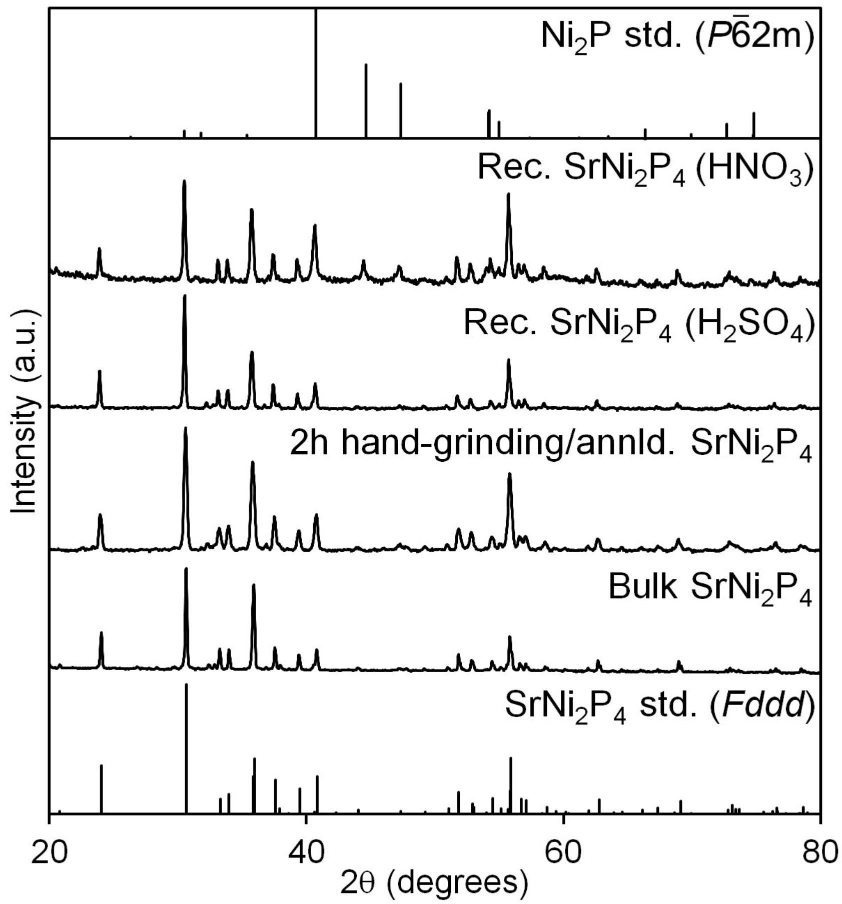


Figure S5. Powder XRD of $SrNi_2P_4$ before and after hand-grinding/H_2-annealing, as well as after catalysis using different acids. Reference XRD patterns are shown for comparison ($SrNi_2P_4$, ICSD429359; Ni_2P, ICSD43395).

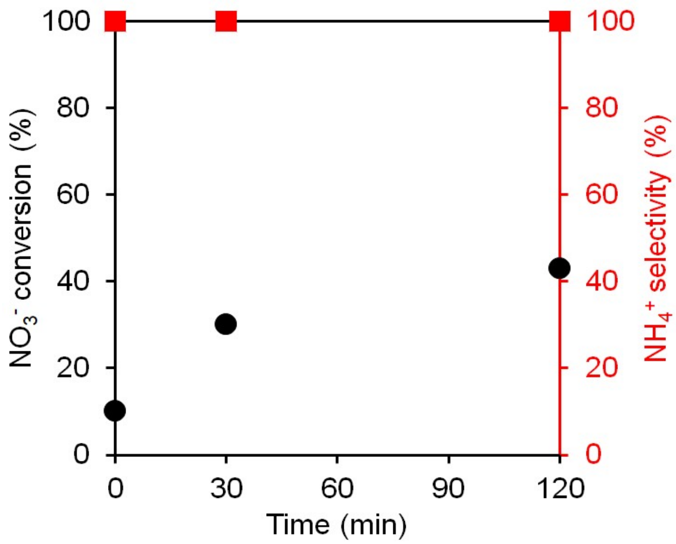


Figure S6. Catalytic activity and selectivity observed during NO_3^- hydrogenation with $BaNi_2P_4$ as a function of ball-milling prior to catalysis; decomposition of the clathrate to binary nickel phosphides was observed by XRD (see text).

