Click on silica: systematic immobilization of Co(II) Schiff bases to the mesoporous silica *via* click reaction and their catalytic activity for aerobic oxidation of alcohols†

Bharat S. Rana,[a] Suman L. Jain,*[b] Bhawan Singh,[a] Asim Bhaumik,[c] Bir Sain[b] and Anil K. Sinha*[a]

Received 26th March 2010, Accepted 21st May 2010
First published as an Advance Article on the web 26th July 2010
DOI: 10.1039/c0dt00208a

The systematic immobilization of cobalt(II) Schiff base complexes on SBA-15 mesoporous silica *via* copper catalyzed [3 + 2] azide–alkyne cycloaddition (CuAAC) "click reaction" involving either step-wise synthesis of silica-bound Schiff base ligand followed by its subsequent complexation with cobalt ions, or by the direct immobilization of preformed Co(II) Schiff base complex to the silica support is described. The catalytic activity of the prepared complexes was studied for the oxidation of alcohols to carbonyl compounds using molecular oxygen as oxidant. The immobilized complexes were recycled for several runs without loss in catalytic activity and no leaching was observed during this course.

Introduction

Surface modifications of mesoporous silica with organosilane groups are of tremendous importance in the development of silica-immobilized transition metal complexes for organic transformations.[1] In particular, SBA-15 silica materials are attractive as supports since these materials can readily be synthesized, have large surface areas (700–900 $m^2 g^{-1}$) and large pore sizes (6–9 nm).[2] Cobalt(II) complexes coordinating with organic base ligands including Schiff bases are well-known to interact with molecular oxygen to form dioxygen adducts and these cobalt-dioxygen complexes have extensively been used as efficient and selective homogeneous catalysts for a variety of oxidation reactions in recent years.[3] However, the difficult separation of the catalyst from the reaction mixture at the end of the reaction and their non-recyclability make them inferior from synthetic, as well as, economical viewpoints. Therefore, much attention has focused on the immobilization of these catalysts onto solid supports as they offer many potential advantages including ease of handling, facile recovery from the reaction mixture by simple filtration and recycling ability.[4] Although many methods have been developed for the heterogenization of homogeneous catalysts, they mainly use inorganic materials,[5] dendrimers[6] and organic polymers[7] as supports. Further, it has been well accepted that covalent immobilization of metal complexes to the solid support offers high catalytic efficiency and better recycling without having the inherent problems of leaching of complex/ligand during the reaction. Immobilization of cobalt Schiff base complexes to the inorganic supports *via* covalent attachment, is well documented,[5] albeit the known methods have some limitations such as need of excess reagents, decomposition of the complex/ligand either due to the properties of support or due to the stringent reaction conditions required to immobilize.

In recent years, azide–alkyne [3 + 2] cycloaddition "click reaction" owing to its simplicity in use, mild reaction conditions and high conversion has proven to be one of the most powerful tools for the covalent attachment between appropriately functionalized molecules or their ligation to solid supports *via* a 1,2,3-triazole linkage.[8] Although, this approach has extensively been used for the functionalization of surfaces with biomolecules,[9] few reports are known for the immobilization of metal complexes using "click" reaction.[10] Although, previous reports have demonstrated the utility of the "click" reaction in the preparation of silica bound Schiff base complexes for organic reactions,[11] a systematic study by using different approaches for the immobilization of Co(II) Schiff base complexes is still unexplored. Recently, we have explored the potential of this efficient and versatile approach for the immobilization of cobalt(II) Schiff base complexes onto polystyrene support.[12] However, poor thermo-oxidative and mechanical stability of polystyrene based supports sometimes causes problems in the regeneration of the catalyst,[12] whereas immobilization on silica supports offers several advantages in terms of thermal stability, high surface areas, tailorable porosities and lower cost. This led our interest towards the use of mesoporous silica based materials as supports for developing efficient catalytic system by using "click" chemistry.

In the present paper, we report a systematic study on the controlled and randomly distributed loadings of an organoazide on the mesoporous silica by a "direct synthesis" route. Subsequent coupling of the organoazide on mesoporous silica with Co(II) Schiff base complexes using azide–alkyne [3 + 2] cycloaddition "click reaction" using different approaches involving either step-wise synthesis of silica-supported Schiff base followed by its complexation with cobalt ions (Fig. 1, **Route I**) or *via* direct immobilization of preformed cobalt Schiff base to the support (Fig. 1, **Route II**), resulted in high catalyst loading under mild reaction conditions. Significant differences in reactivity are demonstrated qualitatively between isolated and dense complexes.

---

[a] *Catalytic Conversion and Process Division, Indian Institute of Petroleum, Dehradun, India 248005. E-mail: asinha@iip.res.in*
[b] *Chemical Sciences Division, Indian Institute of Petroleum, Dehradun, India 248005. E-mail: suman@iip.res.in*
[c] *Department of Materials Science, Indian Association for the Cultivation of Science, Jadavpur, Kolkata, India 700032*

† Electronic supplementary information (ESI) available: Additional data. See DOI: 10.1039/c0dt00208a

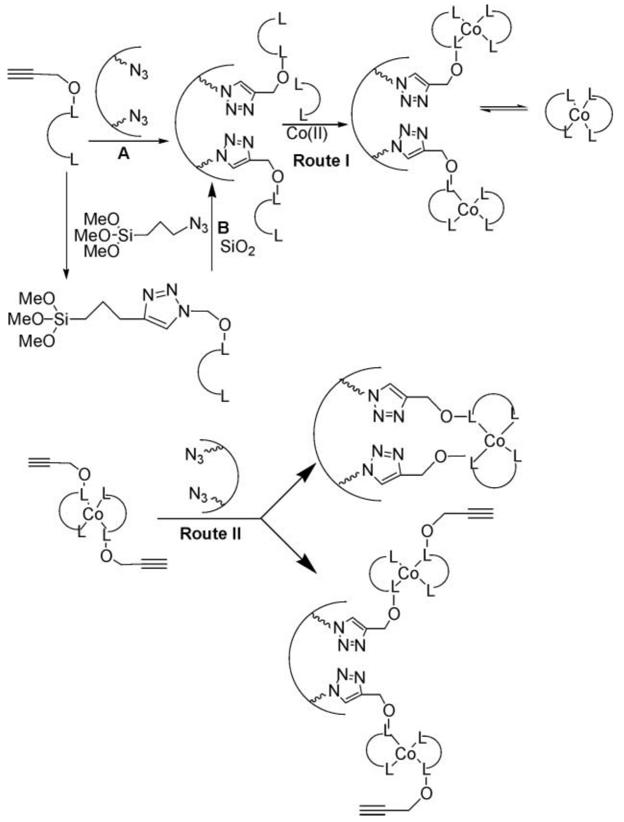


Fig. 1 Strategies applied for the immobilization of Co(II) Schiff base onto SBA-15 materials.

