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An immobilised Co(II) and Ni(II) Schiff base magnetic nanocatalyst *via* a click reaction: a greener approach for alcohol oxidation[†]

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A Schiff base immobilised nanocatalyst was synthesized *via* copper catalysed alkyne azide cycloaddition (CuAAC) on a magnetic support. The nanocatalyst exhibited high accessible active sites with a surface area of 76 m² g⁻¹ for a cobalt complex and 57 m² g⁻¹ for a nickel complex. A strong interaction between the magnetic support and the Schiff base was achieved by avoiding leaching during the course of reaction. The nanocatalyst efficiently oxidised both primary and secondary alcohols to carbonyl with improved yield in a solventless system rendering a greener approach.

Introduction

In recent years, researchers have explored different strategies to improve yielding of immobilized complexes on a support. Covalent anchoring of metal complexes on a silane support provides efficient immobilization.¹ However, a slight amount of leaching is observed. This may be due to the possible interaction between the support and the metal complexes. A strong binding between the support and nanoparticle must withstand the harsh conditions of the reaction.² The immobilization strategy used for linking metal complexes to supports must be mild, preserving the chemical functional activity of the complex and giving quantitative conversion.³ In this respect, click reaction is one of the powerful tools for ligation, which prevents the leaching of the complexes from the support during the reaction.

Immobilization methods that are often used for the attachment of metal complexes to a surface either involve non-covalent interactions based on physical adsorption or direct covalent immobilization to chemically functionalized activated supports. However, these methods suffer from certain drawbacks such as a lower catalyst loading on the support, use of excess metal complex and harsh reaction conditions. Hence, recently, researchers have indulged in determining different immobilization strategies to be carried out under mild reaction conditions with quantitative conversions.

Copper catalysed alkyne azide cycloaddition reaction was first proposed by Sharpless' group and Meldal's group.^{4,5} The simplicity in use, mild reaction conditions and high conversion has proved this reaction to be one of the most powerful tool for covalent attachment.⁶ Usually, the immobilization methods often require harsh conditions with multiple-step syntheses and are complicated by cross-reactivity of the functional groups present.⁷ Therefore, developing a new strategy with mild, selective and water-compatible immobilization of ligands onto magnetic nanomaterials is highly desirable. The 1,2,3-triazole linkage provides a high tolerance functional group for covalent attachment of the functionalized molecule on the support.8 Immobilization of the 1,2,3-triazole linkage on silica supports offers several advantages in terms of thermal stability, high surface areas and tailorable porosities at a lower cost. This approach has been extensively used for functionalization of surfaces by biomolecules and complexes.9-12 However, few studies have been devoted for the immobilization of metal complexes on magnetic nanoparticles (MNP) via a click reaction.13-15 In this respect, we tried to immobilize metal complexes on magnetic nanoparticles via a click reaction.

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Results and discussion

The electronic spectra of the ligands and complexes were recorded by DMSO. The electronic spectra of all the complexes showed bands in the 300–380 nm region. The bands appearing in the 300–400 nm region have been assigned to intra ligand transitions. A band in the range of 380–400 nm corresponds to the ligand to metal charge transfer transition (Fig. 1).

A coordinated Co(n) and Ni(n) complex shows d–d transitions at 650 nm. As a result of coordination, the intra ligand transition bands are red-shifted in the complexes. Magnetic susceptibility measurements of all Co(n) complexes show magnetic moments in the range of 4.08–4.12 B.M., confirming the tetrahedral structure.

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Fig. 1 UV-visible spectra of the (a) cobalt complex, (b) ligand L1, (c) nickel complex, and (d) ligand L2.

The Ni(π) complex was diamagnetic in nature. The HNMR of the ligand exhibited a multiplet at around 6.9–7.9 ppm, which has been assigned to the protons of phenyl groups present in the Schiff base ligand. A peak observed at ~8.5 ppm in complexes has been assigned to azomethine proton (-CH=N-). A peak around 5 ppm gives (O-CH₂) and 3.5 for (HC=CH) confirms propargylation of the ligand (ESI,† Fig. S1). The HNMR of the Co complex could not be obtained due to its paramagnetic nature (Scheme 1).



