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Synthesis and characterization of Silica –Supported azo-based Schiff base copper(II) complex, catalytic activity of Suzuki–Miyaura cross coupling reaction

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Abstract : Cu(II) Schiff base complex was immobilized on silica -supported azoaldehyde from the one pot reaction of azoaldehyde with activated silica gel, 3-aminopropyltriethoxysilane and copper acetate. The synthesized material was completely characterized by FT-IR,XRD, SEM, EDX. The silica- azoaldehyde Schiff base Cu(II) complex catalytic was studied through efficient catalysts for the Suzuki-Miyaura cross coupling reactions in aqueous medium in iodobenzene with phenylbornic acid.

Keywords : Schiff base, Silica, Azo-Cu(II) Complex, cross coupling reaction.

1. Introduction

Schiff base and their metal complexes have been prepared because of their interesting and important properties, exhibit catalytic reaction. Several studies have also shown that diazo compounds exhibit properties similar to those of Schiff bases [1-2]. Azo-based Schiff bases and their metal complexes have additional applications, especially in the dye industry [3]. The role of the Schiff base metal complexes in such applications is related to molecular structure. The Suzuki-Miyaura cross-coupling have been utilized for the construction of biphenyls is one of the most useful synthetic protocols in organic chemistry [4]. It is used extensively in the synthesis of polymers, agrochemicals, and pharmaceutical intermediates. The heterogeneous catalysis has become a major area of research since the potential advantages of these materials such as simplified recovery and reusability over homogeneous systems which have positive environmental effects.Thus, efforts are being made to transform active homogeneous copper catalysts into effective heterogeneous catalysts by adopting various immobilization strategies utilizing solid supports like silica, MCM-41, SBA- 15 and zeolite[5-6].

In the present work, we have used silica having high surface area and high reactivity prepared by reported method. This silica shows strong and a large number of acidic sites in comparison with commercial silica, making it a good support material to prepare copper immobilized catalyst to carry out iodobenzene with phenylbornic acid to biphenyl.

2. Experimental

2.1. Materials and Instruments

Silica gel, 3-aminopropyltriethoxysilane was purchased from Sigma Aldrich and all the other reagents and solvents were purchased from LobaChemie. FT-IR spectra of the samples were recorded in the region of 4000-400 cm^{-1} on Shimadzu spectrophotometer using KBr pellet technique. Powder X-ray diffraction (XRD) patterns were recorded on a Rigaku Mini Flex II diffractometer (Tokyo, JAPAN). The surface morphology of the synthesized material was analyzed by using scanning electron microscope (HRSEM, JSM 840A, JEOL-Japan) equipped with EDX.

2.2. Activated Silica gel

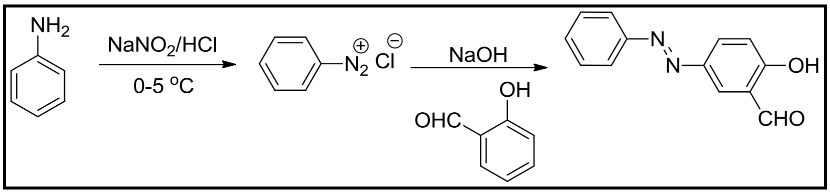
3g of Silica gel with particle size in the range of 60–120 mesh was treated with mixture of nitric acid: water (HNO_3:H_2O = 1:1) at 100°Cfor 3 h, and then with hydrochloric acid (6 mol L^{-1}) at 100°C for 8 h. The treated silica gel was washed doubly with distilled water and dried first at 120°C for 24 h, and the finally calcined in Muffle furnace at 180°C for 2 h.

2.3. Functionalization of silica gel with 3-aminopropyltriethoxysilane (SiO_2@APTES)

3 g activated silica was suspended in 100 ml of dichloromethane and 2.0 mmol of APTES was added and the resultant mixture was refluxed for 24 h. After cooling, the solids were separated by filtration, washed repeatedly with dichloromethane and dried, the obtained material was designated as SiO_2@APTES[7].

