

A fascinating Suzuki homo-coupling reaction over anchored gold Schiff base complexes on mesoporous host

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ABSTRACT

We present a study of the use of chloro-functionalized mesoporous silicas as supports for immobilization of Au(III) Schiff base complex, and use of this composite material as heterogeneous catalyst for homocoupling of aryl boronic acid. The catalyst was characterised by XRD, FTIR, UV–vis DRS, TG-DTA, etc. Catalyst was initially tested using the coupling of phenylboronic acid with bromo benzene in the presence of K_2CO_3 and with xylene as solvent. The reaction was also tested in the absence of the aryl halide and K_2CO_3 . The results indicate that in our catalytic system base is not needed for the activation of phenylboronic acid, and its only role is to neutralize the boric acid. The optimized catalysts are also active in the coupling of a range of aryl boronic acids, and after four catalytic runs they show virtually no drop in activity.

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1. Introduction

Gold was believed to be chemically inert, and with very few exceptions [1–4] the possibilities of homogeneous and heterogeneous gold catalysts for organic reactions were not considered. Recent reports have shown that gold salts, specifically Au(III), can act as a Lewis acid catalyst for a large variety of reactions [5–8]. Gold in homogeneous complexes [2,9] has shown possibilities for several catalytic reactions, including asymmetric aldol condensation, and the asymmetric hydrogenation of alkenes and imines [10,11]. More specifically, it has been recently shown [12] that Au(III) complexes were active and selective catalysts for carrying out the homocoupling of different aryl boronic acids. However, Au(III), unlike Pd complexes, was not able to catalyze cross-coupling reactions. The traditional homogeneous catalysis causes major problems in purification of the product and separation of expensive catalyst that leads to environmental toxic wastes. Immobilized gold catalyst over solid support has been developed in order to overcome these problems facing green chemistry [13–15].

The Suzuki reaction is by far the most versatile synthetic method available for the generation of unsymmetrical biaryl compounds which are important building blocks in natural products and in materials sciences [13,16–22]. Biaryls exhibit a wide variety of physical and chemical properties [23,24] and possess versatile applications in pharmaceuticals, nonlinear optics [25], liquid crys-

tal [26] and optically active ligands [27]. Various metal catalyzed coupling reactions have been recognized as convenient one-step method for assembling complex structures [16,28]. Suzuki coupling has become increasingly popular due to its compatibility with a variety of functional groups, the stability of organoboron precursors, and the ease of working up the reaction mixture. Pd–phosphine complexes [18,29–33] have been the most commonly used catalysts for the Suzuki reaction. However, alternative ligands such as N-heterocyclic carbenes [6,34], imidazol-2-ylidenes [35] and diazabutadienes [36] have been used in Suzuki coupling reactions.

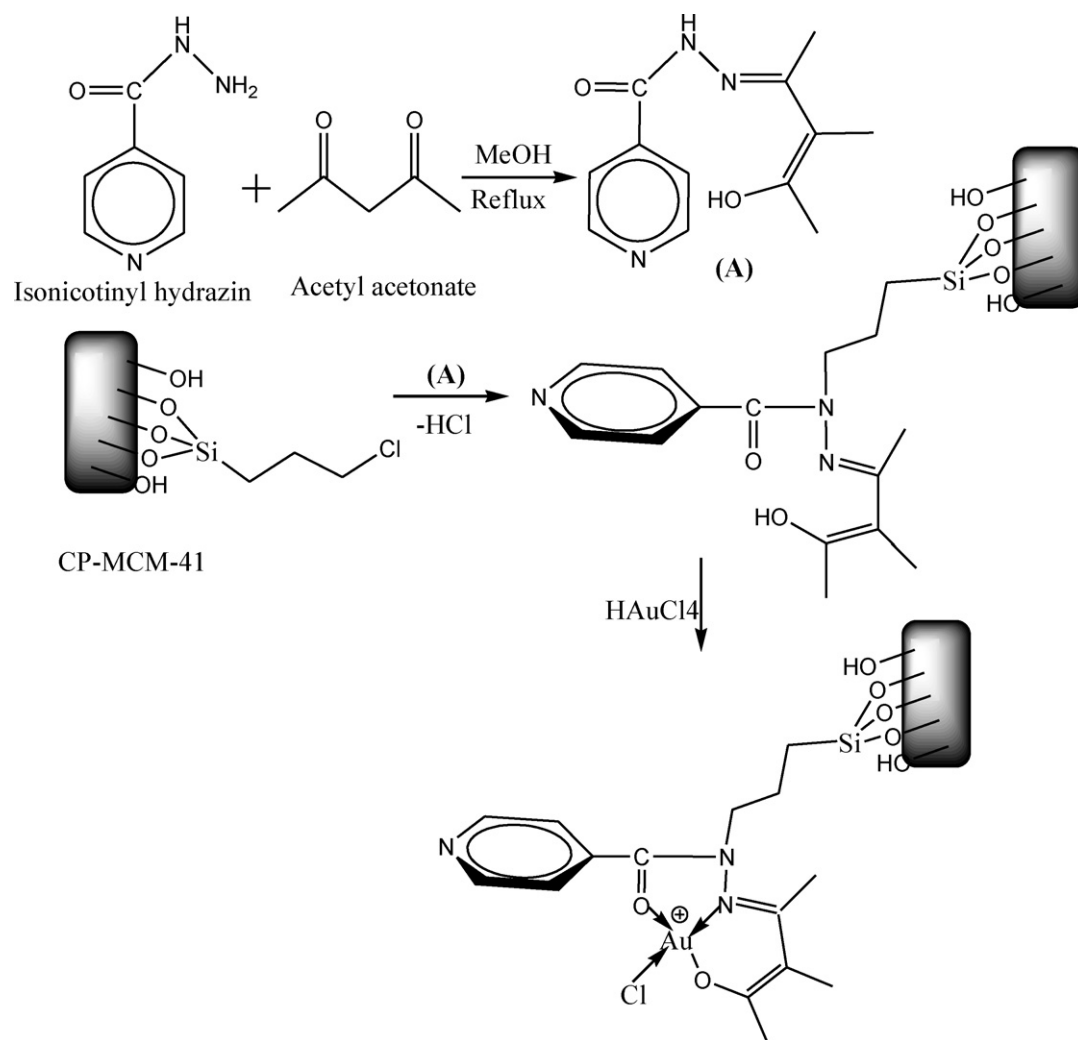
Our interest in this area led us to explore the activity of Au(III) Schiff base complex and anchoring it onto the surface of MCM-41, which can be easily separated from the reaction mixture. MCM-41 is an inorganic support which has some advantageous properties such as excellent stability, good accessibility, and the fact that organic groups can be robustly anchored to the surface [37,38]. Here in we report the synthesis of homogeneous and heterogeneous Au(III) Schiff base complex and its catalytic activity in Suzuki homocoupling reaction. The comparative activity of Pd(II) complexes with same ligands for the same reaction is also studied.

