

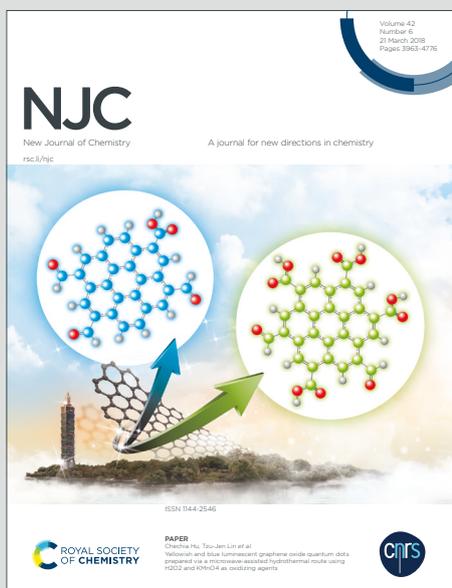
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ARTICLE

Design, preparation and characterization of aerogel NiO-CuO-CoO/SiO₂ nanocomposite as a reusable catalyst for C-N cross-coupling reaction

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Abstract

Aerogels are porous, non-crystalline solid materials with high specific surface space, plentiful three-dimensional (3D) porous construction, ultra-low density and significant porosity. The aerogel nanocomposite is produced using sol-gel and supercritical drying processes. CO₂ supercritical drying (SCD) is the most powerful process, ensuring optimal product properties such as high porosity, low density, and high thermal conductivity. On this account, we used the CO₂ supercritical drying method to produce NiO-CuO-CoO/SiO₂ nanocomposite aerogels and applied it as a reusable catalyst for the C-N cross-coupling reaction (Buchwald-Hartwig amination). Powerful catalytic activity for the C-N cross-coupling reaction was obtained for the new nanocomposite aerogel, that is, NiO-CuO-CoO/SiO₂. The catalyst was characterized by X-ray Powder Diffraction (XRD), field emission scanning electron microscopy (FE-SEM), energy-dispersive X-ray spectroscopy (EDS), elemental mapping and Brunauer-Emmett-Teller (BET). Also, organic compounds were identified by melting point, Fourier-transform infrared spectroscopy (FT-IR) and hydrogen-1 nuclear magnetic resonance (¹H NMR) analyses.

Keyword: Buchwald-Hartwig amination, C-N coupling, carbon-nitrogen bond, nanocatalyst, nanocomposite, composite aerogel, CO₂ supercritical drying.

1. Introduction

Investigation on cross-coupling of amines with aryl halides or pseudohalides to form C-N bonds has improved the universal knowledge about the preparation of aromatic amines^{1,2}. Nitrogen-containing compounds have many applications in agrochemicals, coordination, and biological chemistry³⁻⁶. Nitrogen-based compounds are key construction blocks in the fields of medicinal chemistry⁷ and natural products synthesis⁸.

General and reliable protocols have been produced as a result of advancements of in the production of enhanced catalysts and precatalysts⁹⁻¹¹. Since 1983, there has been a growth in the number of published articles and patents on carbon-nitrogen coupling reactions¹².

Recently, the application of transition metals as heterogeneous catalysts has been increasing in coupling reactions¹³. The reagents and methods include transition metals are significant in modern

organic synthesis because of that cause progress of the difficult reaction^{14,15}.

In most published cross-coupling methods, the C-N bond formation reaction has been applied to homogeneous palladium with different ligands¹⁶⁻²¹. Palladium is not the perfect catalyst as its toxicity, a high price, moisture-sensitive nature and hard catalyst recovery. Therefore, the use of toxic and expensive phosphine ligands was necessary for the palladium catalytic reaction^{22,23}. Thus, producing a simple and safe method for the preparation of promoted catalysts is necessary²⁴. Also, devising methods for the reaction of C-N bond formation can be an attractive challenge. Various methods have been reported for the C-N bond formation reaction in the presence of different catalysts including CuI with DPPT phosphine ligand²⁵, CuI with cesium fluoride²⁶, Pd(OAc)₂²⁷ and Palladium complexes of 2-formylpyridine thiosemicarbazone²⁸. However, some of the reported methods have some drawbacks including long reaction time, use of noxious and non-reusable catalysts and undesirable reaction conditions.

Recently, nanoporous materials have attracted wide attention as a large surface space area nanocatalyst. The large space porous created a great area to the difference of applications, for example, drug delivery, nanoreactor and nanocatalyst²⁹⁻³². Aerogels are porous non-crystallines with high special surface space, high porosity,

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plentiful three-dimensional (3D) porous construction, and ultra-low density^{33,34}.

Due to the importance of the aerogel catalysts prepared by the SCD method and the resulted diphenylamines, we aim to prepare a nanoporous structure by the sol-gel method and CO₂ supercritical drying (SCD) technique for the construction of NiO-CuO-CoO/SiO₂ nanocomposite aerogels. In addition, the catalysis performance of this nanocomposite in the reaction of C–N bond formation has been studied. Therefore, NiO-CuO-CoO/SiO₂ nanocomposite aerogel is an encouraging catalyst for the synthesis of diphenylamines.