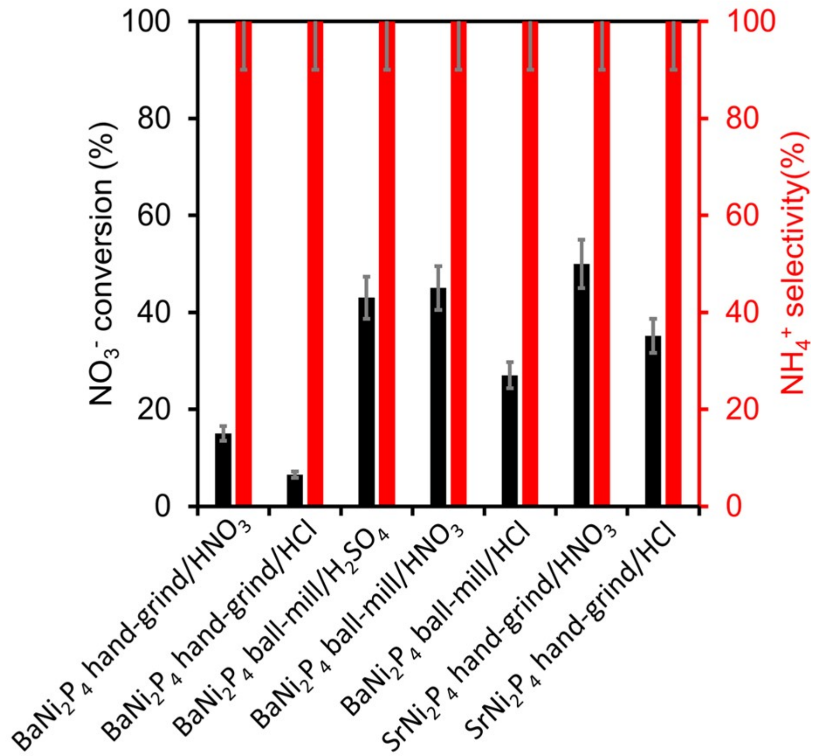


Figure S7. Catalytic activity and selectivity observed during NO_3^- hydrogenation as a function of catalyst and acid used after 12 h. (Conditions: 2 mM NO_3^-, pH 2, 60 °C; catalysts hand-ground or ball-milled for 2 h and annealed under H_2, 10 mg catalyst used; see Experimental).

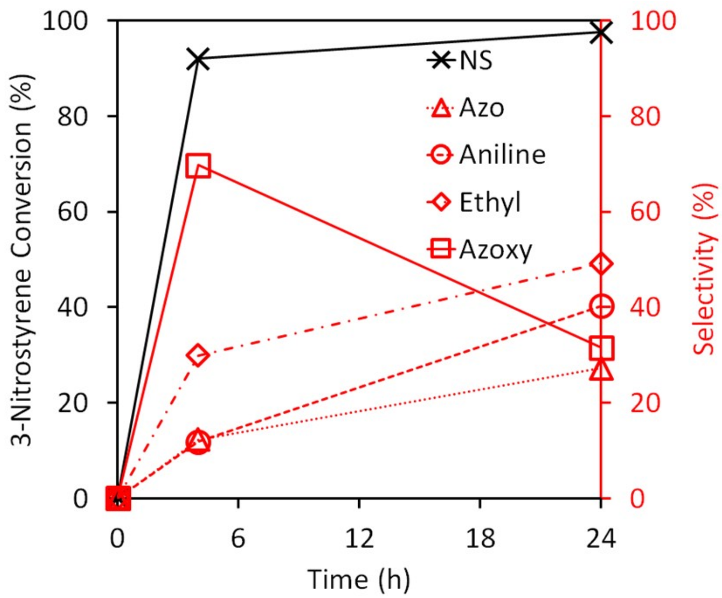


Figure S8. 3-Nitrostyrene reduction in the presence of $SrNi_2P_4$. (Conditions: 50 mM 3-nitrostyrene, ambient temperature; 10 mg of catalyst, 2 h hand-ground and annealed under H_2, see Experimental).

