Supplementary Information for

Selective Synthesis of α-Nickel Hydroxide through a Polyol Process

Koki Kawabata, Shusuke Okamoto, Hironori Hondoh, and Daisuke Nagai*

School of Food and Nutritional Science, University of Shizuoka, 52-1 Yada, Suruga-ku, Shizuoka, Shizuoka, 422-8526, Japan.

Correspondence to: Daisuke Nagai (E-mail: daisukenagai@u-shizuoka-ken.ac.jp)

Table of Contents

S1. XRD

S2. IR

S3. DFT

S1. XRD

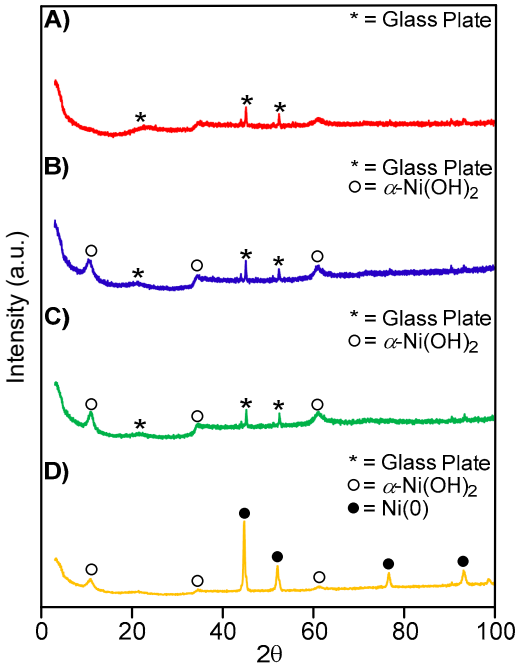


Figure S1. Powder XRD patterns of products using (**A**) potassium hydroxide in Run 4, (**B**) sodium hydrogen carbonate in Run 5, (**C**) potassium carbonate in Run 6, and (**D**) sodium carbonate in Run 7.

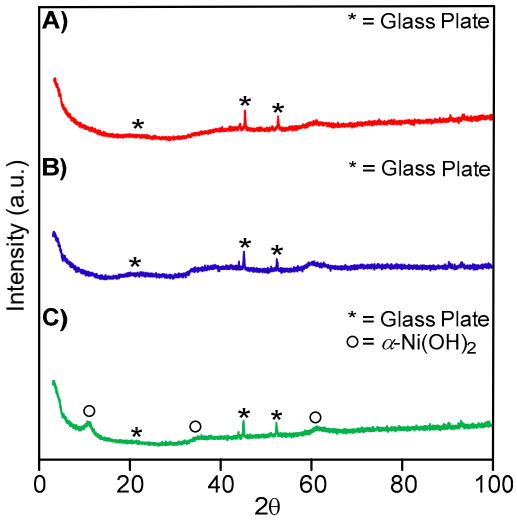


Figure S2. Powder XRD patterns of products using (**A**) TEG in Run 8, (**B**) Poly-EG in Run 9, and (**C**) Gly in Run 10.

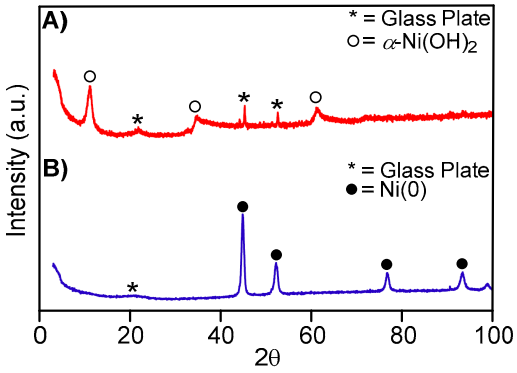


Figure S3. Powder XRD patterns of products using (**A**) nickel nitrate hexahydrate in Run 11, and (**B**) nickel chloride hexahydrate in Run 12.