Experimental

Materials

L-(–)-Tyrosine, salicylaldehyde, *p*-aminobenzoic acid, propargylated bromide (80 wt% solution in toluene) and alcohols were commercially available and used as obtained. $CoCl_2$ was dried at 110 °C for 3–4 h under vacuum before use. Acetonitrile was dried over CaH_2 prior to use. Mesoporous silica functionalized with 3-azidopropylsilyl groups **4** with tailored pore size of 5–20 nm was synthesized using a triblock-copolymer template $EO_{20}PO_{70}EO_{20}$ (MW_n *ca.* 5800), hydrothermal synthesis method and by adding (3-azidopropyl)trimethoxysilane (4–12 mol%) during the synthesis. After the synthesis of mesoporous silica SBA-15 materials, the templates were removed by the soxhlet extraction in ethanol for 24 h.

Techniques used

The melting points were determined in open capillaries on a Buchi apparatus and are uncorrected. ^1H NMR spectra were recorded on Bruker 300 MHz spectrometer and the chemical shifts are expressed in δ parts per million relative to tetramethylsilane (TMS) as the internal standard. The IR spectra were recorded on a Perkin Elmer FTIR X 1760 instrument. Elemental analysis was done by using ASTM D-3828 (Kjeldhal method). Analysis for metal contents were carried out by using inductively coupled plasma atomic emission spectrometer (ICP-AES, PS-3000UV) by Leeman Labs. 10 mg of each sample was dissolved in 1 ml of refluxing 5% KOH, acidified with conc. nitric acid, and diluted to 10 ml. The resulting solutions were filtered and subjected to the analysis for Co content by ICP analysis. Specific surface areas of the SBA-15 materials were determined by the Brunauer–Emmett–Teller (BET) method using N_2 adsorption–desorption isotherms on a Micromeritics ASAP 2010 equipment. The average pore diameters were calculated by the BJH method. Powder X-ray diffraction experiments were performed with a Cu-Kα radiation.

Preparation of (3-azidopropyl)trimethoxysilane

In a 250 ml round bottomed flask was added sodium azide (0.05 mol, 3.66 g) and DMF (75 ml). The slurry so obtained was then cooled in an ice bath and 3-(chloropropyl)trimethoxysilane (0.12 mol, 5.0 g) was added under nitrogen atmosphere. The reaction mixture was warmed to ambient temperature and stirred for 48 h. The mixture was extracted with dichloromethane (3 times) and washed with water. The organic layer was dried over anhydrous sodium sulfate and concentrated under reduced pressure to give 3-azidopropyl)trimethoxysilane as a clear oil (yield 1.5 g, 40%). IR (Nujol, cm^{-1}): 2102 (azide); UV-vis (CH_3CN): 278 nm (azide).

Preparation of 3-azidopropyl SBA-15

3-Azidopropyl modified SBA-15 (N_3PrSBA-15) was synthesized using P123 (the triblock copolymer template ($PEO_{20}PPO_{70}PEO_{20}$)) as a structure-directing agent, 3-azidopropyltrimethoxysilane as a functionalized moiety and an auxiliary molecule 1,3,5-trimethylbenzene (TMB, to expand the pore) over the conventional hydrothermal synthesis method.[13] In a typical synthesis P123 ($EO_{20}PO_{70}EO_{20}$) (1 mmol, 6 g) was dissolved in a 2 M HCl solution (120 ml) and the mixture was stirred for 3 h. A solution of TMB (6 g) in deionized water (50 ml) was added and the resulting solution was stirred for 30 min. This solution was referred to as the surfactant solution. Further, tetraethylorthosilicate (TEOS; 11.44 g, 0.055 mol) and 3-azidopropyltrimethoxysilane (0.56 g, 0.002 mol) in different molar ratios (96 : 4, 92 : 8, 88 : 12) were added drop-by-drop to the surfactant solution and the mixtures so obtained were vigorously stirred for 45 min at 35 °C. After stirring, the mixtures were transferred to a stoppered PTFE bottle and stored at 100 °C for 48 h. The resulting material was collected by filtration and dried at 100 °C. The template was removed by soxhlet extraction in ethanol for 24 h.

Preparation of "click" modified SBA-immobilized Schiff base 5

To the stirred mixture of N_3PrSBA-15 (4 mol%, 0.62 mmol g^{-1}, 1 g) in dry DMF (10 ml) was added CuI (5 mol%), Et_3N (1 ml) and propargylated tyrosinato Schiff base **3** (1 mmol, 0.33 g). The resulting suspension was heated at 50 °C for 24 h under N_2 atmosphere. The solid material was filtered off and washed thoroughly with DMF, methanol and soxhlet extracted in acetonitrile for 24 h and dried under vacuum, yield (1.12 g, 94%). IR (cm^{-1}): 2930 (b), 1737, 1627, 1509.

Preparation of SBA-immobilized Co(II) Schiff base (SBA-click-Co-Schiff base 1A)

A mixture containing "click" modified SBA-immobilized Schiff base **5** (1 g, 0.52 mmol), salicylidine-*N*-(methyl-3(4′-hydroxyphenyl) propionate **6** (0.15 g, 0.52 mmol) and anhydrous

$CoCl_2$ (0.07 g, 0.55 mmol) in dry acetonitrile (15 ml) was stirred at room temperature for 24 h under nitrogen atmosphere. The so obtained green coloured solid was separated by filtration and thoroughly washed with acetonitrile, methanol, soxhlet extracted in acetonitrile and dried under vacuum, yield 0.86 g (72%). IR (cm^{-1}): 3392 (b), 1731, 1652, 1604, 1511, 1082. Analytical calculation for **7**: C, 61.26; H, 5.14; N, 9.16. Found: C, 63.67; H, 5.53; N, 9.98.

