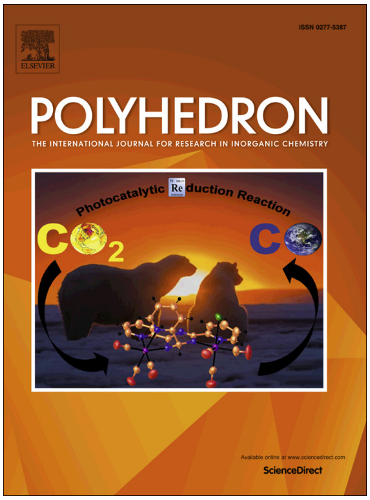

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PII: S0277-5387(16)30482-X
DOI: http://dx.doi.org/10.1016/j.poly.2016.09.052
Reference: POLY 12240

To appear in: *Polyhedron*

Received Date: 31 May 2016
Revised Date: 24 September 2016
Accepted Date: 27 September 2016

Please cite this article as: D. Dumbre, V.R. Choudhary, PR. Selvakannan, Cu-Fe layered double hydroxide derived mixed metal oxide: Environmentally benign catalyst for Ullmann coupling of aryl halides, *Polyhedron* (2016), doi: http://dx.doi.org/10.1016/j.poly.2016.09.052

Cu-Fe layered double hydroxide derived mixed metal oxide: Environmentally benign catalyst for Ullmann coupling of aryl halides

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Abstract

Solid mixed metal oxide derived from Cu-Fe-layered double hydroxide by its thermal decomposition at 600 °C has been demonstrated as novel ligand free catalyst for the synthesis of biphenyls through C-C coupling. The catalytic efficiency of this material has been studied by varying the solvents and bases, thereby their influence in controlling the product formation. The C-C coupling yield of aryl halides were found to be higher, when dimethylformamide and potassium carbonate used as a solvent and base respectively. The catalyst can be easily separated from the reaction mixture, simply by filtration and reused several times without significant loss of its activity. The mixed metal oxide has been characterized by XPS, XRD, SEM, BET, TG analysis and the role of calcined Cu-Fe layered double hydroxide in catalyzing C-C coupling reaction was proposed. Moreover, it is ligand-free C-C coupling reaction and is promising alternative than the conventional homogeneous and heterogeneous Pd catalysts.

Keywords: Cu-Fe-hydrotalcite; Heterogeneous Catalysis; Ullmann coupling, Biaryls

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1. Introduction

The Ullmann condensation reaction has long been studied by chemists for C-C bond formation between two phenyl or substituted phenyl rings to form biaryls because biaryls play an important role in modern synthetic organic chemistry [1]. This coupling reaction between two aryl halide molecules leads to the elimination of two halide groups that result in the formation of the C-C bond towards the synthesis of biaryls. This reaction is usually carried out by converting two moles of aryl halide into a biaryl in the presence of finely granulated metallic copper at temperatures above 170 ºC, wherein halides are eliminated as copper halides. Metallic copper has been demonstrated as an effective reagent for this type of condensation reaction. There have been many reports in the literature about the conventional Ullmann coupling [2 - 4] and the use of stoichiometric amounts of copper, nickel, zinc and palladium as a reagent/catalyst has been comprehensively reviewed [5] due to the significance of biaryls as building blocks for the synthesis of polyketides, terpenes, coumarins, flavonoids, tannins, and alkaloids.

As mentioned earlier, this reaction have the disadvantages that includes high temperature, elimination of copper halides, poor product yields and sensitive to reaction conditions. Therefore, various attempts have been made and reported in the literature to improve the product yield with ambient reaction conditions. In some cases, the reaction rate can be accelerated by carrying out the reaction under the influence of ultrasound [6]. In addition to copper, there are other metals like Nickel, Zinc and palladium were also used for Ullmann coupling. Nickel catalysts have been used to promote C-C coupling [7] to produce natural products and palladium based catalysts were also used to catalyze the couplings in presence of trialkylamine base [8]. Homocoupling of aryl halide by palladium acetate and tetra-n-butylammonium bromide mixture [9] have been reported for the synthesis of various substituted biphenyls. In a recent work, it has been demonstrated that [10] catalytic amount of palladium and zinc mediated reductive coupling of aryl halides at ambient temperature and air in water. Ullmann type coupling were recently carried out under solvent less conditions using stoichiometric amounts of Palladium and zinc in presence of water and liquid carbon dioxide [11] and fluorinated palladium catalyzed coupling reaction in supercritical carbon dioxide [12]. Commercially available zinc dust was also demonstrated as an active catalyst for the synthesis of symmetrical functionalized biaryls from aryl halides using ammonium formate as base [13]. One-pot synthesis of symmetrical biaryls [14] for the synthesis of biologically active secalonic acid, has also been reported. Zinc and carbon supported Pd catalyzed Ullmann homocouplings under sonochemical conditions in aqueous media under CO_2 bubbling have also been demonstrated without using any donor solvents [15]. Very recently, a few catalysts have also been reported using N-heterocyclic carbene (NHC) polymer [16], CuNPs/nanoporous polymer [17], Cu-TDPAT [18] for various Ullmann coupling reactions.

