

Synthesis of diphenyl sulfide from iodobenzene and thiophenol using Metal-Organic Framework $\text{Cu}_2(\text{NDC})_2(\text{DABCO})$ as an efficient heterogeneous catalyst

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ABSTRACT

A metal-organic framework $\text{Cu}_2(\text{NDC})_2(\text{DABCO})$ was synthesized from copper nitrate trihydrate, 2,6-Naphthalenedicarboxylic acid (H_2NDC), and 1,4-diazabicyclo[2.2.2]octane (DABCO) by solvothermal method. Its physicochemical properties were confirmed by several techniques such as X-ray powder diffraction (PXRD), Fourier transform infrared (FT-IR), scanning electron microscopy (SEM), and transmission electron microscopy (TEM). $\text{Cu}_2(\text{NDC})_2(\text{DABCO})$ appeared as well-shaped crystals. To get diphenyl sulfide as desired product from the C-S cross coupling reaction of iodobenzene and thiophenol, the $\text{Cu}_2(\text{NDC})_2(\text{DABCO})$ was used as heterogeneous catalyst in the presence of LiO-t-Bu as base. The results showed that the transformation could proceed with more than 93% reaction conversion being obtained after 6 h at 120 °C when using 5 mol% $\text{Cu}_2(\text{NDC})_2(\text{DABCO})$ catalyst in the presence of LiO-t-Bu. The solid catalyst could be recovered and reused five times without a significant degradation in catalytic activity. The coupling reaction could only proceed to achieve major product in the presence of the $\text{Cu}_2(\text{NDC})_2(\text{DABCO})$ catalyst.

Introduction

Formation carbon-sulfur bonds are indispensable tools in synthetic chemistry to achieve final desired products. Many scientists have been using C-S bonds in various application such as biological chemistry [1], organic synthesis [2], and materials sciences [3]. For preparing these compounds, several methods have been developed. For example, the transition metal catalyzed

cross-coupling reactions are have been usually used to get aryl-sulfur bonds. It was found that this approach involved the coupling of organic halides with thiols. Migita and co-workers reported that $\text{Pd}(\text{PPh}_3)_4$ could be used as a catalyst for the coupling reaction between aryl iodides and bromides with thiols [4]. Similarly, based on bidentate phosphines or diverse organophosphane derivatives, a lot of Pd based catalytic systems have also reported [5]. However, the

limitations of these systems are the preparation of PR_3 ligands which is very complex. To overcome this drawback, other transition metals including iron, cobalt, nickel have been used as catalysts for C-S coupling reactions [6-8]. Unfortunately, these catalysts also have the disadvantages that are low turnover numbers, metal toxicity,...Therefore, many research groups have studied copper based catalytic systems because copper is less toxic and inexpensive [9, 10]. Even though copper is found to be the most suitable catalyst for catalyzing C-S cross coupling reactions, developing an efficient catalyst containing copper system for formation C-S bonds of aryl iodides with thiols remains to be explored.

In recent years, metal-organic frameworks (MOFs) have great attention because they have special structures and properties [11]. Their topological structures contain various metal sites with potential coordinative unsaturation and organic linkers. Besides, MOFs possess structural diversity, high surface areas, adjustable pore sizes, and the ease of processability, flexibility [11]. Therefore, promising applications of MOFs in manifold areas have been exhaustively investigated, particularly in the area of catalysis [12,13]. MOFs could be used as remarkable heterogeneous catalysts in various types of organic reactions, including both carbon-carbon and carbon-heteroatom reactions [12,13]. Compared to several popular MOFs, copper containing metal-organic frameworks (Cu-MOFs) emerge as the most frequently utilized materials. Many research groups reported that copper-based metal-organic frameworks exhibited high catalytic activities in a lot of organic transformations [14]. In this study, we report the direct C-S cross coupling reaction of iodobenzene with thiophenol using $Cu_2(NDC)_2(DABCO)$ as an efficient heterogeneous catalyst.