2. Experimental

2.1. Materials and apparatus

All the commercially available reagents were purchased from Merck and Sigma-Aldrich Chemical Company in high purity. All the reagents were used without any further purification. If needed, the products were purified via a thin-layer chromatography process to obtain the corresponding products in 69–98% yields. Hydrogen-1 nuclear magnetic resonance (¹H NMR) spectra were recorded in CDCl₃ on a Bruker DRX-400 spectrometer with tetramethylsilane (TMS) as an internal reference. IR spectra were recorded as KBr pellets on a Nicolet FT-IR spectrophotometer. A BANDELIN ultrasonic HD 3200 with probe model KE76, with a diameter of 6 mm, was used for homogenizing the reaction mixture. Melting points were measured by Yanagimoto micro melting point equipment. XRD patterns were reported by an X'Pert Pro (Philips) apparatus with 1.54 Ångström wavelengths of the X-ray beam and Cu anode material. Nitrogen adsorption-desorption isotherms were estimated using a BELSORP-mini II apparatus (Microtrac BEL, Japan) at 77 K. The specific surface area of the nanocomposite aerogels samples was measured by the Brunauer-Emmett-Teller (BET) method. The field emission scanning electron microscope (FE-SEM) of nanoparticles was performed on Zeiss that operated at a 15 kV accelerating voltage.

2.2. General procedure for the preparation of nanocomposite aerogels

To prepare Ni⁺² ionic solution, Co⁺² and Cu⁺² were added to 1 mmol of copper (II) chloride, nickel (II) chloride and cobalt (II) chloride and were dispersed in 30 mL distilled water through sonication for 10 minutes. Then, the silica-sol was prepared by mixing tetraethyl orthosilicate (TEOS), distilled water and ethanol in the mole ratio of 1:4:8 at 50 °C for 30 min. The ionic solution and silica-sol were then combined in the mole ratio of 1:1 and the pH was set to 3.0 by adding hydrochloric acid (HCl, 1.2 M) to silica-sol. The pH value of the combined solution was set to 11 by adding liquid ammonia (NH₃, 2.5 M), after about a minute, the reaction container was placed in a constant environment. The reaction mixture became a composite wet gel after 45 minutes. The wet gel was exchanged with ethanol and then aged in ethanol solvent for 3 days to enhance gel firmness.

2.2.3. General procedure for CO₂ supercritical drying (SCD) of NiO-CuO-CoO/SiO₂ nanocomposite wet gels

The wet gel exchanged with liquid CO₂ was dried via cold SCD at 35 °C and 7.3 MPa for 3 h, followed by venting of CO₂ gas for 24 h to obtain nanocomposite aerogels. Then, the dried gel was heated to 500 °C for 3 hours to stabilize the nanoparticles.

2.3. General procedure for the cross-coupling of aniline with aryl halides

In a round-bottomed flask equipped with a magnetic stirrer, aryl halide (1 mmol), aniline (1.2 mmol), catalyst (3 mg, NiO-CuO-CoO/SiO₂ nanocomposite aerogels) and KOH (3 mmol) were stirred in 5 mL DMF under air atmosphere at 130 °C. The progress of the reaction was monitored by Thin-layer chromatography (TLC). After completion of the reaction, ethyl acetate (15 ml) was added and the catalyst was separated by filtration. The organic layer was washed with water (3 × 10 ml) and dried over anhydrous Na₂SO₄. The product was isolated by column chromatography. The recovered catalyst was washed with ethanol and water and dried at 80 °C for further use.

4-(Phenylamino)benzotrile (**3a**); Yellow solid; m.p.: 97–98 °C (Lit. m.p 97–98 °C)³⁵; IR (KBr) ν = 3375, 3086, 3035, 2221, 1590, 745, ¹H NMR (400 MHz, CDCl₃) δ 7.43 (d, J = 8.5 Hz, 2H), 7.31 (t, J = 8.5 Hz, 2H), 7.11 (d, J = 8.5 Hz, 2H), 6.96 (t, J = 8.5 Hz, 1H), 6.82 (d, J = 8.5 Hz, 2H), 5.96 (br, 1H).

4-Nitro-*N*-phenylaniline (**3b**); Orange solid; m.p.: 133–135 °C (Lit. m.p 133–134 °C)³⁶; IR (KBr) ν = 3380, 3099, 3029, 1954, 1594, 1517, 1313, 741, ¹H NMR (400 MHz, CDCl₃) δ 8.3 (d, J = 8.5 Hz, 2H), 7.40 (t, J = 8.5 Hz, 2H), 7.14–7.23 (m, 3H), 6.95 (d, J = 8.5 Hz, 2H), 6.28 (br, 1H).

4-Bromo-*N*-phenylaniline (**3c**); White solid; m.p.: 85–86 °C (Lit. m.p 84–86 °C)³⁷; IR (KBr) ν = 3390, 3059, 3020, 1931, 1581, 1078, 688, ¹H NMR (400 MHz, CDCl₃) δ 7.29–7.35 (m, 4H), 7.13–7.22 (m, 5H), 5.72 (br, 1H).

1-(4-(Phenylamino)phenyl)ethan-1-one (**3d**); Yellow solid; m.p.: 94–95 °C (Lit. m.p 93–95 °C)³⁸; IR (KBr) ν = 3385, 3041, 2922, 1682, 1591, 1495, 1266, 747, ¹H NMR (400 MHz, CDCl₃) δ 7.55 (d, J = 8.0 Hz, 2H), 7.35 (t, J = 8.0 Hz, 2H), 7.20 (d, J = 4.0 Hz, 2H), 7.11 (t, J = 8.0 Hz, 1H), 6.99 (d, J = 8.0 Hz, 2H), 6.22 (br, 1H), 2.52 (s, 3H).