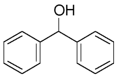
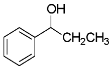
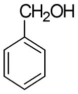
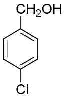
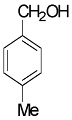
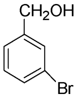
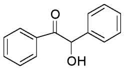
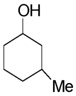
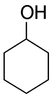
Preparation of "click" modified SBA-immobilized cobalt(II) Schiff base complex (SBA-click-Co-Schiff base II)

To the stirred mixture of Co(II) Schiff base **13** (0.73 g, 1 mmol) in dry DMF (20 ml) was added N_3PrSBA-15 (4 mol%, 0.62 mmol g^{-1}), triethylamine (1 ml) and CuI (5 mol%). The resulting suspension was heated at 50 °C for 24 h under nitrogen atmosphere. The progress was checked by IR as it showed the reduction of N_3 band (2107 cm^{-1}). After completion, the solid was separated by filtration, washed thoroughly with DMF, methanol and soxhlet extracted in acetonitrile for 8 h and then dried under vacuum, yield 1.04 g (72%). IR (cm^{-1}) 3419 (b), 2927, 1731, 1651, 1609, 956. Analytical calculation for **11**: C, 62.84; H, 5.15; N, 8.72. Found: C, 63.88; H, 5.69; N, 8.33.

General experimental procedure for aerobic oxidation of alcohols to carbonyl compounds

To the stirred solution of alcohol (1 mmol) and 2-methylpropanal (1.5 mmol) in dry acetonitrile (3 ml) was added SBA-click-Co Schiff base I-II (2 mol%). The mixture was heated at 50 °C under oxygen atmosphere. The progress of the reaction was monitored by TLC (SiO_2). At the end of the reaction, the catalyst was removed by filtration and the solvent was evaporated under reduced pressure. The residue thus obtained was dissolved in ethyl acetate, washed with saturated sodium bicarbonate solution (3 × 10 ml) and brine solution (2 × 10 ml). The organic layer was dried over anhydrous $MgSO_4$ and reduced under vacuum. The crude product was purified by column chromatography (SiO_2, hexane–ethyl acetate, 6 : 4). The yields of the carbonyl compounds and their reaction times are presented in Table 1.

Table 1 Oxidation of various alcohols[a]

Entry	Substrate	Catalyst	Time/h	Yield (%)[b]
1		SBA-click-Co Schiff base IA **7**	2.0	98
		SBA-click-Co Schiff base II **11**	2.5	97
2		SBA-click-Co Schiff base IA **7**	2.0	92
		SBA-click-Co Schiff base II **11**	2.75	90
3		SBA-click-Co Schiff base IA **7**	3.5	98
		SBA-click-Co Schiff base II **11**	4.25	98
4		SBA-click-Co Schiff base IA **7**	4.0	92
		SBA-click-Co Schiff base II **11**	4.25	90
5		SBA-click-Co Schiff base IA **7**	3.5	94
		SBA-click-Co Schiff base II **11**	3.75	90
6		SBA-click-Co Schiff base IA **7**	4.5	85
		SBA-click-Co Schiff base II **11**	5.0	86
7		SBA-click-Co Schiff base IA **7**	1.0	98
		SBA-click-Co Schiff base II **11**	1.5	98
8		SBA-click-Co Schiff base IA **7**	6.0	94
		SBA-click-Co Schiff base II **11**	7.0	92
9		SBA-click-Co Schiff base I **7**	6.5	92
		SBA-click-Co Schiff base II **11**	7.0	90

[a] *Reaction condition*: substrate (1 mmol), 2-methylpropanal (1.5 mmol), catalyst (2 mol%), acetonitrile (3 ml), under dioxygen atmosphere (1 atm) at 50 °C. [b] *Isolated yields*.

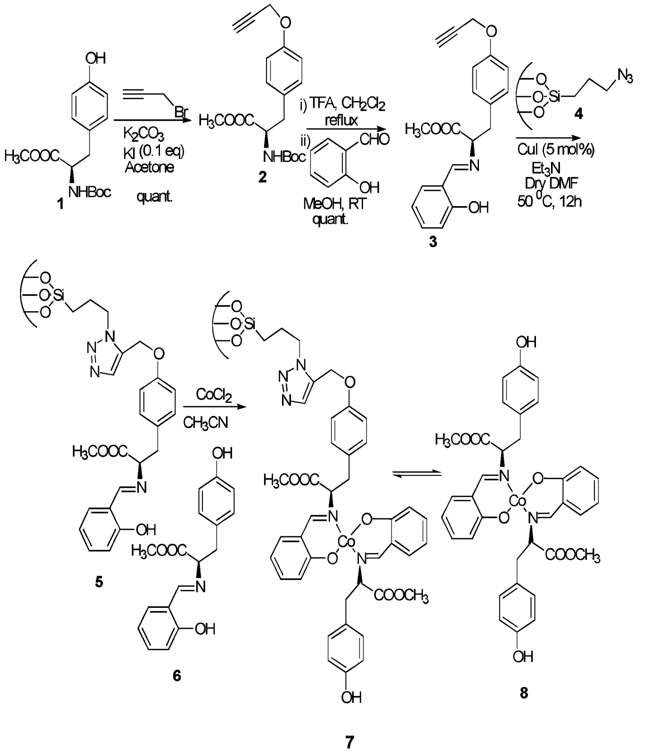
Results and discussion

Synthesis of silica immobilized Co(II) Schiff bases

Large (>5 nm) pore-size 3-azidopropyl-functionalized mesoporous SBA-15 support **4** (0.62 mmol N_3/g) was synthesized using a triblock-copolymer template $EO_{20}PO_{70}EO_{20}$ (MW_n *ca.* 5800) by hydrothermal synthetic method.[10] Azido-functionalization to the SBA-15 mesoporous silica support (4 mol%, 0.62 mmol g^{-1}) was carried out by adding 3-azidopropyltrimethoxysilane as a functional moiety during the synthesis. The incorporation of azido groups into the mesoporous material was confirmed by IR spectroscopy as it showed a clear band at 2106 cm^{-1} of the azido group (ESI, Fig. S1†).