Experimental

Materials and instrumentation

All reagents and starting materials were purchased from Sigma-Aldrich and Acros, and used as received without further purification. X-ray powder diffraction (XRD) patterns were recorded using a Cu $K\alpha$ radiation source on a D8 Advance Bruker powder diffractometer. Fourier transform infrared (FT-IR) spectra were obtained on a Nicolet 6700 instrument. Scanning electron microscopy studies were conducted on a S4800 Scanning Electron Microscope (SEM). Transmission electron microscopy studies were

performed using a JEOL JEM 1010 Transmission Electron Microscope (TEM) at 80 kV.

Gas chromatographic (GC) analyses were performed using a Shimadzu GC 2010-Plus equipped with a flame ionization detector (FID) and an SPB-5 column (length = 30 m, inner diameter = 0.25 mm, and film thickness = 0.25 μ m). The temperature program for GC analysis held samples at 100 $^{\circ}$ C for 1 min; heated them from 100 to 280 $^{\circ}$ C at 10 $^{\circ}$ C/min; held them at 280 $^{\circ}$ C for 8 min. Inlet and detector temperatures were set constant at 280 $^{\circ}$ C. N-dodecane was used as an internal standard to calculate reaction conversions. GC-MS analyses were performed using a Hewlett Packard GC-MS 5972 with a RTX-5MS column (length = 30 m, inner diameter = 0.25 mm, and film thickness = 0.5 μ m). The temperature program for GC-MS analysis heated samples from 60 to 280 $^{\circ}$ C at 10 $^{\circ}$ C/min and held them at 280 $^{\circ}$ C for 10 min. Inlet temperature was set constant at 280 $^{\circ}$ C. MS spectra were compared with the spectra gathered in the NIST library.

Synthesis of $Cu_2(NDC)_2(DABCO)$

In a typical preparation, $Cu(NO_3)_2 \cdot 3H_2O$ (0.169 g, 0.70 mmol), H_2NDC ($H_2NDC = 2,6$ -naphthalenedicarboxylic acid; 0.152 g, 0.70 mmol), and DABCO (DABCO = 1,4-diazabicyclo[2.2.2]octane; 0.039 g, 0.35 mmol) were dissolved in DMF (DMF = *N,N'*-dimethylformamide; 25 mL). The suspension was magnetically stirred for 2 h. After getting clear solution, the solution was distributed to three vial 10 mL vials. These vials were heated at 120 $^{\circ}$ C in an isothermal oven for 2 days. The vials were then cooled to room temperature. The forming blue crystals product was removed by decanting with mother liquid and washed with DMF (3x 10 mL). Solvent exchange was carried out with dichloromethane (3x 10 mL). The solid was then dried under vacuum at 140 $^{\circ}$ C for 6 h, yielding 0.147 g of $Cu_2(NDC)_2(DABCO)$ as blue crystals (75 % based on H_2NDC).

Catalytic studies

In a representative experiment, iodobenzene (0.22 mL, 2.0 mmol) and thiophenol (0.44 g, 4.0 mmol) were added into a three-neck flask containing a predetermined amount of the $Cu_2(NDC)_2(DABCO)$ catalyst and n-dodecane (0.15 mL) as internal standard in DMF (4 mL). The catalyst amount was calculated with respect to the copper/iodobenzene molar ratio. LiO-*t*Bu (0.848 g, 4 mmol) as base was then added. The reaction mixture was magnetically stirred at 120 $^{\circ}$ C for 6 h. The reaction conversion was recorded by withdrawing samples from the reaction mixture at

different time periods. The withdrawn solution was diluted with diethyl ether, and dried with anhydrous Na_2SO_4 before analyzing by gas chromatography (GC). The products were determined by GC-MS. For the leaching test, a catalytic reaction was stopped after 1 h, analyzed by GC, and filtered to remove the solid catalyst. The reaction solution was then stirred for an additional 5 h. Reaction progress, if any, was monitored by GC as previously described.

