

Selective oxidation of alcohols to aldehydes using silica-functionalized cobalt (II) acetate as recyclable heterogeneous catalyst

Tahira Shamim¹, Mousami Sharma²

^{1,2}Department of Chemistry, University of Jammu, Jammu, India

Abstract : Silica-functionalized cobalt (II) acetate, $\text{SiO}_2\text{-Co(OAc)}_2$ was developed and its catalytic activity was evaluated for the selective oxidation of alcohols to aldehydes. Reactions were found to be efficient and selective to afford excellent yields. This method has many advantages such as higher yields and methodological simplicity. Recyclability of the catalyst makes it significant. The catalyst is characterized by FTIR, TGA, SEM, TEM, and AAS.

IndexTerms - Oxidation of alcohols to aldehydes, Recyclability, silica-functionalized cobalt (II) acetate [$\text{SiO}_2\text{-Co(OAc)}_2$]

INTRODUCTION

Alcohol oxidation[1] is an important organic transformation required during the synthesis of complex organic compounds and fine chemicals[2-3]. In general, oxidation of alcohols to corresponding carbonyl compounds is accomplished by an oxidising agent. Common oxidants include chromium reagents, manganese dioxide, silver oxide, *N*-chlorosuccinimide, dimethyl sulfoxide activated by oxalyl chloride[4], and periodanes[5,6]. These oxidants are generally useful on a laboratory scale but are unacceptable on industrial scale because of the toxicity and the amount of chemical waste produced due to the stoichiometric nature of these reagents. However, recently, more and more efforts have been made to develop high valuable selective catalytic oxidizing processes. Among these, protocols based on O_2 , air or H_2O_2 are particularly attractive because of cheap and readily available oxidants, and moreover, formation of H_2O as the only by-product. Numerous methods[7-11] are available for the selective oxidation of alcohols to carbonyl compounds. Saikia *et al.*[12] have reported a transition metal-free protocol for the oxidation of alcohols to corresponding carbonyl compounds using *N,N*-dibromo-*p*-toluenesulfonamide as oxidizing agent. Generally, oxidations that do not require transition metal catalysts are particularly appealing since there is neither leaching nor the need for catalyst regeneration. However, these systems are less attractive for industrial applications and most of them are not environment-friendly. Oxidations catalyzed by transition metals can potentially alleviate problem associated with such systems. Carbon nanotube (CNT)-supported ruthenium catalysts[13], assembled at the interfaces of emulsion droplets, showed activity for the selective oxidation of benzyl alcohols to benzaldehydes with oxygen or air as oxidant in water. Zhang *et al.*[14] have used a combination of FeCl_3 , L-valine and TEMPO to oxidize a wide range of primary/secondary, allylic, benzyl, and heterocyclic alcohols to the corresponding carbonyl compounds in the presence of dioxygen as oxidant in good to excellent isolated yields. Recently, Rostami *et al.*[15] have successfully developed a novel method for the oxidation of alcohols to the corresponding carbonyl compounds using *tert*-butyl hydrogenperoxide (TBHP) in the presence of a catalytic amount of recyclable magnetic nanoparticle-supported oxo-vanadium ephedrine complex ($\text{VO(ephedrine)}_2\text{@MNPs}$) in PEG as a green solvent at 80 °C. The catalyst can be magnetically recycled and reused. Although, a wide range of methods[16-20] are available for the oxidation of alcohols, but most of them, still have poor atom efficiencies, less selective and significant scale-up issues. Therefore, it is of particular importance to develop methods which use cleaner oxidants and minimize the amount and toxicity of the released waste. Moreover, though there is great development of homogeneous cobalt based catalysts, heterogeneous systems are still largely unexplored. Therefore, there is a scope for further development of a highly active heterogeneous catalyst together with environmentally friendly oxidants such as molecular oxygen, which would provide an important addition to the existing protocols for alcohol oxidation.

Owing to the importance of aldehydes in organic syntheses, and in continuation of our research to explore the catalytic activity of $\text{SiO}_2\text{-Co(OAc)}_2$ for useful organic transformations, herein, we report an efficient, selective, cost-effective and green procedure for the selective oxidation of alcohols to aldehydes using silica functionalized cobalt(II) acetate [$\text{SiO}_2\text{-Co(OAc)}_2$] as a recyclable heterogeneous catalyst under mild reaction conditions.