Methyl 4-(Phenylamino)benzoate (**3e**); Yellow solid; m.p.: 110–111 °C (Lit. m.p 109–111 °C)³⁹; IR (KBr) ν = 3390, 3035, 2951, 1720, 1592, 1516, 1111, 1282, ¹H NMR (400 MHz, CDCl₃) δ 7.20 (t, J = 8.5 Hz, 2H), 6.87–6.92 (m, 7H), 5.74 (br, 1H), 3.85 (s, 3H).

N,*N*'-Diphenylbenzene-1,4-diamine (**3f**); white solid; m.p.: 152–153 °C (Lit. m.p 152–154 °C)⁴⁰; IR (KBr) ν = 3380, 3034, 1506, 1517, 1462, 1315, 742, ¹H NMR (400 MHz, CDCl₃) δ 7.37 (t, J = 8.0 Hz, 4H), 7.16–7.22 (m, 8H), 7.11 (t, J = 12.0 Hz, 2H), 5.44 (br, 2H).

3-Chloro-*N*-phenylaniline (**3g**); Yellow Oil; IR (KBr) ν = 3392, 3058, 1596, 1478, 693, ¹H NMR (400 MHz, CDCl₃) δ 8.69 (t, J = 12.0 Hz, 2H), 8.39 (t, J = 16.0 Hz, 1H), 7.55 (d, J = 8.5 Hz, 2H), 7.45 (s, 1H), 7.37 (t, J = 8.5 Hz, 1H), 7.13–7.22 (m, 2H), 6.13 (br, 1H).

Diphenylamine (**3h**); White solid; m.p.: 52–53 °C (Lit. m.p 52–53 °C)⁴¹; IR (KBr) ν = 3382, 3037, 1941, 1596, 1490, 1315, 745, ¹H NMR (400 MHz, CDCl₃) δ 7.36 (t, J = 8.5 Hz, 4H), 7.16 (d, J = 8.5 Hz, 4H), 7.03 (t, J = 8.5 Hz, 2H), 5.72 (br, 1H).

N-Phenylnaphthalen-1-amine (**3i**); Yellow solid; m.p.: 65-66 °C (Lit. m.p 65.9 °C)⁴²; IR (KBr) $\nu = 3391, 3039, 1594, 1494, 746$, ¹H NMR (400 MHz, CDCl₃) δ 8.70 (d, $J = 12.0$ Hz, 1H), 8.40 (d, $J = 16.0$ Hz, 1H), 7.55 (d, $J = 8.0$ Hz, 1H), 7.32-7.38 (m, 4H), 7.11-7.22 (m, 4H), 6.94 (t, $J = 8.0$ Hz, 1H), 5.90 (br, 1H).

3-Methyl-*N*-phenylaniline (**3j**); Yellow solid; m.p.: 31-32 °C (Lit. m.p 30-31 °C)⁴³; IR (KBr) $\nu = 3387, 3064, 1594, 1379, 1379, 1331, 878, 742, 692$, ¹H NMR (400 MHz, CDCl₃) δ 7.23 (t, $J = 4.0$ Hz, 2H), 7.13 (t, $J = 8.0$ Hz, 1H), 7.04 (d, $J = 4.0$ Hz, 2H), 6.88-6.89 (m, 3H), 6.76 (d, $J = 12.0$ Hz, 1H), 5.65 (br, 1H), 2.31 (s, 3H).

4-Methyl-*N*-phenylaniline (**3k**); Yellow solid; m.p.: 89-90 °C (Lit. m.p 89-90 °C)⁴¹; IR (KBr) $\nu = 3399, 3042, 2920, 1593, 1497, 820$, ¹H NMR (400 MHz, CDCl₃) δ 7.20 (d, $J = 8.0$ Hz, 2H), 7.11 (d, $J = 8.0$ Hz, 2H), 7.01-7.03 (m, 4H), 6.88 (t, $J = 4.0$ Hz, 1H), 5.68 (br, 1H), 2.43 (s, 3H).

4-Methoxy-*N*-phenylaniline (**3l**); White solid; m.p.: 105-106 °C (Lit. m.p 104-106 °C)⁴⁴; IR (KBr) $\nu = 3391, 3040, 2930, 1593, 1499, 1309, 820$, ¹H NMR (400 MHz, CDCl₃) δ 7.20 (t, $J = 8.5$ Hz, 2H), 6.87-6.92 (m, 7H), 5.74 (br, 1H), 3.85 (s, 3H).

3. Results and discussion

3.1. Preparation and characterization of catalyst

The NiO-CuO-CoO/SiO₂ nanocomposite aerogels were prepared by the sol-gel method and the CO₂ supercritical drying (SCD) technique. This is described in Fig. 1. At the first step, metal precursors were manufactured in situ on the surfaces of silica sol-gel from a mixed solution of TEOS, Ni²⁺, Cu²⁺, and Co²⁺ by a sol-gel method. The gels exchanged with ethanol were dried via CO₂ supercritical drying (SCD).