2. Experimental

2.1. Materials and methods

All solvents and reagents were purchased from Aldrich and used without further purification. The arylation products were char-

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Scheme 1. Schematic representation of the formation of Au(III) Schiff-base complex within the pore channels of MCM-41.

acterised by comparison of their spectra and physical data with authentic samples.

Powder X-ray diffraction (XRD) patterns of the heterogeneous samples were obtained on Rigaku D/Max III VC diffractometer with Cu K α radiation at 40 kV and 40 mA in the range of $2\theta = 0-10^\circ$. The FTIR spectra of the samples were recorded using Varian 800-FTIR in KBr matrix in the range of $4000-400\text{ cm}^{-1}$. The co-ordination environments of the samples were examined by diffuse reflectance UV-vis spectroscopy. The spectra were recorded in Varian-100 spectrophotometer in the wavelength range of 200–800 nm in BaSO₄ phase. The thermal stability of the material is also characterised by TG-DTA using Toledo-Mettler TG/DTA/851^e. The metal loading and leaching of the reaction solution were determined by atomic absorption spectroscopy (AAS) with a Perkin-Elmer Analysis 300 using acetylene (C₂H₂) flame. Transmission electron microscopy (TEM) analyses were performed on Philips TECHNAI G² operated at 200 kV.

2.2. Preparation of MCM-41-Cl

MCM-41-Cl was prepared by co-condensation method [39] using C₁₆H₃₃N(CH₃)₃Br (CTAB) as template, tetraethyl orthosilicate (TEOS) as silica precursor and chloropropyltriethoxysilane (CPTES) as organoalkoxysilane precursor.

2.3. Preparation of Schiff base ligand

The reactions were performed under inert atmosphere of dry nitrogen using distilled dried solvents. Schiff base ligand (A) was synthesized by co-condensation method taking isoniazid and acetyl acetone in 1:1 molar ratio. In a typical experiment, 10 mmol of isoniazid (1.37 g) was dissolved in 20 ml methanol. To this acetyl acetone (10 mmol) was added and refluxed for 6 h. Then the reacting mixture was cooled and allowed to crystallize. Finally the ligand was recrystallized from methanol.

2.4. Preparation of immobilized ligand on MCM-41

MCM-41-Cl (1 g) was added to a solution of Schiff base ligand (0.123 g, 0.562 mmol) in dry toluene and the resulting suspension was refluxed for 48 h under inert atmosphere. The ligand was thought to be heterogenized by the elimination of HCl. This can be observed as the appearance of pale yellow colour in the reaction mixture. The heterogenized ligand was filtered, washed thoroughly with dry toluene and finally dried at 80 °C.

2.5. Preparation of MCM-41 immobilized metal complexes

Immobilized complex catalyst was prepared under dinitrogen by conventional Schlenk-tube technique, the solvents were care-