Results and discussion

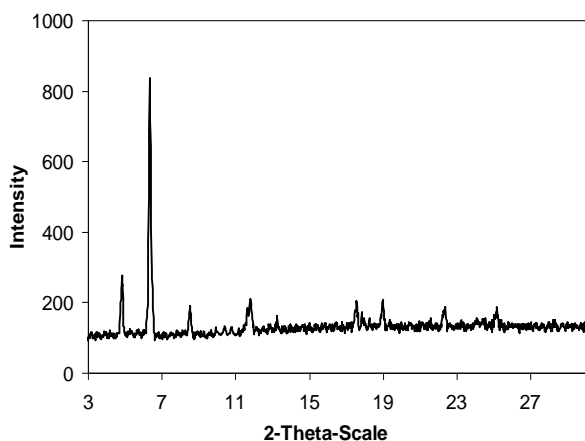


Figure 1: X-ray powder diffractograms of the $\text{Cu}_2(\text{NDC})_2(\text{DABCO})$

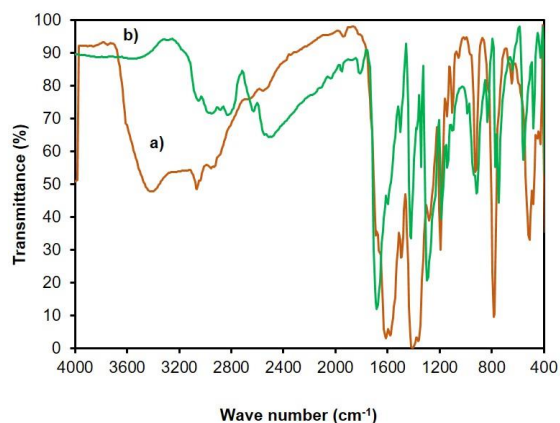


Figure 2: FT-IR spectra of 2,6-Naphthalenedicarboxylic acid (a), and the $\text{Cu}_2(\text{NDC})_2(\text{DABCO})$ (b)

In this work, the $\text{Cu}_2(\text{NDC})_2(\text{DABCO})$ was prepared from the reaction of copper nitrate trihydrate, 2,6-Naphthalenedicarboxylic acid (H_2NDC), and 1,4-diazabicyclo[2.2.2]octane (DABCO) via a solvothermal method, following a literature protocol [15]. The physicochemical properties of $\text{Cu}_2(\text{NDC})_2(\text{DABCO})$ was determined by various techniques. Firstly, the typical reflections of $\text{Cu}_2(\text{NDC})_2(\text{DABCO})$ phase were indicated in XRD pattern (Figure 1). The crystallinity of this

material was demonstrated by the presence of the peaks at 2θ of approximately 7.5° , 9.5° , 15° . Secondly, the presence of bonded carboxylate organic linkers of this Cu-MOF were observed by FT-IR spectra (Figure 2). In details, the protonation of COOH groups in H_2NDC upon the reaction with copper (II) ion was confirmed at 1604 cm^{-1} as the stretching vibration of the carboxylate ion. Compared with the free carboxylic acid, the C=O stretching vibration of $\text{Cu}_2(\text{NDC})_2(\text{DABCO})$ exhibited a lower value. Finally, SEM micrograph demonstrated that $\text{Cu}_2(\text{NDC})_2(\text{DABCO})$ had well-shaped crystals (Figure 3) while TEM image showed a porous structure for the material (Figure 4). In short, the obtained results were good agreements with previous reports [15].