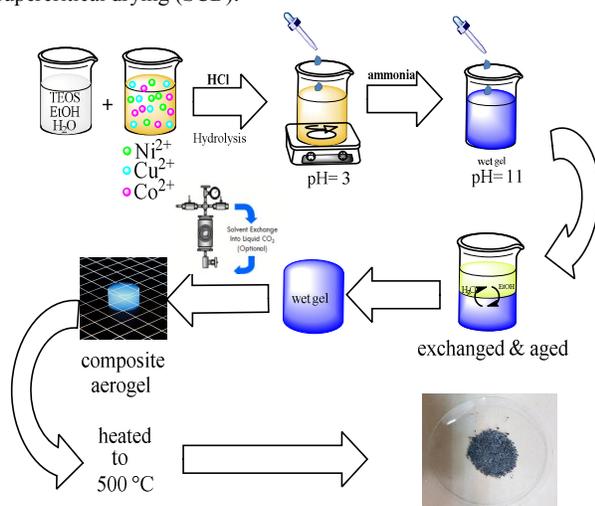


Fig. 1. Preparation of the NiO-CuO-CoO/SiO₂ nanocomposite aerogels

The crystalline structure of the SiO₂ aerogels and NiO-CuO-CoO/SiO₂ nanocomposite aerogels was also studied by XRD characterization. There was no visible crystal diffraction peak in the XRD pattern. Fig. 2a displays a wide peak that could be related to the amorphous nature of the SiO₂ aerogels. Obviously, no

characteristic peaks of copper, nickel and cobalt were seen observed in the XRD pattern of SiO₂ aerogels (Fig. 2a). The XRD diagram displays the related peaks of NiO-CuO-CoO/SiO₂ nanocomposite aerogels at 36, 43 and 62 °2-theta (Fig. 2b).

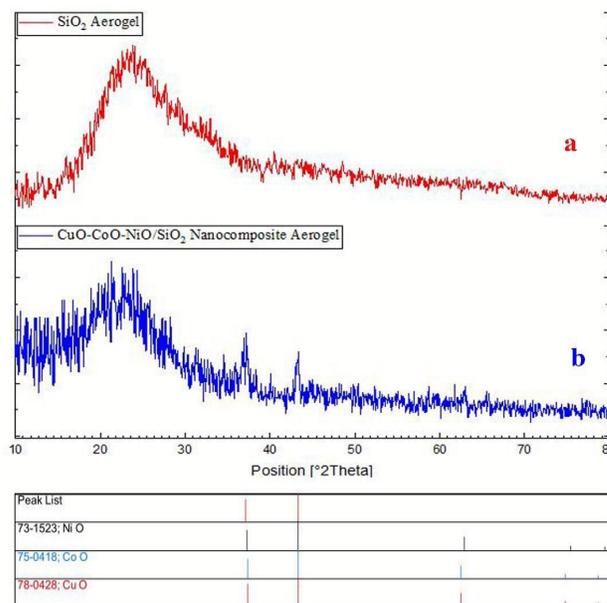
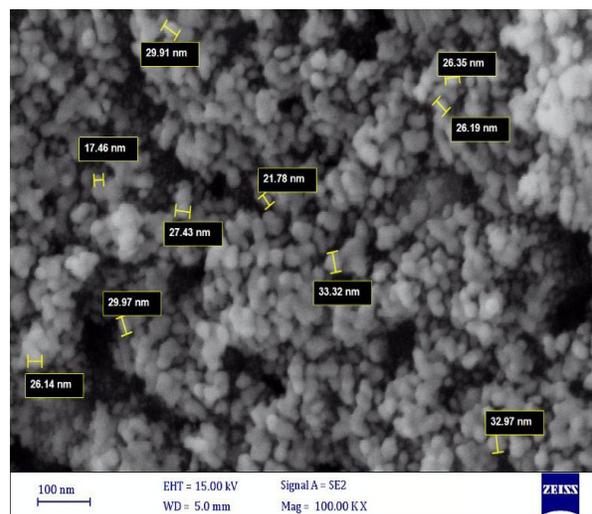


Fig. 2. XRD patterns: (a) SiO₂ aerogels, (b) NiO-CuO-CoO/SiO₂ nanocomposite aerogels

The field emission scanning electron microscopy (FE-SEM) images of NiO-CuO-CoO/SiO₂ nanocomposite aerogels showed the surface morphologies of the catalysts (Fig. 3). The nanoparticles of the transition metal-oxides with a particle size arrangement of 17–33 nm were well-dispersed in pores or on network frames of the nanocomposite aerogels (Fig. 3). Also, FE-SEM images depicted cavities in the nanocomposite structure. Moreover, the size distribution of aerogels nanocomposite particles as small as 25.82 nm with a standard deviation of 9.83 nm was achieved (Fig. 4).



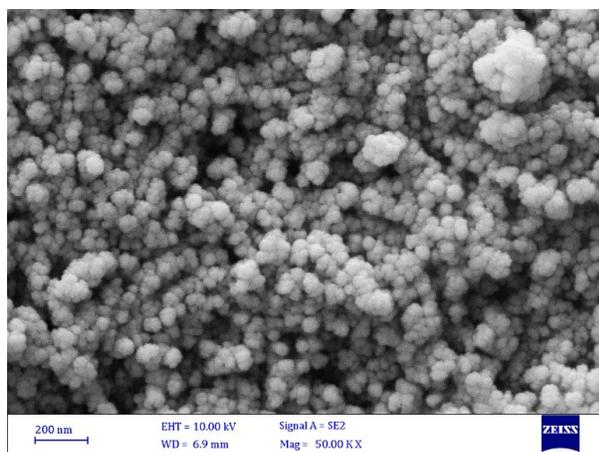


Fig. 3. FE-SEM images of NiO-CuO-CoO/SiO₂ nanocomposite aerogels

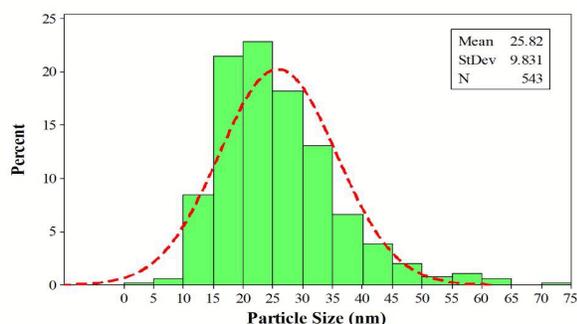


Fig. 4. Histograms representing the size distribution of NiO-CuO-CoO/SiO₂ nanocomposite aerogels

In addition, the elemental energy-dispersive X-ray (EDS) spectrum of the NiO-CuO-CoO/SiO₂ nanocomposite aerogels was investigated. The EDS spectrum confirms the presence of Ni, Co, Cu, O and Si in the matrix (Fig. 5).