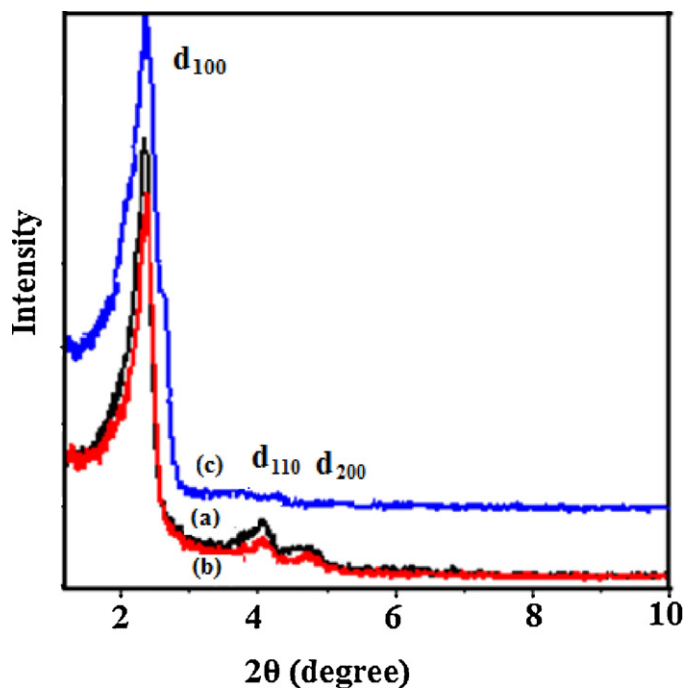


Fig. 1. XRD spectra of (a) MCM-41, (b) CP-MCM-41 and (c) MCM-41–Au(III) complex.

fully degassed before use. Then, an ethanolic solution of HAuCl_4 (0.562 mmol) was added to a suspension of heterogenized ligand in toluene (20 ml) at room temperature. The resulting mixture was under reflux for 12 h, then cooled to room temperature and filtered. The solid was filtered, washed several times with ethanol and dried to afford the respective heterogenized complex in almost quantitative yields. AAS analysis shows that 0.30 mmol Au was anchored in 1.0 g of immobilized complex catalyst. The preparation procedure is summarized in Scheme 1.

2.6. General procedure for Suzuki reaction

Aryl halide (15 mmol), phenylboronic acid (10 mmol), K_2CO_3 (20 mmol) and Au catalyst (3 mg) were mixed in xylene. The mixture was stirred at 80°C in nitrogen atmosphere. The reaction time was idealized as 24 h. Yields were determined, for various catalysts by GC analysis (Shimadzu GC-2010) equipped with a capillary column (ZB-1, 30 m length, 0.53 mm I.D. and $3.0\ \mu\text{m}$ film thickness) using flame ionization detector (FID).

3. Results and discussions

3.1. Characterisation

3.1.1. Powder X-ray diffraction

X-ray diffraction analysis was performed in order to investigate the effect of incorporating gold complex on the texture properties of the materials. In the XRD pattern of parent MCM-41 (Fig. 1a) shows a very intense $d_{100} = 38.85\ \text{\AA}$ diffraction peak at $2\theta \approx 2.27$ and two other weaker peaks at $2\theta \approx 3.99$ and $2\theta \approx 4.58$ for d_{110} and d_{200} , respectively. All the peaks are well resolved indicating MCM-41 has a well defined hexagonal symmetry. The XRD patterns of CP-MCM-41 and MCM-41–Au(III) complex are shown in Fig. 1b and c, respectively. However, after organo-functionalization (here chloropropyltriethoxy silane) and metal complex loading, there was a slight decrease in intensity and broadening of corresponding peaks indicating a slight disorder in the organo-functionalized

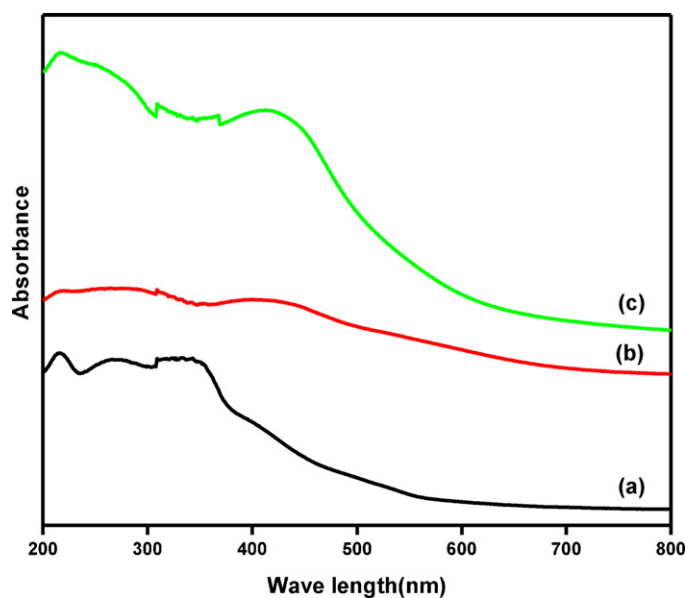


Fig. 2. UV–vis spectra of (a) Schiff base ligand (A), (b) Au(III) complex, and (c) MCM-41–Au(III) complex.

(here chloropropyl) and complex modified MCM-41. This is probably because the addition of organic group distorts the regular liquid crystalline array of the template and lowers the long-range ordering of the MCM-41 mesostructure. This is not interpreted as a severe loss of long range ordering of the silica framework [40,41]. In the XRD pattern of the supported gold catalyst, the $\langle 100 \rangle$ reflection is only present and shifts to a lower angle with respect to MCM-41. Other reflections disappeared probably as a result of the contrast matching between the silicate framework and organic moieties that are located inside the MCM-41 channels [42].

