A highly active nickel-fibre complex as a catalyst for the Heck reaction

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A new amidoxime fibre–nickel catalyst (AOFs–Ni(0)) was synthesised by a coordination and reduction reaction. The X-ray diffraction patterns indicated that the Ni(II) ions were reduced to Ni(0). The scanning electron microscope image showed that the Ni(0) particles which were reduced *in situ* had a diameter of about 300 nm. This catalyst demonstrated high activity in the Heck coupling reaction of aryl iodine and conjugated alkenes without the protection of an inert atmosphere.

Keywords: amidoxime fibres, fibre-nickel complex, heterogeneous catalyst, Heck reaction

The Mizoroki–Heck reaction has become one of the most useful carbon–carbon bond-forming reactions in organic synthesis and it has been intensively developed from both synthetic and mechanistic points of view.^{1–4} The reaction has been applied in many areas, including the synthesis of bioactive compounds, natural products, drug intermediates, fine chemicals, UV absorbers, antioxidants and industrial applications.^{5–10}

Although palladium is the most active catalyst in these carbon-carbon bond forming reactions, nickel was considered the most promising replacement of palladium among the inexpensive transition for metals. The study of nickel catalysed Heck reactions is important in an industrial context. In early studies, NiCl₂(PPh₂) was used to catalyse the reaction of aryl halides with the olefins.¹¹⁻¹² Kelkar¹³ reported the vinylation of bromobiphenyls using NiCl₂ (PPh₃) in the presence of an inorganic base. However, the homogeneous catalysts suffer from the drawbacks of difficult separation and limited lifetime.¹⁴⁻¹⁶ In addition, phosphine or amine ligands are often necessary and the reactions are often sensitive to oxygen.¹⁷ To overcome these problems, heterogeneous catalysts were tentatively employed.18-19 For example, Yu20 reported that polyaniline/ Pd(0) nanocomposites could be a good catalyst for the Heck reaction.

In this paper, we report a new amidoxime fibre–nickel complex (AOFs–Ni(0)) catalyst for the Heck reaction. Scheme 1 shows the synthetic route of AOFs–Ni(0). The AOFs can easily be obtained by the reaction of polyacrylonitrile (PAN) and NH₂OH. The –NH₂ and –OH in AOFs have a high coordinating ability with metal cations.^{21–22} A new amidoxime fibre–nickel catalyst was then synthesised by the 'coordination–reduction' reaction between the amidoxime groups in the fibres and the Ni(II) ions.

The catalytic activity of the AOFs–Ni(0) was tested by using them in the Heck reaction. The results of the AOFs–Ni(0) catalysed Heck reaction showed that the reaction could be carried out under mild conditions without the protection of an inert atmosphere. In addition, the catalyst is environmentally-friendly since phosphine or amine ligands are not used. This method is an efficient alternative for the nickel-catalysed Heck reactions.

Results and discussion

Characterisation of the catalyst

The SEM pattern (Fig. S1 in the ESI) of AOFs–Ni(0) showed that Ni particles had a uniform distribution on the surface of the AOFs and the average size of the Ni particles was about 300 nm. The characteristic peaks of Ni(0) at the 2 θ angles of 46.2° was observed in the XRD pattern (Fig. S2 in the ESI) of AOFs–Ni(0), indicating that Ni(II) was reduced to nickel particles on the surface of the AOFs.

Heck reaction of iodobenzene with phenylethylene

Table 1 (entries 1–4) showed the Heck reaction of iodobenzene with phenylethylene at different temperatures. It can be seen that the reaction temperature has some influences on the catalytic performance. Using DMF as a solvent and K_2CO_3 as a base, the Heck reaction could be carried out at 100 °C with a yield of 78%. When the temperature was increased from 100 °C to 130 °C, the yield increased although when the temperature was above 110 °C, the yield decreased. Hence 110 °C was selected as the optimum reaction temperature.

Different solvents and bases can affect this reaction. We examined DMF, DMSO, i-PrOH and EtOH (Table 1, entries 5–8) in the reaction. The corresponding yield was 95%, 95%, 12%, 13%. Hence DMF is the best solvent for this reaction. We also examined different bases in this reaction, including Bu_3N , Et_3N and K_2CO_3 . The corresponding yield was 40%, 39% and 80% (Table 1, entries 9–11). Hence we choose K_2CO_3 for this reaction.