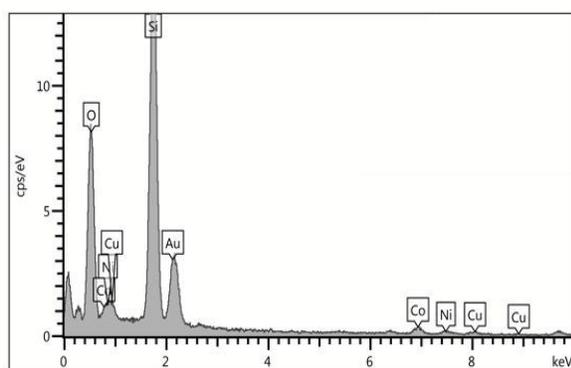


Fig. 5. EDS spectrum of the NiO-CuO-CoO/SiO₂ nanocomposite aerogels

Energy-dispersive X-ray spectrum of elemental mapping pictures of NiO-CuO-CoO/SiO₂ nanocomposite aerogels displayed in Fig. 6 reveal that the Ni, Co, Cu, O, and Si elements scatter homogeneously across the whole nanocomposite aerogels.

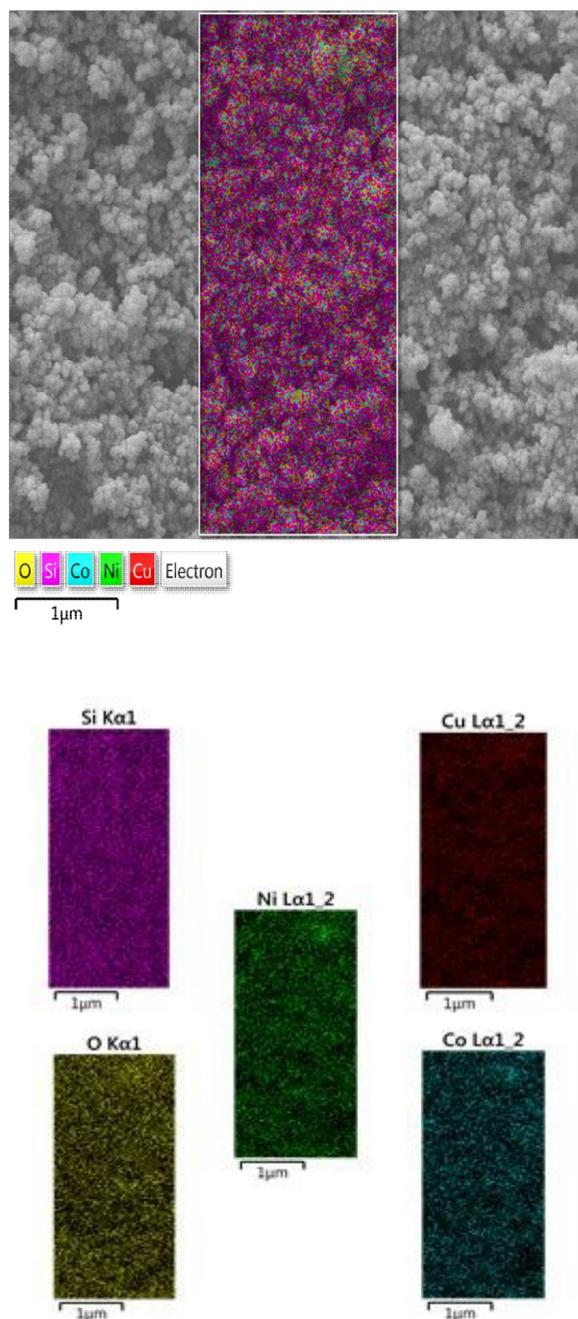


Fig. 6. EDS elemental mapping pictures of NiO-CuO-CoO/SiO₂ nanocomposite aerogels

BET analysis was performed to estimate the surface area, pore volume and pore size of NiO-CuO-CoO/SiO₂ nanocomposite aerogels. The results of the BET analysis of nanocomposite sample,

produced by the CO₂ supercritical drying method, are shown in (Fig. 7).

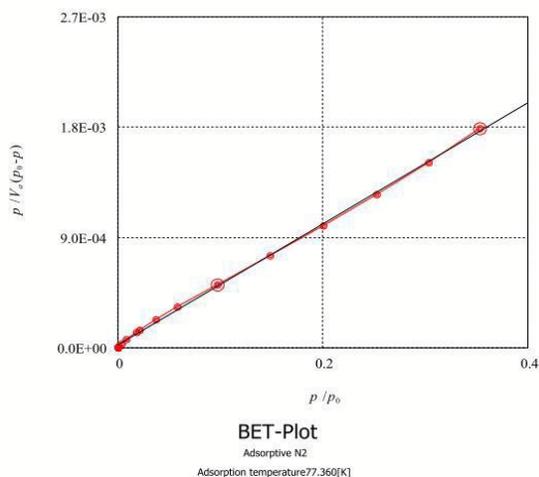


Fig. 7. BET analysis of nanocomposite sample produced by the CO₂ supercritical drying method.