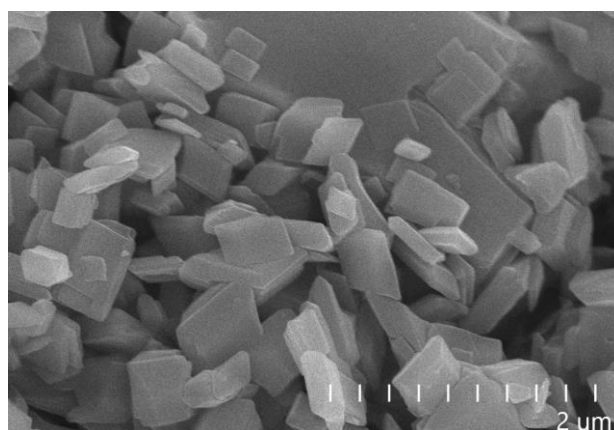


Figure 3: SEM micrograph of the $\text{Cu}_2(\text{NDC})_2(\text{DABCO})$

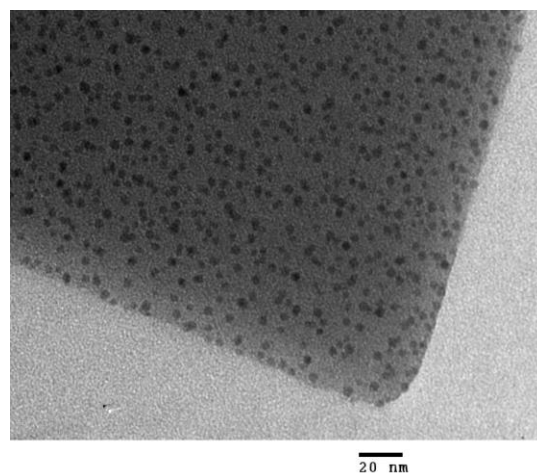
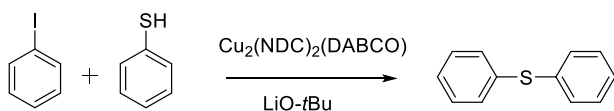


Figure 4: TEM of the $\text{Cu}_2(\text{NDC})_2(\text{DABCO})$

In optimization studies, the catalytic activity of $\text{Cu}_2(\text{NDC})_2(\text{DABCO})$ was demonstrated for the C-S cross coupling reaction of iodobenzene with thiophenol to get diphenyl sulfide as the desired product (Scheme 1). Its structures were confirmed by GC-MS.



Scheme 1: The coupling reaction of iodobenzene and thiophenol using $\text{Cu}_2(\text{NDC})_2(\text{DABCO})$ catalyst

The effect of reaction temperature on reaction conversion was firstly addressed. In the presence of four equivalents of LiO-tBu as base and 5 mol% $\text{Cu}_2(\text{NDC})_2(\text{DABCO})$ catalyst, the C-S coupling reaction was carried out in 4 mL DMF for 6 h, using the iodobenzene and thiophenol molar ratio of 1:2 at 80 °C, 100 °C, and 120 °C, respectively. Interestingly, at low temperature, the results showed that the reaction proceeded hardly. Indeed, only 20 % reaction conversion was observed after 6 h at 80 °C. As expected, increasing the reaction temperature to 100 °C and 120 °C resulted in a significant drop in reaction conversion, with 60% and 93% reaction conversions being obtained after 6 h (Figure 5).

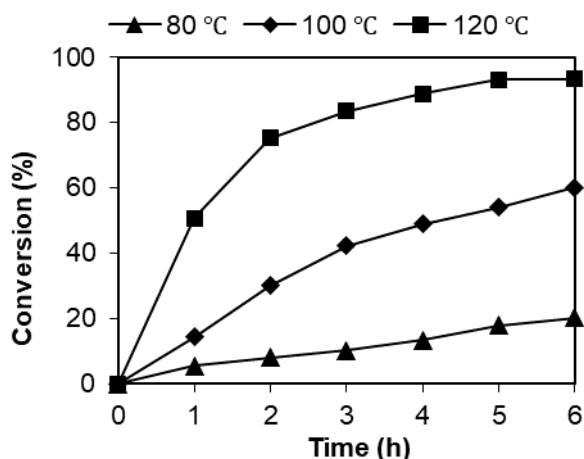


Figure 5: Effect of temperature on reaction conversion

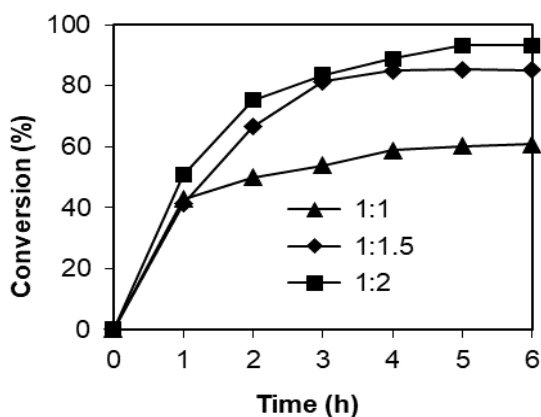


Fig 6: Effect of the molar ratio of iodobenzene and thiophenol on reaction conversion