In Table 1 entries 12–15 we can see the best reaction time is 9 h. We explored the reaction of iodobenzene with phenylethylene catalysed by different amounts of Ni/AOFs ranging from 0.98 mol%, 1.47 mol% and 1.96 mol% at 110 °C. The results are listed in Table 1 (entries 16–18). It can be seen that the best amount of catalyst is 1.47 mol%.

Heck reaction of iodobenzene with acrylic acid

Table 2 (entries 1–4) shows the Heck reaction of iodobenzene with acrylic acid at different temperatures. Using DMF as the solvent and tributylamine as the base, 120 °C was selected as the optimum reaction temperature. We investigated the influence of different alkaline reagents on the Heck reaction. The results are





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 Table 1 Effects of the reaction temperature, catalyst amount, solvent and base on catalytic performance of the Heck reaction of iodobenzene with phenylethylene

	AOFs-Ni(0) Base, Temperature solvent		
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Entry	Temperature/°C	Solvent	Base	AOFs-Ni(0)/ mol%	Time/h	Yield [/] % ^a
1	100	DMF	K, CO3	1.47	9	78
2	110	DMF	K ₂ CO ₃	1.47	9	94
3	120	DMF	K ₂ CO ₃	1.47	9	90
4	130	DMF	K ₂ CO ₃	1.47	9	80
5	110	DMF	K ₂ CO ₃	1.47	9	94
6	110	DMS0	K ₂ CO ₃	1.47	9	94
7	110	i-PrOH	K ₂ CO ₃	1.47	9	12
8	110	EtOH	K ₂ CO ₃	1.47	9	14
9	110	DMF	Bu ₃ N	1.47	9	40
10	110	DMF	Et ₃ N	1.47	9	39
11	110	DMF	K,CO3	1.47	9	95
12	110	DMF	K ₂ CO ₃	1.47	7	54
13	110	DMF	K ₂ CO ₃	1.47	8	60
14	110	DMF	K ₂ CO ₃	1.47	9	94
15	110	DMF	K ₂ CO ₃	1.47	10	73
16	110	DMF	K ₂ CO ₃	0.98	9	78
17	110	DMF	K,CO3	1.47	9	94
18	110	DMF	K,CO,	1.96	9	94

^aYield based on the iodobenzene used.

 Table 3 The Heck reaction of substituted aryl halides with conjugated alkenes catalysed by AOFs-Ni(0)

R	→_I + <i>//</i>	$R_2 = \frac{AC}{DMF}$	PFs-Ni(0) K ₂ CO ₃ /Bu ₃ N R ₁	
Entry	R ₁	R ₂	Products	Yield/%
1	Н	Ph	A	99
2	4-C00H	Ph	В	94
3	4-N0 ₂	Ph	C	85
4	4-H ₃ CO	Ph	D	68
5	Н	-C00H	E	85
6	4-N0 ₂	-C00H	G	86
7	4-H ₃ C0	-C00H	F	93
8	4-C00H	-C00H	H	73

listed in Table 2 entries 5–7. It can be seen that tributylamine is preferred and from entries 8–11 the best solvent is DMF. Entries 12–15 show that 8 h is the best reaction time.

Heck reaction of aryl halides derivatives with conjugated alkenes In order to examine the catalytic activity of the AOFs–Ni(0) catalyst with other substrates, some related experiments are shown in Table 3. This shows that the Heck reaction of acrylic acid or styrene with aryl iodides can be carried out efficiently with a relatively high yield. It was found that the yields were generally high for both electron-donating and electronwithdrawing aryl iodides although the latter gave a higher yield than electron-donating aryl iodides.

Recycling of the catalyst

The catalyst can be easily separated from the reaction mixture by filtration during the work-up procedure. The results were summarised in Table 4 and Table 5.
 Table 2 Effects of the reaction temperature, catalyst amount and base on catalytic performance of the Heck reaction of iodobenzene and acrylic acid