3.1.2. UV–vis spectroscopy

The Schiff-base ligand, homogenous Au(III) complex and complex anchored functionalized MCM-41 were characterised by diffuse-reflectance UV–vis spectroscopy (recorded in 200–800 nm) (Fig. 2). The complexes show several band maxima in the UV region which might be due to intraligand $\pi \rightarrow \pi^*$ and $n \rightarrow \pi^*$ transition in the heteroaromatic ring, azomethine group and charge transfer transitions. Bands correspond to 400–500 nm region is due to $d-d$ transition of planer complexes and MLCT (metal to ligand charge transfer bands). The diffuse reflectance spectra of both homogeneous and heterogeneous complex possess almost identical spectra indicating that complexes maintain their geometry and electronic properties after heterogenization without significant distortion.

3.1.3. FTIR spectroscopy

In the Schiff base ligand (A) IR spectra (Fig. 3b), a very intensive band appears at $1691\ \text{cm}^{-1}$ and a strong band appears at $1668\ \text{cm}^{-1}$, which are assigned to the vibration frequency $\nu(\text{C}=\text{O})$ amide [43] and $\nu(\text{C}=\text{N})$ azomethine [44]. For homogenous gold complex (Fig. 3a), the band group corresponding to amide appear shifted with $29\text{--}38\ \text{cm}^{-1}$ towards lower frequencies, which indicates the involvement of carbonyl group in coordination [45]. Also, a shift towards lower values of $\Delta\nu = 66\text{--}77\ \text{cm}^{-1}$ is observed for the frequencies characteristic to azomethine group of homogenous gold complex with Schiff base ligand (A). This suggests the involvement of azomethine nitrogen in coordination with Au(III) ion [45]. In the IR spectra of the ligand, three mid intensity bands appear at 1548 , 1000 and $743\ \text{cm}^{-1}$, which are assigned to vibration frequency $\nu(\text{Py ring})$, Py ring bending and γ (Pyring outside the plane), respectively. Absence of any shift for these vibrational frequen-

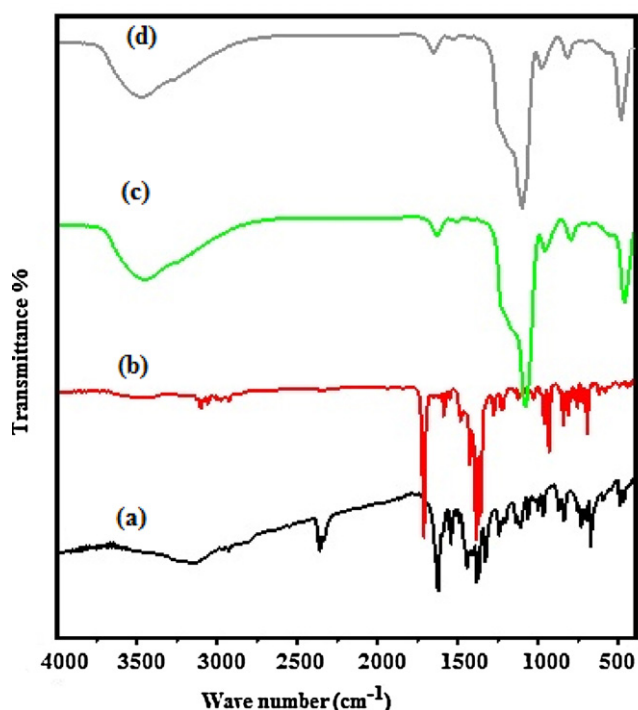


Fig. 3. FT-IR spectra of (a) Au(III) complex, (b) Schiff base ligand, (c) MCM-41–Au(III) complex and (d) recycled catalyst.

cies discards the possibility of attachment of N atom of pyridine ring. A broad band with its centre of gravity around 3425 cm^{-1} in the spectra of both ligand and complex may be assigned to the combined mode of the stretching vibration of adsorbed water molecule and NH_2 groups. Appearance of the additional peak in gold complex around 2367 cm^{-1} may be due to adsorption of atmospheric CO_2 . All data support the idea that in the gold complex, the ligand works as tridentate NOO, being coordinated through the azomethine nitrogen, enolic oxygen and carbonylic oxygen. In the FTIR spectroscopic characterisation of the heterogeneous complex (Fig. 3c), the peaks due to the supports masks the spectra of the immobilized complex. Absence of the N–H stretching in the heterogenized complex (comparing with homogeneous) indicates that complex binds to the support through the N atom of the amide group. A shoulder near 3600 cm^{-1} represents the presence of hydrogen-bonded, isolated and geminal silanols [46]. It can be analyzed that the band appears near 2942 cm^{-1} result due to the C–H stretching of the functionalized chloropropyl group.

3.1.4. Thermal analysis

The anchoring of the complexes was checked by TGA and DTA measurements. The decomposition behaviour of the free complex and anchored complex has been compared in order to understand the effect of anchoring (Fig. 4). The free complex decomposes during heating to 650°C in several welldefined steps. This behaviour indicates that the Au(III) complex decomposes in a relatively welldefined manner and releases defined fragments, which readily burn off. The characteristic mass losses related to water were detected between 90 and 110°C for all curves. The main mass losses in the temperature range of 200 – 700°C corresponds to the splitting of the Schiff base molecules. DTA curve indicates that all weight loss steps are exothermic in nature.

