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Introduction

Montmorillonite is an old but potentially promising candidate to disperse catalytically active metal species and it makes a good support for heterogeneous catalytic processes.¹⁻⁶ However, it is still far from satisfactory for use in scaled-up industrial applications due to poor stabilization of the final catalysts from a practical point of view. The premier development in surface immobilization on any solid support is the covalent attachment of organic compounds/ligands to its surface, followed by complexation with metal ions.⁷ This will enable the active species to interact indirectly, but strongly, with the support surface, preventing their loss to the surrounding medium when used in solution.

Grafting with amines is a relatively in demand method of durably attaching metal ions to many solid support systems. Some successful work has been carried out on amine functionalized zirconia and MCM-41 by our group.^{8–11} Motokura *et al.* have reported a bifunctional catalyst by immobilizing organic primary amines in acidic montmorillonite interlayers using *n*-heptane as a solvent.¹² In our previous report, we have attempted to prepare an organic–inorganic hybrid material by covalent grafting of organic amine moieties on K10 montmorillonite.¹³ Currently, bimetallic catalysts are

A stable amine functionalized montmorillonite supported Cu, Ni catalyst showing synergistic and cooperative effectiveness towards C–S coupling reactions

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The objective of this work is to prepare a cheap and highly stable heterogeneous catalyst. This was done by a simple two step approach. The first step involved the preparation of an organic–inorganic hybrid material by covalent grafting of amines on K10 montmorillonite. In the second step the N atoms of the amine groups were co-ordinated to Cu and Ni ions. Both the covalent and co-ordination forces are strong enough to make the catalyst fairly stable during the catalytic runs. The amine functionalization was confirmed by ²⁹Si CP MAS NMR spectroscopy, FTIR spectroscopy and XPS analysis. The XPS analysis revealed Cu and Ni were present in their +2 oxidation states. This bimetallic system was discovered somewhat by curiosity when Ni was added to a previously well-established Cu catalyzed C–S coupling reaction in an attempt to enhance the catalytic activity. When this catalyst was employed in the C–S coupling reaction, it showed wonderful activity with 99% product yield, due to the synergistic effect of the metal duo.

more in demand than monometallic ones. Clearly, there is great scope for improving the efficiency of organic transformations using two metals instead of one.^{14,15} The introduction of a second metal into a monometallic sample modifies the geometry and electronic properties of the sample. The synergistic effect of both metals is responsible for the higher activity observed for the bimetallic system. Therefore, after using amines to modify the clay, bimetallic immobilization was proposed, where both the metal ions were expected to coordinate with the N atoms of the surface amine groups on the clay.

The coupling reactions offer an essential tool to construct new target molecules in synthetic organic chemistry that exhibit activity against cancer, HIV, Alzheimer's disease, inflammation and asthma.¹⁶ Therefore, we suggested employing the prepared bimetallic catalyst for coupling reactions. Among numerous cross coupling reactions, transition metal-mediated C(aryl)-S bond formation is a much less studied reaction than the corresponding C-N and C-O bond formations due to the deactivation of metal catalysts by organosulfur compounds. Despite this notion, many successful C-S coupling reactions have been reported in the literature using optimised reaction conditions. In a previous report, we successfully carried out the reaction using KOH as the base and DMF as the solvent.¹¹ Aryl sulfur cross coupling reactions can be accomplished by using various transition metals such as Fe, Co, Cu and Ni etc, rather than the costly noble metals.¹⁷⁻²⁰ However, Cu is preferred over various other transition metals because it is cheap and readily available. Compared to copper mediated C-S coupling, there

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has been very little investigation into the potential of nickel to promote this reaction. Therefore, out of curiosity, we chose Ni along with Cu as the two metals for use in the desired reaction. In this work, we report the co-operative effects of a bimetallic Cu, Ni heterogeneous catalyst for the C–S coupling reaction.

Although this coupling reaction has been studied by earlier methods, our approach allows the preparation of the desired product in a shorter time at a low reaction temperature. We also got appreciable results using water as the solvent. In catalysis, reusability of a catalyst/adsorbent is the most important feature of research work,^{21–24} and we found that our catalyst is much more stable towards the reaction conditions compared to the other reports to date.