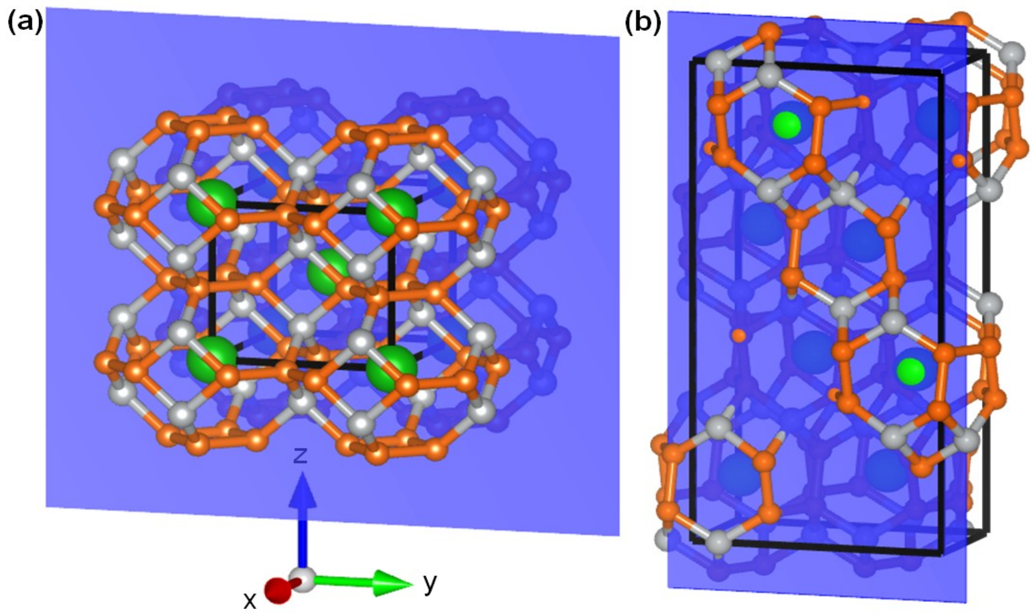


Figure S9. Facets of $BaNi_2P_4$ (a) and $SrNi_2P_4$ (b) used to determine the number of active sites on each catalyst surface.

TOF and TON calculation examples

[$BaNi_2P_4$ example – $PhNO_2$ – 2 h hand-grind; 24 h rxn]

$BaNi_2P_4$ unit cell parameters: a = 0.6620 nm, b = 0.6470, c = 0.5785 nm, V = 0.24778 nm^3, 14 atoms (Z = 2 formula units)

Molar mass of $BaNi_2P_4$ = 378.612 g/mol

Density

$$= \frac{378.612\ g}{1\ mol} \times \frac{1\ mol}{6.02 \times 10^{23}\ formula\ units} \times \frac{2\ formula\ units}{1\ unit\ cell} \times \frac{1\ unit\ cell}{0.24778\ nm^3} = 5.075 \times 10^{-21}\ g/nm^3$$

Volume of an 1150 nm sphere $= \frac{4}{3}\pi r^3 = \frac{4}{3}\pi(575nm)^3 = 796{,}328{,}288\ nm^3$

Surface area of an 1150 nm sphere $= 4\pi r^2 = 4\pi(575nm)^2 = 4{,}154{,}756\ nm^2$

Surface area per gram of 1150 nm sphere

$$= \frac{4{,}154{,}756\ nm^2}{1\ particle} \times \frac{1\ particle}{796{,}328{,}288\ nm^3} \times \frac{1\ nm^3}{5.075 \times 10^{-21}\ g} = 1.03 \times 10^{18} nm^2/g$$

One $BaNi_2P_4$ formula unit approximate area (001) $= 0.6620 \times 0.6470 = 0.4283\ nm^2$

Must divide by 1; there are 2 formula units in the unit cell, but only 1 is at the surface of the cell

Assume 1 $BaNi_2P_4$ formula units provides 1 active site, then 10.0 mg catalysts active sites number

$$(10.0 \times 10^{-3})g \times \frac{1.03 \times 10^{18} nm^2}{1\ g} \times \frac{1\ molecule}{0.4283\ nm^2} = 2.40 \times 10^{16}\ active\ sites$$