According to Table 1, BET analysis proved the superiority of the CO₂ supercritical drying method. The use of the CO₂ supercritical drying (SCD) for the preparation of nanocomposite aerogels has led to a significant increase in the catalyst surface area, enhancing catalyst efficiency. When solvent extraction occurs under supercritical conditions, the network does not shrink and an extremely porous, low-density material known as an aerogel is produced. The SCD method provides beneficial properties such as high special surface space, high porosity, plentiful three-dimensional (3D) porous construction, and ultra-low density to the composite. Heat processing of a xerogel at high temperatures causes viscous sintering and completely changes the porous gel into a compact glass.

Table 1. BET analysis of surface area, pore-volume, and pore size for nanocomposite aerogels.

Catalyst	Surface area ^a (m ² /g)	Pore volume ^a (cm ³ /g)	Pore size ^a (nm)
NiO-CuO-CoO/SiO ₂ nanocomposite aerogels	875.79	0.47	2.15

^a Textural properties measured with N₂ at 77K.

3.2. Investigation of catalytic activity

The catalytic performance of the synthesized NiO-CuO-CoO/SiO₂ nanocomposite aerogels for organic reactions was investigated by applying the Buchwald-Hartwig C–N bond formation reaction. At first, the reaction of iodobenzene and aniline was selected as a model reaction. To determine the optimal conditions, catalyst activity was investigated with a variety of factors including solvent, temperature and catalyst loading (Table 2). Low yields of the products were

observed using toluene (Table 2, entry 5) and CH₃CN (Table 2, entry 2) and DMF was selected as the best solvent for the model reaction at 130 °C (Table 2, entry 12) to produce diphenylamine.

Table 2. Optimization of the reaction conditions^a

Entry	Solvent	T (°C)	Catalyst (mg)	Time (min)	Yield (%) ^b
1	EtOH	Reflux	15	240	92
2	CH ₃ CN	Reflux	15	280	72
3	DMSO	140	15	120	86
4	DMF	140	15	45	96
5	Toluene	Reflux	15	420	68
6	H ₂ O	Reflux	5	260	87
7	PEG	140	5	300	89
8	H ₂ O/ETOH	Reflux	5	260	89
9	DMF	140	10	25	95
10	DMF	140	5	45	92
11	DMF	140	20	40	94
12	DMF	130	3	30	97
13	DMF	120	3	55	90
14	DMF	100	3	70	88

^a Reaction conditions: Iodobenzene (1 mmol), aniline (1.2 mmol) and potassium hydroxide (3 mmol).

^b Isolated yield.

Also, we tried to use several different bases for the C–N bond formation reaction catalyzed by NiO-CuO-CoO/SiO₂ nanocomposite aerogels in DMF. The outcomes showed modest yields of the product with K₃PO₄ and NEt₃ (Table 3, entries 4,5). Superior yields were obtained with KOH and NaOH from among various bases (Table 3, entries 1,2).

Table 3. Optimization of the base reactions

Entry	Base	Time (min)	Yield (%) ^b
1	KOH	30	97
2	NaOH	45	93
3	K ₂ CO ₃	55	87

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4	K ₃ PO ₄	75	66
5	NEt ₃	240	58

^a Reaction conditions: Iodobenzene (1mmol), aniline (1.2 mmol), catalyst (3 mg), and DMF (5 ml) solvent at 130 °C.

^b Isolated yield.

In addition, to optimize the conditions, various types of catalysts for the required transformations were examined (Fig. 8). Conducting the reaction in the presence of 3 mg of NiO-CuO-CoO/SiO₂ nanocomposite aerogels directed to the corresponding products in 97% yield. Other catalysts such as NiO-CuO/SiO₂ nanocomposite aerogels, NiO-CoO/SiO₂ nanocomposite aerogels, NiO/SiO₂ nanocomposite aerogels, CoO/SiO₂ nanocomposite aerogels, and CuO/SiO₂ nanocomposite aerogels caused lower conversions and SiO₂ aerogels completely failed to produce the product. Thus, the improved catalytic activity of NiO-CuO-CoO/SiO₂ nanocomposite aerogels could be due to the synergistic catalytic effect between the metal varieties.

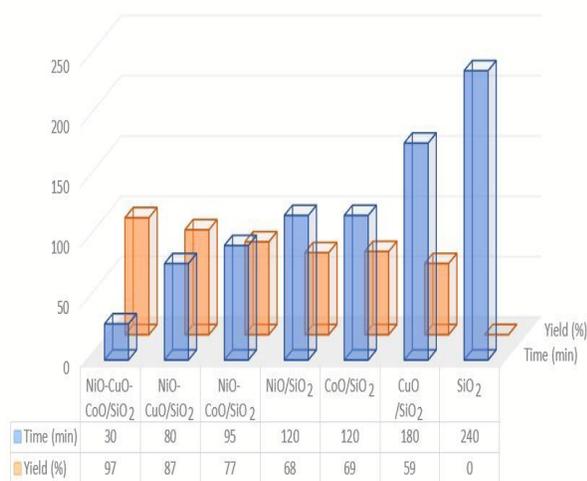


Fig. 8. Catalytic activity of different nanocomposite aerogel catalysts in the C–N bond formation reaction.

