Cobalt Schiff base immobilized on Graphene nanosheet with N,O linkage for Cross-Coupling reaction

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Cobalt Schiff base immobilized on Graphene nanosheet with N,O linkage for

Cross-Coupling reaction

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Abstract:

A simple and direct pathway to synthesize heterogeneous catalyst by covalently immobilizing cobalt Schiff base complex on the surface of amino functionalized graphene oxide for the cross coupling of aryl halides and arylboronic acids is reported. The as synthesized samples were characterized using various spectroscopic techniques and thermal analysis to attain their structural and functional features. The analysis confirmed that the Co bounded to the ligand using bi(N,O) linkage and the Co Schiff base complex immobilized onto the functionalized graphene oxide through its amino moiety. The catalytic investigation confirmed the product yield up to 96.5% for the Suzuki cross coupling using gas chromatography. ICP Analysis shows that the central active metal is 85% in its catalyst even after the 5th iteration. High product yield, environmentally benign, easy workup, easy filtration of catalyst and mild reaction conditions are the main facets of this catalyst.

Keywords:

Schiff base; Functionalized Graphene oxide; Biaryls; heterogeneous catalyst.

Introduction

Nowadays, Graphene and its materials emerged as an interesting moiety having impeccable properties such as high surface area, defective lattice sites with adjustable tuning properties and high thermal and electronic properties[1,2]. Nevertheless, graphene based materials are helpful in

controlling the growth of size of metal nanoparticles (NPs) with adjustable tuning properties which makes them known to be heterogeneous catalysts[1]. In order to overcome the present demand for the design of heterogeneous catalyst, numerous methodologies were developed in carbon based materials, graphene oxide with varied oxygen containing functional moieties capable for anchoring the metal NPs making them as nanocomposites[3,4]. These nanocomposites acts as promising material in catalysis, energy storage devices electronics and sensor applications[5]. Various techniques have been monitored to synthesize graphene-metal nanoparticle composites and the simplest method is the incorporation of metal precursors on to the surface of GO using noncovalent interactions at an elevated temperatures[6,7].

Suzuki-Miyaura cross coupling reaction is extensively known method for the carbon-carbon bond formation in organic synthesis which includes from the manufacture i.e., small complex intermediates to the industrially viable active pharmaceutical ingredients (APIs) [8]. Of all the various transition metals, palladium is predominantly used for this[9–11]. However, palladium being a precious metal, high cost volatility prohibits its usage in huge quantities. Due to the search for alternative catalytic methodology, which employs a suitable transition metal 1st row element such as cobalt and iron transition metals which is an important approach due to its sustainability in its ecofriendly nature[12–16].

For this heterogenization of homogeneous catalysts which contributes to the increase in the efficiency of the catalysts due to its more reactive sites on its surface which further expand its use in industrial application [17,18]. Schiff base first reported by Hugo Schiff and when they coordinated with metals such as Co, Cu, Ni etc., to form metal complexes[19–22]. However these complexes finds its applicability in various oxidative-reduction reactions[16]. Due to the lack of catalyst efficiency as well as stability and recovery is the major issue[23]. Herein, we synthesized Schiff base metal

complexes immobilized to the graphene oxide as catalysts for Suzuki coupling reactions. Immobilization phenomena onto solid support is better than impregnation technique which leads to minimize metal leaching as well as improving the long-stability of catalyst.

LM Kumar reported (2016) Co complexes which includes tridentate pincer (PNCOP) ligands as catalysts which efficiently catalyzes the Suzuki cross coupling reaction using phenylboronic acid with various substituted bromobenzene[24]. Scheuermann et al (2009) reported the palladium supported graphene oxide and chemically derived graphene (CDGs) with a high catalytic activity and also they stated the morphology of carbon support along with functionalization[25]. Feng et al (2014) reported the Pd-Co bimetallic nanoparticle (1:1) ratio supported on graphene by chemical reduction method for the coupling of phenyl acetylene and aryl halide in THF/water mixture using triethylamine as base at 80 ^{o}C[26]. The catalyst retained satisfied catalytic activity after 5th successive runs along with stability. Alamdari (2016) reported a phosphine group functionalized graphene along with palladium nanoparticles and the catalyst were active till 5th successive cycles for Suzuki, Heck and N-arylation reactions[27]. Wang et al (2013) reported a novel catalyst i.e., palladium supported on an ionic liquid modified graphene (GO-NHC-Pd^{2+}) for catalyzing the Suzuki coupling reaction with at least 6th consecutive cycles retained its activity[28]. Mark et al (2018) reported the palladium species supported on hydrogen titanate nanotubes by impregnation method and tested its activity in Suzuki coupling with 10% decrease in catalytic activity after five cycles[29]. Jinhui et al (2016) reported the synthesize of Cu-Pd ferrites on mesoporous SBA-15 and MCM-41 molecular sieves and retained its activity after 10 consecutive cycles[30]. Nesreen et al (2017) reported the CuAl and CoAl double layered hydroxides (LDHs) onto graphene oxide and the catalytic activity in Ullmann reaction is 91% and 98% in 25min[31]. Phuong et al (2018) reported

the graphene oxide framework with encapsulated with palladium species and the catalytic activity in Suzuki coupling reaction using both protic and aprotic solvents with good yield[32].

In these work, we synthesized a cobalt Schiff base immobilized onto graphene oxide using APTMS as a coupling agent for the formation of carbon-carbon bond and varying the catalytic activity in Suzuki Cross coupling reaction. Herein we synthesized the GO and later it is amino functionalized and then Co Schiff base is immobilized on to amino functionalized GO.

Experimental Section

Materials

Graphite powder, 3-aminopropyl trimethoxy silane (APTMS), 2-aminoethanol, arylboronic acids, terephthalaldehyde and various aryl halides were purchased from sigma Aldrich. All the solvents like ethanol, toluene, acetonitrile, DMSO, hydrogen peroxide and along with sulphuric acid, phosphoric acid are obtained from Finar chemicals limited. Caesium carbonate, potassium carbonate, sodium hydroxide, potassium hydroxide, SDS(sodium dodecyl sulphate), sodium nitrate, sodium carbonate, Cobalt nitrate hexahydrate ($CoNO_3$. $6H_2O$), pyridine, PVP (poly(4-vinylpyridine)) and potassium permanganate are obtained from lobo chemie limited.

Synthesis of Graphene oxide (GO):

GO was prepared according to the improved Hummers method[33] 5g of graphite and 2.5g of $NaNO_3$ were mixed with 108ml of H_2SO_4 and 12ml of H_3PO_4 and later maintained in an ice bath along with stirring for 10minutes. After that, 15g of $KMnO_4$ were added slowly by adjusting the temperature at 5 °C. Then it was stirred for 2h in an ice bath and after that the temperature of the reaction was raised to 45 °C for 30 minutes. Later, the mixture is adjusted to 98 °C for 12h and then deionized water dropped slowly to this mixture to get its volume to 400ml. After that 15ml H_2O_2 was added after 5 minutes and stirred vigorously using glass rod. The collected product was

centrifuged, washed several times with deionized water and 5% HCl solution and later it is dried, kept in oven at 50 °C.

Synthesis of 3-aminopropyl trimethoxysilane functionalized-GO (ASGO):

The as prepared 1000mg GO was immersed in 50ml of toluene using ultrasonic bath and was refluxed with 2ml of APTMS under a nitrogen atmosphere for 24h around 110 °C[17]. After that, the black powder obtained was filtered, washed with toluene for several times, and later washed using absolute EtOH to remove any physisorbed traces of APTMS. The sample was dried in vacuum oven around 90 °C for 6 h.

Synthesis of Cobalt oxide particles:

0.2162g of SDS in 50ml of distilled water along with 0.8731g of $CoNO_3$. $6H_2O$ in 10ml of distilled water were prepared separately. Later, the cobalt solution is stirred by adding SDS solution dropwise and kept constant stirring at room temperature. Next, 0.3603g of urea is dissolved in distilled water and the entire mixture were added together and stirred for 2h. After that the solution is transferred to Teflon lined autoclave for 2h at 140 °C. The final product obtained is filtered, washed repeatedly with ethanol and dried in an oven at 80 °C for 12h. Then, it is annealed at 400 °C for 2h in vacuum oven and then the black colored powder is obtained.

Synthesis of graphene oxide immobilized cobalt Schiff base complexes (CoASGO):

The terephthalaldehyde amount (470mg, 1.0mmol) and 2-amino ethanol (229mg, 0.6mmol) along with few drops of acetic acid were added to the mixture and refluxed for 24h. The formed solid product is filtered and washed several times with ethanol. Later the (500mg, 0.05mmol) amino functionalized GO was dispersed in 60ml of absolute ethanol and then the (100mg, 0.01mmol) of Schiff base is added to the mixture and refluxed for 24h. After refluxing, the product cooled down to room temperature and achieved the solid product by filtering and washed with ethanol twice.