Moles of catalyst active sites $= \frac{2.40 \times 10^{16}\ formula\ units}{6.02 \times 10^{23}\ formula\ units/mol} = 3.99 \times 10^{-8}\ mol$

Turnover number of Exp. 1 (98% conversion) $= \frac{9.8 \times 10^{-5}\ mol\ Nitrobenzene}{3.99 \times 10^{-8}\ mol\ Cat.} = 2456$

Turnover frequency of Exp. 1 $= \frac{2456}{24\ hrs} = 102.3\ h^{-1}$

[$SrNi_2P_4$ example – 2 h hand-grind; 24 h rxn]

$SrNi_2P_4$ unit cell parameters: a = 0.51928 nm, b = 0.95598, c = 1.89575 nm, V = 0.94109 nm^3, 56 atoms (Z = 8 formula units)

Molar mass of $SrNi_2P_4$ = 328.902 g/mol

Density

$$= \frac{328.902\ g}{1\ mol} \times \frac{1\ mol}{6.02 \times 10^{23}\ formula\ units} \times \frac{8\ formula\ units}{1\ unit\ cell} \times \frac{1\ unit\ cell}{0.94109\ nm^3} = 4.643 \times 10^{-21}\ g/nm^3$$

Volume of a 909.3 nm sphere $= \frac{4}{3}\pi r^3 = \frac{4}{3}\pi(454.65nm)^3 = 393{,}659{,}010\ nm^3$

Surface area of a 909.3 nm sphere $= 4\pi r^2 = 4\pi(454.65nm)^2 = 2{,}597{,}552\ nm^2$

Surface area per gram of 909.3 nm sphere

$$= \frac{2{,}597{,}552\ nm^2}{1\ particle} \times \frac{1\ particle}{393{,}659{,}010\ nm^3} \times \frac{1\ nm^3}{4.643 \times 10^{-21}\ g} = 1.42 \times 10^{18} nm^2/g$$

One $SrNi_2P_4$ formula unit approximate area (100) $= 0.95598 \times 1.89575 = 1.8123\ nm^2$

Must divide by 4; there are 8 formula units in the unit cell, but only 4 are the surface of the cell

$$\frac{1.8123\ nm^2}{4\ formula\ units\ at\ the\ (100) surface} = 0.45308\ nm^2$$

Assume 1 $SrNi_2P_4$ formula units provides 1 active site, then 10.0 mg catalysts active sites number

$$(10.0 \times 10^{-3})g \times \frac{1.42 \times 10^{18} nm^2}{1\ g} \times \frac{1\ molecule}{0.45308\ nm^2} = 3.13 \times 10^{16}\ active\ sites$$

Moles of catalyst active sites $= \frac{3.13 \times 10^{16}\ active\ sites}{6.02 \times 10^{23} active\ sites/mol} = 5.21 \times 10^{-8}\ mol$

Turnover number of Exp. 1 (58% conversion) $= \frac{5.8 \times 10^{-5}\ mol\ Nitrobenzene}{5.21 \times 10^{-8}\ mol\ Cat.} = 1114$