Following **Route I** (Fig. 1, A), the required Schiff base **3** could readily be prepared from the three step sequence starting from N-Boc protected tyrosine methyl ester **1** according to the earlier report.[14] The prepared Schiff base was reacted with azido-functionalized SBA-15 **4** by using copper(I) iodide (5 mol%) catalyzed [3 + 2]-cycloaddition "click reaction" to give **5** in a virtually quantitative reaction, which is evident by the reduction of the typical IR absorption band of azide (2109 cm^{-1}) (ESI, Fig. S2†). The loading of Schiff base was found to be 0.38 mmol g^{-1}

as determined by elemental analysis. The supported Schiff base **5** was subjected to react with anhydrous cobalt(II) chloride and homogeneous Schiff base **6** in a molar ratio (1 : 1 : 1) in anhydrous acetonitrile for 12 h, to afford the light green colored SBA bound Co(II)-Schiff base **7** (SBA-click-Co-Schiff base IA, Scheme 1), which was isolated by filtration, washed thoroughly with hot methanol and subjected to soxhlet extraction in acetonitrile for 12 h and then dried under vacuum. The covalent attachment and successful synthesis of silica-immobilized Co(II) Schiff base complexes **7** (SBA-click-Co-Schiff base IA) was confirmed by IR spectroscopy (ESI, Fig. S3†). The reduced frequency of phenolic OH, shift of C=N band from 1627 to 1604 cm^{-1} revealed the formation of cobalt Schiff base complex on the support. Nevertheless, the possibility of the formation of the homogeneous Co(II) Schiff base **8** cannot be ruled out, the yield obtained for the silica immobilized catalyst **7** was found to be 72%, indicating the predominant formation of the silica immobilized Co(II) Schiff base during the reaction. Low angle XRD pattern of the prepared catalyst **7** is shown in Fig. 2. Low-angle XRD analysis showed a clear prominent peak at $2\theta = 0.85°$ with d (100) spacing of 9.8 nm, along with higher order peaks indicating that the material has a mesoporous structure with long range ordering of the pores, confirming the periodic hexagonal mesoporous structure of the silica supported material. The nitrogen-sorption analysis (Fig. 3) showed a narrow pore-size distribution with a mean pore-size of 5.9 nm. The material had a surface area of 404 m^2 g^{-1} and pore volume of 0.45 cm^3 g^{-1}, which is considerably lower in comparison to that observed for pristine mesoporous silica support (1.0 cc/g pore volume and 902 m^2 g^{-1} surface area), indicating considerable loading of the complex inside the mesopores.[15] However, even after the surface functionalization through "click reaction", the pore width of the material was as high as 5.9 nm, which justifies the use of auxiliary organic TMB in the synthesis. The loading of Co(II) Schiff base complex to the silica support was found to be 0.15 mmol g^{-1} as determined by the cobalt content through ICP-AES analysis.



Scheme 1 Step-wise synthesis of silica immobilized Co(II) Schiff base (SBA-click-Co Schiff base IA) **7**.

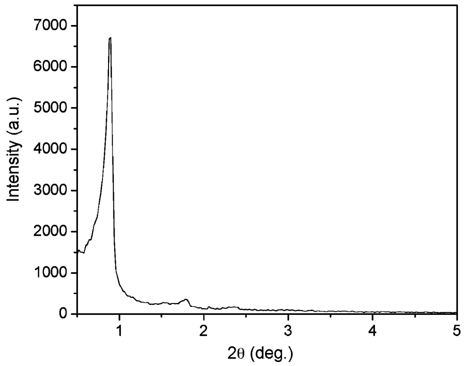


Fig. 2 Low angle XRD of SBA-click-Co Schiff base IA **7**.

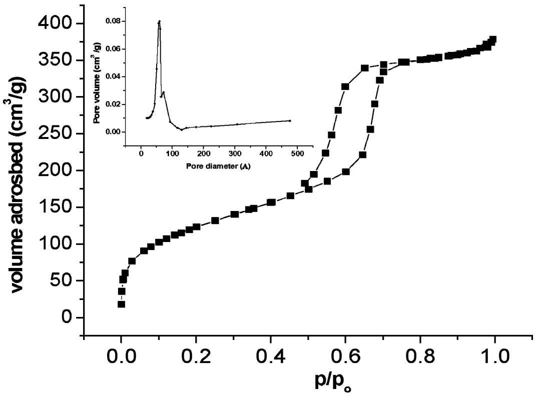
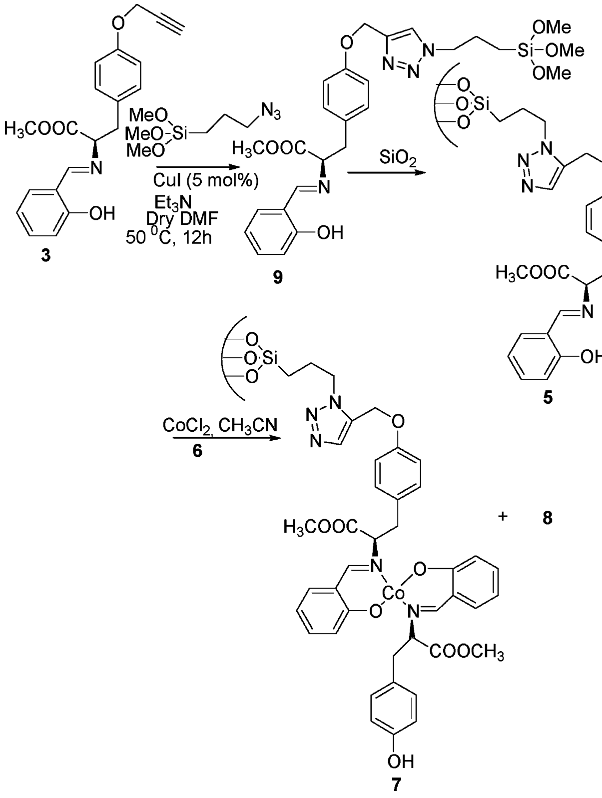


Fig. 3 Nitrogen-sorption isotherm and pore-size distribution of SBA-click-Co Schiff base IA **7**.

When the 3-azidopropyl loading was higher (12%), a lower loading of Co(II) Schiff base complex on the silica support was obtained (<0.1 mmol g^{-1}). This could be due to molecular crowding inside the mesopores at higher loadings which prevents the growth of the Schiff base complex inside the mesopores.