Most of the afore-mentioned methods, either expensive metals like palladium were used as homogeneous catalyst or transition metals like copper, nickel and zinc were used in stoichiometric or excess amounts, which lead to the loss of metals as metal halides. Therefore it is essential to develop a heterogeneous catalyst that contains these metals as active sites, which can catalyze the reaction as well as significant reduction of metal leaching. Hydrotalcites and layered double hydroxides containing these metal ions are the desired candidates for this kind of reaction. However these materials have layered structure and have intercalated hydroxide and carbonate ions commonly, which limits their activity towards these C-C coupling reactions. Thermal treatment of these materials lead to the loss of these ions and resulted in the formation of mixed metal oxides and they can be promising candidates for these kinds of condensation reactions. Moreover, catalyst separation is easier after the reaction completion, thereby the potential of its recycling makes these materials as an important alternative to homogeneous catalysts. In the present work, we have demonstrated a greener process for the Ullmann-type aryl–aryl coupling of aryl iodides or bromides, forming biaryls with excellent yields at low temperature (120 ºC) using easily separable and reusable thermally activated Cu-Fe-hydrotalcite. Presented below are the details.

2. Experimental

2.1 Catalyst preparation and characterization

The precursor of the catalyst is the layered double hydroxide of Cu^{2+} and Fe^{3+} ions was synthesized by co-precipitating these ions together with the addition of base and this method adopted with few modifications from the procedure that we reported earlier [20-23]. To the aqueous solution containing the mixture of 3 mmol of copper nitrate and (3 mmol) and ferric citrate (1 mmol), aqueous solution containing the mixture of ammonium hydroxide and ammonium carbonate mixture were added drop-wise to increase the pH slowly. The precipitated layered double hydroxide of copper and iron (Cu-Fe-LDH, referred hereafter), washed several times with water to remove any free ions and dried at room temperature. After complete drying, this material was calcined at 600 ºC for four hours under static air. This material was used as a catalyst without any further processing and termed as CuFe-MMO hereafter. N_2 physi-sorption analysis of these materials showed that this material has the BET surface area of 130 m^2/g with the pore volume of 0.5 cm^3/g.

Thermo gravimetric data (TGA) of the Cu-Fe LDH were collected using a Perkin Elmer TGA-7 from 35 ºC to 700 ºC with a heating rate of 10 ºC per minute under the flow of nitrogen. XRD measurements were carried out on a Bruker D8 X-ray diffraction system operating at a voltage of 40 kV and current of 40 mA with CuKa radiation and equipped with the Antonn Parr Heating accessory. XPS data of CuFe MMO was collected using a Thermo K-5 Alpha XPS instrument at a pressure better than 1×10^{-9} torr with core levels aligned with C 1s binding energy of 284.6 eV. SEM/EDX studies of these materials were carried out using FEI nova nano SEM, operated at 30 KV.

2.2 Catalyst activity

In a typical reaction, 5 ml of DMF was added with 2.5 mmol of aryl halide (with or without 2.5 mmol of second aryl halide), catalyst (10 wt % in regard to aryl halide) and 3mmol of base. The mixture was stirred at 120 ºC under nitrogen atmosphere for an appropriate time and the reaction was monitored by TLC. After completion of reaction, the catalyst was separated by filtration and washed with DMF (3 x 3 ml). Then the filtrate was diluted with water followed by extraction with ethyl acetate to give the crude product, which was subsequently purified by column chromatography on silica gel with petroleum ether/ethyl acetate as an eluent. The catalyst was further washed with acetone, dried and reused. The reaction products were isolated by column chromatography and were confirmed by NMR, IR, MS and elemental analysis.