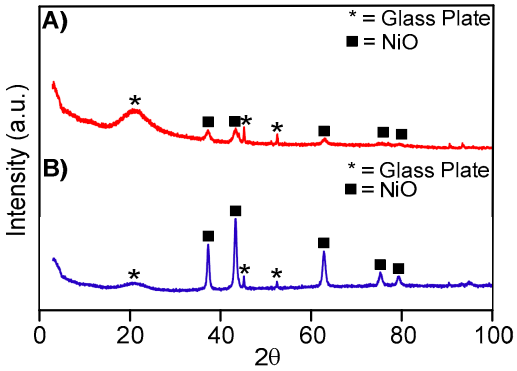


Figure S4. Powder XRD patterns of products after heating at 600 °C under an air atmosphere (**A**) α-nickel hydroxide in Run 2, and (**B**) a commercially available β-nickel hydroxide.

S2. IR

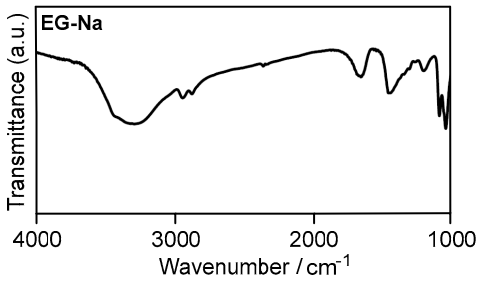


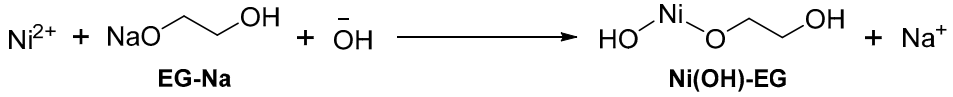
Figure S5. IR spectrum of the crude EG-Na

S3. DFT

All DFT calculations were performed with the Gaussian 09 package using the B3LYP functional combined with the 6-311G(d,p) basis set. The geometry optimizations were accompanied by frequency analyses. Based on the optimized structure, the Gibbs free energies at 473.15 K were calculated using 6-311G(d,p) level. These results are summarized at Table S1.

Table S1. Results of free energies for compounds

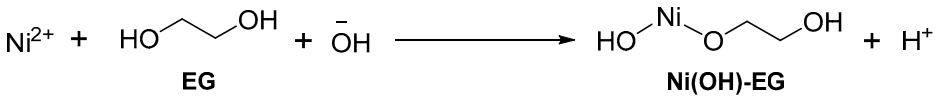
Compound	Free Energy (Hartree) at 473.15 K
H^+	-0.0176
Na^+	-162.112
Ni^{2+}	-1507.173
^-OH	-75.784
EG	-230.283
EG^-	-229.671
EG^{2-}	-228.893
EG-Na	-392.013
Ni(OH)-EG	-1813.778
$Ni(EG)_2$	-1967.607
Ni-EG Cyclic Complex	-1737.313
$Ni(OH)_2$	-1659.946



EG-Na Ni(OH)-EG

ΔG = (-1813.778 + -162.112) - (-1507.173 + -392.013 + -75.784) = -0.920

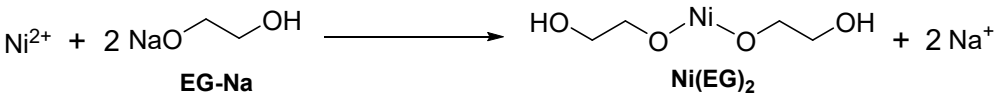
= -0.920 × 627.5095 = -557.31 (kcal/mol).



EG Ni(OH)-EG

ΔG = (-1813.778 + -0.0176) - (-1507.173 + -230.283 + -75.784) = -0.556

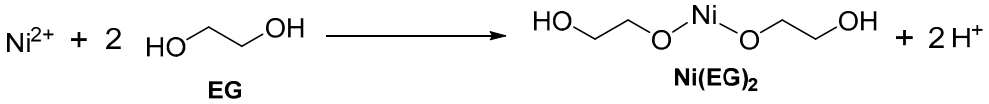
= -0.556× 627.5095 = -348.90 (kcal/mol)