In an alternative approach (Fig. 1, B), Schiff base **3** was first reacted with 3-azidopropyltrimethoxysilane *via* copper catalyzed [3 + 2] azide–alkyne cycloaddition "click reaction" to yield Schiff base **9**. In the next step, Schiff base **9** was used as an organo-functionalized moiety and was added to the reaction mixture (4 mol%) during the synthesis of mesoporous SBA-15 material, which resulted in the formation of silica-immobilized Schiff base **5** (Scheme 2). The silica-immobilized Schiff base **5** was then reacted with anhydrous cobalt(II) chloride and homogeneous Schiff base **6** in a molar ratio (1 : 1 : 1) in anhydrous acetonitrile for 12 h, to afford green colored silica-bound Co(II)-complex **7**, which was separated by filtration, washed thoroughly with hot methanol and soxhlet extracted in acetonitrile for 12 h and then dried under vacuum. Again, the reduced frequency of the alkyne CH band near to 3320 cm^{-1} and bands at 1715, 1642 due to C=O and C=N of the Schiff base (ESI, Fig. S4†) and higher yield revealed the predominant formation of silica immobilized Co(II) Schiff base



Scheme 2 Step-wise synthesis of silica immobilized Co(II) Schiff base (SBA-click-Co Schiff base IB).

complex **7** (SBA-click-Co Schiff base IB). Low angle XRD of the prepared catalyst is shown in Fig. 4. The single low-angle XRD peak indicates that the material has a mesoporous structure but a lack of periodicity in the long range ordering of the pores. The nitrogen-sorption analysis (Fig. 5) showed a clear type IV isotherm due to mesoporous structure. The BET surface area and peak pore diameter of this material were 325 m^2 g^{-1} and 4.1 nm, respectively. The loading of Co(II) Schiff base complex to the silica support was found to be 0.11 mmol g^{-1} as determined by ICP-AES analysis.

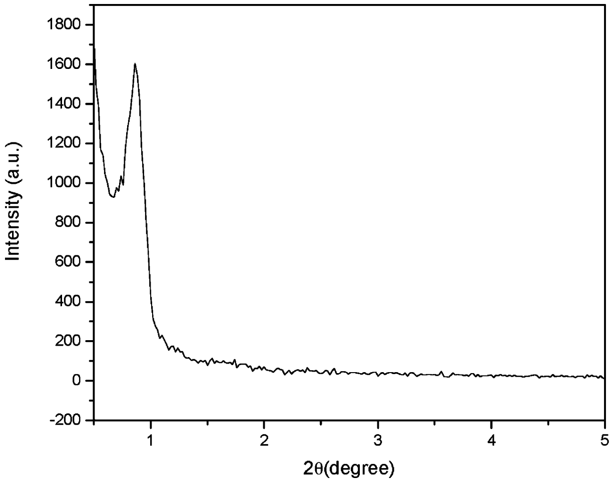


Fig. 4 Low angle XRD of SBA-click-Co-Schiff base IB.

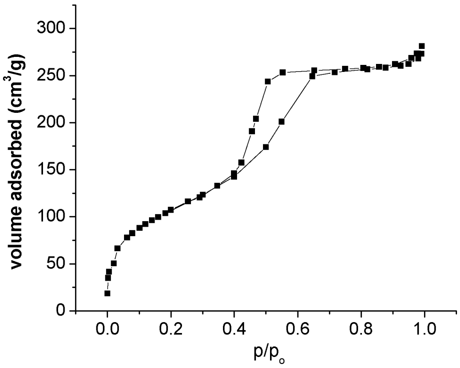


Fig. 5 Nitrogen-sorption isotherm and pore-size distribution of SBA-click-Co-Schiff base IB.

Following another strategy (Fig. 1, **Route II**), *i.e.* direct immobilization of preformed cobalt Schiff base to silica support *via* “click reaction”, the required complex **8** was synthesized by reacting **6** with anhydrous cobalt chloride in a molar ratio of 2 : 1 as reported earlier.[9] Subsequent propargylation **10** and copper(I) iodide catalyzed ligation with pore-expanded azido-functionalized SBA-15 **4** (0.62 mmol N$_3$/g) resulted in covalently attached silica-bound Co(II) catalyst **11** (SBA-click-Co salen II) as a light brown solid which was separated by filtration, washed thoroughly with acetonitrile, methanol, soxhlet extracted in acetonitrile for 24 h and then dried under vacuum. Again, formation of **11** (SBA-click-Co Schiff base II) was evidenced by the reduction of the typical IR frequency at 2104 cm^{-1} for the azide group and appearance of new bands at 3300–3400 cm^{-1} due to alkyne-CH, 1742 cm^{-1} and 1657 cm^{-1} due to C=O and C=N of the Schiff base respectively (ESI, Fig. S5†). Low angle XRD of the prepared catalyst **11** is shown in Fig. 6. The single low-angle XRD peak indicates that the material has a mesoporous structure but lacks in periodicity in the long range ordering of the pores. The mesoporous silica was prepared in the presence of trimethylbenzene to expand the mesopores to accommodate the bulky complex. The nitrogen-sorption analysis (Fig. 7) showed a narrow pore-size distribution with a very large mean pore-size of 23.8 nm. The loading of Co(II) Schiff base was determined by ICP-AES analysis and was found to be 0.18 mmol g^{-1}.

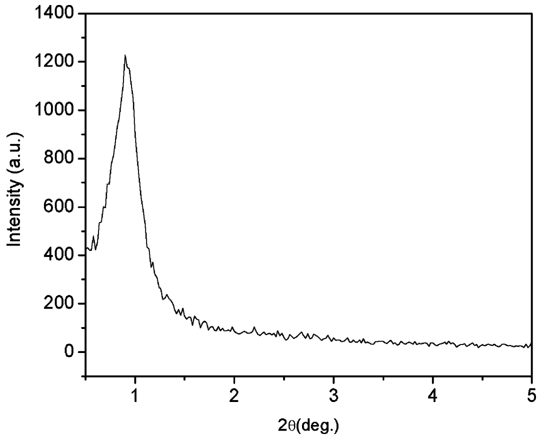


Fig. 6 Low angle XRD of SBA-click-Co Schiff base II.