The covalent attachment and successful synthesis of silicaimmobilized $Co(\pi)$ and $Ni(\pi)$ Schiff base complexes *via* a click reaction was confirmed by FTIR spectroscopy (ESI,† Fig. S2). The FTIR spectral intensity of the MNP-grafted clicked complex is weak due to the low concentration of the complex. The reduced



Scheme 1 Schematic representation of the synthesis of the nanocatalyst.





frequency of Fe–O vibration from 570 cm⁻¹ to 550 cm⁻¹ revealed grafting of a clicked metal complex on the nanoparticle.¹⁶ A Si–O peak at 1057 cm⁻¹ confirms the silane modification on the nanoparticle. A peak at 2067 cm⁻¹ confirms the presence of the azide functional group on the surface of the modified ferrite.¹⁷ The reduced azide peak confirms click immobilization of the metal complexes on the nanoparticle. The X-ray diffraction pattern of MNP-clicked metal complexes was same as raw MNP, clearly indicating that crystallinity and morphology were not altered after grafting (Fig. 2). A widened broad spectrum with reduced intensity confirmed the immobilization of metal complexes on the magnetic nanoparticle.¹⁸

FEG-SEM images of MNP-clicked metal complexes shows further evidence for the attachment of the clicked metal complex to MNP. The morphology of MNP-clicked metal complexes showed a cluster of nanoparticles (Fig. 3). The molecular crowding by a clicked ligand can cause slight agglomeration. These ligands may block the active pores of the nanocatalyst and reduce its surface area. TEM images also further confirmed the size of a nanoparticle to be 20 nm. The TEM images exhibit a layer of the ligand adhered on a nanoparticle (black dots).



Fig. 3 FEG-SEM of (a) FCoL1, (b) FCoL2, (c) FNiL1 and (d) FNiL2.



Fig. 4 FEG-SEM of (a) FCoL1, (b) FNiL1 and (c) SAED image of FCoL1.

The SAED image confirms the crystalline nature of the nanocatalyst (Fig. 4c). Energy dispersive X-ray analysis (EDAX) further confirmed the presence of 'Si', 'Ni', 'Co', 'Fe' in the anchored clicked metal complexes on the MNP (ESI,† Fig. S3)

The nitrogen-sorption analysis showed a narrow pore-size distribution with a mean pore-size of 5 nm. The nanocatalyst had a surface area of 76 m² g⁻¹ for the cobalt complex (Fig. 5) and 57 $m^2 g^{-1}$ for the nickel complex (Fig. 6), which is considerably lower in comparison to that observed for bare ferrite (330 m² g⁻¹ surface area),¹⁹ indicating considerable loading of the complex inside the active pores of the nanocatalyst. Thermal behavior of the complexes was determined in a nitrogen atmosphere (20 ml min^{-1}) with a heating rate of 10 °C min⁻¹ in the temperature range of 30-800 °C. The thermograms of MNP-grafted complexes showed a two-step weight loss at temperatures ranging from 30 to 800 °C. The ferrite showed only one step weight loss at 300 °C. The first region at temperatures between 35 °C and 250 °C corresponds to the removal of physically adsorbed water. The second region is mainly related to the decomposition of Schiff base groups in the temperature range from 450 °C to 800 °C. A higher rate of weight loss of clicked metal complexes compared to ferrite further confirms the immobilization of the clicked complexes on the ferrite (Fig. 7).



Fig. 5 (a) Nitrogen sorption isotherm and (b) pore size distribution of FCoL1.



Fig. 6 (a) Nitrogen sorption isotherm and (b) pore size distribution of FNiL1.



Fig. 7 Thermogravimetric analysis of (a) Fe₃O₄, (b) FCoL1 and (c) FNiL1.

The oxidation of primary and secondary alcohols catalyzed by the magnetic core grafted clicked Schiff base complexes occurs readily to form the corresponding aldehydes and ketones as major products. The oxidation of benzyl alcohol was studied as a model substrate in more detail to optimize the reaction variables such as solvent, alcohol/oxidant, the alcohol/catalyst molar ratio and length of the reaction time. In order to study the effect of time on the activity, the product analysis was done at regular intervals of time under similar reaction conditions (Fig. 8). A total reaction time of 140 min gave a maximum conversion. A significant change in conversion was not observed with increase in time above 140 min. An increase in GC conversion by 3% was achieved for acetonitrile solvent. This can be due to the solvent effect observed due to acetonitrile (the chelating ligand). However, the MNP-immobilised clicked metal complexes via a click azide reaction exhibited comparable good efficiency for the solvent-less system. Hence, further studies were carried out in the solvent-less system. The water content present in hydrogen peroxide (30%) can act as a solvent to the catalytic system rendering a green synthesis. In order to study the effect



Fig. 8 Effect of time on nanocatalyst (a) FCoL1 and (b) FNiL1.

of the concentration of a catalyst with respect to the substrate, the reaction was also studied at different substrate to catalyst ratios. The reaction was also studied in the absence of a catalyst. No conversion was observed in this case (Table 1, entries 1 and 6). This observation ruled out the possibility of the reaction taking place due to the thermal decomposition of the oxidants. 0.02 g of catalyst was sufficient for the effective transformation of benzyl alcohol to benzaldehyde. The reactions were also studied at various substrate-to-oxidant ratios. From the Table 1, it is observed that a minimum quantity of 5 mmol of the oxidant was sufficient for the effective oxidation of 1 mmol benzyl alcohol to benzaldehyde.