The anchored complex (MCM-41–Au(III) complex) shows somewhat different decomposition behaviours due to covalent bonding. The TGA curve of MCM-41 anchored complex shows less defined steps of weight loss. Decomposition of the complex is complete at

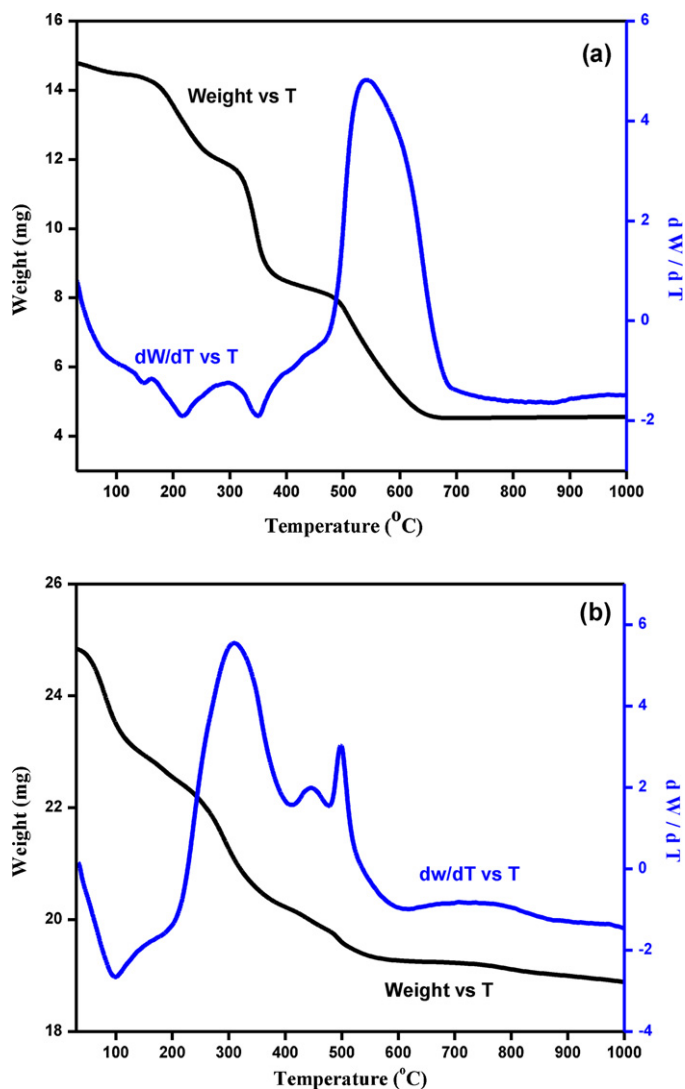


Fig. 4. Thermo gravimetric and differential thermo gravimetric results of (a) homogeneous gold complex and (b) MCM-41–Au(III) complex.

900°C . The shifts of the onset temperature of decomposition of the anchored complex in comparison with free complex is due to the mutual stabilization of propyl amino groups and the complexes and are indirect proofs for the entrapment of complex moieties inside the pore channels MCM-41.

3.1.5. TEM studies

Transmission electron micrographs of (a) MCM-41–41 and (b) MCM-41–Au(III) complex are shown in Fig. 5. Both MCM-41 and MCM-41–Au(III) complex feature an open-ended lamellar type arrangement of hexagonal porous tubules. But in case of MCM-41–Au(III) complex the channels are slightly less ordered due to immobilization of the complex in the pore channels.

3.2. Analysis of Suzuki coupling reaction

3.2.1. Catalytic study

To test the reactivity of Au(III) complex for Suzuki coupling, reactions were carried out between Br–Ph and I–Ph with a series of aryl boronic acids. The general utility of the reaction conditions with a variety of aryl boronic acid substrates (aryl = Ph, 4-MeOPh and 4-MePh) and aryl halides (BrPh, IPh) was studied. We observed that the expected cross-coupling product was not formed while the aryl

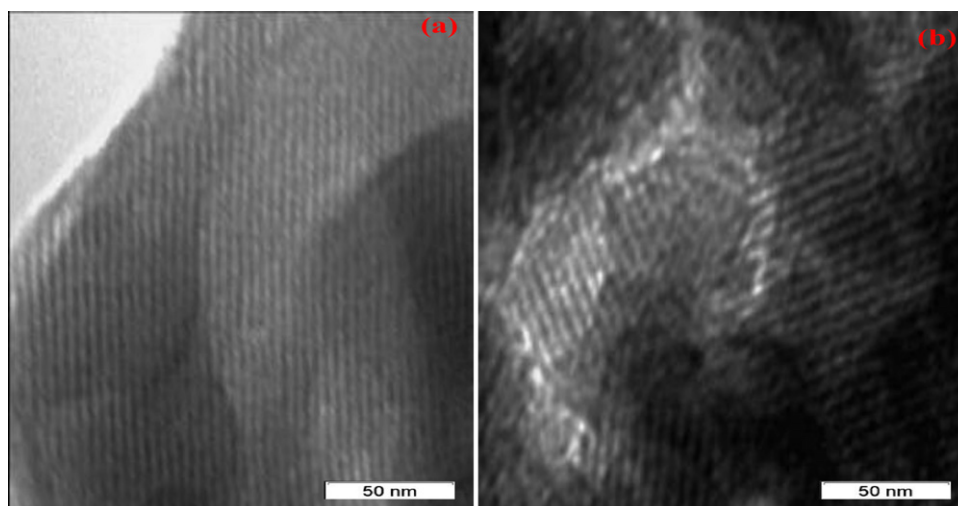


Fig. 5. TEM of (a) MCM-41 and (b) MCM-41-Au(III) complex.

boronic homocoupling compound was obtained as the exclusive product (Table 1).