3. Results and Discussion

Under the optimized conditions (presented later), the coupling reaction of aryl halides were investigated to know the scope of our method, in DMF with K_2CO_3 as a base at 120 ^{0}C to obtain coupling products in good to excellent yields (Scheme 1). The results are presented in Table 1.

3.1 Effect of nature of aryl halide:

Results showing a strong influence of the nature of aryl halide on the biphenyl yield in the coupling reaction are presented in Table 1. For the different halobenzenes, the biphenyl yield was in the following order: iodobenzene > bromobenzene >> chlorobenzene >>> flurobenzene (Table 1, entries 1-5). In the case of fluorobenzene, there was no biphenyl formation even for a longer reaction time (Table 1, entry 5). The electronegativity of the halogen controls the strength of C-X bond, thereby highly electronegative chlorides and fluorides didn't show much conversion into biaryls. In the absence of any catalyst the product yield was found to be negligibly small. Previous studies were shown that reaction temperature, bases and solvents play a key role in controlling C-C conversion, therefore this reaction was carried out under different reaction temperature, various bases and solvents to optimize the product yield. The obtained results showed strong influence of reaction temperature and various bases and solvents on the product (biphenyl) yield in the coupling reaction over the Cu-Fe-hydrotalcite catalyst (calcined at 600 ^{o}C) are given in Table 2 and 3 respectively.

3.2 Influence of the reaction temperature

To identify the optimum reaction temperature, the reaction between 4-iodoanisole over the catalyst was carried out at different temperatures (50 ^{o}C – 120 ^{o}C). As expected the product yield increased with increasing the reaction temperature; show a strong influence of temperature on the reaction. The catalyst showed its activity above 50 ^{o}C and the product yield increased exponentially with increasing the bath temperature from 50 ^{o}C to 120 ^{o}C.

3.3 Influence of the various base

In order to optimize the reaction conditions, the reaction between 4-iodoanisole over the catalyst was carried out using different bases such as Na_2CO_3, NaOAC, trimethyl amine, pyridine and zinc dust. The results in Table 2 showed a strong influence of base on coupling of aryl halides, K_2CO_3 was found to be the best base for this reaction. When K_2CO_3 was replaced by Na_2CO_3, sodium acetate, trimethyl amine and pyridine or zinc dust in the coupling reaction, the product yield was much smaller, even for higher reaction time, than that achieved with K_2CO_3. This revealed that, among the bases, K_2CO_3 is the most suitable base for the CuFe MMO catalyzed Ullmann coupling. In the absence of base, the formation of biphenyl in the coupling reaction is quite small. Thus, the coupling reaction is strongly influenced by the base concentration.

3.4 Influence of the various solvents

To check the efficiency of the catalyst and to optimize the reaction conditions, different solvents have been used in the Ullmann coupling of *p*-iodoanisole, under similar reaction conditions. Even though other polar solvents like NMP, ethanol and water can be used, but DMF showed best results with more or less active aryl halides (Table 3). The other solvents like CH_3CN and xylene gave lower yield and required longer reaction time. However, no reaction was observed with solvents like water, 1,4-dioxan, toluene and ethanol. Among the different solvents, DMF was found to be the best solvent most probably due to increased competitive adsorption on the catalyst surface of the solvents for providing very good conversion in the reaction.

The reusability of the Cu-Fe-hydrotalcite was thoroughly investigated. The catalyst showed excellent reusability in the reaction without a significant loss in its activity in five reuses; the biphenyl yield in the five reuses was 78 ± 2%. The catalyst (after the reaction) was removed from the reaction mixture by filtration, washed with DMF first and then with acetone, dried and then reused in the coupling reaction at 120 °C. This was repeated several times. The results showing the reusability of the catalyst are presented in Table 1 (entry 6). Since, all the products (Table 1) of the reaction are known/reported earlier; we have provided spectral data only for a few representative products.

Spectral data

4, 4'-Dimethoxy biphenyl

^{1}H NMR ($CDCl_3$+CCl_4, 50 MHz): δ 7.47 (d, 4H, J=8 Hz), 6.95 (d, 4H, J=8 Hz), 3.85 (s, 6H). IR (chloroform): 3019, 2957, 1608, 1500, 1215, 1182, 1041, 824 cm^{-1}; GC Mass**:** m/z 214

Biphenyl

^{1}H NMR ($CDCl_3$, 50 MHz): δ 7.47 (m, 6H), 7.61 (d, 4H, J = 6 Hz); IR (Neat): 3060, 1638, 1456, 1210, 898, 698, 728 cm^{-1}.