Finally, the obtained product was mixed with Co oxide particles (488.1mg, 2.0mmol) in ethanol and reacted for 24h room temperature. The product was filtered and washed with ethanol, and dried in an oven at 50 °C. The scheme 1 shows the synthesis of CoASGO complex.
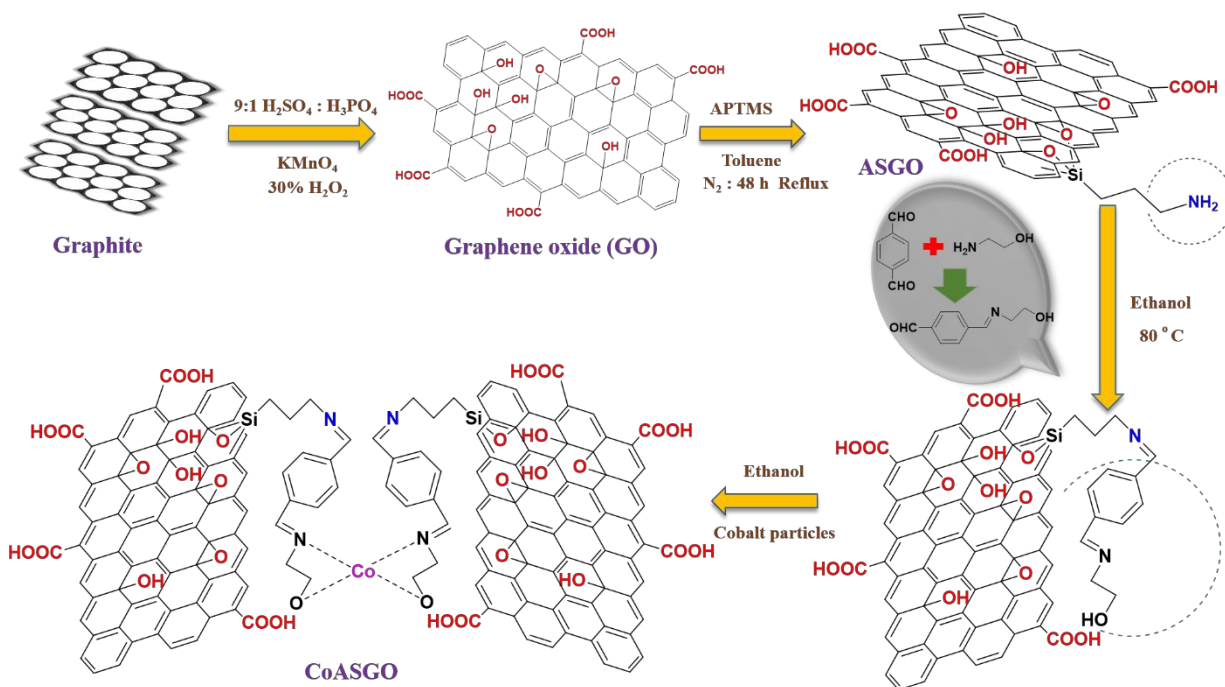
Scheme 1: Schematic mechanism for the synthesis of CoASGO complex

Experimental procedure:

Aryl halide (1mmol) and arylboronic acid (1.5mmol) taken in a flask along with the catalyst (0.32mol%) and base Cs_2CO_3 (3mmol) in ethyl alcohol (5ml). The flask was charged in a parallel synthesizer Talboys at 80 °C under reflux conditions up to 12h. Once the reaction is completed (monitored by using thin layer chromatography) the product was analyzed using Gas Chromatography (GC) (Shimadzu 2014, japan), siloxane Restek capillary column (30m length and 0.25mm diameter) and flame Ionization Detector (FID).

Hot Filtration Test:

The catalytic reaction between phenylboronic acid (1.5mmol) and aryl bromides (1mmol) was performed at 60 °C in presence of base Cs_2CO_3, CoASGO catalyst (0.32 mol%) and ethanol as

solvent for the hot-filtration test. After the reaction time 4h, half of the reaction mixture is taken and filtered while it is hot into a preheated vial and continued the reaction. Later, the unfiltered and filtrate solution were analyzed using Gas Chromatography at the predestined time.

Poisonous Test:

In order to investigate the homogeneity/ heterogeneity of catalytic system, catalyst-poisoning test was conducted for the Suzuki coupling reaction. Due to the addition of catalyst poisons, the catalytic activity of the active Co species can be removed and further decrease in the product formation. Here, the poisons like pyridine are used which binded strongly to Cobalt metal ions and insoluble PVP (poly(4-vinylpyridine)) used as a trapping agent which confirmed the presence of leached soluble Co ion in the reaction medium. Organic polymer resin i.e., 3-aminopropyl trimethoxy silane was also studied to determine the activity of catalyst.

Sample Characterization:

In this work, the CoASGO catalyst shows improved reactivity due to the covalent interaction of amino functionalized GO with cobalt Schiff base complex. Herein, we reported a series of physicochemical characterizations such as ICP-AES, FTIR, TGA, PXRD, SEM, EDX, TEM and XPS were conducted on the catalyst to understand the structure and composition as well as to identify an efficient means to enhance the stability of the catalyst. The infrared spectra were recorded using KBr disks in a Bruker-Alpha ECO-ATR FTIR in the range 500-4000cm^{-1}. PXRD measurements were carried out using Cu Ka radiation on a Rigaku 600 diffractometer Miniflex. Diffractions were carried out in the ranges (2y) of 5-80º at the scanning speed of 2º per minute for the XRD patterns of GO and their covalently attached amino functionalized Schiff base metal complex catalysts. HR-TEM Analysis were taken on a FIE Tecnie-F20 with an acceleration voltage of 200kV. X-Ray photoelectron spectroscopy (XPS) was measured on a Kratos XSAM800

X-ray electron photometer using Al K radiation. TG analysis performed on a Hitachi DTA-6300

in N_2 stream with a heating rate of 5 °C per minute in the range of 25-800 °C. The samples were

heated at a constant rate of 10 °C/min under N_2 flow from 200-800 °C. Metal content was calculated

by inductively coupled plasma atomic emission spectroscopy (ICP-AES) analysis on a Agilent

5100 Synchronous vertical Dual view ICP-AES with Dichroic Spectral Combiner (DSC)

Technology. Electron paramagnetic resonance spectroscopy were done on a JEOL JES FA200

ESR spectrometer, X-band with LN2 VT accessories) were obtained with a frequency of 9.65GHz

Results and discussion

i) Characterization of the catalyst:

FTIR:

FT-IR spectra of the pure GO and CoASGO shown in Figure 1. In GO, a strong band is around

$1710cm^{-1}$ (C=O) represented the carboxylic acid and they were bands at 1058, 1220 and 1621 cm^{-1}

represented the epoxy(C-O), phenol, C=C etc., in their scaffold[6,7,33,34]. The hydroxyl groups in GO

around 3394 cm^{-1} which indicated the stretching mode of O-H bonds. In ASGO, there is a doublet

band around 2850 and 2917 cm^{-1} exhibited the symmetric and asymmetric stretching vibrations of

methyl and methylene alkyl groups in ASGO[35,36]. Further, the other bands in ASGO around

1121.5, 1029 and 1629 cm^{-1} intended to be Si-O-Si, Si-O-C linkages and bending N-H vibrations

which indicated that the grafting of APTMS onto GO by chemical bonding have taken place. Two

bands around 3423.7 and 1629 cm^{-1} i.e., N-H group which confirmed that the amino

functionalization successfully taken place on its surface i.e., ASGO shown in supplementary

information (figure S1)[36]. A band around 692 cm^{-1} proved that the silylation process taken place

on GO shown in supplementary information (figure S2). The band around $1629cm^{-1}$, in amino

functionalized GO disappeared and moved to lower frequency (C=N cm^{-1}) at 1610cm^{-1} confirmed

that the -NH$_2$ groups in ASGO undergone condensation reaction with the other side carbonyl group

of terephthalaldehyde to form C=N bond on the heterogeneous support which confirmed the

binding of amino functionalized GO surface with the organic Schiff base moiety. A peak around

660 cm^{-1} confirmed the presence of cobalt moiety on the heterogeneous catalyst shown in figure