RESULTS AND DISCUSSION

Synthesis and characterization of silica-functionalized cobalt(II) acetate

Fig. 1 represents the preparation procedure for silica functionalized cobalt(II) acetate [$\text{SiO}_2\text{-Co(OAc)}_2$]. It involves building up a suitable ligand structure onto the surface of commercial silica (K100) followed by complexation with cobalt(II) acetate. In order to make the process completely heterogeneous, $\text{SiO}_2\text{-Co(OAc)}_2$ was conditioned for 12 h by refluxing each in acetonitrile (2×2 h), ethanol (2×2 h) and toluene (2×2 h) so as to remove the physisorbed cobalt(II) acetate.

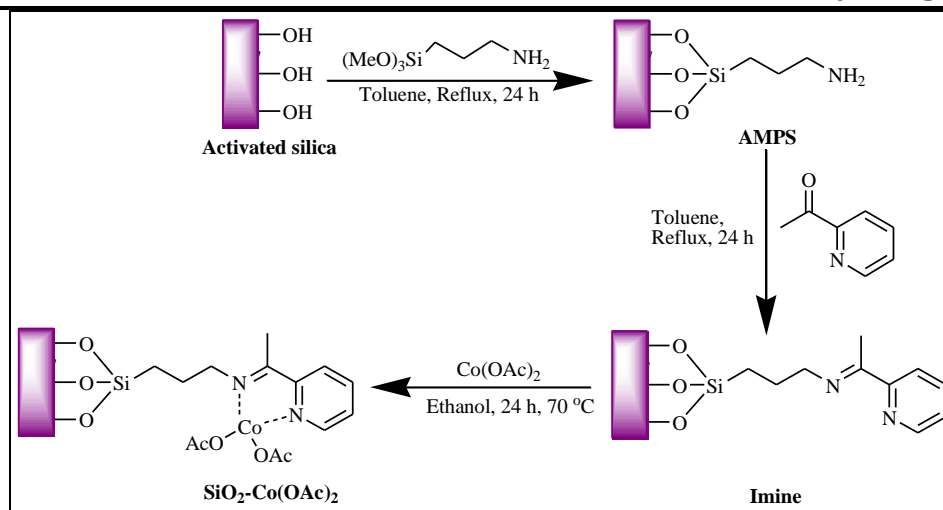


Fig. 1 Preparation of silica-functionalized cobalt(II) acetate [$\text{SiO}_2\text{-Co}(\text{OAc})_2$]

The characterization of silica-functionalized cobalt(II) acetate [$\text{SiO}_2\text{-Co}(\text{OAc})_2$] was carried out by FTIR, TGA, AAS, SEM and TEM.

FTIR

The FTIR of chemically modified silica (imine) (Fig. 2) showed a sharp peak at 1638 cm^{-1} due to C=N bond, which on complexation with cobalt(II) acetate disappeared and appeared as a band at 1617 cm^{-1} (Fig. 3). The lowering in frequency of the C=N peak indicates the formation of the metal-ligand bond[21].

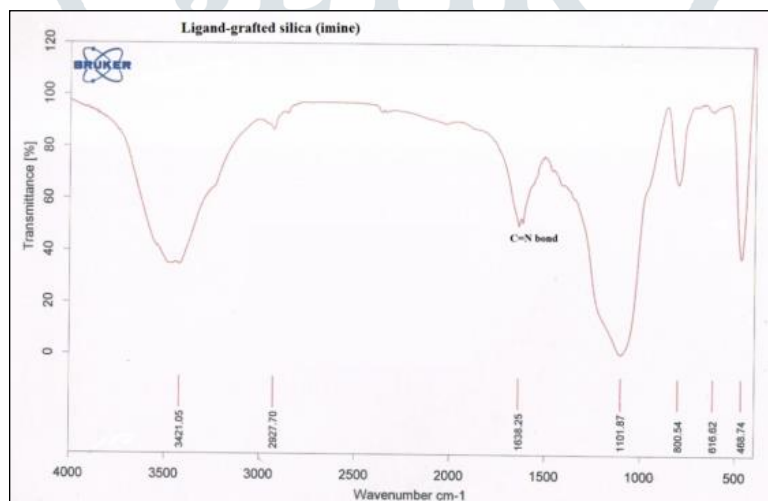


Fig. 2 FTIR of ligand-grafted silica (imine).