The oxidation was extended to a variety of alcohols, including aromatic and aliphatic alcohols. All the synthesized MNPgrafted clicked Schiff base complex were found to catalyse the oxidation of alcohols to corresponding carbonyl compounds in good yield (Table 2). Among the various alcohols studied, those containing aromatic substituents were found to be more reactive than aliphatic alcohols. It is clear from GC analysis that no side reaction took place during the course of catalytic oxidation. All the experiments were carried out in air at room temperature because there is no significant change in conversion observed when the experiments are carried out under a higher temperature of 80 $^{\circ}$ C. This indicates that oxidation

Table 1	Optimisation	of the catalyst	amount and	oxidant	concentration
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		Amount of	Conversion ^a (%)		
Entry	Catalyst (g)	oxidant (mmol)	FCoL1	FNiL1	
1	0	5.00	2.6	2.23	
2	0.01	5.00	47.0	43.5	
3	0.02	5.00	82.0	79.8	
4	0.04	5.00	53.2	48.7	
5	0.06	5.00	39.2	32.4	
6	0.02	0	1.3	1.8	
7	0.02	2.00	36.2	32.8	

^{*a*} Reaction conditions: 1 mmol substrate, time 140 min. Average of 3 GC trials.

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Table 2	Oxidation of alcohols	catalyzed b	y MNP-clicked metal	complexes

		Conversion ^a (%)			
Substrate	Product	FCoL1	FCoL2	FNiL1	FNiL2
ОН	0	82.0	80.1	79.8	76.2
ОН	O	98.5	97.3	96.6	98.0
ОН		96.2	94.3	92.5	95.3
Н3С ОН	H ₃ C 0	70.3	76.8	70.5	77.2
Н3СО ОН	H ₃ CO 0	68.4	66.7	64.5	67.1
ОН	O OH	64.6	62.9	62.4	60.4
OH CI	O CI	58.7	59.3	57.6	58.9
CI	CI CI CI	72.3	70.5	69.2	73.1
но ОСН3	HO OCH3	74.2	70.6	66.9	71.5
ОН	0	33.6	30.3	35.7	36.2
$(CH_3)_2CH_2OH$	(CH ₃) ₂ CH ₂ CHO	24.2	27.3	26.4	21.9

^{*a*} Reaction conditions: substrate (1 mmol); oxidant (H₂O₂, 30%, 5 mmol); catalyst (0.02 g); time 140 min; solventless. Average of 3 GC trials.

involves peroxide adsorption on the surface of nanoparticles. This also confirmed that the magnetic nanoparticle had a sole role of a catalyst support. All the reactions occurred with complete selectivity for aldehydes and no other products were detected in the reaction mixture. A higher rate of oxidation was observed for the clicked Co complex than for Ni complexes. This can be due to feasibility of the Co^{2+} cation with a higher number of unpaired electrons for orbital overlap. In the nanorange, the ligands may passivate the active pores on the nanocatalyst due to molecular crowding, thereby decreasing the catalytic activity.

Catalyst reusability was checked by the extraction of the nanocatalyst by a simple external magnet after the reaction. The active surfaces of the nanocatalyst were activated by washing with ethanol followed by sonication. The oxidation reaction was carried out nearly 5 times under identical reaction conditions to check the significant change in the catalytic activity observed.



Fig. 9 Vibrating sample magnetometry analysis of (a) FNiL1, (b) FNiL2, (c) FCoL1, (d) FCoL2 and (e) Fe_3O_4 .

All the catalyst exhibited better stability (ESI,† Fig. S4). A decrease in the catalytic activity of FNiL1 can be attributed to the overcrowding of the oxidised products entrapped within the pores. The magnetic curve obtained from vibrating sample magnetometry showed a hysteresis curve without coercivity (Fig. 9). This indicated super-paramagnetism of the ferrite nanoparticle.

The metal loading observed for clicked metal complexes was 4.6 wt% (Co complex) and 5.2 wt% (Ni Complex). The loading of the azide group was confirmed by TGA as 0.36 mmol g^{-1} . An improved yielding was observed for the model substrate with 80% conversion. Furthermore, leaching experiments were undertaken to demonstrate that the catalysis with MNPs are truly heterogeneous and that no catalytically active Ni or Co species are dissolved in the solution. For these experiments, the reactions were allowed to occur until around 50% of conversion and the catalyst was extracted by an external magnet. The filtrate was subjected to atomic absorption spectroscopy (AAS) to determine the amount of the leached product (ESI,† Table S1). Clearly, it was observed that a negligible amount of leaching was observed during the oxidation process. This confirms the catalyst to be heterogeneous.

