

Supporting Information

for

Ni nanoparticles on RGO as reusable heterogeneous catalyst: effect of Ni particle size and intermediate composite structures in C–S cross-coupling reaction

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Powder XRD patterns of Ni/RGO-20 and Ni/RGO-40; Table showing comparative catalytic performance and effect of NP sizes; ¹H and ¹³C NMR spectral data for compounds 3a–p

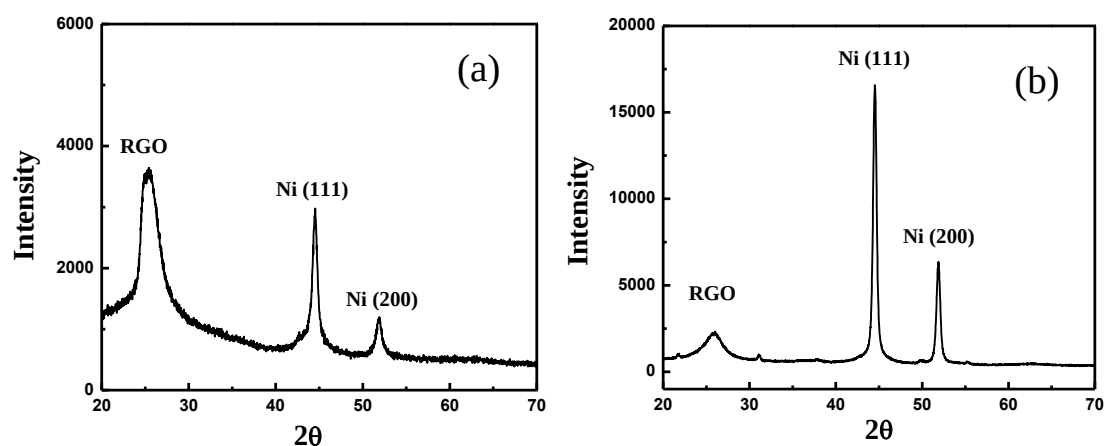


Figure S1: P-XRD patterns of (a) Ni/RGO-20 and (b) Ni/RGO-60.

Table S1: Comparative Table showing catalytic performance and NP sizes.

Comparison of various heterogeneous nickel catalysts in C–S cross-coupling reaction

Entry	Ni-Catalyst	Average particle size (nm)	Amount of Ni (mmol)	Temp (°C)	Time (h)	Yield (%)	TOF (h ⁻¹)	Ref.
1	Ni/RGO-40	11	0.15	100	2	93 ^a	3.10	–
2	After 1 st cycle	12 & 4	0.15	100	2	93 ^a	3.10	–
	Ni/Ni(OH) ₂ /RGO							
3	Ni(OH) ₂ /RGO (30 wt %)	13	0.15	100	2	82 ^a	2.73	–
4	NiO–ZrO ₂	7	0.078	80	24	89 ^b	0.47	§

^aIsolated yield of (4–Methoxyphenyl)(phenyl)sulfane.

^bIsolated yield of (4–Chlorophenyl)(4–methoxyphenyl)sulfane.

§ Pal, N.; Bhaumik, A. *Dalton Trans.* **2012**, 41, 9161–9169.

NMR spectral data for compounds listed in Table 2

(4-Methoxyphenyl)(phenyl)sulfane (3a)¹

Colourless liquid

¹H NMR (CDCl₃, 300 MHz): δ ppm 3.82 (s, 3H, OCH₃), 6.90 (dd, J = 2.1 and 6.6 Hz, 2H, ArH), 7.14–7.26 (m, 5H, ArH), 7.42 (dd, J = 2.1, 6.9 Hz, 2H, ArH); ¹³C NMR (CDCl₃, 75 MHz): δ ppm 55.3, 114.9, 124.1, 125.7, 128.1, 128.9, 135.3, 138.6, 159.7.