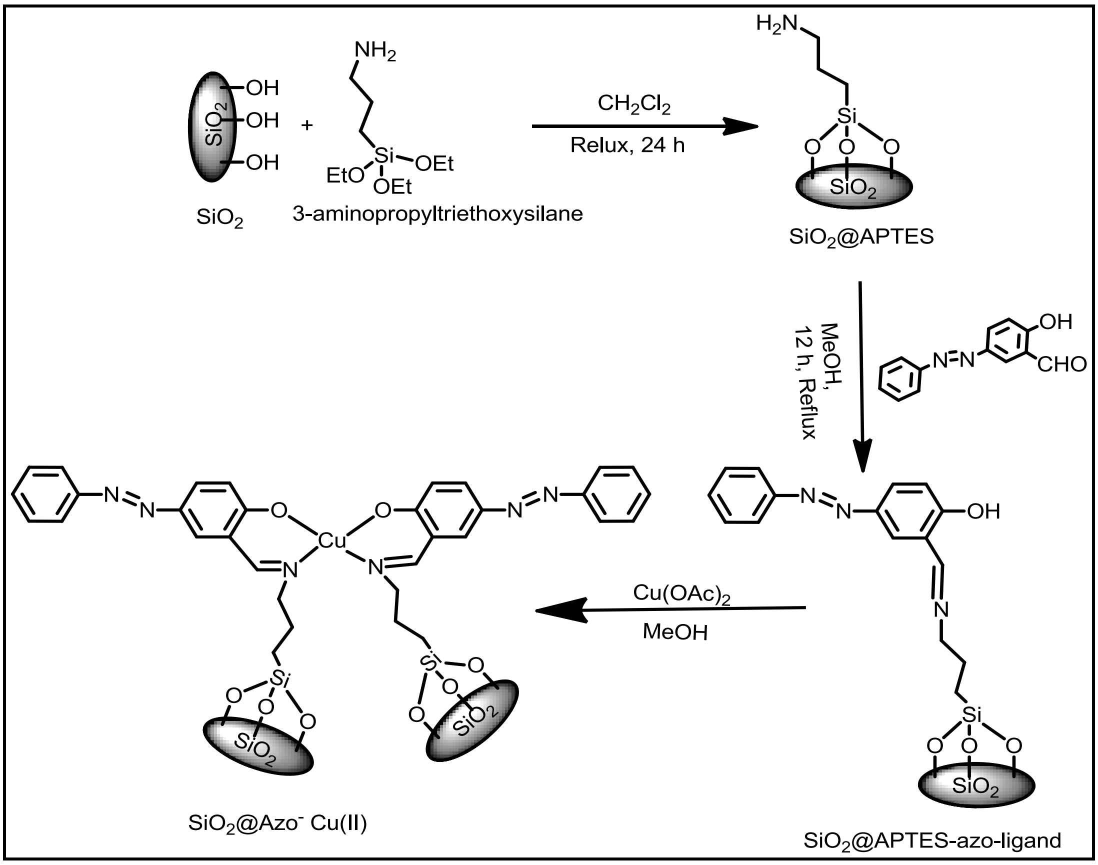
2.4. Synthesis preparation of azo-compounds

Aniline (10mmol) or its derivatives in HCl (36ml) and water (16ml) were heated to 70 °C. Then the clear solution was poured in to an ice-water mixture and were diazotized between 0 °C to 5 °C with sodium nitrate (10mmol) dissolved in water (5ml). The cold diazo solution was added to a solution of salicylaldehyde (10mmol) in water (19ml) contain sodium hydroxide NaOH (10mmol) during the period of 30 min at 0 °Cwith vigorous stirring. Finally, the products were collected by simple filtration and washed with water. Then the crude solid was dried under vacuum at 80°C.



Scheme 1.Syntheses of azo-Aldehyde

Preparation of silica-supported azo containing Schiff base copper complex (SiO_2@Azo- Cu(II)3 g of SiO_2@APTES was added to a stirred solution of azo-aldehyde (0.2g) and the mixture was refluxed at 60 °C for 12 h. The brown solid was filtered, washed with excess amount of MeOH, and dried at 90 °C for 12 h. Then 0.5 mmol of copper acetate was added to the 3g of synthesized azo ligand-grafted silica in MeOH. Then the mixture was refluxed for 24 h at 50 °C (pH 7-8). After completion, the complex was filtered, washed with excess amount of water and dried in vacuum at 80 °C. Silica-supported azo-containing Schiff base copper complex with a possible structure are shown in Scheme 2[8-9].