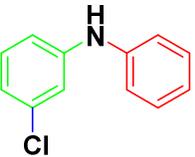
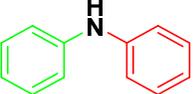
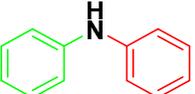
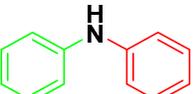
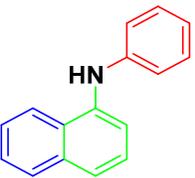
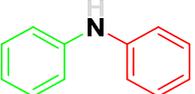
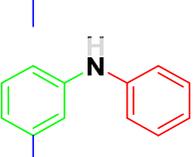
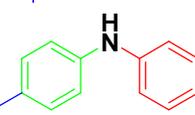
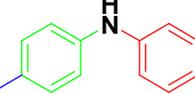
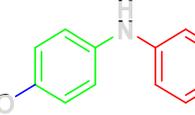
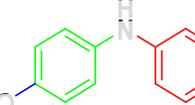
After the optimization of the conditions with various solvents, bases, catalyst loading, and temperatures, we carried out the C–N bond formation reaction of aniline with a variety of aryl halides. The results are presented in Table 4. A variety of aryl iodides, bromides, and chlorides including electron-withdrawing and electron-donating substituents react efficiently with aniline. The laboratory outcomes show that the aryl iodides are found to be more reactive than the aryl bromides and aryl chlorides.

The existence of electron-withdrawing groups, such as; -Cl, -Br, -NO₂, -CN, and H₃CCO, on the aryl halides, give the corresponding diphenylamine products highest yields (Table 4, entries 1–9). The aryl halides bearing electron-donating groups, such as; CH₃ and OCH₃, reacted efficiently with aniline with good yields (Table 4, entries 14–19), but not better than the aryl halides containing electron-withdrawing groups.

These findings indicated that the simultaneous dual coupling of aniline on 1,4-dibromobenzene has triarylamine compounds in excellent yields (Table 4, entry 8).

Table 4. Synthesis of diphenylamine derivatives ^a

Entry	R/X	Product	Time (min)	Yield ^c (%)
1a-l	2	3a-l		
1	CN/I		8	98
2	CN/Br		12	89
3	NO ₂ /I		15	88
4	NO ₂ /Br		19	92
5	Br/Br		24	69
6	H ₃ CCO/Br		24	72
7	H ₃ CO/CO/I		26	78
8 ^b	Br/Br		33	91

9	Cl/Br		29	68
10	H/I		30	97
11	H/Br		38	86
12	H/Cl		45	84
13	H/Br		47	88
14	CH ₃ /Br		69	78
15	CH ₃ /Cl		88	84
16	CH ₃ /I		89	86
17	CH ₃ /Br		95	78
18	H ₃ CO/I		98	79
19	H ₃ CO/Br		112	77

^aReaction conditions: aryl halides (1mmol), aniline (1.2 mmol), KOH (3 mmol), catalyst (3 mg), and DMF (5 ml) solvent at 130 °C.

^bReaction conditions: aryl halides (1mmol), aniline (2.4 mmol), KOH (6 mmol), catalyst (3 mg), and DMF (5 ml) solvent at 130 °C.

^c Isolated yield.

To compare the performance of the NiO-CuO-CoO/SiO₂ nanocomposite aerogel with the previous reported catalysts the synthesis of diphenylamine from Iodobenzene was carried out and

the results are presented in Table 5. As shown in Table 5, the aerogel NiO-CuO-CoO/SiO₂ nanocomposite is superior to the reported catalysts. As expected, the increased surface area due to the high porosity of the aerogel catalyst prepared with the SCD method and the synergistic catalytic effect between the metal varieties, enhanced the reactivity of the catalyst (Entry 5 vs entries 1-4, Table 5).

Table 5. Comparison of the catalytic activity of the aerogel NiO-CuO-CoO/SiO₂ nanocomposite with the other reported catalysts for the synthesis of diphenylamine from Iodobenzene

Entry	Catalyst (conditions)	Time (min)	Yield ^a (%)	Ref.
1	CuI, DPPT (CuI: 0.28 mmol; ligand: 0.28 mmol, KOBu-t, toluene, 115 °C)	300	24	25
2	CuI (10mol %, CsF, DMSO, 130 °C)	24 h	39	26
3	Pd(OAc) ₂ (3mol %, KotBu, 1,4-dioxane, 100 °C)	120	75	27
4	C ₃₁ H ₂₆ N ₄ PPdS ^{(1+)*Cl⁽¹⁻⁾ (0.01mol %, NaO^t-Bu, toluene, 95 °C)}	600	100	28
5	aerogel NiO-CuO-CoO/SiO ₂ nanocomposite (3 mg, KOH, DMF, 130 °C)	30	97	This work

^a Isolated yield.

3.3. Reusability

From the perspective of green chemistry, reusability is one of the most essential properties of metal catalysis that should be investigated. The reusability of NiO-CuO-CoO/SiO₂ nanocomposite aerogels was studied by consecutive C-N bond formation reactions of iodobenzene with aniline under optimized reaction conditions (Fig. 9).

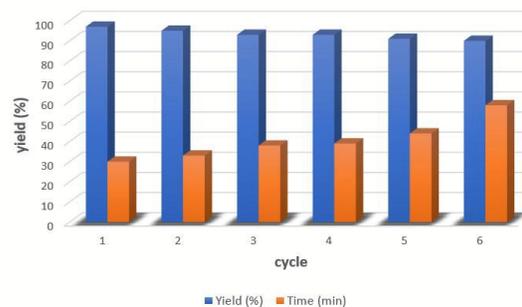


Fig. 9. The C-N bond formation reaction of iodobenzene with aniline in the presence of reused NiO-CuO-CoO/SiO₂ nanocomposite aerogels.