Secondly, the impact of the iodobenzene and thiophenol molar ratio on reaction conversion should be then assessed. The transformation was carried out at 120 °C for 6 h in the presence of 4 mL DMF, four equivalents of LiO-tBu as base and 5 mol% $\text{Cu}_2(\text{NDC})_2(\text{DABCO})$ catalyst, using the iodobenzene and thiophenol molar ratio of 1:1, 1:1.5, and 1:2, respectively. It was found that the molar ratio exhibited a profound effect on reaction conversion. The obtained results indicated that increasing molar ratio to 1:1 and 1:1.5 led to a significant enhancement in the reaction rate, reaching 61% and 85% conversions after 6 h. As expected, the reaction could afford 93% reaction conversion after 6 h when using the iodobenzene and thiophenol molar ratio of 1:2 (Figure 6).

Another important factor that should be seriously considered is the catalyst amount of $\text{Cu}_2(\text{NDC})_2(\text{DABCO})$. The coupling reaction was conducted at 120 °C in 4 mL DMF for 6 h, using the iodobenzene and thiophenol molar ratio of 1:2 in the presence of four equivalents of LiO-tBu as base, with 0 mol%, 1 mol%, 3 mol%, and 5 mol% $\text{Cu}_2(\text{NDC})_2(\text{DABCO})$ catalyst, respectively. It was found that the catalyst played an important role in this transformation. Indeed, no reaction conversion was observed for the C-S coupling reaction without the presence of $\text{Cu}_2(\text{NDC})_2(\text{DABCO})$. The reaction conversion should be improved to 56% and 72% after 6 h when increasing the catalyst amount from 1 mol% and 3 mol%, respectively. By employing 5 mol% catalyst, reaction conversion was achieved 93% after 6 h (Figure 7). Therefore, using 5 mol% $\text{Cu}_2(\text{NDC})_2(\text{DABCO})$ was necessary for the reaction to obtain desired product.

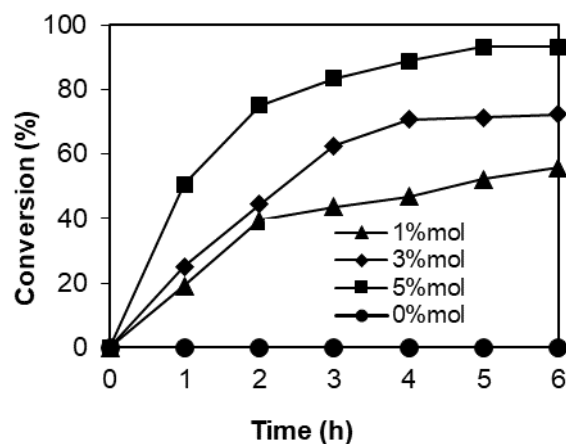


Figure 7: Effect of the catalyst amount on reaction conversion

Investigate the effect of different bases on reaction conversion was conducted with LiO-*t*Bu, NaO-*t*Bu, CH₃COONa, CH₃ONa, K₃PO₄ and K₂CO₃. The coupling reaction was carried out at 120 °C in DMF for 6 h, at the iodobenzene and thiophenol molar ratio of 1:2, in the presence of 5 mol% Cu₂(NDC)₂(DABCO) catalyst, using four equivalents of the base. The obtained results showed that the presence of base in the C-S coupling reaction was necessary. Indeed, with the presence of K₂CO₃ in the coupling reaction, 64% reaction conversion was obtained after 6 h. Similarly, reaction conversion was slightly increased to 68% in the case of CH₃CONa. Interestingly, when using CH₃COONa, K₃PO₄, as base for the transformation, reaction conversions should be improved to 82% and 87%, respectively. As expected, LiO-*t*Bu, NaO-*t*Bu were found to be good base for the coupling reaction, with 93% and 97% reaction conversions being achieved after 6 h (Figure 8).