3.4 Catalyst characterization

In the previous section, it was shown that thermally activated CuFe-MMO was found to be an active catalyst as compared to its precursor Cu-Fe LDH. In order to study the influence of thermal activation and its role in forming the mixed metal oxide phase formation, XRD patterns of CuFe LDH material was collected as a function of temperature. Figure 1 shows the XRD profile of the CuFe LDH at room temperature and when it was heated up at higher temperatures until 600 ^{o}C. Hydrolysis of Cu(II)/Fe(III) ions under basic conditions resulted in the formation of layered double hydroxides, wherein ions like hydroxide and carbonate intercalated between the layers. The CuFe LDH exhibit a broader and intense X-ray reflections at 2θ 11.4 was the characteristic diffraction peak for the layered structure and this peak shifted to higher 2θ values and disappeared completely when CuFe LDH was heated above 400 ^{o}C. This was an indication of layered structure of CuFe LDH initially decreased the interplanar distance and later transformed into new crystalline phase that corresponds to the mixed metal oxide. At 400 ^{o}C, a new broad diffraction observed at 38.6, which corresponds to the (111) CuO phase and no peaks correspond to iron oxide was observed. This is a general phenomenon, when hydrotalcite and layered double hydroxide materials were calcined, the crystalline phase contain predominantly the oxide phase of the divalent metal ion, while the trivalent metal ion gets incorporated in the framework of the divalent metal oxide. There are few other small diffraction peaks observed, which correspond to the $CuFe_2O_4$, mixed metal oxide phase. In order to investigate the textural properties of these particles during calcination, SEM imaging of CuFe LDH and CuFe MMO has been done and the images are shown in Figure 2. CuFe HT exhibit many irregular shaped particles but each of these particles tend to have layered structure that was shown as inset in Figure 2B. After calcination, the size of the particles tends to decrease, even though are few larger aggregates were present and may be formed as a result of calcination induced sintering of particles. Energy Dispersive X-Ray (EDX) analysis of these materials clearly showed the presence of Cu and Fe, even though there was no diffraction peaks corresponds to iron oxide. To investigate the thermal degradation of the CuFe LDH during the calcination, thermo gravimetric analysis of these materials were carried out and the results are presented in Figure 3. In general, LDH kind of materials tend to rehydrate it and partly restore their layered structure, therefore TG analysis of the calcined material was also carried out and the results are given in the Figure 3. Interestingly CuFe LDH exhibits its major sharp weight loss between 300 ^{o}C – 380 ^{o}C and after 400 ^{o}C there was no significant weight loss. This result is in agreement with the XRD results, where the phase transformation of LDH to mixed metal oxide was observed at 400 ^{o}C. However, CuFe-MMO showed continuous weight loss due to the loss of adsorbed water and hydrated ions like hydroxide and carbonate. This shows that this material tend to rehydrate after calcination. This gives an important insight why this material don’t require any ligand during the Ullmann coupling because DMF as a donor solvent tend to rehydrate the CuFe MMO and act as weak ligand to bind with the metal site.

The surface chemistry of the CuFe-MMO needs to be studied to understand the catalytic role of this material towards Ullmann coupling. Figure 4 shows the XPS analysis of CuFe MMO, wherein Cu2p, O1s and Fe2p core level spectra were presented. The binding energy of Cu2p$_{3/2}$ level was observed at 934.4 eV, corresponds to the Cu2p binding energy in the CuO phase. However, the increase in the Cu2p binding energy as compared to standard Cu 2p binding energy in CuO may be probably due to its interaction with iron ions in the framework. In the case of iron, the binding energy of the Fe 2p$_{3/2}$ core level in the CuFe MMO material (Fig. 4C inset) material appeared at 712 eV, slightly higher than the binding energy value observed for iron oxy hydroxides and iron oxide. Another interesting observation, the presence of iron was found to be lower than the iron content observed in the EDX analysis. This was probably due to the presence of iron in the bulk CuO framework and the resultant electronic interaction may be responsible for the shift in binding energy. Analysis of O1s core level binding energies appeared in the case of CuFe MMO material (Fig. 4B) showed two chemically distinct oxygen species. The binding energy values of the O1s levels observed at 530.3, 531.9 were assigned to metal oxide and surface bound hydroxyl groups. Based on this analysis, calcination of CuFe LDH led to the formation of crystalline CuO, wherein iron oxide is incorporated. The role of copper in Ullmann coupling reaction was mainly its oxidative addition reaction with the aryl halides and subsequent reductive elimination of copper halides. Thermally activated CuFe MMO consists of CuO phase doped with Fe^{3+} ions, which was derived from its layered precursor CuFe LDH, The addition of base K_2CO_3 during the reaction partially regenerates the layered structure and enable the copper active sites. This material has high surface area and tends to get rehydrated with the presence of DMF. Since DMF is a donor solvent and its ability to bind with these copper site that eventually led copper to undergo oxidative addition with aryl halides and release of halide ions. The electronic interaction between the Copper and iron in the oxide framework promote the halide adsorption on these sites and enable the Ullmann condensation reaction.