1[37]. There is a band around 598cm^{-1} which signified the stretching of Co-N bond and it proved the

coordination of cobalt with N, O sites on the catalytic surface of the heterogeneous catalyst shown

in figure 1[17].
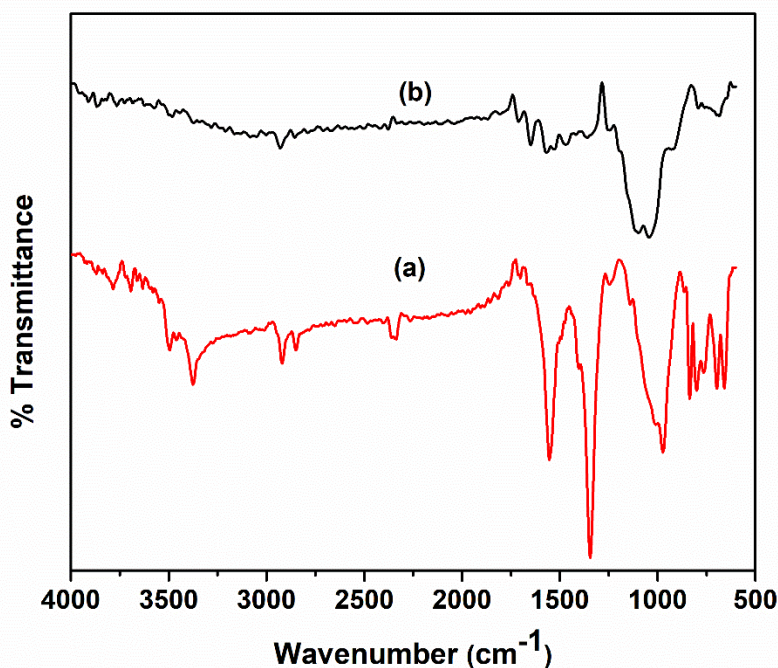
Figure 1. FTIR spectra of a) CoASGO complex and b) GO

XRD analysis:

In GO, a broad peak around 2θ = 10.91 confirmed that the graphene oxide has been formed with

oxygen moieties which got amalgamated on the basal planes of graphitic layers having hydroxyl

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groups which increase the interlayer distance between the graphitic sheets shown in supplementary information (figure S3)[33,34]. In ASGO, the diffraction peak around 2θ = 10.9 represented that graphene oxide chemical morphology not damaged due to the amino functionalization of GO[35,36] Due to the functionalization of GO with APTMS, the peak intensity reduces and a new broad peak appears around 20.1º respectively shown in supplementary information (figure S3). The peak weakening is due to the saturation of spaces between interlayer exhibiting amorphous morphology[36]. However, due to the shattering of varied range of stacking equal to GO nanosheet exfoliation and the newly protruded peaks nearest to the reduced GO confirmed that some of the oxygen moieties possessing hydroxyl group in GO have been successfully functionalized. A broad peak around 2θ = 22.24 confirmed the oxygen groups on graphene oxide surface have been successfully functionalized due to the amino functionalization and which in turn lead to encapsulation of metal complex. The cobalt crystallites peaks in cobalt oxide particles were around 18.9, 32.3, 36.7, 42.7, 56.2 shown in figure 2b [14]. The peaks in synthesized catalyst CoASGO around 18.9, 31.2, 37.4, 44.7, 59.2 and 65.2 respectively shown in figure 2a. The intensity of a weak peak indicates the cobalt oxide molecules were in smaller in size [14,37]. A weak peak around 10.9 represented that the immobilization had taken place with the simultaneous introduction of organometallic species which resembles the complex prepared successfully[18]. However, the broader peaks of diffraction pattern explained that the synthesized catalysts is amorphous in nature.
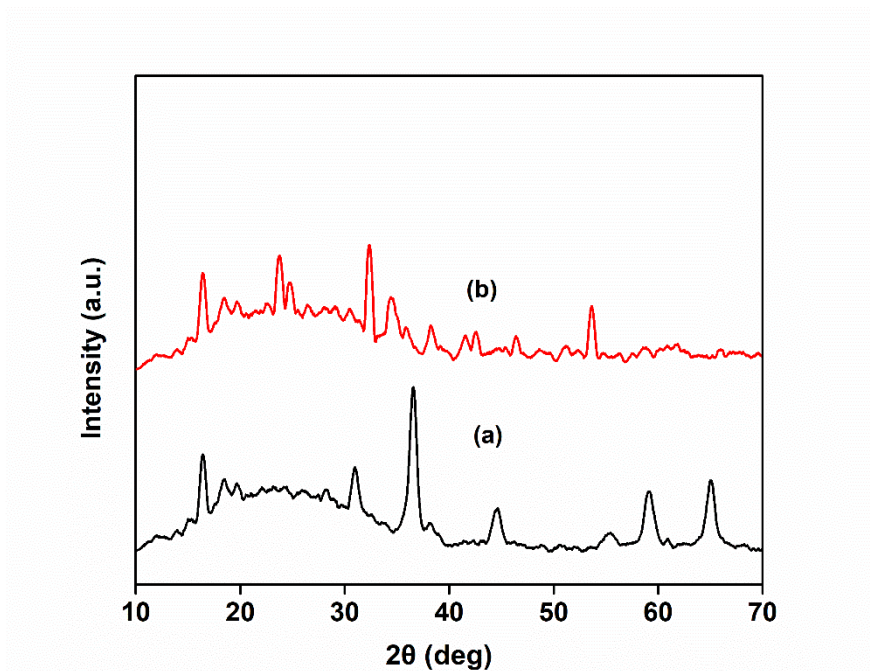
Figure 2. XRD graph of a) CoASGO complex and b) Cobalt oxide particles

SEM & EDX (Scanning Electron Microscopy & Energy Dispersive X-ray Analysis):

The morphology and structural features of GO, catalyst CoASGO and ASGO were analyzed using

FE-SEM analysis and EDX analysis. In GO, the 2D structure represented twist in its nanosheets

which resemble to be not in ordered phase with a lot of crumpling feature shown in figure 3a [34].

The carbon in GO is sp^2 hybridized with a lot of protrusion and folded edges enabling the Co

Schiff base complexes to get immobilized onto the graphitic surface. The reactive sites on these

heterogeneous support acts as idealistic patterns which in turn enables the reactant moieties

undergo target oriented modification on GO. Therefore the stacking phenomena which is more in

synthesized catalyst due to the amino modification using APTMS shown in figure 3b along with

organometallic species introduction compared to the basal planes of pure GO shown in figure
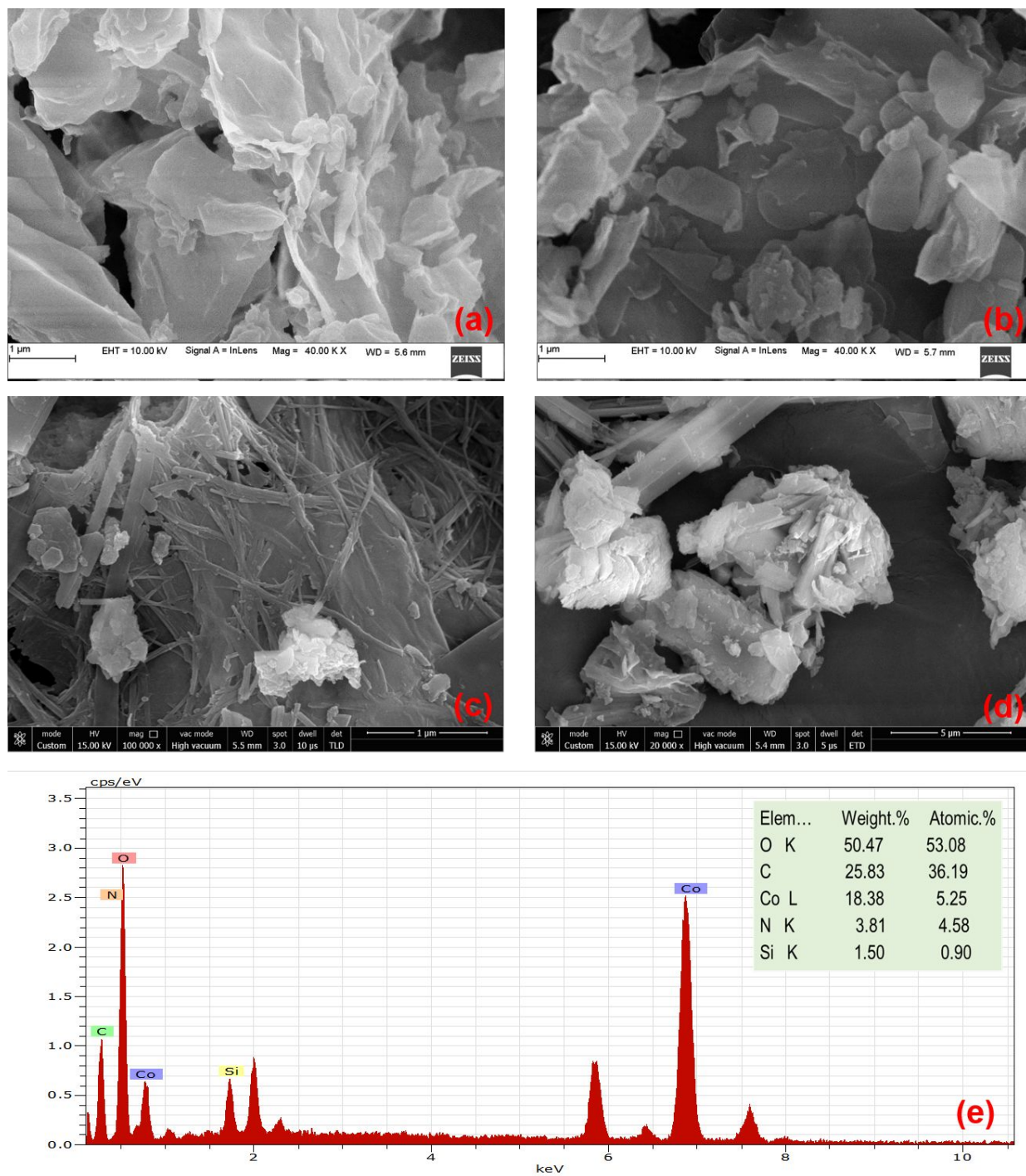
3(c,d) [14,16,35,36].