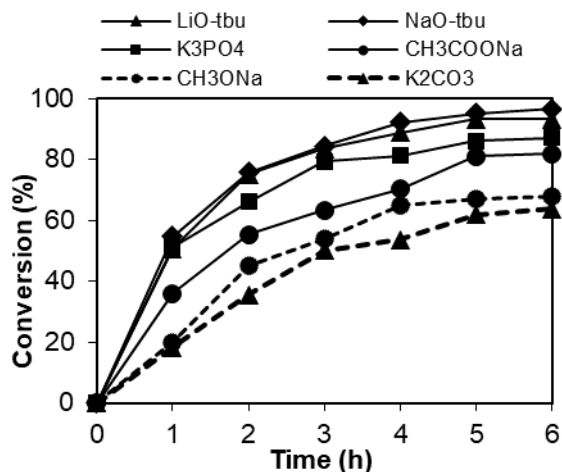


Figure 8: Effect of base on reaction conversion

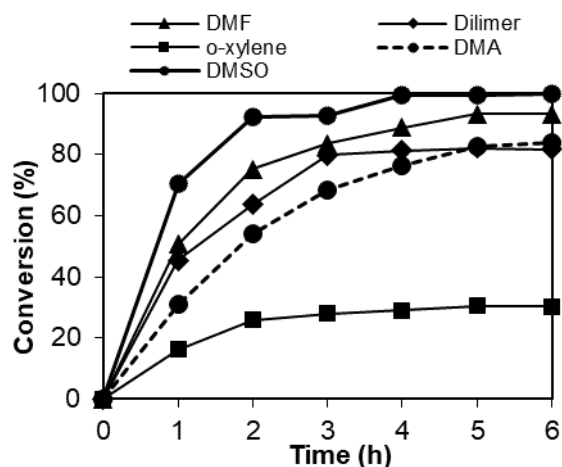


Figure 9: Effect of solvent on reaction conversion

Depending on the nature of the catalyst, the presence of solvent in reaction could significantly accelerate or

slow down the transformation [16]. In the next studies, the effect of different solvents on reaction conversion should be then investigated. The coupling reaction was studied at 120 °C for 6 h with 5 mol% Cu₂(NDC)₂(DABCO) catalyst and four equivalents of LiO-*t*Bu as a base, using the iodobenzene and thiophenol molar ratio of 1:2 in different solvents such as DMF, *o*-xylene, Dimethyl sulfoxide (DMSO), Dilimer, and *N,N'*- Dimethylacetamide (DMA), respectively (Figure 9). It was observed that the transformation could proceed well in polar solvents than non-polar solvents. In details, the results showed that only 30% reaction conversion was achieved after 6 h in the presence of *o*-xylene as solvent. Both Dilimer and DMA exhibited better performance than *o*-xylene, with 82% and 84% conversions being observed after 6 h. With the presence of DMF as solvent, the transformation could afford 93% reaction conversion after 6 h. Interestingly, DMA was found to be the best solvent for the reaction, with 100% reaction conversion being achieved after 6 h.

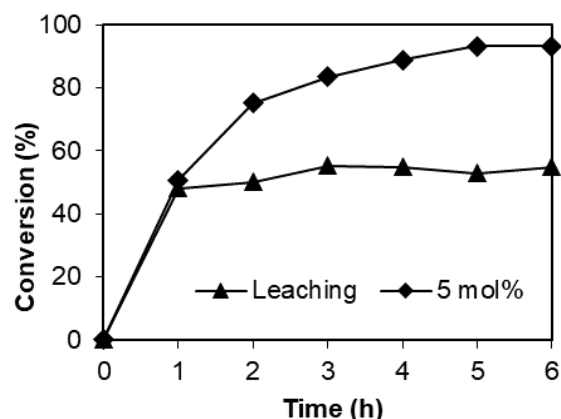


Figure 10: Leaching test demonstrated that no donation from homogeneous catalysis to the generation of diphenyl sulfide was detected