Interestingly, the reaction also proceeds with the same conversion and selectivity in the absence of the aryl halide and K_2CO_3 . When the reaction is carried out without K_2CO_3 , the only difference observed is the degradation of the catalyst. The base is known to activate phenylboronic acid [47,48] however, our results indicate that with our catalytic system base is not needed for the activation of phenylboronic acid, and its only role is to neutralize the boric acid. We have also tested the reaction by taking K^tOBu , sodium acetate, and butyl amine as base. Under optimal reaction conditions K_2CO_3 is found to be best among all.

The effects of electron-donating and electron-withdrawing substituents in the boronic acid on reactivity are also given in Table 1. In general, moderate to excellent yields and good selectivity towards the homo-coupling product are found with Au(III) complexes. The best reactivity is found with phenylboronic acid as the substrate. It can be concluded that electron donating and electron withdrawing substituent did not significantly change the yield.

For comparison purposes, Pd(II) complex with same ligand was prepared and tested under the same reaction conditions, the results (Table 1) show that Pd-catalysts are highly selective towards cross-coupling reactions, and only when the reaction was very slow, some homocoupling reaction between boronic acids also occurred.

3.2.2. Heterogeneous activity and catalyst reuse

In order to ascertain whether the catalysts were behaving in a truly heterogeneous manner, we repeated several reactions and fil-

tered the catalysts under optimal reaction conditions, and allowed the reactions to continue in the absence of catalyst. No additional conversion was seen in any case after filtration of the catalyst. Furthermore, small fractions of liquid were removed from reactions, which were underway, rapidly filtered and added to a fresh mixture of different coupling partners and base. In these cases, the fresh mixture did not react, indicating that no catalytic activity could be ascribed to the liquid aliquot from the first reaction. On the other hand, the first reaction continued, indicating that the solid catalyst remained active.

Again, we turn our attention to the reusability of present heterogeneous Au(III) complex. To test the stability and recycling ability as well as leaching of gold metal from MCM-41 under reaction conditions, recycling experiments were carried out using xylene as solvent. The typical recycling procedure was as follows: after the initial reaction, the catalyst was separated from the reaction mixture, washed, dried under vacuum and the catalytic run was repeated with further addition of substrates in appropriate amount under same reaction conditions. The recovered catalyst is found to exhibit almost the same catalytic activity for homo-coupling reaction. From Fig. 6, it is seen that there was almost

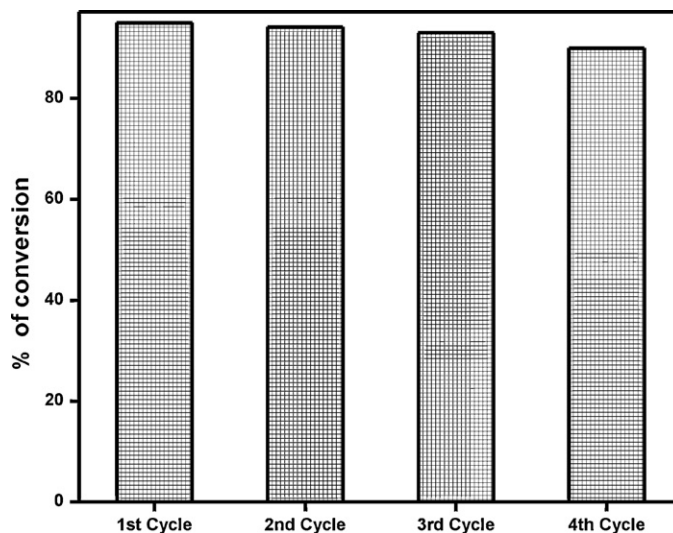


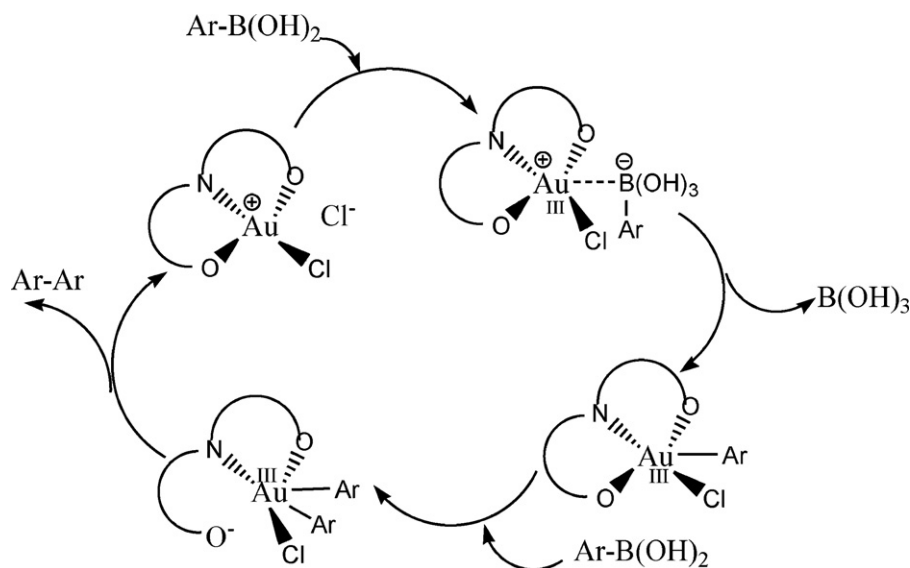
Fig. 6. Bar chart showing catalyst activity for MCM-41-Au(III) complex over several recycle (homocoupling of phenylboronic acid with iodo benzene in K_2CO_3 /xylene at $80^\circ C$).