EG-Na **$Ni(EG)_2$**

ΔG = (-1967.607 + 2×-162.112) - (-1507.173 + 2×-392.013) = -0.632

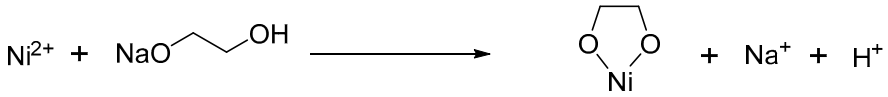
= -0.632 × 627.5095 = -396.59 (kcal/mol)



EG **$Ni(EG)_2$**

ΔG = (-1967.607 + 2×-0.0176) - (-1507.173 + 2×-230.283) = 0.097

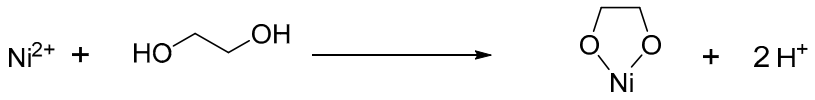
= 0.097 × 627.5095 = 60.87 (kcal/mol)



EG-Na **Ni-EG Cyclic Complex**

ΔG = (-1737.313 + -162.112 + -0.0176) - (-1507.173 + -392.013) = -0.257

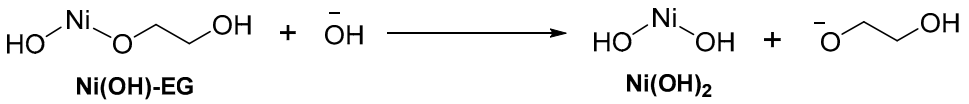
= -0.257 × 627.5095 = -161.27 (kcal/mol)



EG **Ni-EG Cyclic Complex**

ΔG = (-1737.313 + 2×-0.0176) - (-1507.173 + -230.283) = 0.108

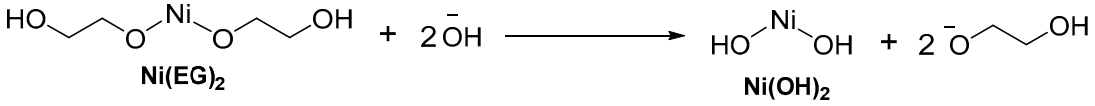
= 0.108 × 627.5095 = 67.77 (kcal/mol)



$Ni(OH)$-EG **$Ni(OH)_2$**

ΔG = (-1659.946 + -229.671) - (-1813.778 + -75.784) = -0.055

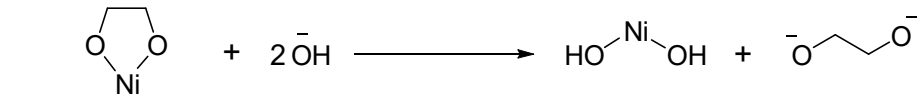
= -0.055 × 627.5095 = -34.51 (kcal/mol)



$Ni(EG)_2$ **$Ni(OH)_2$**

ΔG = (-1659.946 + 2×-229.671) - (-1967.607 + 2×-75.784) = -0.113

= -0.113 × 627.5095 = -70.91 (kcal/mol)



Ni-EG Cyclic Complex **$Ni(OH)_2$**

$\Delta G = (-1659.946 + -228.893) - (-1737.313 + 2\times-75.784) = 0.042$

$= 0.042 \times 627.5095 = 26.36$ (kcal/mol)



H^+

#p opt freq=readisotopes b3lyp/6-311g(d,p)

1 1

H 0.00000000 0.00000000 0.00000000



Na^+

#p opt freq=readisotopes b3lyp/6-311g(d,p)

1 1

Na 0.00000000 0.00000000 0.00000000

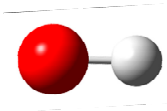


Ni^{2+}

#p opt freq=readisotopes b3lyp/6-311g(d,p)

2 1

Ni 0.00000000 0.00000000 0.00000000



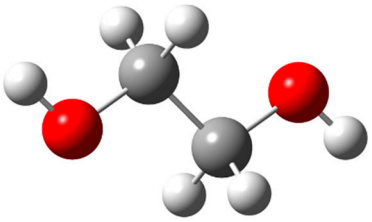
^-OH

#p opt freq=readisotopes b3lyp/6-311g(d,p)