The superiority of the CuAAC for covalent immobilization of the cobalt Schiff base to the silica support was reflected from the fact that it is a simple process and gave high catalyst loading

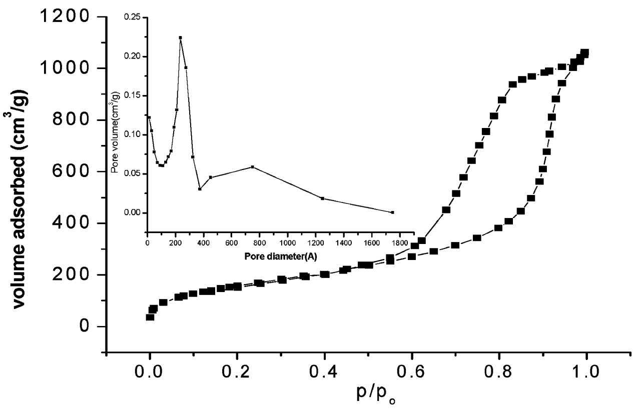
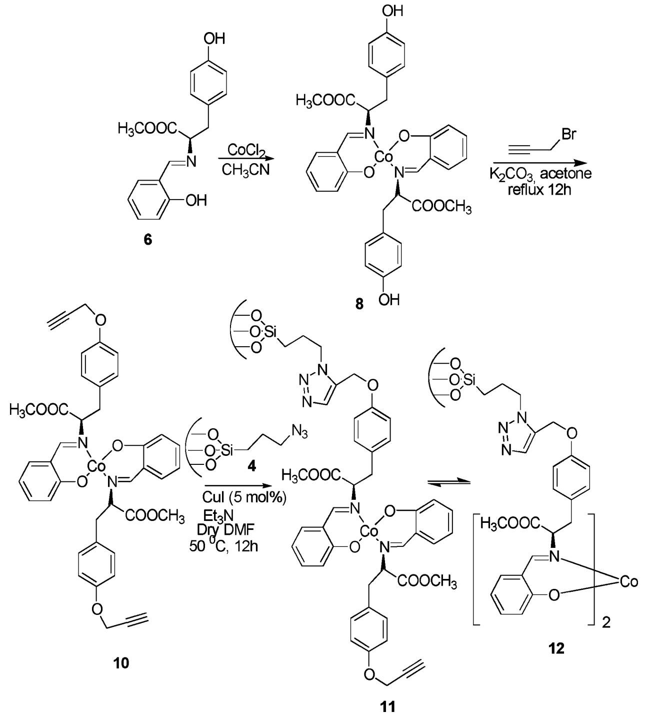


Fig. 7 Nitrogen-sorption isotherm and pore-size distribution of SBA-click-Co Schiff base II.

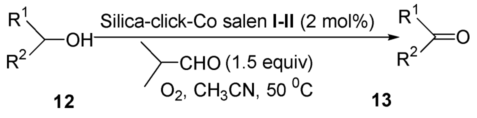
without using excess reagents under mild reaction conditions. This is in contrast to the existing methods, where covalent immobilization of functionalized ligand or complex on an inorganic support mainly requires excess reagents, multi-step synthetic procedures and gave lower yields either through ligand/complex decomposition due to the properties of the inorganic support or due to the relatively extreme conditions required to immobilize.[11a]

Catalysis

The catalytic activity of prepared silica immobilized cobalt(II) Schiff bases I and II were tested for the oxidation of alcohols **12**, both primary and secondary, to the corresponding aldehydes and ketones **13**, respectively, using molecular oxygen as oxidant and 2-methylpropanal as a reducing agent (Scheme 4).



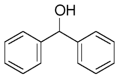
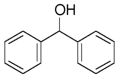
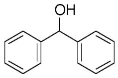
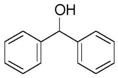
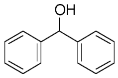
Scheme 3 Immobilization of preformed Co(II) Schiff base to silica support (SBA-click-Co Schiff base II).



Scheme 4 Oxidation of alcohols.

The protocol developed consists of the addition of silica-immobilized cobalt(II) Schiff base complex (2 mol%) to a stirred solution of alcohols **12** and 2-methylpropanal (1.5 equiv.) in acetonitrile under dioxygen atmosphere at 50 °C. This afforded corresponding carbonyl compounds **13** in high to excellent yields. After completion of the reaction as monitored by TLC analysis, the catalyst was separated by filtration and reused as such for subsequent runs. We did not observe any leaching of metal or ligand during the recycling experiments, and importantly, analysis by inductively coupled plasma atomic emission spectroscopy (ICP-AES) confirmed that the metal content of fresh and recovered catalyst was almost the same (detection limit 1 ppm). To examine the recyclability of the silica-immobilized cobalt Schiff base complexes, we selected benzhydrol as a representative substrate (Table 2). In all cases, the catalyst was recovered from the reaction mixture by simple filtration, washed with methanol, dried and subjected to subsequent experiments (4 cycles) without further activation. All the immobilized catalysts could be recycled without significant loss in activity and there was no metal/ligand leaching observed. Next, we studied the oxidation of a variety of primary and secondary alcohols under the described reaction

Table 2 Results of recycling experiments[a]

Entry	Substrate	Catalyst	Time/h	Yield (%)[b]
1		SBA-click-Co Schiff base IA **7**	2.0	98
		SBA-click-Co Schiff base II **11**	2.5	97
2		SBA-click-Co Schiff base IA **7**	2.0	98
		SBA-click-Co Schiff base II **11**	2.5	97
3		SBA-click-Co Schiff base IA **7**	2.0	98
		SBA-click-Co Schiff base II **11**	2.5	97
4		SBA-click-Co Schiff base IA **7**	2.0	98
		SBA-click-Co Schiff base II **11**	2.5	96
5		SBA-click-Co Schiff base IA **7**	2.0	98
		SBA-click-Co Schiff base II **11**	2.5	96

[a] *Reaction condition*: benzhydrol (1 mmol), 2-methylpropanal (1.5 mmol), catalyst (2 mol%), acetonitrile (3 ml), under dioxygen atmosphere (1 atm) at 50 °C. [b] *Isolated yields.*

conditions. The results of these experiments are presented in Table 1. Primary benzyl alcohols afforded the corresponding aldehydes selectively without any evidence for the formation of acids due to further oxidation. However, among the various secondary alcohols studied, those having aromatic substituents were found to be more reactive than alicyclic alcohols (Table 1, entry 8–9). The presence of 2-methylpropanal was found to be vital for this transformation, in its absence the oxidation of alcohols to carbonyl compounds did not occur. The reactions were found to be slow at room temperature, however 50 °C was found to be optimum temperature for this transformation. Likewise, in a controlled blank experiment, *i.e.* the stirring of a reaction mixture containing benzhydrol (1 mmol), 2-methylpropanal (1.5 mmol) and acetonitrile (3 ml) at 50 °C, no reaction occurred in the absence of catalyst even after prolonged reaction time (3.5 h). Similarly, the oxidation of benzhydrol did not occur when the reaction was performed with 2-methylpropanal alone in the absence of catalyst and molecular oxygen under otherwise similar reaction condition.