Experimental section

Materials and methods

Preparation of the catalyst. 0.5 g K10 montmorillonite (MMT) was added to a 15 ml solution of 3-aminopropyltrimethoxysilane (APTMS) (1.2 mmol) using *n*-heptane as the solvent, and stirred at room temperature for 2 h. Then the solvent was removed by filtration and the functionalized clay was washed with the same solvent, followed by drying under vacuum.

Different wt% of metal loading on NH2-MMT was done by an incipient wetness impregnation method. In the first step, to an aqueous suspension of NH₂-MMT, an aqueous solution of the metal nitrates (copper nitrate and/or nickel nitrate) was added dropwise. The suspension was vigorously stirred on a magnetic stirrer for 4 h. It was then kept on a water bath at 80 °C to evaporate the water. The resulting solid was ground into a powder. This was followed by drying at 110 °C for 8 h. These monometallic/bimetallic samples are denoted as different wt% Cu NH₂-MMT, Ni NH₂-MMT, and Cu, Ni NH₂-MMT (Cu and Ni in a 1 : 1 molar ratio). For the sake of comparison, other molar ratios of Cu and Ni (1:0.5, 1:0.75, and 1:1.5) were impregnated on NH₂-MMT. Cu and Ni in a 1:1 ratio were also impregnated onto neat MMT following the above incipient wetness impregnation procedure. These samples are denoted as different wt% Cu, Ni MMT.

Catalyst characterization. Elemental analysis was performed by ICP-OES using a Perkin-Elmer Optima 2100 DV instrument. ^{29}Si CP MAS spectra were recorded at 79.49 MHz applying 90 $^\circ$ pulses, with 300 s pulse delays and 5.0 ms contact time. Both spectra were obtained by using a Bruker Avance 400 MHz spectrometer. The FT-IR spectra of the samples were recorded using a Varian FTIR-800 spectrometer in a KBr matrix in the range 4000–400 cm⁻¹. The PXRD patterns of the samples were obtained on a Rigaku D/Max III VC diffractometer with Cu-Ka radiation at 40 kV and 40 mA in the range 2θ = 5–80°. The specific surface area and pore size distribution of the catalysts were determined by N2 adsorption-desorption at 77 K using an ASAP 2020 (Micromeritics) instrument. Known amounts of the samples were evacuated for 2 h at 110 °C to remove physically adsorbed water prior to the surface area measurements. The X-ray photoelectron spectra of various elements present were recorded using a KRATOS apparatus with Mg, Al and Cu-K α as X-ray sources. The transmission electron microscopy images were recorded using an FEI TECNAI G^2 20 TWIN instrument and the images were recorded using a Gatan CCD camera. The samples for electron microscopy were prepared by dispersing the powder in ethanol and dropping a very dilute suspension onto carbon coated Cu grids. FE-SEM was performed with a ZEISS 55 microscope. The metal leaching into the reaction solution was determined by atomic absorption spectroscopy (AAS) with a Perkin-Elmer Analysis 300 instrument using an acetylene (C_2H_2) flame.

General procedure for aryl-sulfur coupling reaction of thiophenol with aryl iodide. A two neck round bottom flask was charged with KOH (2 mmol). Then the liquid reagents (iodobenzene = 1 mmol; and thiophenol = 1.1 mmol) and solvent (3 ml DMF) were added and finally the catalyst (0.02 mg) was added. The reaction mixture was stirred in a preheated oil bath at 80 °C for 4 h. Then it was allowed to cool to room temperature and diluted with acetonitrile (5 ml), and diethyl ether (0.425 mmol) was added as an external standard. Samples were analyzed by gas chromatography.

Results and discussion

Characterization

Direct metal impregnation on MMT is inhibited by the low stability of the metals on the surface of montmorillonite due to weak electrostatic forces of attraction. To improve the catalytic process, this clay was functionalized *via* a two-step process. As proposed in Scheme 1, this process includes the attachment of surface amines and binding of Cu and Ni ions to these amines. Similar structures have been proposed in the literature, where the metals are co-ordinated to the pseudo NH₂ ligands.^{25,26} The characteristic evidence in favour of the proposed structure is discussed below.

ICP-OES

The results of elemental analysis of the prepared materials (Table 1) suggest that N was grafted onto the clay at 0.8 mmol g^{-1} . It also showed complete uptake of both Cu and Ni, with a Cu : Ni ratio of nearly one in the bimetallic samples. The slightly lower loading of Cu than Ni may be due to the fact that Ni is a little more electronegative than Cu and hence can be more easily co-ordinated to the electron donating N atom of the NH₂ group present on the amine modified clay surface.