4. Conclusions

In conclusion, we have developed a novel ligand-free, highly efficient and environmentally more benign method for the synthesis of biphenyls with high yields under mild conditions, using a novel solid mixed metal oxide catalyst derived from Cu-Fe-hydrotalcite (by its thermal decomposition at 600 ^{o}C). In the coupling reactions of different halo benzenes, high biphenyl product yields were achieved for iodobenzenes and bromobenzenes but for chlorobenzenes and flurobenzenes poor product yields were obtained. We have investigated the role of various solvents and bases in controlling the product yield and reaction rate. It was observed that DMF and K_2CO_3 when they were used as solvent and base respectively, the Ullmann condensation product was increased significantly. The CuFe

MMO catalyst showed high activity/selectivity and excellent reusability in the reaction. Moreover, this catalyst is inexpensive and requires mild base like K_2CO_3. It can also be easily separated from the reaction mixture and reused for the reaction without significant loss of its activity. All these facts make this catalyst a highly promising alternative to the palladium based homogenous or other heterogeneous solid catalysts. The high catalytic activity seems to be attributed to the uniformly distributed Cu- and Fe-species on the catalyst surface.

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Captions of Figures

Table 1: Ullmann-type coupling of 4-iodoanisole to 4,4-dimethoxy biphenyl over Cu-Fe-hydrotalcite catalyst

Table 2: Influence of the various Bases

Table 3: Influence of the various solvents

Figure 1: XRD profile of as-synthesised Cu-Fe LDH as a function of temperature

Figure 2: SEM images and of as-synthesized Cu-Fe layered double hydroxide and after calcination and EDX spectra of Cu-Fe layered double hydroxide.

Figure 3: Thermo gravimetric data of as synthesised Cu-Fe LDH (1) and calcined Cu-Fe MMO (2)

Figure 4: XPS core level spectra of Cu2p (A), O1s (B) and Fe2p (c) from Cu-Fe layered double hydroxide after calcination.

Scheme 1: C-C coupling of aryl halides

Table 1: Results of Ullmann coupling of substituted aryl halides over Cu-Fe MMO catalyst at 120 °C [reaction mixture = 2 mmol aryl halide (with or without 2 mmol of second aryl halide) + 5 ml DMF + 3 mmol Base + catalyst (10 wt% w.r.to aryl halide)]

Entry	Substrates	Reaction Time (h)	Product	Yield (%)
1	*p*-Iodoanisole	5	4,4’-Dimethoxy-biphenyl	80
2	Iodobenzene	5	Biphenyl	78
3	*P*-Bromoanisole	12	4,4’-Dimethoxy-biphenyl	50
4	*p*-chloroanisole	20	4,4’-Dimethoxy-biphenyl	5
5	*p*-Fluroanisole	20	4,4’-Dimethoxy-biphenyl	nil
6	*p*-Iodoanisole	5	4,4’-Dimethoxy-biphenyl	78[a]
7	*p*-Iodoanisole	20	4,4’-Dimethoxy-biphenyl	<5[b]
8	*p*-Iodoanisole	20	4,4’-Dimethoxy-biphenyl	45[c]
9	*p*-Iodoanisole	20	4,4’-Dimethoxy-biphenyl	nil[d]