Conclusions

In summary, we have demonstrated the successful application of the copper catalyzed [3 + 2] azide–alkyne cycloaddition (CuAAC) "click reaction" for grafting cobalt(II) Schiff base complexes to mesoporous silica supports. Either step-wise synthesis of silica immobilized Schiff bases followed by their subsequent complexation with cobalt ions or direct immobilization of already prepared homogeneous complexes onto the support *via* "click reaction" could be successfully achieved. The key features of the "click reaction" such as its simplicity in use, versatility and high efficiency with respect to the catalyst loading without using excess reagents, makes it an attractive and superior tool for the preparation of immobilized catalysts. The so obtained silica-immobilized cobalt(II) Schiff base complexes could readily be recycled for several runs with consistent activity and without observable metal or ligand leaching to the aerobic oxidation of alcohols to give the corresponding aldehydes or ketones in excellent yields.

Acknowledgements

We kindly acknowledge the Director, IIP for his kind permission to publish these results. We thank the analytical division of Institute for providing analysis. BS thanks CSIR for his fellowship. DST, New Delhi is acknowledged for research funding.

Notes and references

1 (*a*) B. G. Trewyn, I. I. Slowing, S. Giri, H.-T. Chen and V. S. Y. Lin, *Acc. Chem. Res.*, 2007, **40**, 846–853; (*b*) G. E. Fryxell, *Inorg. Chem. Commun.*, 2006, **9**, 1141–1150; (*c*) Y. Wan and D. Y. Zhao, *Chem. Rev.*, 2007, **107**, 2821–2860; (*d*) T. J. Terry and T. D. P. Stack, *J. Am. Chem. Soc.*, 2008, **130**, 4945–4953; (*e*) G. D. Pirngruber, L. Frunz and M. Luchinger, *Phys. Chem. Chem. Phys.*, 2009, **11**, 2928–2938; (*f*) L. Li and J.-l. Shi, *Adv. Synth. Catal.*, 2005, **347**, 1745–1749; (*g*) C. Baleizao, B. Gigante, H. Garcia and A. Corma, *J. Catal.*, 2003, **215**, 199–207; (*h*) Bialek Marzena, Garlowska Anna and Liboska Ozanna, *J. Polym. Sci., Part A: Polym. Chem.*, 2009, **47**, 4811–4821; (*i*) C. Sanchez, B. Julian, P. Belleville and M. Popall, *J. Mater. Chem.*, 2005, **15**, 3559–3592; (*j*) D. E. De Vos, M. Dams, B. F. Sels and P. A. Jacobs, *Chem. Rev.*, 2002, **102**, 3615; (*k*) A. Schlossbauer, D. Schaffert, J. Kecht, E. Wagner and T. Bein, *J. Am. Chem. Soc.*, 2008, **130**, 12558–12559.

2 (*a*) D. Zhao, J. Feng, Q. Huo, N. Melosh, G. H. Fredrickson, B. F. Chmelka and G. D. Stucky, *Science*, 1998, **279**, 548–552; (*b*) F. Martinez, G. Morales, A. Martin and R. van Grieken, *Appl. Catal., A*, 2008, **347**, 169–178.

3 (*a*) T. Punniyamurthy, S. Velusamy and J. Iqbal, *Chem. Rev.*, 2005, **105**, 2329–2363; (*b*) L. I. Simandi, *Catalytic Activation of Dioxygen by Metal Complexes*, Kluwer Academic Publishers, Dordrecht, 1992; (*c*) A. L. Gavrilova, C. J. Qin, R. D. Sommer, A. L. Rheingold and B. Bosnich, *J. Am. Chem. Soc.*, 2002, **124**, 1714–1722; (*d*) R. A. Sheldon, J. K. Kochi, *Metal Catalyzed Oxidations of Organic Compounds*, Academic Press, New York, 1981; (*e*) D. H. R. Barton, A. E. Martell, D. T. Sawyer, *The Activation of Dioxygen and Homogeneous Catalytic Oxidation*, Plenum Press, New York, 1993.

4 (*a*) C. A. McNamara, M. J. Dixon and M. Bradley, *Chem. Rev.*, 2002, **102**, 3275–3299; (*b*) M. Benaglia, A. Puglisi and F. Cozzi, *Chem. Rev.*, 2003, **103**, 3401–3430; (*c*) A. Sakthivel, W. Sun, G. Raudaschl-Sieber, A. S. T. Chiang, M. Hanzlik and F. E. Kühn, *Catal. Commun.*, 2006, **7**, 302–307; (*d*) B. Pugin and H.-U. Blaser, *Comprehen. Asymm. Catal. I-III*, 1999, **3**, 1367–1375.

5 (*a*) C. E. Song and S. Lee, *Chem. Rev.*, 2002, **102**, 3495–3524; (*b*) J. M. Notestein and A. Katz, *Chem.–Eur. J.*, 2006, **12**, 3954–3965; (*c*) A. Corma and H. Garcia, *Adv. Synth. Catal.*, 2006, **348**, 191–1412.

6 (*a*) G. R. Newkome, H. He and C. N. Moorefield, *Chem. Rev.*, 1999, **99**, 1689–1746; (*b*) L. J. Twyman, A. S. H. King and I. K. Martin, *Chem. Soc. Rev.*, 2002, **31**, 69–82; (*c*) R. van Heerbeek, P. C. J. Kamer, P. W. N. M. van Leeuwen and J. N. H. Reek, *Chem. Rev.*, 2002, **102**, 3717–3756; (*d*) Y. Ribourbouille, G. D. Engel and L. H. C. R. Gade, *Chim.*, 2003, **6**, 1087–1096; (*e*) P. A. Chase, R. J. M. Klein Gebbink and G. J. van Koten, *J. Organomet. Chem.*, 2004, **689**, 4016–4054; (*f*) A. Berger, R. J. M. Klein Gebbink and G. van Koten, *Top. Organomet. Chem.*, 2006, **20**, 1–38(Dendrimer Catalysis); (*g*) R. Andres, E. De Jesus and J.-C. Flores, *New J. Chem.*, 2007, **31**, 1161–1191; (*h*) S.-H. Hwang, C. D. Shreiner, C. N. Moorefield and G. R. Newkome, *New J. Chem.*, 2007, **31**, 1192–1217.