Scheme2.Synthesis of silica supported Azo Containing Schiff Base Copper Complex (SiO_2@Azo- Cu(II)

2.5. General procedure for the Suzuki-Miyaura coupling reactions of aryl halides using SiO_2@Azo-Cu(II))

A mixture of iodobenzene with phenylboronic acid, K_2CO_3, SiO_2@Azo- Cu(II)catalyst (0.05g) and solvent (3 mL) were charged in a RB flask and the mixture was refluxed under stirring at 100 °C until the completion [10]. The process was monitored by thin layer chromatography (TLC). After completion, the catalyst was separated by filtration and the filtrate was extracted with dichloromethane. The combined organic layer was washed with brine and dried over Na_2SO_4 and then solvent was evaporated under vacuum to give the crude product. The products were purified by column chromatography by usingethyl acetate/hexane (1:9) as an eluent.

3. Results and discussion

Silica supported, azo- Cu(II) Complex, was successfully synthesized and characterized by FTIR, XRD and SEM-EDAX, BET analysis. Then as synthesized complex was used as a catalyst for Suzuki–Miyaura cross coupling reactions.

3.1. Infrared spectroscopy

FT-IR spectroscopy was used to confirm the modification of silica surface. The spectra of azo-Aldehyde, SiO_2, SiO_2@APTES, SiO_2@APTES-Azo-ligand and SiO_2@APTES-Azo-Cu(II) are presented in Fig. 1. The FT-IR spectrum of azo-Aldehyde exhibited a band at 1506 cm^{-1} due to the stretching vibration of N=N group. In addition, a strong stretching vibration at 1610 cm^{-1}confirm the presence of aldehyde carbonyl group and this C-H bond vibration appeared at 2843 cm^{-1}. In the case of silica a strong absorption band characteristic of the support matrix appeared at 1095 and 798 cm^{-1} which can be assigned to Si–O–Si asymmetric and symmetric stretching vibrations, respectively.

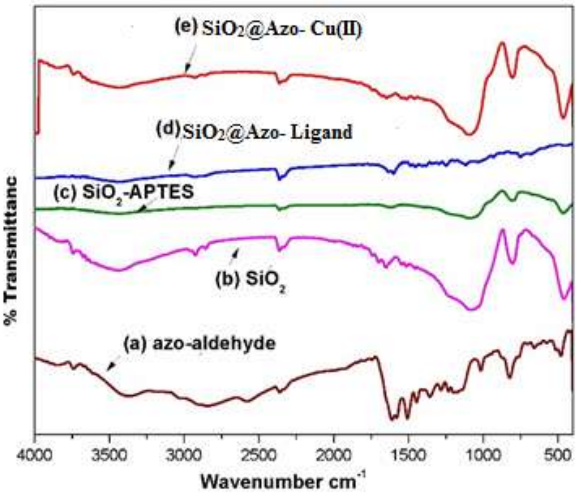


Fig 1. FTIR-Spectra of (a) azo-aldehyde (b) SiO_2, (c) SiO_2-APTES, (d)SiO_2@APTES-Azo-ligand (e) SiO_2@Azo- Cu(II) Complex.

In addition, a broad peak centered at around 3448 cm^{-1} was also observed, that can be attributed to the O– H stretching mode of terminal silanol groups located on the surface of silica spheres. Si–O bending absorbs at 462 cm^{-1}. In the IR spectrum of SiO_2@APTES a broad band in the range 3633 cm^{-1} and at 1095 cm^{-1} can be attributed to silanol OH group stretching and Si-O-Si bonds respectively. The band appeared at 3431 cm^{-1}may be due to the $–NH_2$ stretching vibration of silica supported APTES. A band belonging to $–NH_2$ group was disappeared when azo aldehyde bound to SiO_2@APTES. Furthermore, after coordination of the ligand to the metal ion the relative intensity of the C=N 1635 cm^{-1} (1010 cm^{-1}) is weakened. Where as in the SiO_2@ Azo-Cu(II) (fig.1.e.) the disappearance of the –OH band indicates its coordination to the metal ion after deprotonation. [11-12].

3.2. XRD studies

X-ray diffraction patterns of modified silica supported SiO_2@ Azo- Cu(II) catalyst are shown in Fig.3. The XRD patterns of pure silica showed a single broad diffraction peak at around 2□ = 23° indicated the amorphous nature of silica particles. But the XRD patterns of SiO_2@Azo- Cu(II) exhibited the diffraction peak at 2□ = 22.52° indicates that the topological structure of parent framework remains intact even after surface functionalization. There is a decrease in the reflection intensity of the diffraction peaks after functionalization of linking agent and successive metalation because of the presence of the immobilized species within the pores which reduces the electron density contrast between the silicate walls and pores, thereby causing a decrease in the intensity of the diffraction lines.The overall XRD pattern of the catalyst was found to be similar to modified silica gel, confirming that crystallinity of silica is maintained after modification reaction [13].