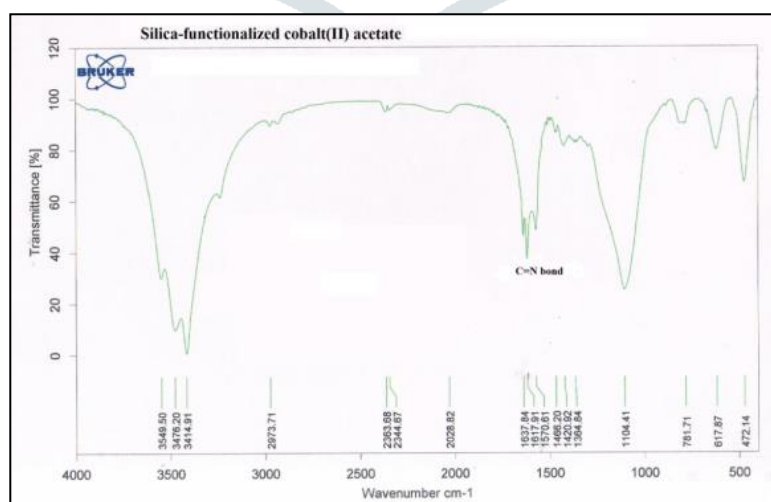


Fig. 3 FTIR of $\text{SiO}_2\text{-Co}(\text{OAc})_2$.

Thermogravimetric analysis (TGA)

The stability of $\text{SiO}_2\text{-Co}(\text{OAc})_2$ was determined by thermal analysis (TGA). The TGA curve (Fig. 4) showed an initial weight loss upto $100\text{ }^\circ\text{C}$ and then a very little upto $250\text{ }^\circ\text{C}$. Afterwards a gradual weight loss occurs till $580\text{ }^\circ\text{C}$. The weight loss upto 100

°C may be due to the loss of residual solvent and water present onto the surface of the catalyst. Further, weight loss from 250 to 580 °C was attributed to the loss of organic functionality. Thus, the TGA of $\text{SiO}_2\text{-Co(OAc)}_2$ indicated that the catalyst is stable upto 250 °C and hence it is safe to carry out all reactions at 90 °C.

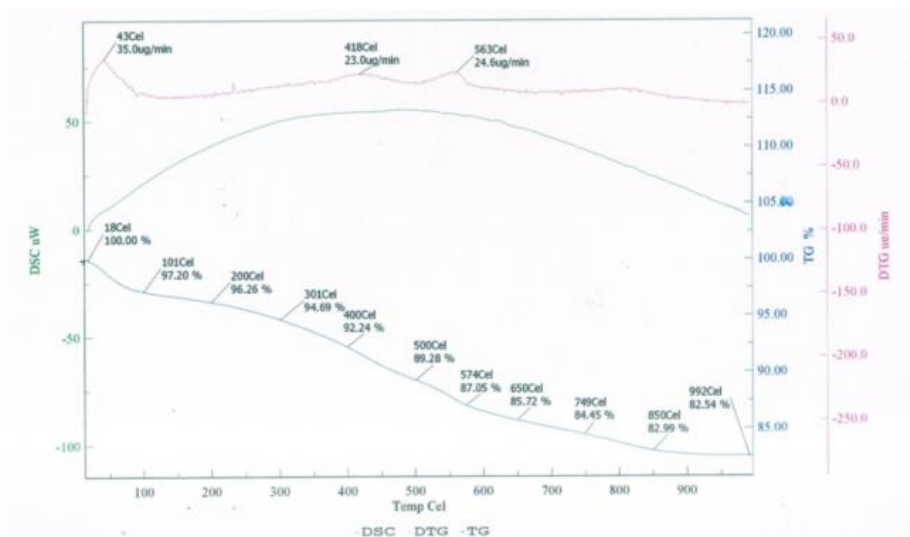


Fig. 4 TGA of $\text{SiO}_2\text{-Co(OAc)}_2$.

Atomic Absorption Spectrophotometric Analysis (AAS)

The amount of the cobalt loaded onto the surface of silica in $\text{SiO}_2\text{-Co(OAc)}_2$ was determined by AAS analysis. The catalyst was stirred in dil. HNO_3 and the solution was subjected to AAS analysis. $\text{SiO}_2\text{-Co(OAc)}_2$ was found to contain 0.01236 g of Co per gram of the catalyst.