Although a solid catalyst is used for the liquid-phase organic reaction, it might not occur under real heterogeneous catalysis conditions in several cases [17]. It was therefore decided to carry out the leaching test in order to determine if active species leached from the solid Cu₂(NDC)₂(DABCO) catalyst could play an important role in the catalytic activity for the C-S formation (Figure 10). The reaction was studied in DMF at 120 °C for 6 h, using the iodobenzene and thiophenol molar ratio of 1:2 and 5 mol% Cu₂(NDC)₂(DABCO) catalyst, in the presence of four equivalents of LiO-*t*Bu as base. After the first 1 h reaction time with 51% conversion being obtained, the

solid catalyst was removed from the reaction mixture by simple filtration. The liquid phase was then transferred to a new round bottom flask, stirred for an additional 5 h at 120 °C with aliquots being samples at different time intervals, and analyzed by GC. As expected, almost no further conversion was observed in the absence of the solid $\text{Cu}_2(\text{NDC})_2(\text{DABCO})$ catalyst. The observation would indicate that the C-S cross coupling reaction could proceed in the presence of solid catalyst. Moreover, it was negligible if the active copper species was dissolved in the liquid phase.

To underline the remarkable feature of $\text{Cu}_2(\text{NDC})_2(\text{DABCO})$ in the C-S coupling reaction between iodobenzene and thiophenol to form diphenyl sulfide, one point that must be explored is the catalyst reusability. For the development of more environmentally benign processes, it should be possible to reuse the solid catalyst for abundant times. The reaction was then performed in DMF at 120 °C for 6 h, using the iodobenzene and thiophenol molar ratio of 1:2 and 5 mol% $\text{Cu}_2(\text{NDC})_2(\text{DABCO})$ catalyst, in the presence of four equivalents of LiO-*t*Bu as base. After the first run, the solid catalyst was separated from the reaction mixture by simple centrifugation, washed with copious amounts of DMF and dichloromethane, dried 140 °C under vacuum in 2 h, and reused in new experiments. The $\text{Cu}_2(\text{NDC})_2(\text{DABCO})$ was accordingly studied for reusability in the reaction over five consecutive runs. Figure 11 showed that, 84% reaction conversion was still detected in the 5th run.

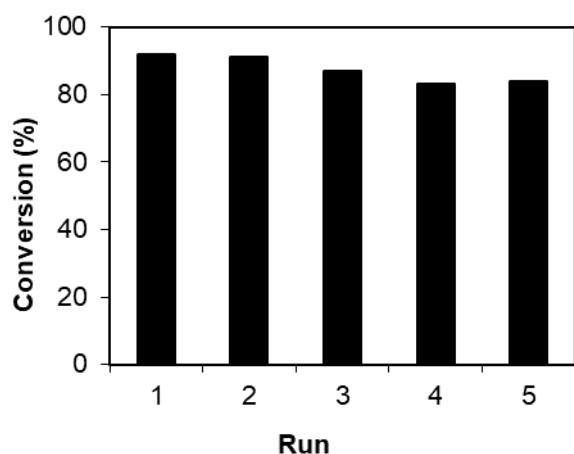


Figure 11: Catalyst recycling studies

Conclusions

In conclusion, the $\text{Cu}_2(\text{NDC})_2(\text{DABCO})$ was successfully prepared by solvothermal method, and characterized by several techniques. This solid could be used as an efficient catalyst for the reaction between iodobenzene

and thiophenol to form diphenyl sulfide. It was found that the transformation could only proceed in the presence of $\text{Cu}_2(\text{NDC})_2(\text{DABCO})$. The reaction afforded 93% reaction conversion at 120 °C after 6 h, in the presence of 5 mol% $\text{Cu}_2(\text{NDC})_2(\text{DABCO})$ catalyst and four equivalents of LiO-*t*Bu as base. The solid catalyst could be recovered and reused five times without a significant degradation in catalytic activity.

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