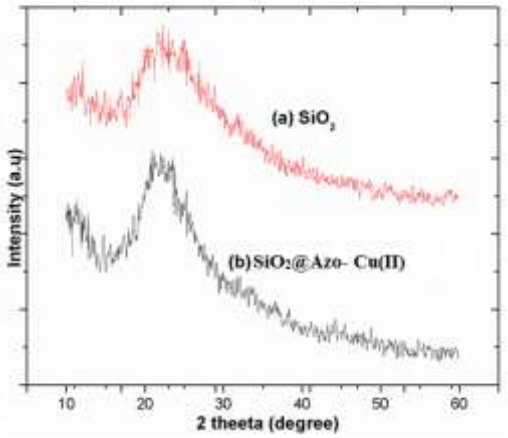


Fig 3. X-ray diffraction patterns of patterns of (a) SiO_2 and (b)SiO_2@Azo- Cu(II) complex

3.3. SEM-EDX analysis

The SEM images (Fig. 4a, 4b) of activated pure silica and the functionalized SiO_2@Azo- Cu(II) complex clearly indicates the changes in the surface morphology of the catalyst before and after introduction of metal complex on silica wall. It was seen that from the Fig. 4 the morphology of the both samples are quite similar appearance with well dispersed stone like structure.

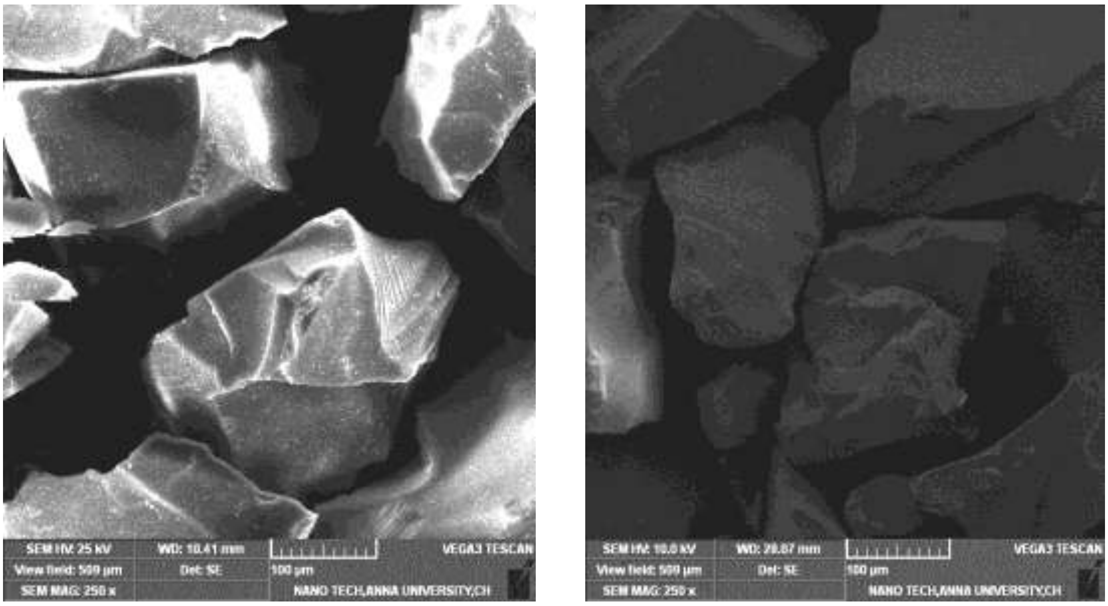


Fig 4. SEM images (a) SiO_2, (b) (SiO_2@Azo- Cu(II) complex,

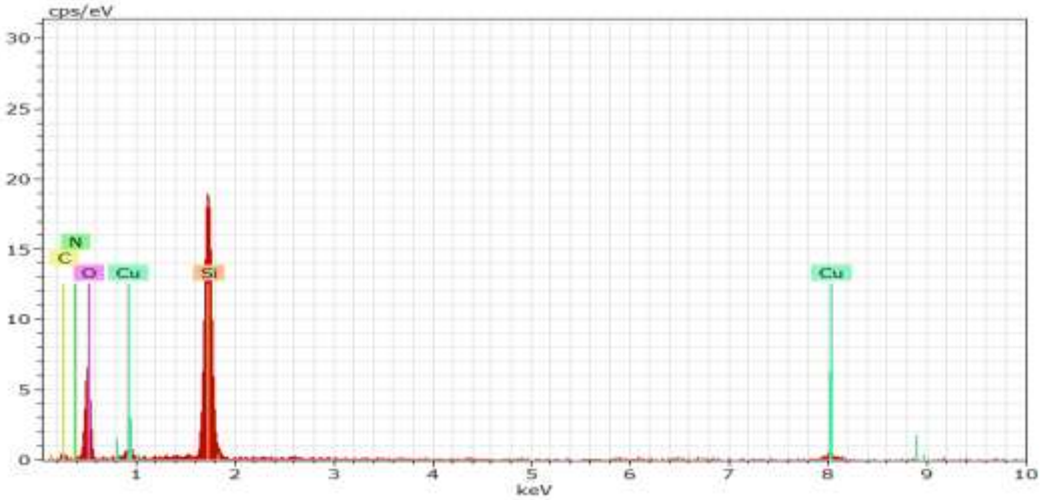
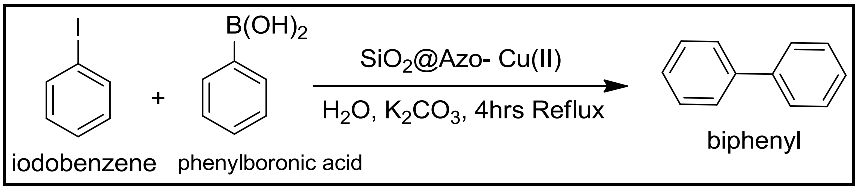


Fig 5. EDX spectrum of (SiO_2@Azo- Cu(II))Schiff base complex.

But, in the case of silica functionalized SiO_2@Azo- Cu(II) complex particle size was increased, because upon functionalization the huge surface area was produced on the silica wall. This is the main reason for the synthesized catalyst possess good catalytic behavior. Furthermore, EDX spectrum of silica functionalized SiO_2@Azo- Cu(II) complex confirms the presence of Copper into the catalyst represents the formation of the copper complex (Fig. 5).

3.4. Catalytic applications

The catalytic activity of the synthesized material (SiO_2@Azo- Cu(II)) was evaluated by the Suzuki coupling reaction (Scheme 3). Initial trials were performed to optimize reaction conditions using iodobenzene and phenylboronic acid as a substrate to evaluate the suitable reaction parameters like bases, solvent and temperature. From this screening results, we observed that K_2CO_3 as a base and H_2O as a solvent