-1 1

O 0.00000000 0.00000000 0.10867000

H 0.00000000 0.00000000 -0.86936200

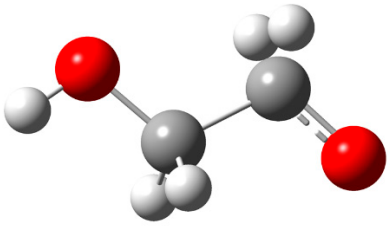


EG

#p opt freq=readisotopes b3lyp/6-311g(d,p)

0 1

C	0.57372200	-0.49603000	0.00002500
H	0.49151000	-1.13473600	0.88940300
H	0.49150400	-1.13479100	-0.88931400
O	1.78036300	0.26076100	0.00001100
H	2.51851400	-0.35386100	-0.00007700
C	-0.57361800	0.49608100	-0.00002300
H	-0.49179700	1.13491200	-0.88931900
H	-0.49186200	1.13495500	0.88924500
O	-1.78036500	-0.26084400	-0.00004100
H	-2.51847500	0.35387800	0.00029600

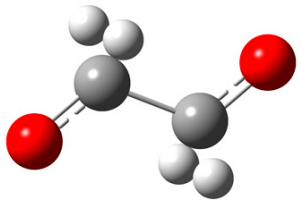


EG$^-$

#p opt freq=readisotopes b3lyp/6-311g(d,p)

-1 1

C	0.73970500	0.47269100	-0.00027400
H	0.55961900	1.17120100	-0.89270600
H	0.55922900	1.17163300	0.89173600
O	1.86644100	-0.21818600	0.00029800
C	-0.50130900	-0.46316300	-0.00020300
H	-0.42028300	-1.10793800	0.88957700
H	-0.42066900	-1.10726000	-0.89048700
O	-1.77255200	0.24806900	0.00038700
H	-2.45938100	-0.42386700	-0.00073300

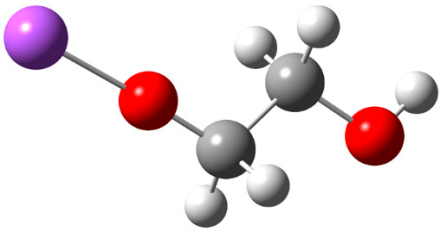


EG^{2-}

#p opt freq=readisotopes b3lyp/6-311g(d,p)

-2 1

C	-0.68077422	0.43391174	0.00000039
H	-0.48969820	1.15584157	-0.89805330
H	-0.48970084	1.15585493	0.89804693
O	-1.84894767	-0.19642177	-0.00000091
C	0.68082236	-0.43357131	0.00000041
H	0.48928113	-1.15567266	-0.89814611
H	0.48928265	-1.15564587	0.89816964
O	1.84901598	0.19611920	-0.00000183

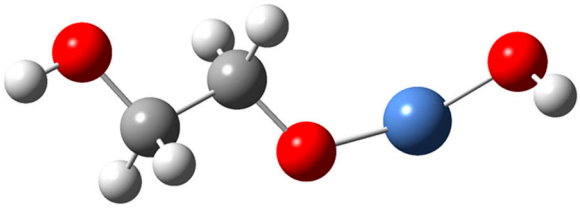


EG-Na

#p opt freq=readisotopes b3lyp/6-311g(d,p)

0 1

O	0.93979500	0.26016900	0.00004100
C	-0.36542200	0.68590200	0.00002300
H	-0.61862300	1.30756300	-0.88331400
H	-0.61864300	1.30757300	0.88334600
C	-1.33971700	-0.49554200	0.00001600
H	-1.13962300	-1.11147600	-0.89007700
H	-1.13972600	-1.11140700	0.89017700
O	-2.68532000	-0.00432200	-0.00008500
H	-3.27506700	-0.76234200	0.00027700
Na	2.81697400	-0.25625900	-0.00002600