Scheme 1 A schematic diagram of the two-step process of amine functionalization and metal loading on MMT.

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Samples	N (mmol g^{-1})	Cu/Ni ratio	Surface area $(m^2 g^{-1})$	Pore volume (cm ³ g ⁻¹)
MMT	_	_	241.41	0.41
NH ₂ -MMT	0.81	_	149.37	0.29
1 wt% Cu, Ni NH ₂ -MMT	0.80	0.98	129.45	0.23
5 wt% Cu, Ni NH ₂ -MMT	0.81	0.99	69.06	0.17
10 wt% Cu, Ni NH ₂ -MMT	0.80	0.99	43.19	0.15

²⁹Si CP MAS NMR spectroscopy

²⁹Si CP MAS NMR spectroscopy is the most reliable method to confirm the covalent linking of the organosilanes on the clay surface. From the solid state NMR spectrum (Fig. 1), the observed Q^n peaks, where $Q^n = \text{Si}(\text{OSi})_n - (\text{OH})_{4-n}$, n = 2-4, are the characteristic peaks of the silicate layers present in the clay. These three peaks were observed at Q^4 ($\delta = -111$ ppm), Q^3 ($\delta = -102$ ppm), and Q^2 ($\delta = -93$ ppm). Again the presence of T^3 ($\delta = -60$ ppm) and T^2 ($\delta = -55$ ppm) peaks confirmed the existence of the covalent linkage between the organic silane moieties of the amine groups and the silicate layers of the clay. The high intensity of the T^3 peak reveals the high degree of condensation of the amine moiety with the clay surface. This confirms the successful covalent attachment of the organosilanes on the surface of the clay.

FTIR

In the FTIR spectrum (Fig. 2) of MMT, it is possible to assign the bands at 3594 and 1034 cm⁻¹ to the Al-O-H and Si-O-Si stretching vibrations. Other bands related to H-O-H stretching and bending vibrations could be found at 3416 and 1636 cm^{-1} respectively. In the case of NH₂-MMT, the CH₂ peaks were used instead of the NH₂ peaks to confirm the APTMS functionalization because of the overlap between the signal of NH₂ at 3200-3500 cm⁻¹ with the Al-O-H and H-O-H stretching vibrations of the unmodified clay. The weak bands at 2941 cm⁻¹ and 2879 cm⁻¹ correspond to the asymmetric and symmetric CH₂ stretch as shown in the literature.^{27,28} However the presence of amide moieties is evident from the appearance of a relatively weak amide band (1536 cm⁻¹, N-H stretching) compared to that of neat MMT. Since both the CH₂ and NH₂ groups are attached to the APTMS skeleton, the above observations suggest the presence of APTMS on the surface of



Fig. 1 ²⁹Si CP MAS NMR spectrum of NH₂-MMT.

MMT. This is in agreement with the results of the ²⁹Si CP MAS NMR spectroscopy.

The sharp peak observed at 1384 cm^{-1} in the case of the 5 wt% Cu, Ni NH₂-MMT sample is due to the nitrate group of the metal precursor. While the positions of other peaks remain unaltered, the weak amide stretching band at 1536 cm^{-1} has undergone a shift towards a lower wavenumber (1512 cm^{-1}). This may be due to metal interactions with the NH₂ groups of the NH₂-MMT.

XPS

The bonding nature of the amine groups with the clay surface (covalent/non-covalent) and the metal loading were further evaluated by X-ray photoelectron spectroscopic (XPS) analyses. The MMT which underwent a two-step process of amine grafting and metal loading exhibited XPS peaks for N, Cu, Ni and Si at different binding energies as shown in Fig. 3. The presence of a Si peak suggests that the surface of MMT has not been completely covered by grafted amines.

The features of the spectra for Cu (Fig. 4) and Ni (Fig. 5) present on the NH_2 -MMT surface reveal information regarding the chemical nature of the metal ions. The narrow survey XPS spectrum of the sample shows that the Cu $2p_{1/2}$ and $2p_{3/2}$ peaks are at 953.3 and 932.9 eV respectively. When the outgoing electron interacted with a valence electron and excited it (shook it up) to a higher energy level, the energy of the core electron was reduced and a satellite structure



Fig. 2 FT-IR spectra of NH₂-MMT (a), MMT (b), and 5 wt% Cu, Ni NH₂-MMT (c).