Temperature/°C	Base	solvent	Time/h	Yield/% ^a
100	Bu ₃ N	DMF	8	15
110	Bu ₃ N	DMF	8	20
120	Bu ₃ N	DMF	8	83
130	Bu ₃ N	DMF	8	80
120	Bu ₃ N	DMF	8	83
120	Et ₃ N	DMF	8	80
120	K,CO3	DMF	8	21
120	Bu ₃ N	DMF	8	83
120	Bu ₃ N	DMS0	8	55
120	Bu ₃ N	EtOH	8	20
120	Bu ₃ N	Acetone	8	17
120	Bu ₃ N	DMF	6	20
120	Bu ₃ N	DMF	7	40
120	Bu ₃ N	DMF	8	83
120	Bu ₃ N	DMF	9	57
	Temperature/°C 100 110 120 130 120 120 120 120 120 120 120 120 120 12	Temperature/°C Base 100 Bu ₃ N 110 Bu ₃ N 120 Bu ₃ N 130 Bu ₃ N 120 Bu ₃ N	Temperature/°C Base solvent 100 Bu_3N DMF 110 Bu_3N DMF 120 Bu_3N DMF 130 Bu_3N DMF 120 K_2CO_3 DMF 120 Bu_3N </td <td>Temperature/°C Base solvent Time/h 100 Bu_3N DMF 8 110 Bu_3N DMF 8 120 Bu_3N DMF 8 130 Bu_3N DMF 8 120 Bu_3N DMF 8 120 Bu_3N DMF 8 120 Bu_3N DMF 8 120 Et_3N DMF 8 120 Bu_3N Acetone 8 120 Bu_3N DMF 6 120 Bu_3N DMF 7 120 Bu_3N DMF 8 120 Bu_3N DMF 8 120</td>	Temperature/°C Base solvent Time/h 100 Bu_3N DMF 8 110 Bu_3N DMF 8 120 Bu_3N DMF 8 130 Bu_3N DMF 8 120 Bu_3N DMF 8 120 Bu_3N DMF 8 120 Bu_3N DMF 8 120 Et_3N DMF 8 120 Bu_3N Acetone 8 120 Bu_3N DMF 6 120 Bu_3N DMF 7 120 Bu_3N DMF 8 120 Bu_3N DMF 8 120

^aYield based on the iodobenzene used.

 Table 4 Successive trials using recycled AOFs-Ni(0) catalysts in the reaction of iodobenzene and phenylethylene^a

Recycling times	Time/h	Yield/%
1st recycle	9	88
2nd recycle	9	75
3rd recycle	9	65
4th recycle	9	40

^aAll reactions were carried out with iodobenzene (9 mmol), phenylethylene (15 mmol), K₂CO₃ (30 mmol), AOFs-Ni(0) (1.47 mol %) and DMF (6 mL) at 110 °C in the air.

Table 5 Successive trials using recycled AOFs-Ni(0) catalysts in the reaction of iodobenzene and acrylic acid^a

Recycling times	Time/h	Yield/%
1st recycle	8	88
2nd recycle	8	80
3rd recycle	8	75
4th recycle	8	50

 a All reactions were carried out with iodobenzene (9 mmol), acrylic acid (15 mmol), Bu $_{\rm s}$ N (30 mmol), AOFs–Ni(0) (1.47 mol%) and DMF (6 mL) at 120 °C in the air.

It could be seen that the catalytic activity of AOFs–Ni(0) decreased a little after the second recycling. But at the fourth recycling the yield decreased considerably. This was ascribed to Ni leaching.

Experimental

Materials

Reagents were purchased from Beijing Chemical Reagents Co. (Beijing, P.R. China) and Sinopharm Chemical Reagent Co., Ltd (Shanghai, P.R. China). The PAN fibres were provided by the Jilin Carbon Co., Ltd. (Jilin, P.R. China).

The morphologies of sample fibres was observed by SEM (Hitachi S-4800 field-emission). The phase structures of sample fibres were examined using a Philips X' Pert PRO SUPER (XRD) with CuK α radiation in step-scan mode. Reaction products were characterised by their ¹HNMR spectra (Bruker ARX-300 spectrometer), GC-MS spectra (GCMS-QP2010 Hra 5MS/NP) and HRMS spectra (solariX 70 FT-MS Bruker, Germany).

Preparation of the catalysts

The PAN fibres (1.0 g) were first immersed in 100 mL 1 mol L⁻¹ NH₂OH aqueous solution at 70 °C for 1.5 h to introduce $-NH_2$ and -OH groups onto the fibre surface. The resultant fibres were termed amidoxime fibres (AOFs). Subsequently, the AOFs were rinsed with distilled water and then immersed in 100.0 mL 0.129 mol L⁻¹ NiSO₄ aqueous solution at about 45 °C for 1 h to allow the AOFs to coordinate with Ni²⁺ ions. Then the fibres were further immersed into 50.0 mL 25% N₂H₄•H₂O aqueous solution at room temperature for 30 min to reduce the Ni(II). The products were rinsed with distilled water and dried, to give the black AOFs–Ni(0) catalysts.