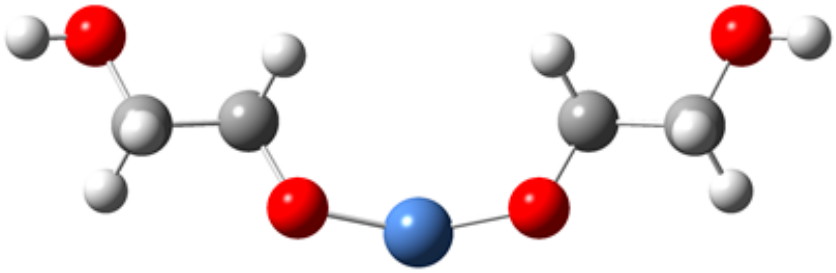


Ni(OH)-EG

#p opt freq=readisotopes b3lyp/6-311g(d,p)

0 1

O	-0.17533900	-0.61570200	0.25040900
C	-1.21675700	0.17732300	-0.27658100
H	-1.29968000	0.09522000	-1.36912900
H	-1.04800200	1.23493500	-0.03465700
C	-2.52994600	-0.26006400	0.35793700
H	-2.69902700	-1.32189200	0.13360900
H	-2.45083900	-0.14751000	1.44709500
O	-3.55344200	0.56442700	-0.19108500
H	-4.39496300	0.28272400	0.17678400
Ni	1.45136600	-0.28296300	-0.13418300
O	2.58177600	0.95910200	0.17072600
H	2.91052300	1.01331800	1.07490200

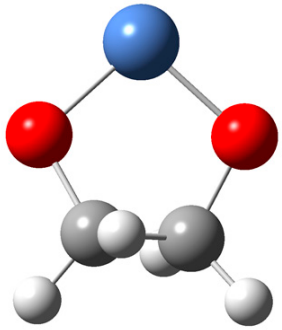


Ni(EG)$_2$

#p opt freq=readisotopes b3lyp/6-311g(d,p)

0 1

Ni	0.00008001	-1.06357136	-0.15030862
O	-1.63261857	-0.73506776	0.22883798
O	1.63299904	-0.73575062	0.22884480
C	-2.29980666	0.43399737	-0.18368081
H	-1.81970357	1.32080597	0.25447572
H	-2.29665227	0.56315189	-1.27515620
C	-3.73970484	0.37986682	0.30963499
H	-3.73407716	0.28074097	1.40276764
H	-4.22961074	-0.50733659	-0.11365771
O	-4.37105946	1.58434924	-0.11452750
H	-5.28869611	1.55770256	0.16846350
C	2.30022065	0.43272357	-0.18520667
H	1.81910331	1.32038897	0.24995660
H	2.29890093	0.55928730	-1.27695018
C	3.73940217	0.38055529	0.31054363
H	3.73208725	0.28322033	1.40376883
H	4.23055254	-0.50691961	-0.11056080
O	4.37036621	1.58482401	-0.11461042
H	5.28768997	1.55925894	0.16942818

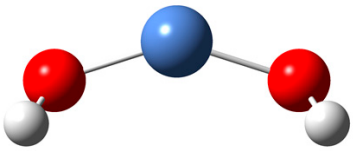


Ni-EG Cyclic Complex

#p opt freq=readisotopes b3lyp/6-311g(d,p)

0 1

C	-1.43073400	-0.72292500	-0.23944800
C	-1.43063700	0.72288400	0.23962500
H	-2.24275300	-1.32236500	0.19173200
H	-1.52522200	-0.74378000	-1.33538400
H	-1.52462900	0.74367900	1.33561000
H	-2.24287100	1.32232200	-0.19115000
O	-0.18093600	-1.28978200	0.17221100
O	-0.18107900	1.28980400	-0.17262500
Ni	0.98570800	0.00000800	0.00005200



$Ni(OH)_2$

#p opt freq=readisotopes b3lyp/6-311g(d,p)

0 1

Ni	0.00000693	0.22481904	0.04280925
O	-1.61421830	-0.28691044	-0.14275550
H	-1.98642194	-0.85214207	0.54282549
O	1.61415372	-0.28699303	-0.14281718
H	1.98674448	-0.85156346	0.54309698