[a] Fifth time reuse of the catalyst,

[b] In the absence of catalyst : control

[c] Reaction temperature 100 °C

[d] At Room temperature to 50 °C

Table 2: Results of Ullmann coupling of 4-iodoanisole to afford 4,4'-dimethoxybiphenyl in the presence of different bases at 120 °C [reaction conditions = 2 mmol iodoanisole + 3mmol base + 5ml DMF + catalyst (10 wt % w.r.to 4-iodoanisole)

Base used	Reaction time (hrs)	Product yield (%)
Sodium Acetate	20	29
Sodium Carbonate	20	25
Triethyl amine	20	10
Pyridine	20	5
Zinc dust	20	30
Potassium carbonate	6	80

Table 3: Results of Ullmann coupling of 4-iodoanisole to afford 4, 4'-dimethoxybiphenyl in the presence of different solvents at reflux temperature [reaction conditions = 2 mmol 4-iodoanisole + 3 mmol K_2CO_3 + 5 ml solvent + catalyst (10 wt % w. r. to 4-iodoanisole]

Solvent used	Reaction time (h)	Product yield (%)
DMF	6	80
NMP	10	20
Xylene	12	6
Water	20	--
Toluene	20	5
1, 4-Dioxan	20	--
Acetonitrile	12	17

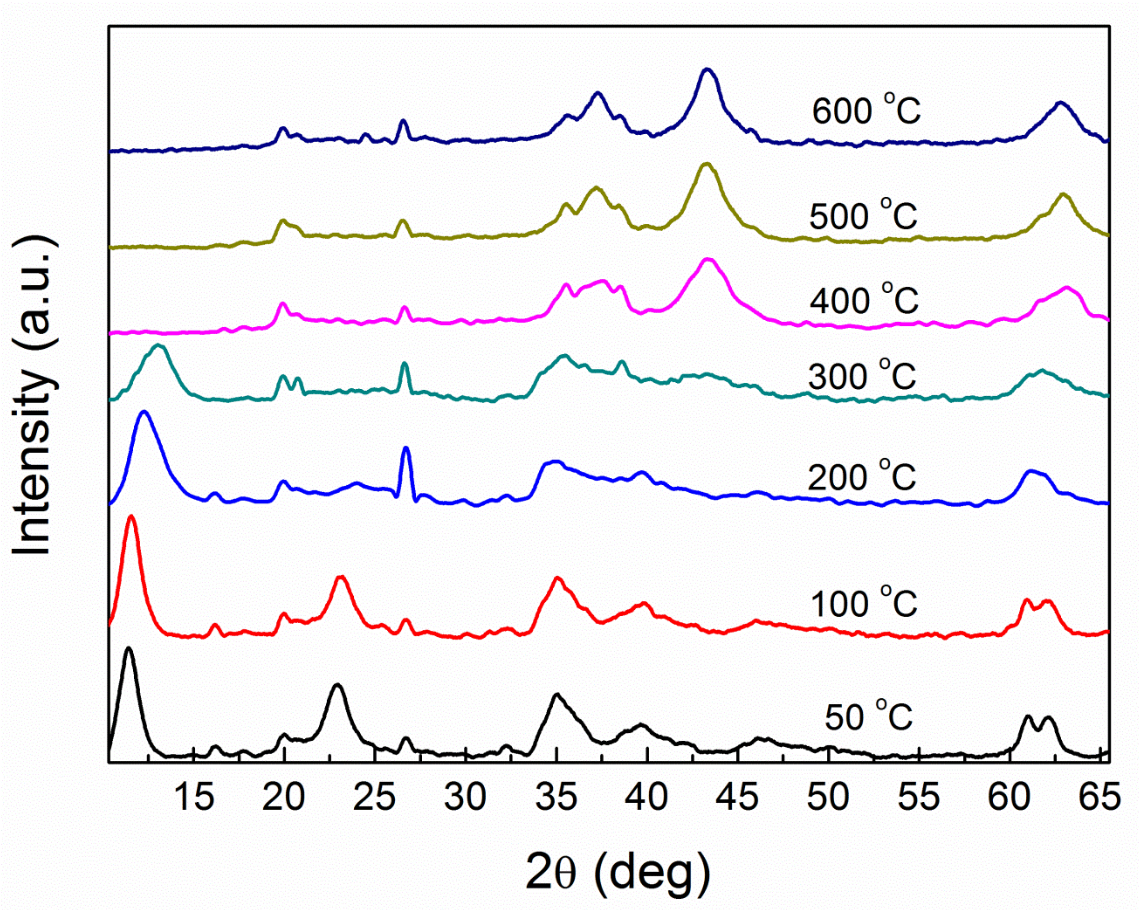


Figure 1: XRD profile of as-synthesised Cu-Fe layered double hydroxide as a function of temperature