Analysis of nickel content in AOFs-Ni(0) catalysts

AOFs–Ni(0) complex was immersed in nitric acid solution (50 mL, 50% HNO_3) and the nickel was dissolved. The content of Ni in AOFs–Ni(0) surface was then analysed by a coordination titration method with EDTA as the indicator, and the result was 1.47 mol%

Typical procedure for the Heck reaction

In a typical reaction, aryl halides (9 mmol), phenylethylene (15 mmol) (or acrylic acid), tributylamine (30 mmol) and DMF (10 mL) were placed in a round-bottomed flask with 1.47 mol% AOFs–Ni(0) as catalyst. The reaction was carried out in a temperature controlled oil bath. After completion of the reaction, the mixture was cooled to room temperature. Then the AOFs–Ni(0) was separated from the mixture by filtration and washed sequentially with hot ethanol and reused in the next reaction. The filtrate was extracted with ethyl acetate (30 mL) and washed with distilled water (3×15 mL). The solvent was then removed by rotary evaporation to give a crude product. The crude product was purified by column chromatography on H 60-silica powder using mixed solvent (petroleum ether/ethyl acetate = 3/1). The pure products were characterised by melting point, ¹H NMR, HRMS and GC-MS spectroscopy.

Diphenylethene (**a**): m.p. 124–126 °C (lit.²³ 123–125 °C). ¹H NMR (300 M Hz, CDCl₃): δ 7.12 (s, 2H), 7.26–7.53(m, 10H). GC-MS (5MS/ NP, CH₃OH): $C_{14}H_{12}$ (M = 180).

1-methoxy-4-(styryl)benzene (**b**): m.p. 154–157 °C (lit.²⁴ 155–157 °C). ¹H NMR (300 M Hz, CDCl₃): δ 3.829(s, 3H), 6.90(d, J = 8.4 Hz, 2H), 7.00–7.47(m, 10H). GC-MS (5MS/NP, CH₃OH): C₁₅H₁₄O (M = 210).

1-nitro-4-(styryl)benzene (c): m.p. 132–134 °C (lit.²⁵ 132–133 °C). ¹H NMR (300 M Hz, CDCl₃): δ 8.22 (d, J = 8.1 Hz, 2H), 7.63(d, J = 8.1 Hz, 2H), 7.11–7.54(m, 7H); HRMS (CH₃OH): C₁₄H₁₁O₂ N ([M + H]⁺: calcd: 226.08625; found: 226.08827).

l-carboxyl-4-(styryl)benzene (**d**): m.p. 249–251 °C (lit.²⁶ 250–253 °C). ¹H NMR (300 M Hz, CDCl₃): δ 8.08 (s, 2H), 7.60(d, *J* = 7.5 Hz, 2H), 7.16–7.53(m, 7H); HRMS (CH₃OH): C₁₅H₁₂O₂ ([M – H]⁻: calcd: 223.07535; found: 223.07354).

Cinnamic acid (**f**): m.p. 133–134 °C (lit.²⁷ 133–134 °C). ¹HNMR (300 M Hz, CDCl₃): δ 6.46 (d, J = 15.9 Hz, 1H), 7.79 (d, J = 15.9 Hz, 1H), 7.16–7.55(m, 5H); HRMS (CH₃OH): C₉H₈O₂ ([M – H]⁻: calcd: 147.04405; found: 147.03919).

4-nitrocinnamic acid (g): HRMS (CH₃OH): $C_9H_7O_4N$ ([M – H]⁻: calcd: 192.02913; found: 192.02621).

4-methoxycinnamic acid (**h**): m.p. 174–175 °C (lit.²⁸ 175 °C). ¹HNMR (300 M Hz, CDCl₂): δ 3.84(s, 3H), 6.31(d, *J* = 15.9 Hz, 1H), 7.73 (d,

J = 15.6 Hz, 1H), 6.90–7.51(m, 4H); HRMS (CH₃OH): C₁₀H₁₀O₃ ([M – H]⁻: calcd: 177.05462; found: 177.05103).

4-carboxycinnamic acid (i): m.p. 254–258 °C (lit.²⁷ 253–259 °C). HRMS (CH₃OH): $C_{10}H_{10}O_3$ ([M – H]⁻: calcd: 191.03388; found: 191.03094).

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Electronic Supplementary Information

The SEM pattern and the XRD pattern of AOFs–Ni(0), are available through:

stl.publisher.ingentaconnect.com/content/stl/jcr/supp-data

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