Scanning Electron Microscopy (SEM)

The microstructure and morphology of $\text{SiO}_2\text{-Co(OAc)}_2$ was studied using Scanning Electron Microscopy (SEM), which showed uniform surface morphology. The SEM image (Fig. 5) showed a very slight roughening of the top surface of the catalyst, which may be due to the interaction of Co(OAc)_2 with the surface of silica.

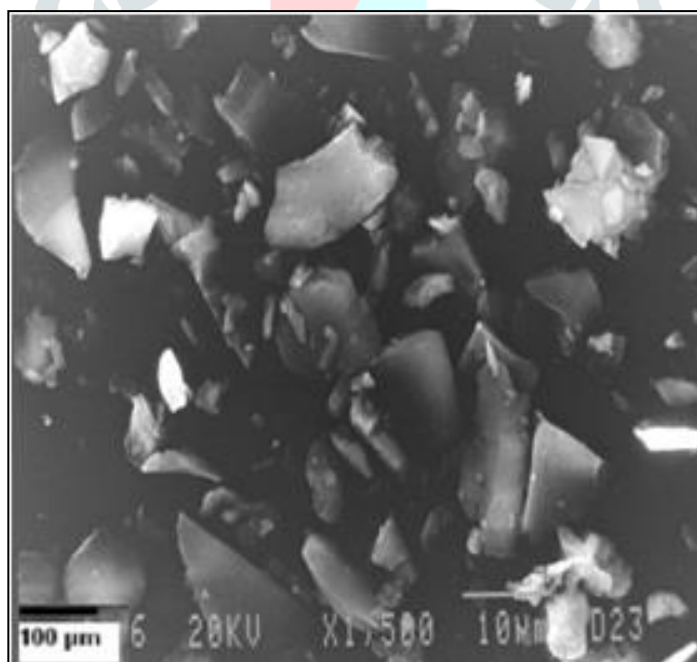


Fig. 5 SEM image of $\text{SiO}_2\text{-Co(OAc)}_2$

Transmission Electron Microscopy (TEM)

TEM micrograph (Fig. 6) showed the distribution of cobalt onto the surface of silica. Cobalt is uniformly distributed with average diameter of about 2.2 nm.

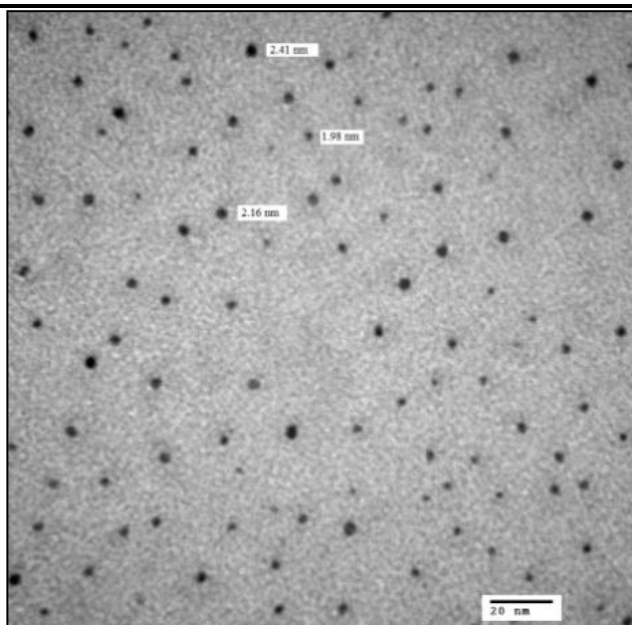
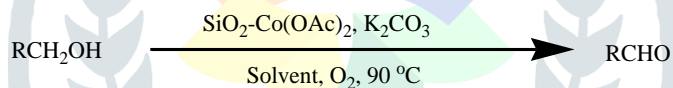


Fig. 6 TEM Micrograph of $\text{SiO}_2\text{-Co(OAc)}_2$.

Catalyst testing for the selective oxidation of alcohols to aldehydes

Oxidation of alcohols was carried out by stirring in toluene at 90 °C in the presence of $\text{SiO}_2\text{-Co(OAc)}_2$ and molecular oxygen. To optimize the reaction conditions, 4-Chlorobenzyl alcohol was selected as the test substrate and oxidation was carried out using K_2CO_3 as base in various solvents like toluene, ethanol, acetonitrile and water (Table 1) at different temperatures in order to select the more effective solvent in terms of selectivity, reaction time, yield and recyclability of the catalyst. In water, 50% conversion of the alcohol was obtained along with over oxidation to acid, while in acetonitrile and ethanol, the reaction didn't go to completion even up to 15 h (70% conversion). However, in toluene, the same reaction under similar reaction conditions got completed in 11 h with 100% conversion and 4-Chlorobenzaldehyde was obtained in 92% isolated yield. The results are shown in Table 1, which indicated that toluene is the excellent reaction medium in terms of selectivity.