(3-Methoxyphenyl)(phenyl)sulfane (3b)²

Colourless liquid

¹H NMR (CDCl₃, 300 MHz): δ ppm 3.71 (s, 3H, OCH₃), 6.75 (dd, J = 2.7 and 8.4 Hz, 1H, ArH), 6.85-6.91 (m, 2H, ArH), 7.14-7.37 (m, 6H, ArH); ¹³C NMR (CDCl₃, 75 MHz): δ ppm 55.1, 112.6, 115.8, 122.8, 127.1, 129.1, 129.8, 131.3, 135.2, 137.1, 159.9.

(2-Methoxyphenyl)(*p*-tolyl)sulfane (3c)¹

Colourless liquid

¹H NMR (CDCl₃, 300 MHz): δ ppm 2.35 (s, 3H, CH₃), 3.88 (s, 3H, OCH₃), 6.80–6.88 (m, 2H, ArH), 6.94 (dd, J = 1.5 and 7.8 Hz, 1H, ArH), 7.13–7.20 (m, 3H, ArH), 7.31 (d, J = 8.1 Hz, 2H, ArH); ¹³C NMR (CDCl₃, 75 MHz): δ ppm 21.1, 55.8, 110.6, 121.2, 125.7, 127.4, 129.7, 129.8, 130.1, 132.9, 137.7, 156.5.

(4-Fluorophenyl)(4-methoxyphenyl)sulfane (3d)³

Colourless liquid

¹H NMR (CDCl₃, 300 MHz): δ ppm 3.80 (s, 3H, OCH₃), 6.86-6.98 (m, 4H, ArH), 7.17-7.22 (m, 2H, ArH), 7.34-7.37 (m, 2H, ArH); ¹³C NMR (CDCl₃, 75 MHz): δ ppm 55.3, 115.0, 116.0 (d, ² J_{C-F} = 21.8 Hz), 125.2, 131.0 (d, ² J_{C-F} = 7.9 Hz), 133.1, 134.5, 159.6, 161.6 (d, ² J_{C-F} = 243.4 Hz).

(4-Methoxyphenyl)(*p*-tolyl)sulfane (3e)⁴

Colourless liquid

¹H NMR (CDCl₃, 300 MHz): δ /ppm 2.29 (s, 3H, CH₃), 3.79 (s, 3H, OCH₃), 6.86 (d, *J* = 9.0 Hz, 2H, ArH), 7.05 (d, *J* = 8.1 Hz, 2H, ArH), 7.13 (d, *J* = 8.1 Hz, 2H, ArH), 7.35 (d, *J* = 9.0 Hz, 2H, ArH); ¹³C NMR (CDCl₃, 75 MHz): δ /ppm 20.9, 55.3, 114.8, 125.6, 129.3, 129.7, 134.3, 136.1, 159.4.

(4-Methoxyphenyl)(2,5-dimethylphenyl)sulfane (3f)⁵

Colourless liquid

¹H NMR (CDCl₃, 300 MHz): δ /ppm 2.20 (s, 3H, CH₃), 2.32 (s, 3H, CH₃), 3.80 (s, 3H, OCH₃), 6.85–6.92 (m, 4H, ArH), 7.06 (d, *J* = 7.5 Hz, 1H, ArH), 7.29 (dd, *J* = 2.1 and 6.6 Hz, 2H, ArH); ¹³C NMR (CDCl₃, 75 MHz): δ /ppm 19.8, 20.9, 55.3, 114.9, 124.9, 127.2, 130.1, 130.2, 133.9, 134.3, 136.0, 136.1, 159.2.

1-(4-(Phenylthio)phenyl)ethanone (3g)²

White solid, mp 62-63 (Lit. mp 63-64 °C)

¹H NMR (CDCl₃, 300 MHz): δ /ppm 2.52 (s, 3H, COCH₃), 7.20 (d, *J* = 8.7 Hz, 2H, ArH), 7.36-7.49 (m, 5H, ArH), 7.78-7.81 (m, 2H, ArH); ¹³C NMR (CDCl₃, 75 MHz): δ /ppm 26.3, 127.3, 128.6, 128.7, 129.5, 131.9, 133.7, 134.3, 144.7, 196.9.