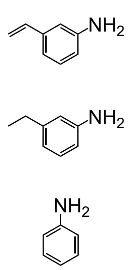
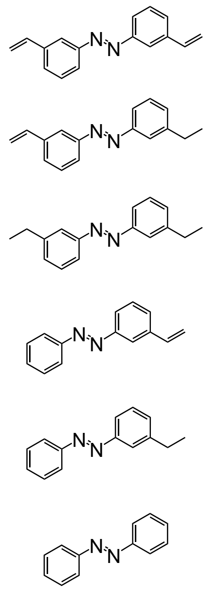
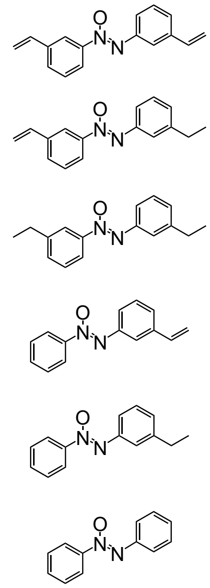
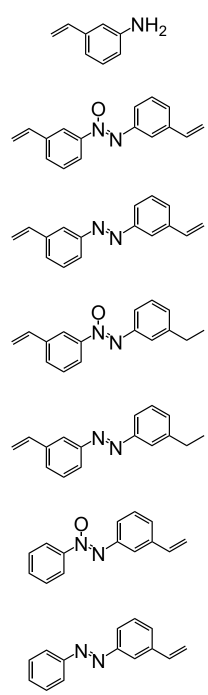
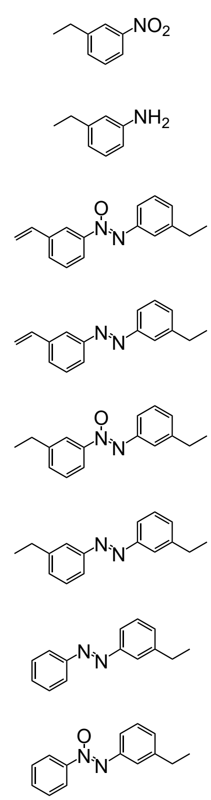
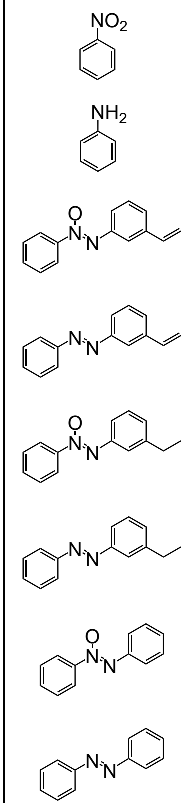
Turnover frequency of Exp. 1 $= \frac{1114}{24\ hrs} = 46.4\ h^{-1}$

Table S1. Nitrate and nitroarene reductions using nickel phosphide and clathrate catalysts.

Catalyst	Pretreatment[a]	Pretreated XRD (size/nm)[b]	Reactant[c]	t (h)	Conversion (%)	Product(s) (Selec./%)	Recovered XRD (size/nm)	TON[d] (TOF[e]/h)
$BaNi_2P_4$[h]	2 h Ball-mill, annld.[f]	73% NiP (20±6), 27% NiP_2 (27±1)	NO_3^-	12	45	NH_4^+ (100)	-	-
$BaNi_2P_4$[i]	2 h Ball-mill, annld.[f]	73% NiP (20±6), 27% NiP_2 (27±1)	NO_3^-	12	27	NH_4^+ (100)	-	-
$SrNi_2P_4$[i]	2 h Hand-grind, annld.[f]	$SrNi_2P_4$ (40±15)	NO_3^-	12	35	NH_4^+ (100)	-	-
None	-	-	NO_2^-	4	99	NO_3^- (9)	-	-
$BaNi_2P_4$[g]	2 h Hand-grind, annld.[f]	$BaNi_2P_4$ (44±5)	NO_2^-	4	100	NO_3^- (14)	-	-
None	-	-	$PhNO_2$	16	48	Aniline (2)	-	-
$BaNi_2P_4$	Annld.[f]		$PhNO_2$	4	66	Aniline (32), azo (19), azoxy (49)	-	-
$BaNi_2P_4$	Annld.[f]		$PhNO_2$	24	57	Aniline (4), azo (2), azoxy (94)	-	-
$BaNi_2P_4$	Annld.[f]		3-Nitrostyrene	4	98	Aniline[j] (16), azo[j] (8), azoxy[j] (70), ethyl[j] (28)	-	-
$BaNi_2P_4$	Annld.[f]		3-Nitrostyrene	24	95	Aniline[j] (28), azo[j] (11), azoxy[j] (62), ethyl[j] (40)	-	-
$SrNi_2P_4$	2 h Hand-grind, annld.[f]		3-Nitrostyrene	4	92	Aniline[j] (12), azo[j] (12), azoxy[j] (70), ethyl[j] (30)	-	-
$SrNi_2P_4$	2 h Hand-grind, annld.[f]		3-Nitrostyrene	24	98	Aniline[j] (40), azo[j] (27), azoxy[j] (32), ethyl[j] (50)	-	1882 (78)

[a]10 mg cat. [b]Estimated from XRD peak widths using the Scherrer equation when <100 nm; reported in nm unless specified otherwise. [c]2.0 mM NO_3^- or NO_2^-, 60 °C, pH = 2/H_2O; or 50 mM nitroarene, RT/EtOH. [d]TON = moles of converted reactant / moles of surface-active catalyst sites (calculated for select cases, only); [e]TOF = TON/catalysis time. [f]1 atm H_2, 1h, 400 °C. Adjusted pH with: [g]H_2SO_4, [h]HNO_3, [i]HCl,. [j]Multiple products containing functional group (see SI). [k]Multiple Ph–vinyl (C–C) breaking products.