Table 1 Effect of solvent on $\text{SiO}_2\text{-Co(OAc)}_2$ catalyzed oxidation of 4-Chloro benzyl alcohol to 4-Chlorobenzaldehyde in toluene at 90 °C^a



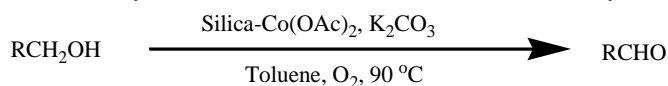
Entry	Solvent	Time (h)	Yield (%)
1	Water	15	40 ^b
2	Acetonitrile	15	60 ^b
3	Ethanol	15	65 ^b
4	Toluene	11	92 ^c

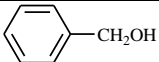
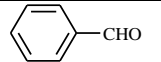
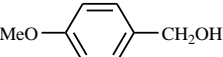
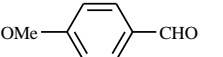
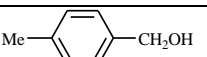
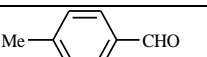
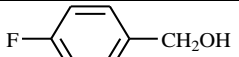
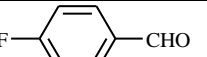
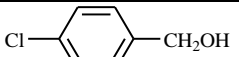
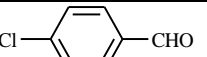
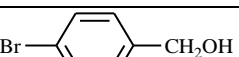
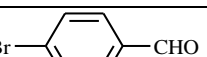


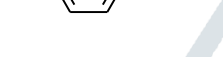

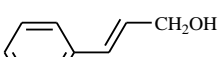
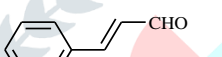
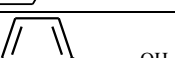

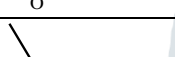

^aReaction Conditions: 4-chlorobenzyl alcohol (0.142 g, 1 mmol), K_2CO_3 (0.276 g, 2 mmol), $\text{SiO}_2\text{-Co(OAc)}_2$ (0.2 g, 4 mol%), Solvent (5 mL), 90 °C as the reaction temperature and O_2 as oxidant.

^bColumn chromatography Yields.

^cIsolated Yields.

The reaction conditions were also screened for various temperatures between room temperature to 90 °C. Reaction didn't go to completion even after 15 h at room temperature but when the reaction temperature was increased to 90 °C, it got completed in 11 h. Hence 90 °C was selected as the optimum reaction temperature. Since molecular oxygen is considered as the green oxidant, so we carried out the test reaction using oxygen as an oxidant in the presence of $\text{SiO}_2\text{-Co(OAc)}_2$.

Table 2. SiO₂-Co(OAc)₂ catalyzed selective oxidation of alcohols to aldehydes in toluene at 90 °C^a

Entry	Reactant	Product	Time (h)	Yield (%)	m.p or b.p/ Lit. m.p or b.p (°C)
1			11	93 ^b	Liq./b.p. 178-179[22]
2			11	92 ^b	Liq./b.p. 248-249[22]
3			12	92 ^b	Liq./b.p. 204-205[22]
4			12	91 ^b	Liq./b.p. 181[22]
5			11	92 ^c	48-49/45-50[22]
6			12	85 ^c	54-55/54-56[22]
7			14	83 ^c	104-105/103-106[22]
8			14	82 ^c	57-58/55-58[22]
9			15	86 ^b	Liq./b.p. 250[22]
10			15	88 ^b	Liq./b.p. 162[22]
11			17	84 ^b	Liq./b.p. 90[22]

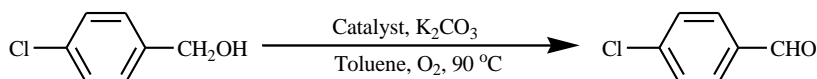
^aReaction conditions: Alcohol (1 mmol), K₂CO₃ (0.276 g, 2 mmol), SiO₂-Co(OAc)₂ (0.2 g, 4 mol% Co), toluene (5 mL), 90 °C was the reaction temperature and O₂ as the oxidant.