Fig. 3 XPS survey spectrum of 5 wt% Cu, Ni NH₂-MMT.



For nickel compounds the spin-orbit splitting of the $2p_{3/2}$ and $2p_{1/2}$ peaks is, in most cases, large enough, so that only the more intense $2p_{3/2}$ signal need be considered. The measured nickel $2p_{3/2}$ binding energy at 855.9 eV is consistent with a $3d^8$ Ni(II) ion which may be coordinated to a nucleophilic moiety *i.e.* the organic amine.²⁹ The satellite peak for nickel at 863 eV and the measured binding energy are both characteristic of a Ni(II) ion in an octahedral environment. This conclusion is supported by the data collected by Matienzo *et al.*, who found that binding energies in the region of 856–857 eV are characteristic of octahedral Ni(II).³⁰

The shifting of the Cu and Ni 2p peaks towards lower binding energies and the N 1s peak (403. 1 eV) (Fig. 3) towards a higher energy suggests that Cu and Ni both accept lone pairs of electrons from the N atoms of the amine functionalized clay, according to the results and valance bond theory.³¹

XRD



The broad angle XRD spectra of MMT, NH_2 -MMT and 5 wt% Cu, Ni NH_2 -MMT are shown in Fig. 6. The *hkl* and two

Fig. 4 The narrow survey XPS spectrum of Cu in 5 wt% Cu, Ni NH₂-MMT.

Fig. 5 The narrow survey XPS spectrum of Ni in 5 wt% Cu, Ni NH₂-MMT.

dimensional *hk* reflections for montmorillonite can be clearly seen in all the samples. Along with these peaks, a number of peaks are also present due to many impurities such as quartz, cristobalite and feldspar. The similarities in the spectra of the three samples suggests no structural changes have occurred in the clay matrix.

However, expansion of the clay layers due to amine modification can only be monitored by low angle XRD. The shifting of the (001) peak towards a lower two theta value suggests the intercalation of primary amines into the clay layers. The low angle XRD spectra of MMT and NH₂-MMT are shown in Fig. 7. However, these did not provide any information regarding the intercalation procedure, since there is an absence of the (001) peak due to the lack of a sufficiently ordered and oriented silicate layer structure. The poor long range ordering may be due to damage to the clay layers caused during acid treatment of the synthetic clay. However, the peak observed at 9° creating the ambiguity as to the presence of the (001) peak is due to the illite impurities present in the clay.

Fig. 6 Broad angle XRD spectra of MMT (a), NH_2-MMT (b) and 5 wt% Cu, Ni NH_2-MMT (c).

Fig. 7 Low angle XRD spectra of MMT (a), and NH₂-MMT (b).

N2 adsorption-desorption studies

Fig. 8 depicts typical nitrogen adsorption-desorption isotherms for MMT, NH_2 -MMT, and 5 wt% Cu, Ni NH_2 -MMT. All the prepared samples were examined by this technique and the main results are summarized in Table 1. All the samples behave according to the same trend. As can be seen from the curves, all the samples demonstrate type IV isotherms according to the BDDT classification.³² They show large hysteresis loops, indicative of mesoporous structures, in accordance with our previous reports on acid activated montmorillonite based materials.^{33,34}

The grafting of organic groups and the loading of both Cu and Ni brought about a substantial reduction in the N_2 adsorption capacity of the samples, reflected in a decrease in surface area and pore volume of the samples. Such a drastic decrease in these parameters could be attributed to the space occupied by the grafting agent along with the metals. This means the amine groups and the Cu and Ni ions have been anchored onto the mesopores of the clay, thereby blocking the pores and making them inaccessible to N_2 .⁶

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Fig. 9 TEM micrograph of MMT. Different areas A and B shown with their EDAX spectra and SAED patterns.

TEM

The TEM observations show that the untreated starting material consisted mainly of montmorillonite particles. However, additional mineral phases were also identified, *e.g.* in Fig. 9, the circled portion 'A' showing the fibre like structure is due to illite impurities. Analysis by EDAX showed that the fibrous features consist of elements such as Si, Al, Mg, K, and O. The distinct peak observed in the low angle XRD spectrum at around 9° due the crystalline illite impurity was also confirmed from the dotted SAED pattern.