Table 1

Summary of yields for Suzuki coupling reactions catalyzed by Au and Pd heterogeneous phases $Ar-X + Ar'-B(OH)_2 \xrightarrow[Arylene]{Au, Pd} Ar'-Ar' + Ar'-Ar' + Ar'-OH$.

Ar	X	Ar'	Au			Pd		
			%A	%B	%C	%A	%B	%C
Ph	Br	Ph	91	0	2	0	87	3
Ph	I	Ph	95	0	0	2	62	0
4-OMePh	Br	Ph	82	0	1	9	79	0
Ph	Br	4-MePh	85	0	2	0	69	-
Ph	I	4-MePh	85	0	0	0	67	0
Ph	Br	4-OMePh	84	0	3	0	68	0
Ph	Br	4-MePh	90	2	0	0	65	0

Condition: Aryl boronic acid (10 mmol), aryl halide (15 mmol), Au(III) or Pd(II) catalyst (3 mg) and K_2CO_3 (20 mmol) in xylene at $80^\circ C$. Reaction time 24 h.



Scheme 2. The possible mechanistic pathway for Suzuki coupling using Au(III) Schiff-base complex.

no change in catalytic activity even after fourth recycle. From atomic absorption spectroscopy (AAS) analysis it was found that metal content of the recycled catalyst remained unaltered indicating no leaching of the metal from MCM-41. In this context, the catalyst was removed from the solution after approximately 50% conversion at the reaction temperature. The isolated solution did not exhibit any further reactivity under similar reaction conditions. These studies indicate that the loss of Au active site is negligible, which could account for the preservation of catalytic activity. IR spectra for the recycled catalyst has provided along with the fresh catalyst in Fig. 3d. Similar spectra suggest retention of all types of properties of the recycled catalyst to that of fresh catalyst.

3.2.3. Reaction mechanism

The contrast selectivity can be explained by the mechanistic difference between gold and palladium catalyst. With regard to the possible reaction mechanism Suzuki cross coupling involve an oxidative addition of phenyl halide to the palladium as the first step. Oxidative addition does not take place in gold complex and homocoupling may occur through an “aromatic transmetallation” from boron to gold according to the mechanism proposed by Corma et al. [12,49,50]. In a second step the gold complex binds to a second aromatic ring which finally gives biphenyl by reductive elimination regenerating the original gold complex through ligand rearrangement (Scheme 2).

4. Conclusion

In summary, this work gives evidence that readily synthesizable gold complex supported on organically modified mesoporous silica can be advantageously employed to homocoupling of aryl boronic acid. XRD patterns show mesoporosity is retained even after multiple synthesis procedure. FT-IR and diffuse reflectance UV-vis spectra confirm the formation of the complex. The gold complex shows high selectivity towards homocoupling of aryl boronic acid, in contrast the palladium complex shows selectivity for cross-coupling. Furthermore the catalyst could be simply recovered and reused up to four cycles without a significant loss in catalytic activity.

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References

- [1] G.J. Hutchings, *Catal. Today* 100 (2005) 55–61.
- [2] A.S.K. Hashmi, *Gold Bull.* 37 (2004) 51–65.
- [3] D. Chandra, B.K. Jena, C. Retna Raj, A. Bhaumik, *Chem. Mater.* 19 (2007) 6290–6296.
- [4] G. Cortial, M. Siutkowski, F. Goettmann, A. Moores, C. Boissiere, D. Grosso, P. Le Floch, C. Sanchez, *Small* 2 (2006) 1042–1045.
- [5] A. Corma, H. García, *Chem. Rev.* 103 (2003) 4307–4365.
- [6] Ch. Wei, Ch.-J. Li, *J. Am. Chem. Soc.* 125 (2003) 9584–9585.
- [7] X. Yao, Ch.-J. Li, *J. Am. Chem. Soc.* 126 (2004) 6884–6885.
- [8] G. Dyker, *Angew. Chem. Int. Ed.* 39 (2000) 4237–4239.
- [9] A.S.K. Hashmi, J.P. Weyrauch, M. Rudolph, E. Kurpejovic, *Angew. Chem. Int. Ed.* 43 (2004) 6545–6547.
- [10] Y. Ito, M. Sawamura, T. Hayashi, *J. Am. Chem. Soc.* 108 (1986) 6404–6405.
- [11] C. González Arellano, A. Corma, M. Iglesias, F. Sánchez, *Chem. Commun.* (2005) 3451–3453.
- [12] C. González-Arellano, A. Corma, M. Iglesias, F. Sánchez, *Chem. Commun.* (2005) 1990–1992.
- [13] N.E. Leadbeater, M. Marco, *Chem. Rev.* 102 (2002) 3217–3274.
- [14] L. Yin, J. Liebscher, *Chem. Rev.* 107 (2007) 133–173.
- [15] S. Paul, J.H. Clark, *Green Chem.* 5 (2003) 635–638.
- [16] F. Diederich, P.J. Stang, *Metal-Catalyzed Cross-Coupling Reactions*, Wiley-VCH, New York, 1998.
- [17] S. Kotha, K. Lahiri, D. Kashinath, *Tetrahedron* 58 (2002) 9633–9695.
- [18] T.E. Barder, S.D. Walker, J.R. Martinelli, S.L. Buchwald, *J. Am. Chem. Soc.* 127 (2005) 4685–4696.
- [19] F. Diederich, P.J. Stang (Eds.), *Oligoacetylenes-Modern Acetylene Chemistry*, Wiley-VCH Verlag Gmbh, 2007.
- [20] D.J. Coza, E. Carita, *Synthesis* (2002) 2183–2186.
- [21] Y. Liua, X. Fenga, D. Baob, K. Li, M. Baoa, *J. Mol. Catal. A: Chem.* 323 (2010) 16–22.
- [22] K. Sarkar, M. Nandi, M. Islamb, M. Mubarak, A. Bhaumik, *Appl. Catal. A: Gen.* 352 (2009) 81–86.
- [23] M. Guinóa, A.C. Sullivanb, J.R.H. Wilsona, *J. Mol. Catal. A: Chem.* 293 (2008) 25–30.
- [24] G. Bringmann, R. Walter, R. Weirich, *Angew. Chem. Int. Ed. Eng.* 29 (1990) 977–991.
- [25] D.S. ChemLa, J. Zyss (Eds.), *Non Linear Optical Properties of Organic Molecules and Crystals*, Academic Press, Orlando, 1987.
- [26] G.W. Gray, *Molecular Structures and the Properties of Liquid Crystals*, Academic Press, London, New York, 1962.
- [27] C. Rosini, L. Franzini, A. Rafael, P. Salvadori, *Synthesis* (1992) 503–517.
- [28] M. Beller, C. Bolm, *Transition Metals for Organic Synthesis*, 2nd ed., Wiley-VCH, Weinheim, 2004.