^bColumn chromatography yields.

^cIsolated yield.

To make this procedure more green, the test reaction was also tried under air atmosphere, and found that only 60% conversion was observed in 20 h. However, with oxygen as an oxidant, the corresponding aldehyde was obtained in 92% isolated yield in 11 h. The reaction conditions were also screened for bases like Na₂CO₃, K₂CO₃, NaOH and KOH and found that when the reaction was carried out using KOH or NaOH, the reaction was not selective as over oxidation to acids was observed, and with Na₂CO₃, the reaction was comparatively slow, while the same reaction with K₂CO₃ under similar conditions dramatically got selective and moreover K₂CO₃ enhanced the rate of reaction completing it in 11 h. Hence, K₂CO₃ was selected as the base for the test reaction. Thus, the optimum conditions selected are: 4-chlorobenzyl alcohol (1 mmol), K₂CO₃ (2 mmol), SiO₂-Co(OAc)₂ (0.2 g, 4 mol% Co), toluene (5 mL), 90 °C as the reaction temperature and molecular oxygen as the oxidant.

In order to demonstrate the versatility of the catalytic system for the oxidation, benzyl alcohols substituted with various electron-releasing groups (entries 2 and 3, Table 2) and electron-withdrawing (entry 7 and 8, Table 2) were chosen and excellent results were obtained. After carrying out the oxidation of benzyl alcohols efficiently, attempts were made to perform the oxidation of aliphatic alcohols. For this, 3-methylbutanol was selected as the test substrate and found that the catalyst was quite effective and selective for the oxidation of aliphatic alcohols as well (entry 10, Table 2), although the yields were somewhat low and the reaction required longer time. Cinnamyl alcohol also gave good results with high selectivity (entry 8, Table 2). In order to find out the role of SiO₂-Co(OAc)₂ for the oxidation of alcohols, we have carried out the reaction in case of (entry 5, Table 2) without catalyst, in presence of APS, imine, Co(OAc)₂ and SiO₂-Co(OAc)₂ under the similar conditions. The results are summarized in Table 3, which indicates that SiO₂-Co(OAc)₂ catalyzes the selective oxidation of alcohols to aldehydes. It is also observed that reaction also takes place in absence of any catalyst but conversion is very low (40% yield in 15 h at 90 °C), and with Co(OAc)₂, the reaction was not selective, overoxidation to acid was observed.

Table 3. Effect of the catalyst on the selective oxidation of alcohols to aldehydes in toluene at 90 °C^a

Entry	Catalyst	Time (h)	Yield ^b (%)
1	No catalyst	15	40 ^b
2	APS	15	45 ^b
3	Imine	15	45 ^b
4	Co(OAc) ₂	15	65 ^c
5	SiO ₂ -Co(OAc) ₂	11	92 ^d

^aReaction conditions: 4-Chlorobenzyl alcohol (0.142 g, 1 mmol), K₂CO₃ (0.276 g, 2 mmol), APS (0.2 g) or imine (0.2 g), Co(OAc)₂ (0.0071 g, 4 mol% Co), SiO₂-Co(OAc)₂ (0.2 g, 4 mol% Co), toluene (5 mL), 90 °C was the reaction temperature and O₂ as the oxidant.

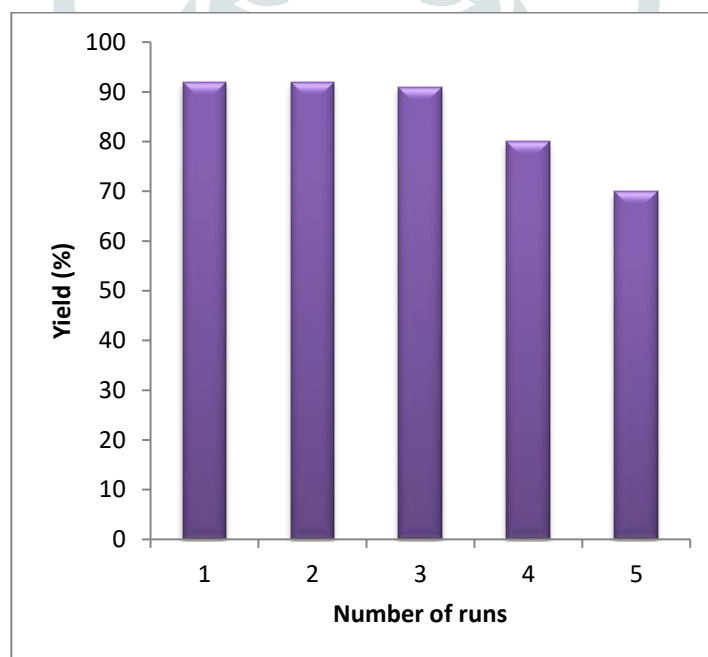
^bColumn chromatography yield.