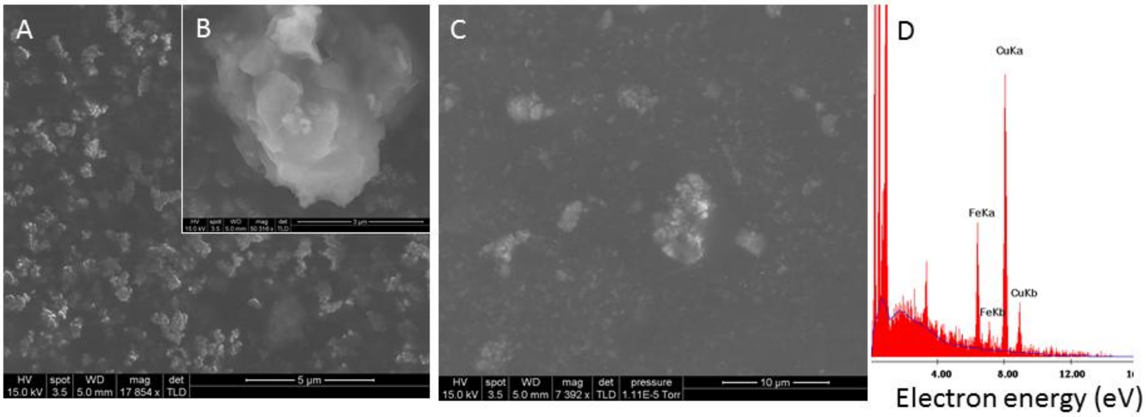


Figure 2: SEM images and of as-synthesized Cu-Fe layered double hydroxide and after calcination and EDX spectra of Cu-Fe layered double hydroxide.

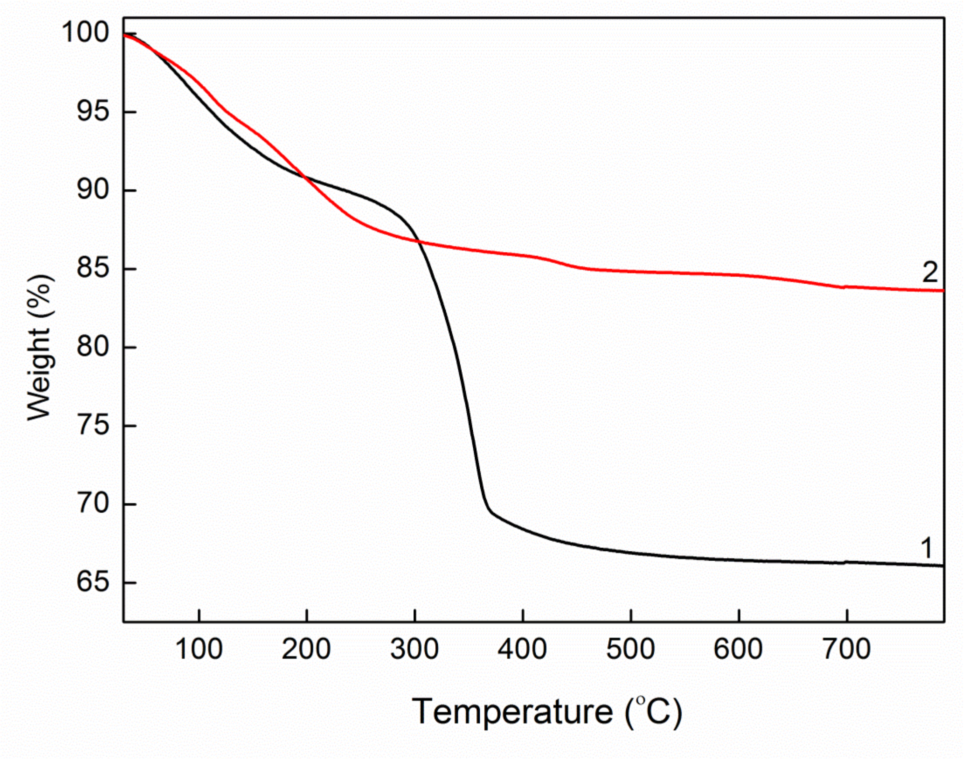


Figure 3: Thermo gravimetric data of as synthesised Cu-Fe layered double hydroxide (1) and calcined Cu-Fe layered double hydroxide (2)