- [29] D.W. Old, J.P. Wolfe, S.L. Buchwald, *J. Am. Chem. Soc.* 120 (1998) 9722–9723.
- [30] J.P. Wolfe, S.L. Buchwald, *Angew. Chem. Int. Ed.* 38 (1999) 2413–2416.
- [31] J.P. Wolfe, R.A. Singer, B.H. Yang, S.L. Buchwald, *J. Am. Chem. Soc.* 121 (1999) 9550–9561.
- [32] J. Yin, S.L. Buchwald, *J. Am. Chem. Soc.* 122 (2000) 12051–12052.
- [33] J. Yin, M.P. Rainka, X.-X. Zhang, S.L. Buchwald, *J. Am. Chem. Soc.* 124 (2002) 1162–1163.
- [34] V.P.W. Bohm, C.W.K. Gstottmayr, T. Weskamp, W.A. Herrmann, *J. Organomet. Chem.* 595 (2000) 186–190.
- [35] C. Zhang, J. Huang, M.L. Trudell, S.P. Nolan, *J. Org. Chem.* 64 (1999) 3804–3805.
- [36] G.A. Grasa, A.C. Hillier, S.P. Nolan, *Org. Lett.* 3 (2001) 1077–1080.
- [37] D.D. Das, A. Sayari, *J. Catal.* 246 (2007) 60–65.
- [38] S. Ray, S.F. Mapholie, J. Darkwa, *J. Mol. Catal. A: Chem.* 267 (2007) 143–148.
- [39] S. Huh, J.W. Wiench, J. Yoo, M. Pruski, W.-S.-Y. Lin, *Chem. Mater.* 15 (2003) 4247–4256.
- [40] M. Kruk, M. Jaroniec, Y. Sakamoto, O. Terasaki, R. Ryoo, C.H. Ko, *J. Phys. Chem. B* 104 (2000) 292–301.
- [41] W. Hammond, E. Prouzet, S.D. Mohanti, T.J. Pinnaviam, *Micropor. Mesopor. Mater.* 27 (1999) 19–25.
- [42] M.H. Lim, A. Stein, *Chem. Mater.* 11 (1999) 3285–3295.
- [43] S.C. Mojumdar, P. Simon, A. Krutosikova, *J. Therm. Anal. Calorim.* 96 (2009) 103–109.
- [44] A. Kriza, C. Parnau, N. Popa, *Rev. Chim. (Bucharest)* 52 (2001) 346–348.
- [45] K. Nakamoto, *Infrared Spectra of Inorganic and Coordination Compounds*, 2nd ed., Wiley, New York, NY, 1970.
- [46] T. Takei, K. Kato, A. Meguro, M. Chikazawa, *Colloids Surf. A* 150 (1999) 77–84.
- [47] A. de Meijere, F. Diederich, *Metal-Catalyzed Cross-Coupling Reactions*, vols. 1–2, Wiley-VCH, Weinheim, 2004.
- [48] G.C. Fu, A.F. Littke, *Angew. Chem.* 114 (2002) 4350–4386.
- [49] D.V. Partyka, A.J. Esswein, M. Zeller, A.D. Hunter, T.G. Gray, *Organometallics* 26 (2007) 3279–3282.
- [50] D.V. Partyka, M. Zeller, A.D. Hunter, T.G. Gray, *Angew. Chem. Int. Ed.* 45 (2006) 8188–8191.