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The catalyst could be separated easily from the reaction solution by filtration. The recovered catalyst was washed with ethanol and water to remove any organic materials and salts. In recycling tests, the catalyst showed no visible loss of catalytic activity after six times of reusability (Fig. 9), while longer times were needed for the reaction to be completed in cycles 5 and 6.

According to the FE-SEM image of the used catalyst after six recycles, no significant change in the morphology of the NiO-CuO-CoO/SiO₂ nanocomposite aerogels from that of the fresh catalyst was identified (Fig. 10).

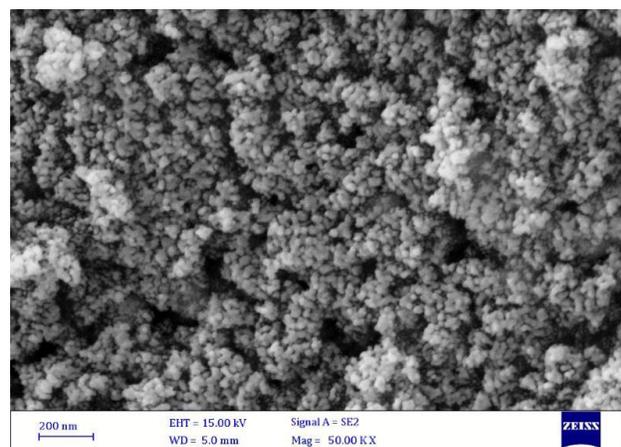


Fig. 10. The FE-SEM image of the used catalyst after six recycles

4. Conclusion

The CO₂ cold SCD method could prepare homogeneous NiO-CuO-CoO/SiO₂ nanocomposite aerogels with high pore volumes and pore diameters, which is beneficial to the development of catalysts with smaller crystal sizes and higher surface areas compared to the other methods. The yield of C–N bond formation reactions catalyzed by the novel supported catalyst is much more powerful than that of other porous catalysts under ligand-free conditions. The range of reaction using NiO-CuO-CoO/SiO₂ nanocomposite aerogels is extensive: various aryl halides form both electron-donating and electron-withdrawing groups react with amines. The highest yields were obtained in approximately short reaction times in both electron-donating and electron-withdrawing groups.

Acknowledgments

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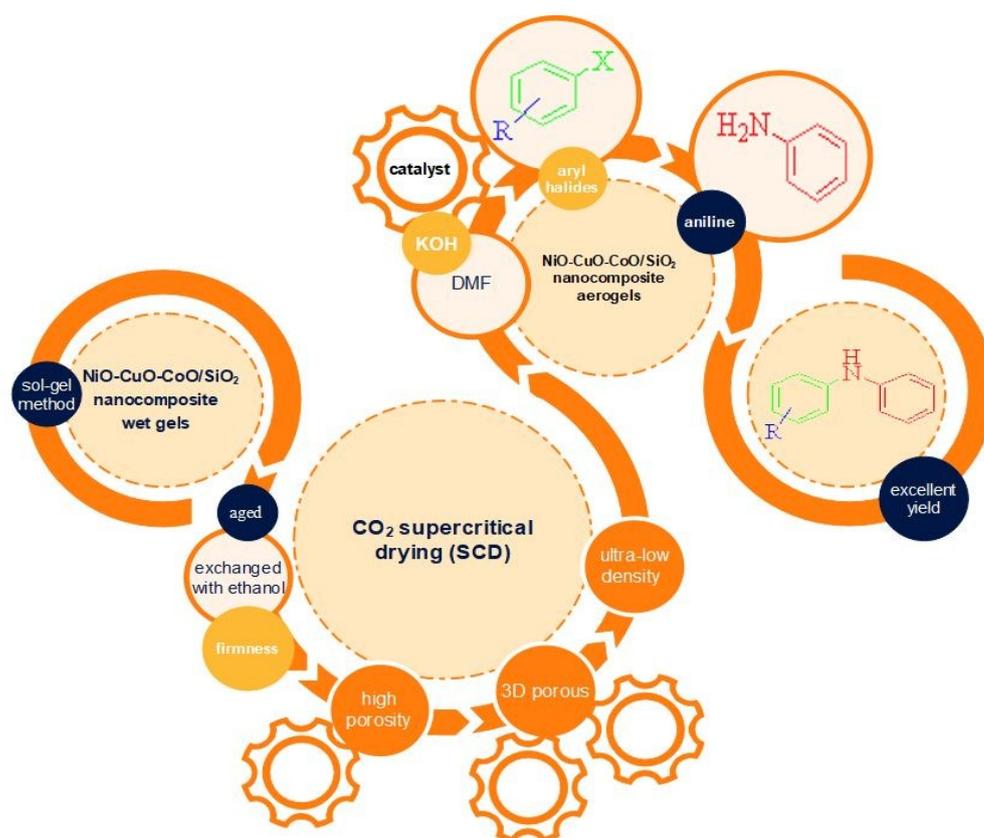
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Design, preparation and characterization of aerogel NiO-CuO-CoO/SiO₂ nanocomposite as a reusable catalyst for C-N cross-coupling reaction

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The aerogel nanocomposite produces using the sol-gel and supercritical drying method processes. The CO₂ supercritical drying (SCD) was taken as the most powerful process, ensuring the best properties of the product.