^cOver-oxidation to 4-chlorobenzoic acid was observed.

^dIsolated yield.

Recyclability of the catalyst

To test the recyclability of SiO₂-Co(OAc)₂ for the selective oxidation of alcohols, a series of 5 consecutive runs in case of entry 5 (Table 2) under the selected conditions were carried out with the same catalyst. The results are shown in Fig. 7, which clearly indicate that the catalyst is stable upto 3rd run and after 3rd run it loses its activity. This is due to leaching of metal under the reaction conditions. Leaching of cobalt (2%) has been indicated by AAS of the catalyst.

**Fig. 7** Recyclability of SiO₂-Co(OAc)₂.

Reaction conditions: 4-Chlorobenzyl alcohol (0.142 g, 1 mmol), K₂CO₃ (0.276 g, 2 mmol), SiO₂-Co(OAc)₂ (0.2 g, 4 mol% Co), toluene (5 mL), 90 °C as the reaction temperature and O₂ as the oxidant.

Proposed Mechanism

The possible mechanism for the oxidation of alcohols to aldehydes using SiO₂-Co(OAc)₂ in the presence of molecular oxygen is outlined in Fig. 8. An oxygen molecule reacts with cobalt to form an oxocobalt complex 'A' which undergoes oxidative addition with alcohol to form an intermediate 'B'. Finally, 'B' undergoes reductive elimination to give aldehyde and Co(II) is regenerated back with the elimination of water as the side product.

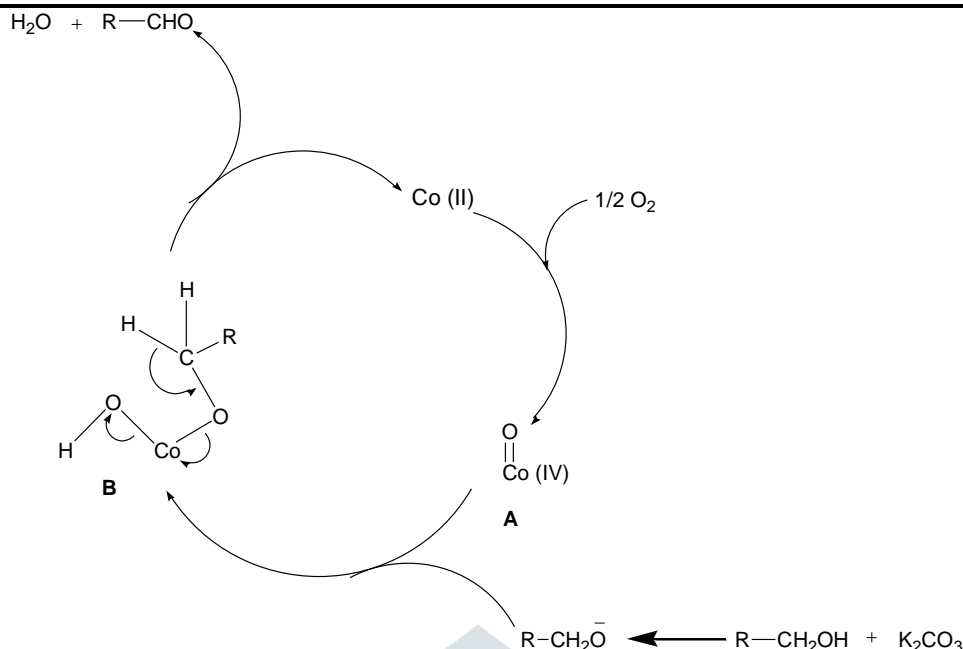


Fig. 8 Proposed mechanism for the oxidation of alcohols to corresponding aldehydes using $\text{SiO}_2\text{-Co(OAc)}_2$ in the presence of oxygen.