at 100°C were most suitable for this suzuki couples reaction. Using this optimized reaction conditions, the scope of this Suzuki reaction was further explored by using iodobenzene with phenylboronic acid and their results are 4hrs 94 % yield obtained.Next, we have find out the suitable solvents for this reaction, same reaction was performed with different solvents (3 ml) like THF, DMSO, EtOH, H_2O and toluene under refluxing conditions and found that **H_2O** was most efficacious one in the terms of yield and time.



Scheme 3.The Suzuki–Miyaura cross coupling reactions of iodobenzene with phenylboronic acid

Table.2.Suzuki-Miyaura cross-coupling reactions of iodobenzene with phenylboronic acid different solvent using (SiO_2@Azo- Cu(II)[a]

Entry	Solvent	Yield[b](%)
1	THF	70
2	DMSO	75
3	EtOH	90
4	**H_2O**	**94**
5	MeOH	88
6	Toluene	70
7	Without solvent	-

[a]Reaction Conditions: Iodobenzene with arylboronic acid(1 mmol), Solvent (3 ml), catalyst loading (0.05g) at temperature 100 °C for 4 h.

All the products are known compounds and physical and spectral data and good agreement with literature.

[b]Isolated yields.

4. Conclusion

In summary, we have successfully synthesized the silica functionalized Azo based Schiff base Cu(II) complex. The synthesized catalyst was fully characterized by FT-IR, XRD, SEM, EDX. The Silica-Supported azo-Cu(II) complex was used as efficient heterogeneous catalyst towards the Suzuki–Miyaura cross coupling reactions of iodobenzene withphenylboronic acid under greener conditions. The catalyst was recycled and reused for more than five times without any loss in its activity.

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