The remaining part 'B' of the figure shows a layered platelike structure. The EDAX analysis showed that the core of the particle consists of Si, Al, Fe, Mg, and O which is consistent with the constituents of montmorillonite. Due to highly disordered stacking of the montmorillonite crystallites, the electron diffraction patterns obtained of these aggregates contained diffuse reflections resulting from a mixture of several disordered crystallites. This is in good agreement with the absence of the (001) peak in the XRD spectrum.

A hen-shaped particle of NH_2 -MMT (A) and another flaky particle of 5 wt% Cu, Ni NH_2 -MMT (B) shown in Fig. 10 reveal

Fig. 8 N₂ adsorption–desorption isotherms of MMT (a), NH₂-MMT (b), and 5 wt% Cu, Ni NH₂-MMT (c).

Fig. 10 TEM micrographs of NH_2 -MMT (A), and 5 wt% Cu, Ni NH_2 -MMT (B). EDAX spectra of NH_2 -MMT (C), and 5 wt% Cu, Ni NH_2 -MMT (D).

Fig. 11 FESEM images of MMT (a), NH₂-MMT (b), and 5 wt% Cu, Ni NH₂-MMT (c).

the retention of the plate like structure of the parent clay. No spectacular changes in the TEM images can be seen when the MMT is functionalized with APTMS, followed by impregnation with Cu and Ni. However, the EDAX analyses reveal the changes. In the NH₂-MMT material, the presence of N can be seen while in the case of 5 wt% Cu, Ni NH₂-MMT an additional peak due to Ni can be seen, though Cu is common in all the samples as it was used as the grid.

FESEM

FESEM observations show that the parent MMT is a multilayered material consisting of many parallel arrays of broken plates (Fig. 11). The corresponding bright field TEM image of the material also shows similar characteristics. Without any significant morphology changes to the parent MMT, NH₂-MMT also consists of some self-stacked ruptured plates. Also, there are no visible changes in the microstructure after Cu and Ni loading.

Catalytic reaction

In the last few decades, organosulfur chemistry has been widely studied. One of the earliest reports of Mitiga's $Pd(Ph_3)_4$ system for the coupling of aryl halides and thiols came to the forefront in the 1980s.³⁵ Reports of this kind led to extensive efforts towards replacing noble metal systems with more desirable transition metals. Recently, Mondal *et al.* reported a C–S coupling catalyst based on a stable Cu-grafted furfural

Table 2 A study of the effectiveness	of the present system compared with
previous reports	

Catalyst	Yield (%)	Reference
5 wt% Cu, Ni NH ₂ -MMT Cu-grafted furfural functionalized mesoporous organosilica	99 85.2	Present work 36
CuI nanoparticles	93	38

functionalized mesoporous organosilica, where they observed 85.2% product yield in 8 h.³⁶ In another article, the same group had reported the significant role of NiO supported on zirconia towards the synthesis of substituted diaryl sulphides using water as a solvent.³⁷ Very recently, employing CuI nanoparticles at 50 °C in the presence of water using nBu₄NOH as the base, Xu *et al.*, achieved a 93% diaryl sulphide yield in 24 h (Table 2).³⁸

As far as we are aware, here for the first time we report a bimetallic Cu, Ni catalyst system for the coupling reaction of iodobenzene and thiophenol. In our previous studies of Cu/amine-zirconia catalyzed C–S coupling reactions, DMF and KOH were found to be the preferred solvent and base, respectively, so we used these conditions first.¹¹ In this study, we achieved a 99% product yield in just 4 h (Table 2). We also observed the possibility of carrying out the reaction in the presence of water. The various observations made during the course of the study are described in detail below.

At first we studied the activity of neat MMT and NH₂-MMT towards the reaction. It should be noted that both show a small amount of catalytic activity towards the reaction (Fig. 12). This may be due to the presence of Fe in the neat sample as is evident from the EDAX analysis.

Then various wt% of the monometallic Cu samples were tested on the reaction. It can be seen from Fig. 12 that 5 wt% Cu showed the highest activity. In order to test whether another metal can influence the catalytic activity, we chose Ni

Fig. 12 Product yield achieved using different samples; K10-montmorillonite (a), NH₂-MMT (b), 1 wt% Cu NH₂-MMT (c), 2 wt% Cu NH₂-MMT (d), 3 wt% Cu NH₂-MMT (e), 4 wt% Cu NH₂-MMT (f), 5 wt% Cu NH₂-MMT (g), and 6 wt% Cu NH₂-MMT (h). Reaction conditions; temperature: 80 °C, time: 4 h, catalyst amount: 0.02 mg.