EXPERIMENTAL SECTION

General Remarks

The chemicals used were purchased from Aldrich chemical company and Merck. The products were characterized by their spectral data and comparison of their physical data with those of known samples. The ^1H NMR data were recorded in CDCl_3 or $\text{CDCl}_3+\text{DMSO-}d_6$ on Bruker DPX 200 (200 MHz) spectrometer using TMS as an internal standard. The FTIR spectra were recorded on Perkin-Elmer FTIR spectrophotometer using KBr windows and mass spectral data were recorded on Bruker Esquires 3000 (ESI). Thermal analysis was carried out on DTG-60 Shimadzu make thermal analyzer.

General procedure for the preparation of silica-functionalized Co(OAc)_2

Preparation of 3-aminopropyl silica (AMPS)

Silica gel (15 g, K 100) was added to a solution of 1:1 HCl (300 mL) in a round-bottom flask (500 mL) and the reaction mixture was stirred at 120°C for 24 h. The activated silica was filtered at pump, washed with distilled water till washings were neutral and dried in air at 110°C for 5 h. To a mixture of activated silica (10 g) and 3-aminopropyl(trimethoxy) silane (1.79 g, 10 mmol) in a round bottom flask (250 mL), dry toluene (150 mL) was added and the reaction mixture was stirred at 120°C for 24 h. The 3-aminopropyl silica (AMPS) was filtered, washed with toluene and dried in hot air oven at 110°C for 5 h. The yield of 3-aminopropyl silica (AMPS) obtained was 9.8 g.

Preparation of ligand-grafted silica (imine)

3-Aminopropyl silica (8 g) and 2-acetylpyridine (0.968 g, 8 mmol) were added to toluene (150 mL) in a round bottom flask (250 mL) and the reaction mixture was refluxed under stirring for 24 h. The water produced *in situ* was removed using Dean-Stark apparatus. Ligand-grafted silica (imine) was filtered at the reaction temperature and washed with toluene (150 mL) to remove unreacted 2-acetylpyridine. Finally, it was dried at 110°C for 5 h in an oven. The yield of ligand-grafted silica obtained was 7.8 g.

Preparation of silica-functionalized cobalt(II) acetate [$\text{SiO}_2\text{-Co(OAc)}_2$]

To a mixture of ligand-grafted silica (imine, 6 g) and Co(OAc)_2 (1.062 g, 6 mmol/gm) in a round bottom flask (250 mL), ethanol (100 mL) was added and the reaction mixture was stirred at 70°C for 24 h. The solid was filtered off at pump and washed with ethanol till washings were colourless. It was dried in an oven at 95°C for 5 h and then conditioned for a total of 12 h (2×2 h each refluxing in acetonitrile, ethanol and toluene). The conditioned catalyst (5.3 g) was dried under vacuum for 5 h before use.

General procedure for the selective oxidation of alcohols to aldehydes using $\text{SiO}_2\text{-Co(OAc)}_2$ as catalyst and molecular oxygen as an oxidant

To a mixture of alcohol (1 mmol), K_2CO_3 (2 mmol) and $\text{SiO}_2\text{-Co(OAc)}_2$ (0.2 g, 4 mol% Co) in a round-bottom flask (25 mL), toluene (5 mL) was added and the reaction mixture was stirred at 90°C for an appropriate time (Table 2). After completion of the reaction (monitored by TLC), the reaction mixture was filtered while hot and the residue was washed with hot toluene (2×5 mL). The product was obtained after removal of the solvent under reduced pressure followed by crystallization or column chromatography. The catalyst was recovered from the residue after washing with methylene chloride (3×15 mL) followed by distilled water (200 mL) and then CH_2Cl_2 (30 mL), and dried at 110°C for 2 h. It was used further for carrying out the reaction (Fig. 7).

The structures of the products were confirmed by IR, ^1H NMR, ^{13}C NMR, mass spectral data and comparison with authentic samples available commercially or prepared according to the literature methods.

CONCLUSIONS

In conclusion, a facile, economical and efficient method has been reported for the selective oxidation of alcohols to aldehydes in the presence of $\text{SiO}_2\text{-Co(OAc)}_2$ in toluene. Moreover, use of ecologically favourable green oxidant i.e. atmospheric oxygen and recyclable catalyst $\text{SiO}_2\text{-Co(OAc)}_2$ makes this methodology a benign alternative to the existing methods.

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