Click immobilization on silane coated ferrite support exhibited negligible amount of leaching with good yield. This confirms a very strong interaction between the magnetic support and the clicked metal complexes. 1,2,3-Triazole as a linker provides stabilized magnetic nanoparticle. In addition, the heterocyclic molecule assisted in enhancing the catalytic activity of the nanocatalyst.

Conclusions

We have successfully synthesized MNP-immobilised clicked metal complexes. The developed nanocatalyst showed a promising greener route with high catalytic activity for oxidation of primary and secondary alcohols. A solventless greener approach with improved yield was achieved. The superiority of the copper catalysed alkyne azide cycloaddition for the covalent immobilization of the cobalt Schiff base to the silica support provided a simple process with high catalyst loading without using excess reagents under mild reaction conditions. Magnetic nanoparticles provided a strong binding interaction to the metal complexes on the support, thereby avoiding low yields possible due to ligand/ complex dissociation.

Experimental

(a) Synthesis of ligands and complexes

Synthesis of N,N'-bis-(4 bromo-2-propynoxybenzylidine)-1,4phenylenediamine (L1) and N,N'-bis-(2-propynoxynapthalidine)-1,4 phenylenediamine (L2). The precursor ligands were prepared by the drop wise addition of a methanolic solution of p-phenylenediamine (0.1 mol) to methanolic solution of 4-bromo-2-hydroxy benzaldehyde (0.2 mol) or 2-hydroxynapthaldehyde (0.2 mol). The resulting solution was refluxed on water bath for 2 h. A yellow coloured and bright red coloured solid mass was separated out, which was filtered, washed and subsequently dried. The ligand was found to be insoluble in non-polar solvents such as acetone and benzene and soluble in polar solvents such as DMF and DMSO (yield 90%). The ligand was treated with propargyl bromide and potassium carbonate (base) at room temperature for 6 h. The product was quenched with water and extracted with ethylacetate. The propargyl armed ligand was soluble in polar solvent like DMSO (vield 80%).

The ligand (0.1 mol) in the minimum quantity of methanol solution was mixed with a methanolic solution of nickel(II) acetate tetrahydrate or cobalt(II) acetate tetrahydrate (0.2 mol). The resulting solution was refluxed with stirring on a magnetic stirrer equipped with a heater at 80 $^{\circ}$ C for 2 h. The bright red (Ni) or brown (Co) colour complex separated out, which was filtered, washed and dried.

(b) Synthesis of iron oxide nanoparticle

Magnetic nanoparticles were prepared by chemical coprecipitation technique. Aqueous solution of salts $Fe_2SO_4 \cdot 7H_2O(1 \text{ mmol})$ and $FeCl_3 \cdot 6H_2O(2 \text{ mmol})$ are mixed in D.I. water at 80 °C with a slow addition of $NH_4OH(25\%, 15 \text{ mL})$ under anaerobic conditions to yield a black ppt.²⁰ The precipitate was aged overnight to obtain monodisperse nanoparticles. Furthermore, the black precipitate was washed with ethanol (10 mL) and water (5 mL) and dried at 80 °C.

(c) Azide functionalized nanoparticle

A solution of sodium azide (0.05 mmole) in DMF solution at 0 °C was treated with 3-chloropropyltrimethoxysilane (ClPTES; 1 mmole). The slurry was heated at 50 °C and stirred for 48 h to yield 3-azidopropyltrimethoxysilane.^{3,21,22} The reaction mixture was quenched in water and extracted with ethylacetate. The organic layer was dried with anhydrous sodium sulfate and concentrated at reduced pressure. This yielded a viscous oil solution. FTIR: 2097 cm⁻¹. ¹H NMR (CDCl₃): 0.7 (2H), 1.7 (2H), 3.27 (2H), 3.5 (9H).

1 g of magnetic nanoparticles was treated with 1.1 g of azidopropyltrimethoxysilane in the presence of toluene at 80 $^\circ\mathrm{C}$

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for 6 h in an argon atmosphere. The product was aged for 1 h, centrifuged with toluene and ethanol and dried at 80 $^\circ C.$

(d) Immobilisation *via* a click-azide reaction of metal complexes on magnetic iron oxide

One gram of azide functionalized ferrite nanoparticles was added to a solution of ligand (100 mg) in $1:1 H_2O_2:tert$ -butanol system. CuSO₄ (0.5 mmol) was added to initiate the reaction with sodium ascorbate (1 mmol). The solution was reacted for 6 h. The brown coloured nanoparticles were separated using a magnet and were washed several times with dichloromethane and toluene.

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