(3-Nitrophenyl)(phenyl)sulfane (3h)⁶

Yellowish liquid

¹H NMR (CDCl₃, 300 MHz): δ /ppm 7.41-7.53 (m, 7H, ArH), 8.00-8.05 (m, 2H, ArH); ¹³C NMR (CDCl₃, 75 MHz): δ /ppm 120.9, 123.1, 128.9, 129.6, 129.8, 132.1, 133.4, 134.2, 140.6, 148.7.

(4-Chlorophenyl)(3-nitrophenyl)sulfane (3i)⁶

Yellow solid, mp 72-73 (Lit. mp 70-71 °C)

^1H NMR (CDCl_3 , 300 MHz): δ ppm 7.36-7.51 (m, 6H, ArH), 8.03-8.06 (m, 2H, ArH);

^{13}C NMR (CDCl_3 , 75 MHz): δ ppm 121.3, 123.4, 129.8, 130.0, 130.8, 134.4, 134.5, 135.1, 139.7, 148.6.

(3-Bromophenyl)(*p*-tolyl)sulfane (3j)⁷

Colourless liquid

^1H NMR (CDCl_3 , 300 MHz): δ ppm 2.36 (s, 3H, CH_3), 7.10–7.18 (m, 4H, ArH), 7.24–7.28 (m, 1H, ArH), 7.32–7.35 (m, 3H, ArH); ^{13}C NMR (CDCl_3 , 75 MHz): δ ppm 21.2, 122.9, 127.2, 129.0, 129.4, 130.2, 130.3, 131.1, 133.2, 138.5, 140.3.

(3-Chlorophenyl)(*p*-tolyl)sulfane (3k)⁸

Colourless liquid

^1H NMR (CDCl_3 , 300 MHz): δ ppm 2.36 (s, 3H, CH_3), 7.07–7.19 (m, 6H, ArH), 7.34 (dd, $J = 1.8$ and 6.3 Hz, 2H, ArH); ^{13}C NMR (CDCl_3 , 75 MHz): δ ppm 21.2, 126.1, 126.7, 128.3, 129.4, 129.9, 130.3, 133.3, 134.8, 138.6, 140.0.

(4-Methoxy-3-methylphenyl)(phenyl)sulfane (3l)

Colourless liquid

^1H NMR (CDCl_3 , 300 MHz): δ ppm 2.22 (s, 3H, CH_3), 3.87 (s, 3H, OCH_3), 6.85-7.35 (m, 8H, ArH); ^{13}C NMR (CDCl_3 , 75 MHz): δ ppm 16.1, 55.4, 110.8, 123.6, 125.6, 128.1, 128.9, 132.9, 136.3, 138.9, 158.1.

1,2-Bis(*p*-tolylthio)benzene (3m)⁹

White solid, mp 76-77 °C (Lit mp. 75.5 °C)

^1H NMR (CDCl_3 , 300 MHz): δ ppm 2.34 (s, 6H, CH_3), 7.04-7.05 (m, 4H, ArH), 7.13-7.17 (m, 4H, ArH), 7.28-7.31 (m, 4H, ArH); ^{13}C NMR (CDCl_3 , 75 MHz): δ ppm 21.1, 127.0, 130.1, 130.5, 132.5, 137.5, 137.8.

1,3-Bis(*p*-tolylthio)benzene (3n)¹

White solid, mp 84–85 °C

¹H NMR (CDCl₃, 300 MHz): δ ppm 2.34 (s, 6H, CH₃), 6.98–7.01 (m, 2H, ArH), 7.06–7.13 (m, 6H, ArH), 7.27 (dd, *J* = 1.5 and 6.3 Hz, 4H, ArH); ¹³C NMR (CDCl₃, 75 MHz): δ ppm 21.1, 126.6, 129.0, 129.3, 130.1, 132.9, 138.0, 138.7.