Figure 3. SEM of a) GO, b) ASGO, c,d) CoASGO, and e) EDS image of CoASGO

EDX analysis showed the atomic wt% of the GO, ASGO, CoASGO. In GO, it is a cluster of both carbon and oxygen moieties with different functional groups shown in supplementary information (figure S4). In amino functionalized GO ASGO, the elemental mapping showed the composition of elements such as carbon, oxygen, silicon and nitrogen which confirmed that APTMS successfully loaded onto the surface of GO given in supplementary information (figure S5). The elemental composition of the synthesized catalyst showed the composition of various elements like cobalt, nitrogen, oxygen, carbon and silicon with different atomic wt% ratio shown in figure 3e. However, the presence of various elements confirmed the loading of Co Schiff base onto amino functionalized GO surface. The results from EDX mapping depicted that the homogeneous distribution of Co, N and Si on the GO support.

TEM:

TEM sample preparation was done by fixing some pieces of composite on a carbon coated copper grid by gentle pressing and making them to adhere to their surface firmly. The figure 4a showed that the synthesized GO with a nanoscopic morphology having wrinkled structures with a few layers or sheets[25]. After the amino functionalization on GO ASGO, the figure 4b showed the layered morphology is due to the binding of silane groups onto the GO surface. It also confirmed that the GO nanosheets structure not damaged during the amino functionalization. Figure 4 (c, d) indicates the Selective area diffraction pattern (SAED) that the catalyst is polycrystalline phase. Numerous crumpling feature with a layered fashion in nanosheets which justified the cobalt schiff base is immobilized onto amino functionalized GO shown in figure 4c. The average size of CoASGO in HR-TEM image confirmed that it is 6nm in its size and the TEM image of the catalyst CoASGO it is 15nm in its size shown in figure 4 (d, e).
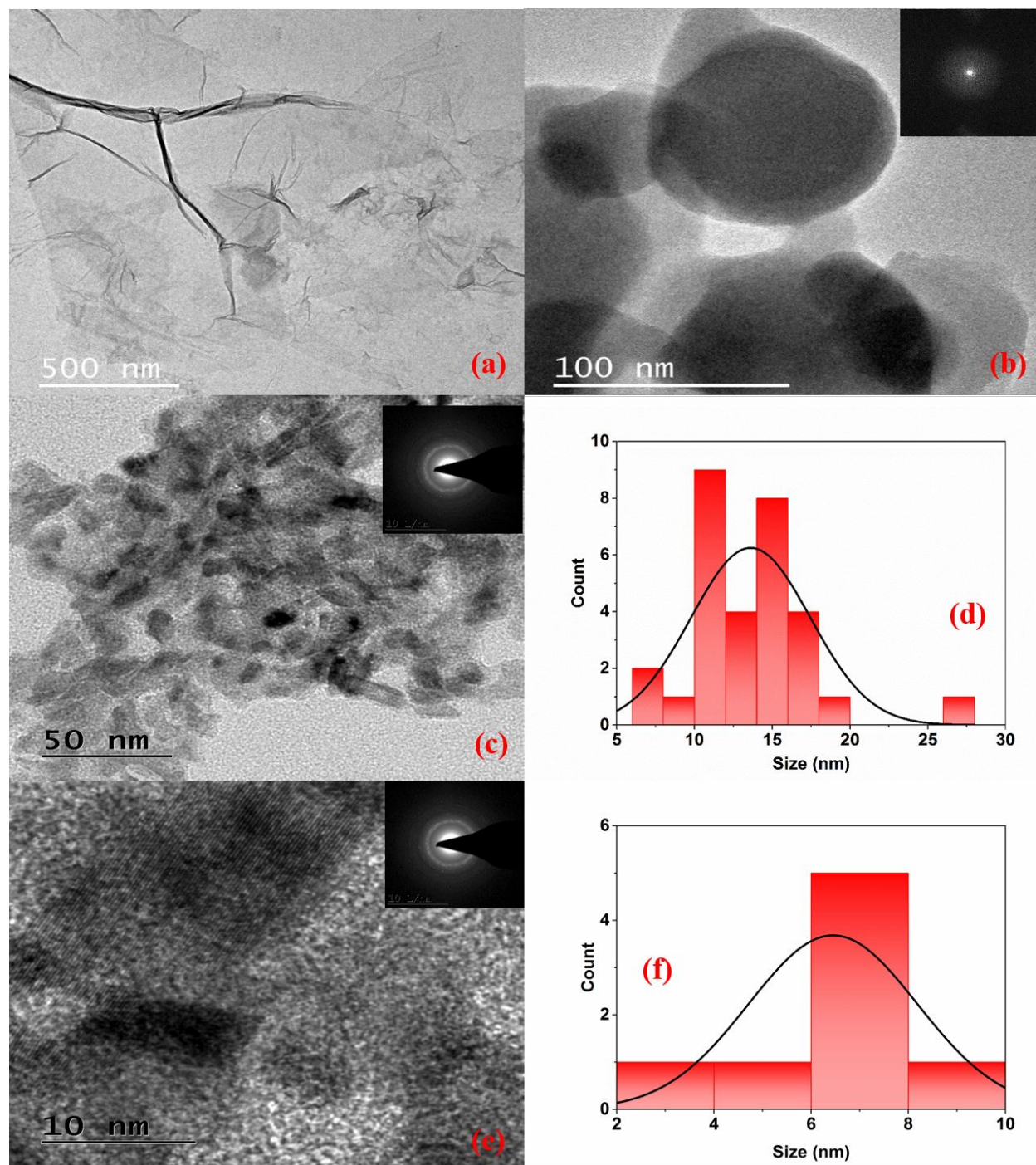
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Figure 4. TEM images of a) GO, b) ASGO, c) CoASGO, d) average size of TEM image of

CoASGO e) HR-TEM of CoASGO and f) average size of HR-TEM image of CoASGO

XPS:

The binding energies of synthesized catalyst CoASGO were 284.5 eV and 531.5 eV which were shown in the deconvoluted XPS spectra of C 1s and O 1s in figure 5 [16]. In deconvoluted C 1s XPS spectra there are four peaks around 284.3, 285.4, 287.4, 289.1 eV which represented the C=C, C-OH, C-O-C and COO$^-$ groups respectively [15,37]. A band around 102.6 eV confirmed that the silicon is bonded to oxygen in Si 2p spectra[38]. And further it had confirmed that the silylation reaction taken place on the hydroxyl group of GO surface with APTMS as a coupling agent. The silylation process also explained the presence of Si and N atom along with Cobalt signal in the wide spectra of synthesized catalyst. In N 1s XPS spectra, there is a signal around 399.75 eV which confirmed that the N-H group converted to C=N is due to the Schiff base formation i.e., involves the condensation of terephthalaldehyde and 2-aminoethanol. Further, there is a shift at 399.75 eV because of the electron pair effect of nitrogen atoms and central cobalt ions. The satellite peak of Co $2p_{1/2}$ and Co$2p_{3/2}$ spectra of synthesized complex shows two typical bands at 795.6 and 779.3 eV confirmed the binding energy of Cobalt atom with Co^{2+} ion and the coordination of cobalt metal with the nitrogen and oxygen groups[37]. There is a satellite peak around 795.6.0 eV i.e., Co 2p3/2 which confirmed the electrostatic interaction with the ligand and cobalt metal. Finally, the wide survey of XPS spectra confirms that all elements Co, Si, N, C and O atoms are present on the synthesized catalyst.
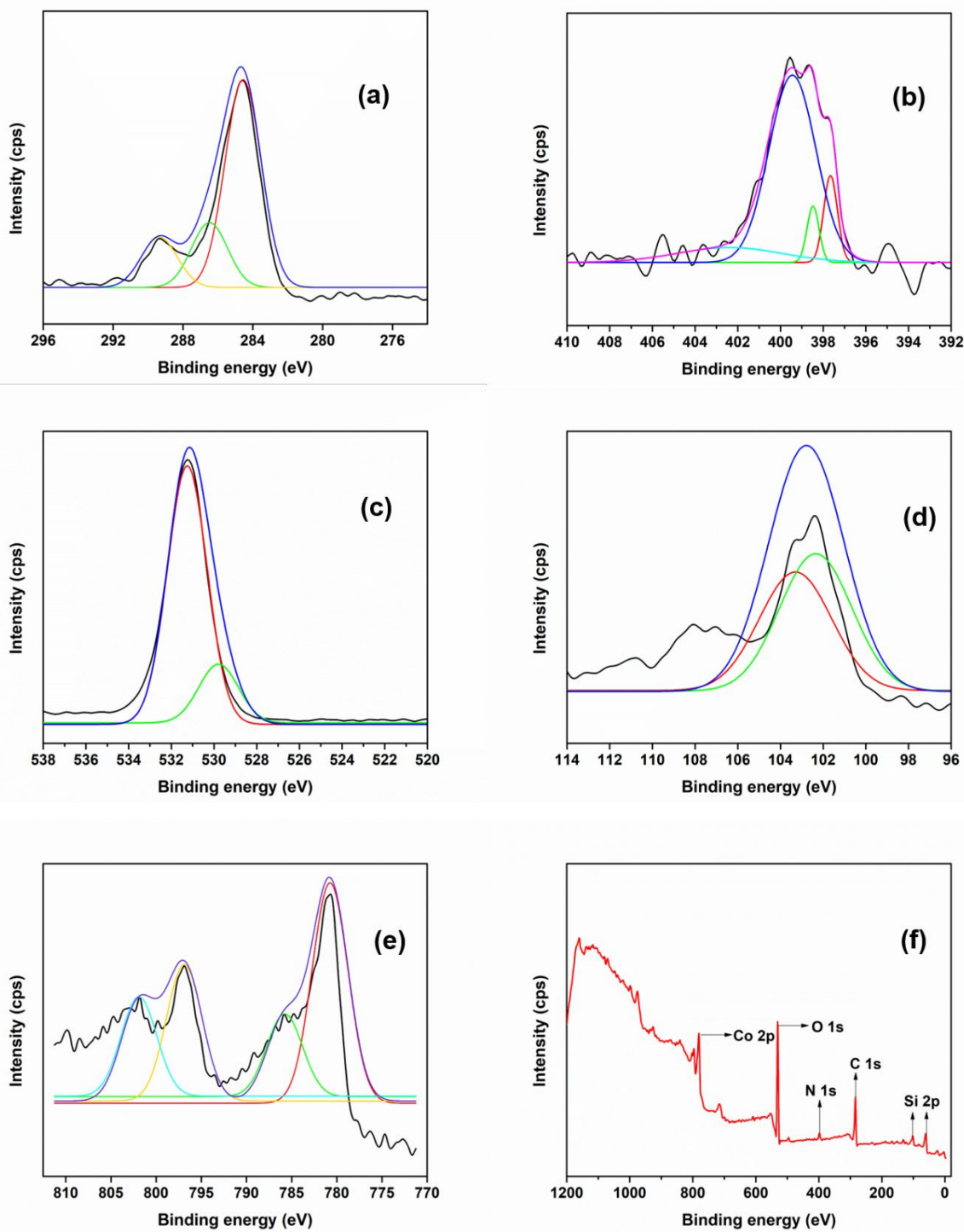
Figure 5. XPS analysis of CoASGO catalyst with a) C 1s scan b) N 1s scan c) O 1s scan, d) Si

2p scan, e) Co 2p scan, and f) elemental survey

Thermal analysis:

Thermogravimetric analysis (TGA):

Figure 6 showed the weight loss in GO is in two degradation step i.e., at first 90-190 °C which is due to the removal of physisorbed water trapped in the GO as well as C-O-C functional groups which remained in the water molecules [18]. The second step is 220-600 °C explained the removal of all the left over oxygen groups along the destruction of carbon ring. Further, the synthesized catalyst CoASGO observed in three steps shown in figure 5: first, there is a loss observed around 4.59% at 90-190 °C represented physisorbed hydroxyl groups and second weight loss is 33% around 250-450 °C confirmed the removal of undigested oxygen functionalities along with unreacted APTMS. Final weight loss is 42.5% around 320-600 °C represented the gradual degradation of the synthesized catalyst CoASGO in figure 6b.
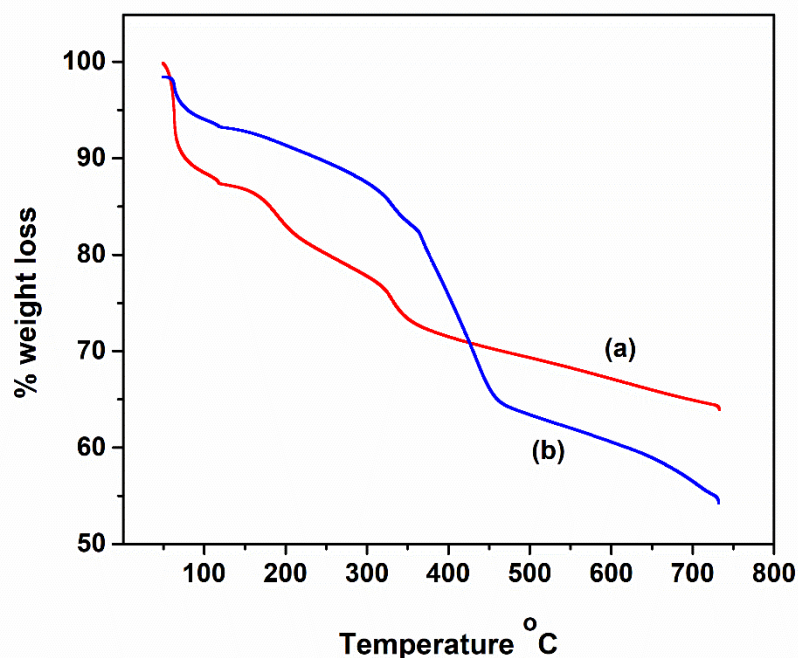

Figure 6: TGA graph shows the a) GO and b) the synthesized catalyst

ICP-AES Analysis:

Before the measurements were done, the catalyst was digested in concentrated nitric acid which were diluted to volume and mixed. The Co complex is 0.31mmol/g represented the weight loss during the immobilization of Co Schiff base complex onto amino functionalized GO surface. Here, the ligand to metal molar ratio is 1:1 during the synthesis of catalyst and then the molar ratio calculated from ICP analysis is 0.34mmol/g respectively. The results suggests that the metal complex successfully supported onto GO.

ii) Catalytic activity of the catalyst:

Suzuki coupling reaction:

The synthesized catalyst CoASGO explored and tested for the Suzuki cross coupling of some arylboronic acids with various substituted aryl halides as a model reaction for determining the catalytic performance[8]. Here the activity of the catalyst substantiated using the coupling reactions by following some of the suitable variations in base, solvents, catalyst amount as well as reactants variations. The cross coupling reaction which involves the substituted aryl halides and arylboronic acids with the catalyst amount along with EtOH as solvent and Cs_2CO_3 base at a specified temperature at 80 °C is given in table S1 in supplementary information.
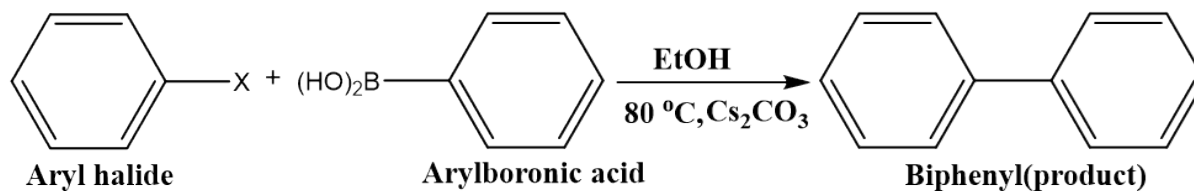

| Aryl halide | Arylboronic acid | Biphenyl(product) |

Table 1. Effect of various solvents and bases on yield at temp 80 °C

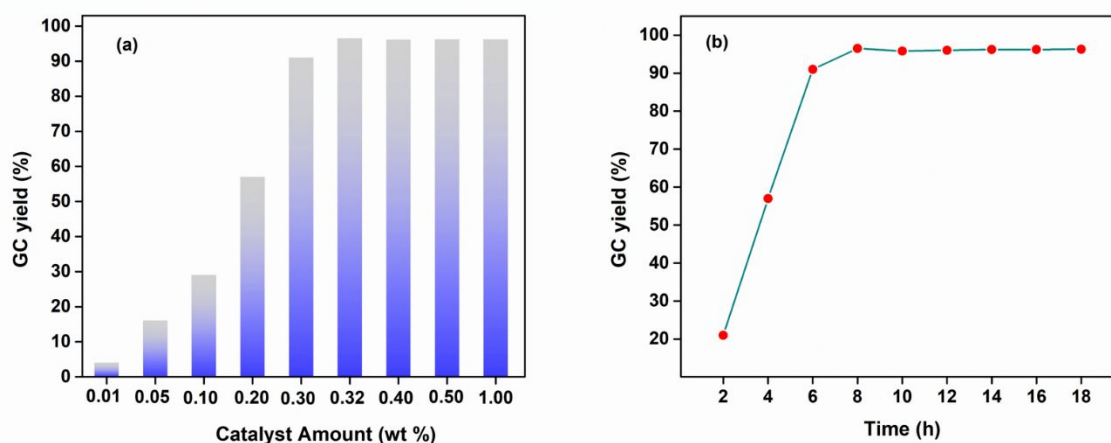| Sl. No.	Solvent	Base	Temperature	Catalyst (mol%)	GC Yield (%)
1	EtOH	Cs_2CO_3	80	0.32	96
2	EtOH	K_2CO_3	80	0.32	79
3	EtOH	Et_3N	80	0.32	55
4	EtOH	KOH	80	0.32	12
5	EtOH	NaOH	80	0.32	35
6	Acetonitrile	Cs_2CO_3	80	0.50	75
7	Dimethyl sulfoxide	Cs_2CO_3	80	0.50	71
8	Tetrahydrofuran	Cs_2CO_3	80	0.50	60.5
9	Toluene	Cs_2CO_3	80	0.50	52

Figure 7. The effect of (a) catalyst amount and (b) reaction time on the GC yield of Suzuki coupling reaction

In case of aryl halides such as iodo and bromo substituents, the yield of the products is 96.5 % with phenylboronic acid using ethanol as solvent and a specified temperature around 80 °C using caesium carbonate as base with a reaction time of 6.5 h showing in table 1. The results from the table S1 in supplementary information stated the rate of reaction with variation to product

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formation taken place with a time of 1 to 24 h and also depends on the type of substrates either

electron donating or withdrawing group. Here the model reaction were done using coupling of

bromobenzene with phenylboronic acid with different solvents and time variation along with base

studies. Six bases have been tested with yield as follows: KOH (12%), K_2CO_3 (79%), Et_3N (55%),

NaOH (35%) and Cs_2CO_3 (96.5%). From the base variation, the better base is Cs_2CO_3 which gave

good yield and abundantly available in nature. Here, we studied the time variation from 1h to 24h

and recorded as follows; 1h (11%), 2h (21%), 4h (57%), 6h (91%), 10h (95.8%), 12h (96.2%) and

24h (96.3%) and the best time period is 6.5h with 96.5% for bromobenzene shown in figure 7b.

However, the product yield for iodobenzene is 97.1% at 6.5h at 80 °C. And the solvents variation

shown in the table 1 which confirmed that EtOH is best solvent for the reaction. On the other hand,

the catalyst loading is 0.01 mol% to 1.00 mol% in the experiments and the maximum yield is

obtained at 0.32 mol% catalyst loading shown in figure 7a. In determining the catalytic behavior

of the catalyst under certain optimized conditions, the biphenyl product gave maximum yield with

iodobenzene and bromobenzene i.e., 97.1% and 96.5%. Electron withdrawing groups such as NO_2

and CHO gave 89% and 87% higher biphenyl yield. Aryl bromides having donor groups takes

long time to form biphenyl product which is due to the migration of electron through pi bond on

aryl bromides. Since the aryl chlorides are more attractive substrates, due to its low cost and

availability but its poor reactivity and high bond dissociation energy C-Cl bond (96 kcal/mol) is a

major problem restricting it in industrial application [39]. Hence, a lot of attempts can be made which

can fulfill the gap in future work in this area. Apart from the coupling reaction mechanism, with

respect to certain evaluation the efficiency of a heterogeneous catalyst in nanocatalysis depends

on its size[6]. However, the smaller the size of particle is, greater will be its catalytic activity[40]. But

due to the good dispersion and cobalt nanoparticles formation without any aggregation along with

GO meant for tuning the surface of cobalt nanoparticle improved the catalytic performance throughout the reaction [24,41]. The high product formation is due to the cobalt oxide average particle size which is confirmed from the HR-TEM image of the CoASGO complex found to be 6nm and the heterogeneous support being GO enhances the surface area of the catalyst which leads to the more reactive sites on its surface.

Recyclability studies were done to prove the reusability of the heterogeneous catalyst which may be beneficial for reliable application[23]. The model reactions done using bromobenzene and phenylboronic acid with 0.32 mol% catalyst under the optimized conditions. Once the reaction is done, the catalyst is filtered using simple filtration and washed twice with acetonitrile (2*10ml) and stirred in ethanol for 30 min at room temperature finally dried in an oven at 60 °C. The catalyst shown in figure 8, can be reused for 5times without any significant loss of its catalytic activity. After that, there is a decrease in product yield. Further analysis, i.e., the catalyst studies done using ICP-AES analysis. For fresh catalyst, the concentration of Co metal is 1.24 wt% and the catalyst after 5th cycle is 1.20wt% confirmed that the metal leaching was very less in the consecutive cycles. Later, the next 6th, 7th, 8th cycles the catalyst metal leaching increased by 10% i.e, 1.116%. However, till the 5th consecutive cycles the catalyst supporting material played a key role, hence carbon supported material especially graphene which enhances the thermal stability of the catalytic system as well as functional groups on these heterogeneous support to prevent further leaching of metal ions. The catalyst deactivation can be explained to some extent with the loss of Co metal ion in the reaction process. The other cause is due to the recycling reactions which results in the decrease in catalytic activity because of the agglomeration of Co nanoparticle. The TEM analysis of the fresh catalyst and the 5th cycle catalyst confirmed that the metal leaching during the coupling

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reaction is less shown in figure 9. The results justified that the complex catalyst remains stable