7 (*a*) S. J. Shuttleworth, S. M. Allin and P. K. Sharma, *Synthesis*, 1997, 1217–1239; (*b*) D. E. Bergbreiter, *Catal. Today*, 1998, **42**, 389–397; (*c*) S. J. Shuttleworth, S. M. Allin, R. D. Wilson and D. Nasturica, *Synthesis*, 2000, 1035–1074; (*d*) B. Clapham, T. S. Reger and K. D. Janda, *Tetrahedron*, 2001, **57**, 4637–4662; (*e*) T. J. Dickerson, N. N. Reed and K. D. Janda, *Chem. Rev.*, 2002, **102**, 3325–3344; (*f*) P. Mastrorilli and C. F. Nobile, *Coord. Chem. Rev.*, 2004, **248**, 377–395.

8 (*a*) L.- J. Chen, F.-M. Mei and G.-X. Li, *Catal. Commun.*, 2009, **10**, 981–985; (*b*) J. P. C. Robert, L.-B. Emmanuelle, M. Ahmad, R. Catherine, B. Stephane and G. Roger, *J. Mater. Chem.*, 2002, **12**, 1355–1362; (*c*) C. Wang, S. Lim, G. Du, C. Z. Loebicki, N. Li, S. Derrouiche and G. L. Haller, *J. Phys. Chem. C*, 2009, **113**, 14863–14871; (*d*) A. Kumar, G. Mishra and A. Kumar, *J. Mol. Catal. A: Chem.*, 2003, **201**, 179–188; (*e*) J. Hu, K. Li, W. Li, F. Ma and Y. Guo, *Appl. Catal., A*, 2009, **364**, 211–220.

9 (*a*) C. W. Tornøe, M. Meldal, *In American Peptide Symposium*M. Lebl, R. A. Houghten, Eds, American Peptide Society and Kluwer Academic Publishers: San Diego, CA, 2001, p 263,; (*b*) V. V. Rostovtsev, L. C. Green, V. V. Fokin and K. B. Sharpless, *Angew. Chem., Int. Ed.*, 2002, **41**, 2596–2599; (*c*) Q. Wang, T. R. Chan, R. Hilgraf, V. V. Fokin, K. B. Sharpless and M. G. Finn, *J. Am. Chem. Soc.*, 2003, **125**, 3192–3193; (*d*) R. Huisgen, *Pure Appl. Chem.*, 1989, **61**, 613–628; (*e*) A. Gissibl, M. G. Finn and O. Reiser, *Org. Lett.*, 2005, **7**, 2325–2328; (*f*) E. M. Ryu and Y. Zhao, *Org. Lett.*, 2005, **7**, 1035–1037; (*g*) A. Gheorghe, A. Matsuno and O. Reiser, *Adv. Synth. Catal.*, 2006, **348**, 1016–1020; (*h*) E. Fernandez-Megia, J. Correa, I. Rodriguez-Meizoso and R. Riguera, *Macromolecules*, 2006, **39**, 2113–2120; (*i*) P. Wu, M. Malkoch, J. N. Hunt, R. Vestberg, E. Kaltgrad, M. G. Finn, V. V. Fokin, K. B. Sharpless and C. J. Hawker, *Chem. Commun.*, 2005, 5775–5777.

10 (*a*) J. Nakazawa, T. Daniel and P. Stack, *J. Am. Chem. Soc.*, 2008, **130**, 14360–14361; (*b*) A. Schlossbauer, D. Schaffert, J. Kecht, E. Wagner and T. Bein, *J. Am. Chem. Soc.*, 2008, **130**, 12558–12559.

11 (*a*) A. R. McDonald, H. P. Dijkstra, B. M. J. M. Suijkerbuijk, G. P. M. van Klink and G. van Koten, *Organometallics*, 2009, **28**, 1082–4699; (*b*) A. Schätz, M. Hager and O. Reiser, *Adv. Funct. Mater.*, 2009, **19**, 2109; (*c*) A. R. McDonald, N. Franssen, G. P. M. van Klink and G. van Koten, *J. Organomet. Chem.*, 2009, **694**, 2153–2162; (*d*) J. Y. Ying, J. Lim, S. S. Lee, S. N. B. Riduan *Int. Appl. No.*: PCT/SG2008/000088 (WO/2008/115154); (*e*) G. Lv, W. Mai, R. Jin and L. Gao, *Synlett*, 2008, 1418–1420; (*f*) X.-Y. Wang, A. Kimyonok and M. Weck, *Chem.*

Commun., 2006, 3933–3935; (*g*) G. Lv, W. Mai, R. Jin and L. Gao, *Synlett*, 2008, **9**, 1418–1422; (*h*) M. Tilliet, S. Lundgren, C. Moberg and V. Levacher, *Adv. Synth. Catal.*, 2007, **349**, 2079–2084; (*i*) S. Jain, J. K. Joseph, F. E. Kuhn and O. Reiser, *Adv. Synth. Catal.*, 2009, **351**, 230–234; (*j*) S. Jain and B. Sain, *Adv. Synth. Catal.*, 2008, **350**, 1479–1483.

12 S. Jain and O. Reiser, *ChemSusChem*, 2008, **1**, 534–541.

13 (*a*) G. J. D. A. Soler-IIlia, E. L. Crepaldi, D. Grosso and C. Sanchez, *Curr. Opin. Colloid Interface Sci.*, 2003, **8**, 109–126; (*b*) B. Yan and Y. Li, *Dalton Trans.*, 2010, **39**, 1480–1487.

14 A. Katiyara, S. Yadava, P. G. Smirniotisa and N. G. Pinto, *J. Chromatogr., A*, 2006, **1122**, 13.

15 K. Sarkar, K. Dhara, M. Nandi, P. Roy, A. Bhaumik and P. Banerjee, *Adv. Funct. Mater.*, 2009, **19**, 223–234.