(4-Methoxyphenyl)(pentyl)sulfane (3o)¹⁰

Colourless liquid

¹H NMR (CDCl₃, 300 MHz): δ ppm 0.88 (t, *J* = 7.2 Hz, 3H, CH₃), 1.26–1.40 (m, 4H, CH₂–CH₂), 1.56–1.61 (m, 2H, CH₂), 2.81 (m, 2H, S–CH₂), 3.79 (s, 3H, OCH₃), 6.83 (dd, *J* = 2.1 and 6.6 Hz, 2H, ArH), 7.33 (dd, *J* = 2.1 and 6.6 Hz, 2H, ArH); ¹³C NMR (CDCl₃, 75 MHz): δ ppm 13.9, 22.2, 29.0, 30.8, 35.7, 55.3, 114.4, 126.9, 132.9, 158.6.

(3-Methoxyphenyl)(heptyl)sulfane (3p)

Colourless liquid

¹H NMR (CDCl₃, 300 MHz): δ ppm 0.85–0.90 (m, 3H, CH₃), 1.26–1.68 (m, 10H, –(CH₂)₅–), 2.91 (t, *J* = 7.2 Hz, 2H, S–CH₂), 3.79 (s, 3H, OCH₃), 6.696 (ddd, *J* = 0.9, 2.4 and 8.1 Hz, 1H, ArH), 6.85–6.91 (m, 2H, ArH), 7.16–7.25 (m, 1H, ArH); ¹³C NMR (CDCl₃, 75 MHz): δ ppm 14.0, 22.6, 28.8, 29.1, 31.3, 31.7, 33.3, 55.2, 111.2, 114.0, 120.8, 129.6, 138.5, 159.8.

References

1. Basu, B.; Mandal, B.; Das, S.; Kundu, S. *Tetrahedron Lett.* **2009**, *50*, 5523–5528. doi: 10.1016/j.tetlet.2009.07.076

2. Park, N.; Park, K.; Jang, M.; Lee, S. *J. Org. Chem.* **2011**, *76*, 4371–4378.
doi: 10.1021/jo2007253
3. Lin, Y.; Cai, M.; Fang, Z.; Zhao, H. *Tetrahedron* **2016**, *72*, 3335–3343.
doi: 10.1016/j.tet.2016.04.063
4. Jammi, S.; Sakthivel, S.; Rout, L.; Mukherjee, T.; Mandal, S.; Mitra, R.; Saha, P.; Punniyamurthy, T. *J. Org. Chem.* **2009**, *74*, 1971–1976.
doi: 10.1021/jo8024253
5. Fernandez–Rodriguez, M. A.; Shen, Q.; Hartwig, J. F. *Chem. Eur. J.* **2006**, *12*, 7782–7796. doi: 10.1021/jo0003347
6. Wu, W. -Y.; Wang, J. -C.; Tsai, F. -Y. *Green. Chem.* **2009**, *11*, 326–329.
doi: 10.1039/B820790A
7. Campbell, J. R. *J. Org. Chem.* **1962**, *27*, 2207–2209.
doi: 10.1021/jo01053a504
8. Sengupta, D.; B, Basu. *Org. Med. Chem. Lett.* **2014**, *4*:17.
Doi: 10.1186/s13588-014-0017-7
9. Nakayama, J.; Tajiri, T.; Hoshino, M. *Bull. Chem, Soc. Jpn.* **1986**, *59*, 2907–2908. doi: 10.1246/bcsj.59.2907
10. Suter, C. M.; Hansen, H. L. *J. Am. Chem. Soc.* **1932**, *54*, 4100–4104.
doi: 10.1021/ja01349a039