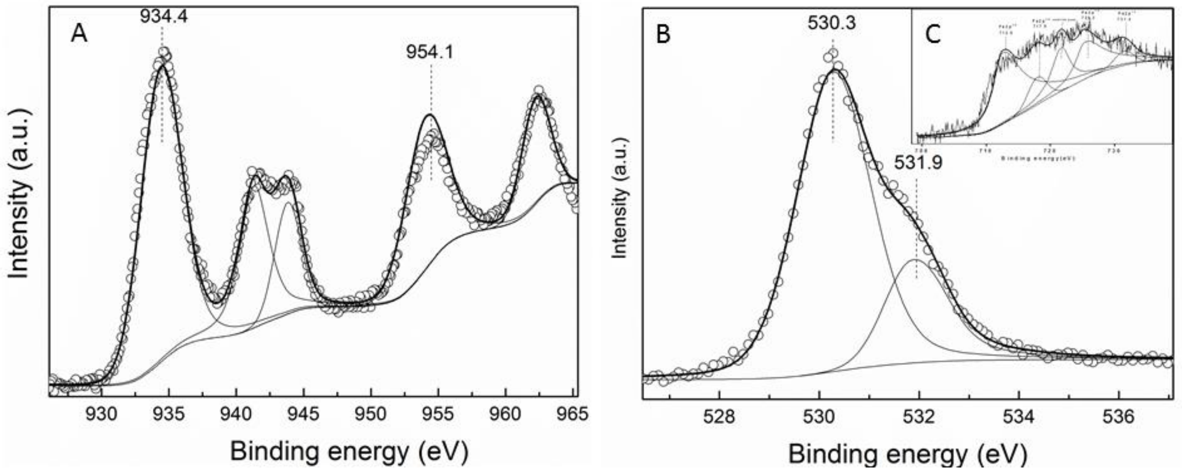
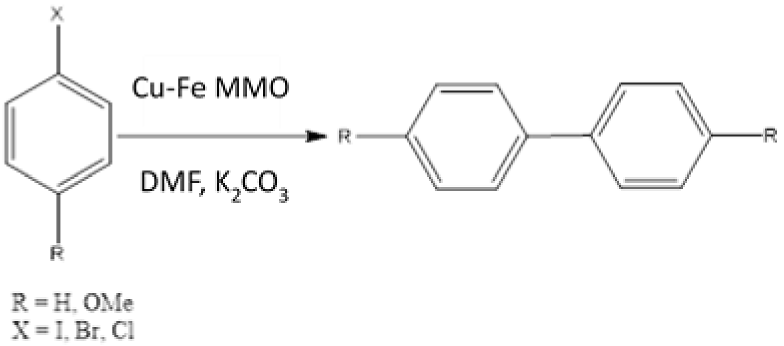
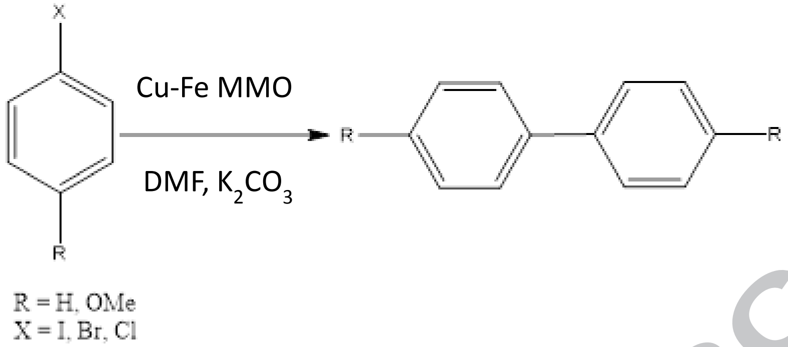


Figure 4: XPS core level spectra of Cu2p (A), O1s (B) and Fe2p (c) from Cu-Fe layered double hydroxide after calcination.



Scheme 1: Ullmann coupling reaction of aryl halides

Graphical Abstract



Mixed metal oxide derived from CuFe layered double hydroxide was demonstrated to be an efficient catalyst for Ullmann coupling between aryl halides to synthesize biaryls.