Fig. 13 Effect of Cu : Ni ratio on the product yield. Reaction conditions; temperature: 80 °C, time: 4 h, catalyst amount: 0.02 mg.

along with Cu for the same reaction. The influence of the Cu, Ni ratio on the catalytic activity prompted us to vary their ratio in Cu, Ni NH₂-MMT. It can be seen from the results, as shown in Fig. 13, that the synergistic effect of Cu and Ni was strongest when the ratio of these two elements approached 1 : 1. The increased catalytic activity of the bimetallic sample suggests that the addition of a second metal in a proportionate amount causes some changes in the geometric and electronic properties of the monometallic Cu sample, thereby increasing the catalytic performance.

Temperature and time have an enormous effect on the reaction. We studied the progress of the reaction varying these two parameters (Fig. 14). Performing the reaction at 80 °C for 4 h resulted in a 99% product yield. However by changing the solvent to water, and keeping other parameters like time and temperature constant, an interesting yield of 67.3% was achieved. Hence, keeping the tenets of green chemistry in mind, we were delighted to find the potential to perform the reaction in the presence of water as a solvent.

On this basis a plausible mechanism has been proposed (Scheme 2). Upon addition of thiophenol, a catalyst thiol complex (I) is formed. After this, the oxidative addition of

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Scheme 2 A plausible reaction mechanism for the C–S coupling reaction by 5 wt% Cu, Ni–NH $_2$ MMT.

iodobenzene in the presence of KOH generates an intermediate (II). Finally, reductive elimination of intermediate (II) *via* species (III) gives the desired product with the regeneration of the catalyst during the catalytic reaction process.

To test whether there was any leaching of copper or nickel into the reaction mixture during the catalytic reactions a hot filtration test was conducted. During the study, the reaction mixture was filtered under hot conditions from the suspended catalyst after 3 h of the reaction and the reaction was continued using the filtrate at the same temperature for another 3 h. It was observed that there was almost no increase in product yield compared to the yield after 3 h (81.9 and 81.7% yield for before and after hot filtration, respectively). This result suggests that no leaching of Cu/Ni occurred during the course of the reaction and the catalyst is purely heterogeneous in nature.

The most important part of the research finding is the stability of the catalyst. NH₂-MMT plays an important role in

Fig. 14 Effect of time and temperature on the product yield

Fig. 15 Results of recycling tests. Y = yield%

Fig. 16 FTIR spectra of fresh 5 wt% Cu, Ni NH_2-MMT (a), and recycled 5 wt% Cu, Ni NH_2-MMT (b).

improving the stability of the metal duo, due to the strong interactions of the metals with the support surface *via* the amine functionality. Eight test recycles were performed to evaluate the reusability of 5 wt% Cu, Ni NH₂-MMT, as shown in Fig. 15. The catalyst still retained high catalytic performance similar to that of the fresh catalyst after several recycles; no decrease in catalytic activity was observed after six uses.

Fig. 16 shows the FTIR spectra of the reused catalyst. Although the peaks are lower in intensity, the proximity of all the peaks to those of the original sample strongly support the stability of the catalyst.

The primary role of amine functionalization can only be recognized by carrying out the reaction on 5 wt% Cu, Ni MMT. Though almost the same results were observed *i.e.* 98% product yield under the same reaction conditions as for 5 wt% Cu, Ni NH₂-MMT, traces of Cu and Ni could be detected in the filtrate after the 2nd cycle, when subjected to AAS analysis. There was also a significant (10%) decrease in the yield obtained in the 3rd cycle. These results confirm that the amine groups on the surface of MMT are good binders with respect to Cu, Ni NH₂-MMT.

Conclusions

The easy to prepare, cheap and stable mixed metal catalyst system reported here shows ultra-high catalytic activity for the C–S coupling reaction. The effectiveness of having both copper and nickel present in the reaction can be rationalized by carrying out the reaction with the monometallic catalysts. This catalytic procedure offers general applicability and simplicity, avoiding expensive and time consuming protocols. The development of other stable bimetallic (transition metal) nano-catalysts dispersed over the same support, in order to avoid costly noble metal catalyzed reactions in favour of more cost effective ones is a future research prospect for our group.

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