Table S2. 3-Nitrostyrene reduction products using clathrate catalysts.

Anilines	Azo arenes	Azoxy arenes	Vinyl arenes	Ethyl arenes	Devinylation
					

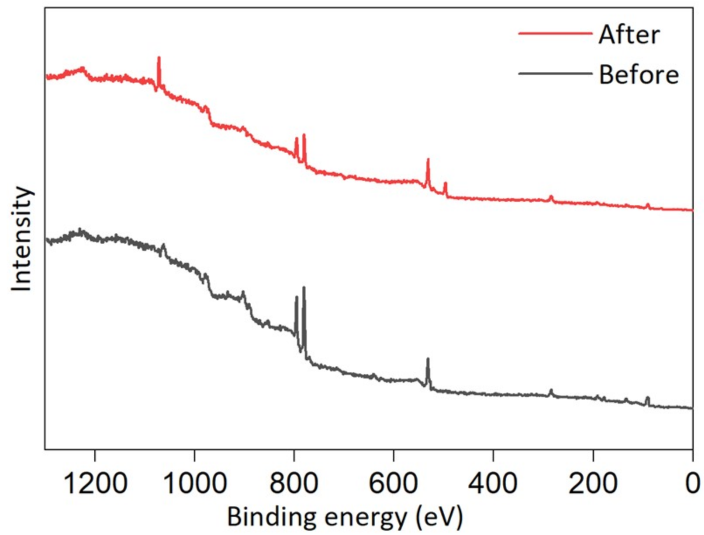


Figure S10. XPS survey spectra of $BaNi_2P_4$ before (black) and after (red) catalytic hydrogenation of 3-nitrostyrene. (Conditions: 50 mM 3-NO_2-styrene, R.T.; catalyst hand-ground for 2 h and annealed under H_2).

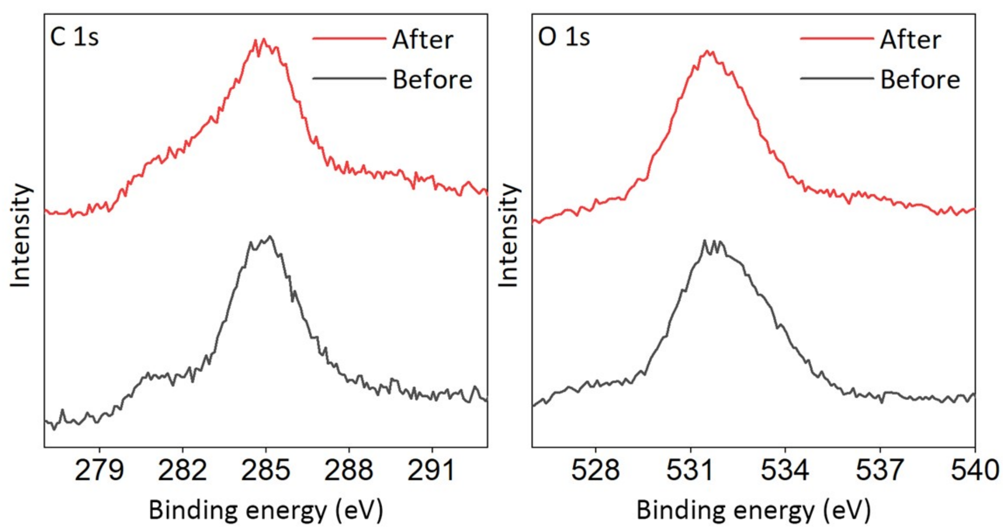


Figure S11. O 1s and C 1s peak XPS regions of $BaNi_2P_4$ before (black) and after (red) catalytic hydrogenation of 3-nitrostyrene. (Conditions: 50 mM 3-NO_2-styrene, R.T.; catalyst hand-ground for 2 h and annealed under H_2).