without any metal leaching.
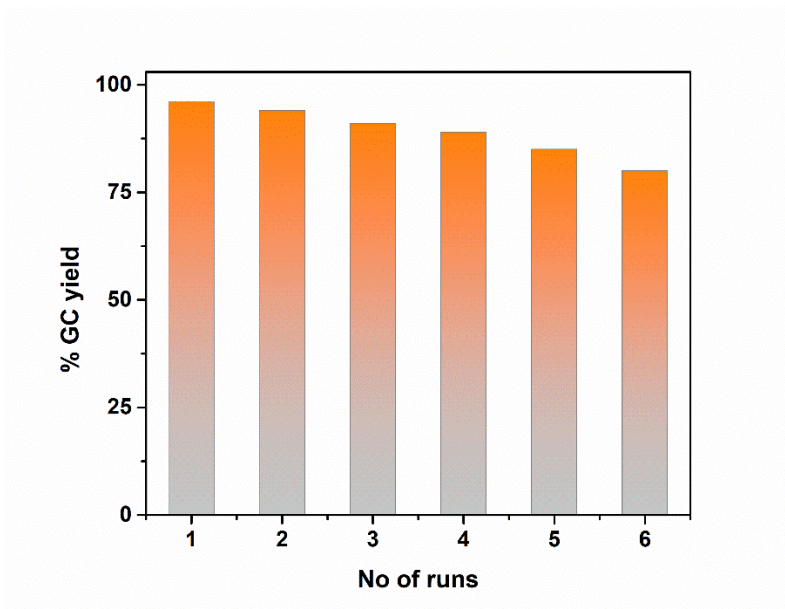
**Figure 8.** Recycling ability of CoASGO as catalyst for Suzuki coupling reactions
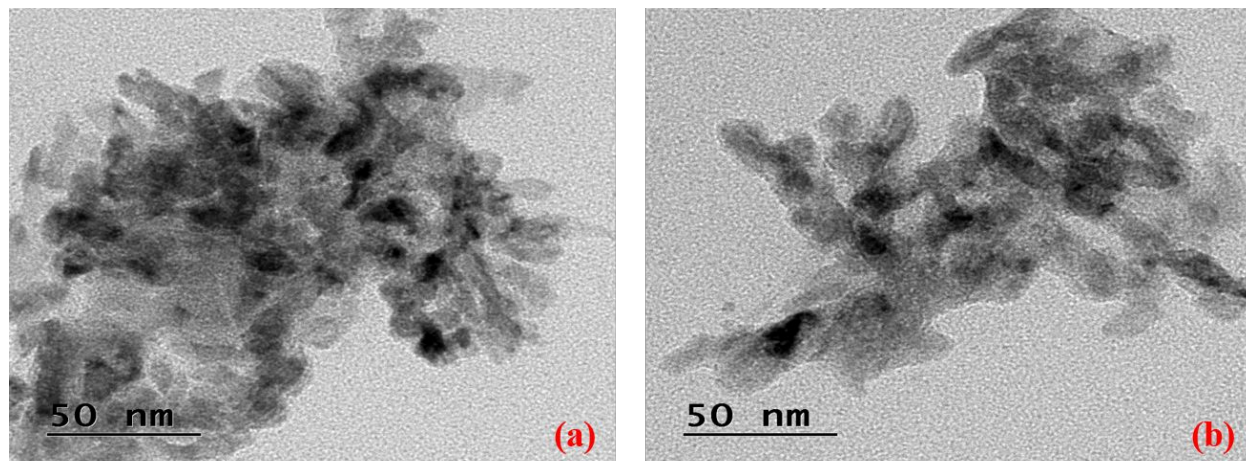
Figure 9. TEM images of Fresh and used catalyst after 5th cycle a) Fresh catalyst b) used catalyst

In order to determine the hot filtration test for the CoASGO catalyst in figure 10, the reaction of

phenylboronic acid (1.5mmol) and bromo benzene (1mmol) in presence of Cs_2CO_3 base and

ethanol solvent was performed at 80 °C until the biphenyl product of 21% yield is achieved within

a time period of 2h (Fig. 10). Later, the CoASGO catalyst was filtered from the hot reaction mixture and the filtrate was then allowed to undergo reaction with the addition of phenylboronic acids (0.5mmol) for 24h. During the initiation of the reaction the formation product was very less, it may be due to an instatement time which encourages the CoASGO catalytic system which leaches out in to the solution as Co nanoparticles which gets enclosed with the Schiff base silane moiety around it[42]. There is no significant change in the product formation indicating that the leached cobalt ions from the supported catalyst are not effective for the catalytic activity which can be proved using ICP-AES analysis. The observed results confirmed that the catalyst is heterogeneous in nature with a maximum stability and the leached cobalt species doesn't have any effect in the reaction medium.
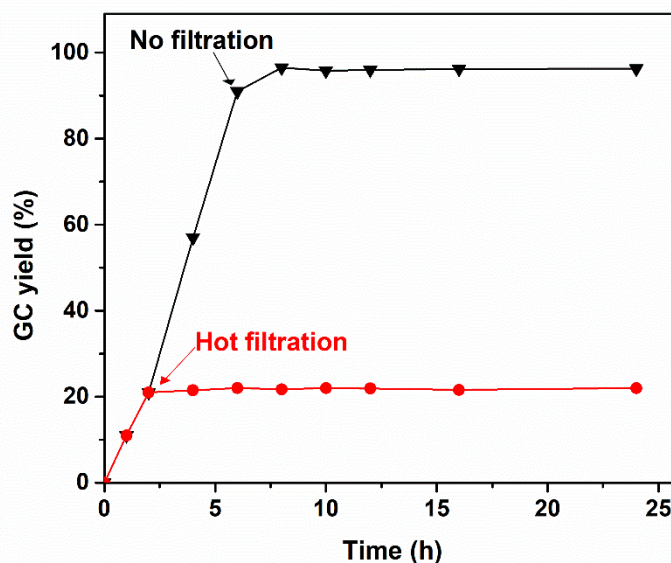
Figure 10. Hot filtration test of CoASGO catalyst

Figure 11 shows the poisoning effect of CoASGO catalytic system in the Suzuki coupling reaction. However, after the addition of the poisons, the catalytic activity of the catalyst readily quenched and no longer growth of bromobenzene conversion with increase in reaction time. Further addition

of the catalytic poisons simply decreases the activity by reducing the feasibility of the reactants to the active catalytic sites in the reaction mixture and thus creating the mass-transfer limitations as well as varying diffusion constants[43]. This explicitly states that the catalytic poisons are responsible for the Suzuki cross coupling reaction.
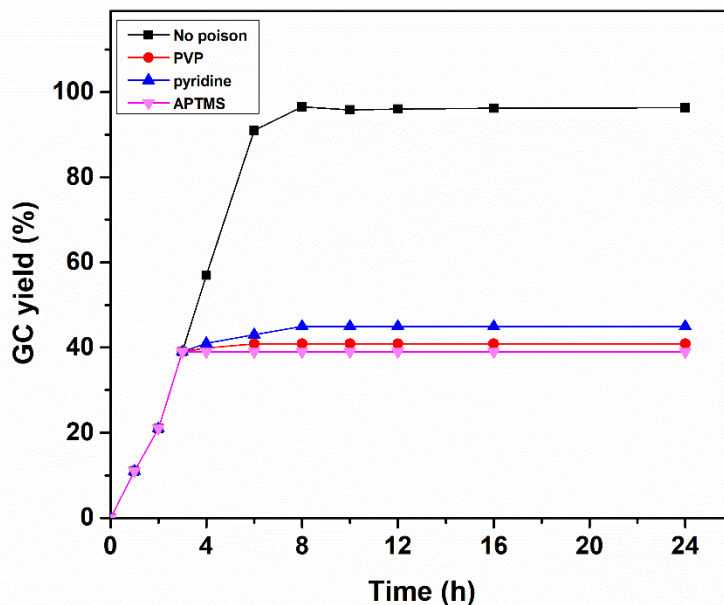

Figure 11. Poisoning test for CoASGO catalyst with No poison, PVP, pyridine and APTMS.

In order to find out the delocalized electron for the CoASGO catalyst which are having characteristic peaks with g-factor values at room temperature, Lorentzian curves with higher intensities investigated the samples for Co. Two pairs of Gaussian curves and broader peaks obtained which indicates localized spins shown in figure 12. The cobalt(II) ions present at tetragonal sites generate a single EPR signal with the Lorentzian curves having a g-factor about 2.005 with an average g value of 1.992 which confirms that it is low spin[44,45]. The isotropic EPR signals observed at room temperature where (I) ½) hyperfine splitting was performed at 50 K in

toluene. Usually the line width depends mainly on the sample preparation temperature along with

calcination temperature.
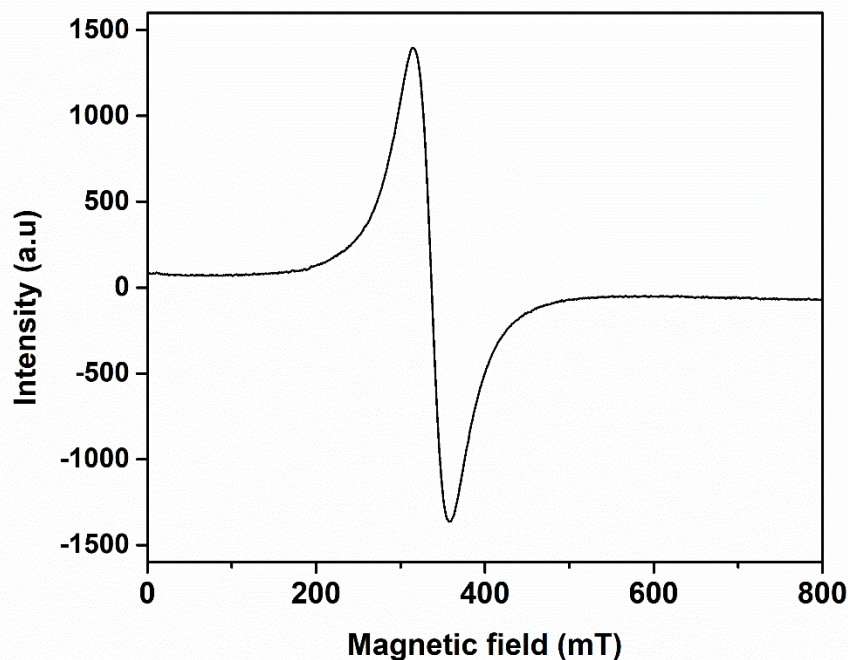
Figure 12. EPR Spectra of CoASGO catalyst

Schematic illustration:

We reported a plausible mechanism for the CoASGO catalyst which facilitates a detailed study to

comprehend the process of C-C coupling reaction. At first, the Co metal in CoASGO (Fig.13 a)

may be reduced to either Co (0) or Co (I) is just a possibility and determing the active species is

quite difficult. Here, we tentatively speculate that the Co (0) (Fig. 13 b) might be formed by

reaction with arylboronic acid ($R_1B(OH)_2$) and Cs_2CO_3 base. Then, the central Co (0) reacts with

aryl halide (R_2-X) affords to form an X-Co(II)-R_2 intermediate (Fig. 13 c) which is an oxidative

addition and further nucleophilic substitution of halo group and followed by transmetallation

between arylboronic acid and GOAS-Co-R_2-CO_3 intermediate (Fig. 13 d) could results in biaryl

R_1-GOAS-Co-R_2 species (Fig. 13 e). In the final step, reductive elimination takes place to form

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the target biaryl (R_1-R_2) (Fig. 13 f) product along with regeneration of CoASGO complex to complete the catalytic cycle.
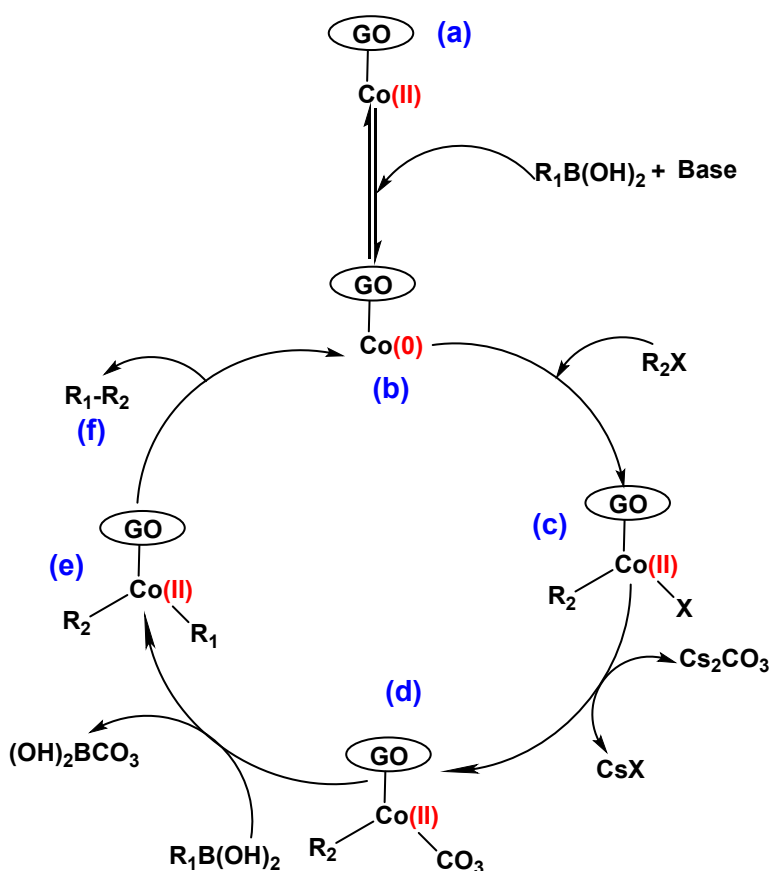

Figure 13. A plausible mechanism of CoASGO catalyst in Suzuki cross coupling reaction

Conclusions

In conclusion, an effective in-situ strategy has been developed to prepare a Schiff base metal complex onto graphene oxide through surface functionalization using APTMS. The product formation i.e., biaryls in the Suzuki Cross coupling reaction of various substituted aryl halides and phenylboronic acid proves that the synthesized catalyst is effective for the Suzuki cross coupling reaction. Therefore, GO support due to its outstanding properties and the robustous synthetic methodology becomes a powerful supporting material for the homogeneous complexes to attain

their practical applications. These heterogeneous nanocatalysts possessing high surface area, along with thermal and chemical stabilities were confirmed using various characterization technique through spectroscopic methods and surface analysis. The catalyst is easily recoverable, reusable, benign and can be handled easily. There is a need for more wide and in-depth studies in heterogeneous coordination catalysis were to be done in future studies in which various organic reactions were envisaged.

Acknowledgements:

Supplementary information: FTIR, PXRD, EDX and Tables are placed in Supplementary information.

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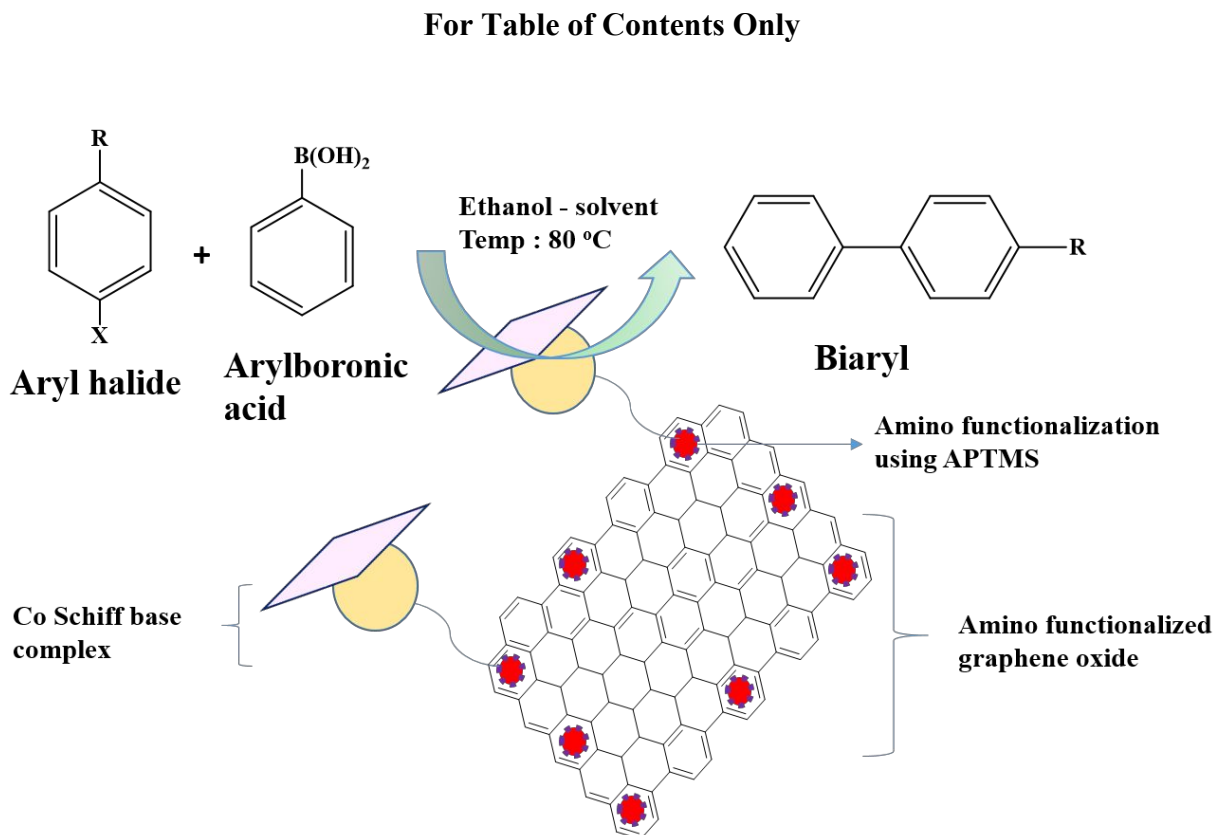
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R

B(OH)$_2$

+

**Ethanol - solvent
Temp : 80 ºC**

X

Aryl halide

**Arylboronic
acid**

R

Biaryl

**Amino functionalization
using APTMS**

**Co Schiff base
complex**

**Amino functionalized
graphene oxide**

Graphical representation of Suzuki cross-coupling reaction using heterogeneous catalyst

(CoASGO).