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# Cobalt(II) Schiff Base Functionalized Mesoporous Silica as an Efficient and Recyclable Chemoselective Acetalization Catalyst

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Cobalt(II) Schiff base functionalized mesoporous silica was synthesized from covalent attachment *via* the introduction of $Co(OAc)_2$ to salicylaldimine functionalized mesoporous silica. The catalyst proved to be chemoselective one for the acetalization of aldehydes to the corresponding acetals in alcohol. The immobilized catalyst can be easily recovered and reused for at least ten reaction cycles without significant loss of its catalytic activity.

**Keywords:** Mesoporous silica, Chemoselective, Acetalization, Cobalt(II), Carbonyl compounds

## INTRODUCTION

Supported catalysts have had a major impact on chemicals and fuels production, environmental protection and remediation. Thus, the design of improved supported catalysts is considered crucial for the successful development of the chemical industry in the future [1]. One approach to obtain supported catalysts is through inorganic-organic hybrid processing of mesoporous materials [2]. Inorganic-organic hybrid materials serve as stable catalytic supports for fixing bulky organometallic catalytic complexes enabling the extension of supported catalysis to new areas [3-6]. Several grafting and tethering procedures have been employed to covalently attach transition metal complexes to a variety of supports such as organic polymer [7], silicas, zeolites, and other microporous or mesoporous inorganic materials [8-12].

The transformation of aldehydes and ketones to acetals is one of the most efficient methods for the protection of carbonyl groups in multi-step synthesis [13-16]. Moreover, chiral acetals are efficient chiral auxiliary groups for enantioselective syntheses [17-19].

Acetals are commonly prepared from alcohol and/or corresponding trialkyl orthoformate with Brønsted and Lewis acid catalysts [20-35]. Although many efficient and reliable reactions for the conversion of carbonyl compounds to their corresponding acetals have been reported, there are, however, some drawbacks such as long reaction times, tedious work-up and separation of catalyst, toxic metal waste, unwanted side reaction and nonselectivity regarding these methods. As mentioned earlier, one way to overcome these problems is immobilization of the homogeneous catalyst. Recently, a number of environmentally friendly solid supported catalysts have been developed for the acetalization of carbonyl compounds, *e.g.*, $NH_4^+OTf^-@SiO_2$ [36], ITQ-2 [37], H-ZSM-5 [38], mesoporous aluminosilicate [39], HMS-sulfonic acid [40], SBA-15-sulfonic acids [41], HMS-supported zinc triflate [42], MCM-sulfonic acid [43], Ga/PS-IL [44], and $CBr_4$/TPPMS [45]. Although significant progress has been achieved in improving the catalytic activity, selectivity, and reagent scope, in many cases, however, they require a high catalyst loading and suffer from catalytic activity losses during reuse. Therefore, there is still a need for a low loading, more

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*Corresponding author. E-mail: f_rajabi@pnu.ac.ir economic, and environmentally benign solid catalysts.

Previously, the application of amine functionalized mesoporous silica to anchor covalently tethered cobalt(II) Schiff base complex was reported [46-49]. Herein, We wish to disclose for the first time, our findings about the catalytic activity of the Co(II) Schiff base functionalized mesoporous silica as a recyclable catalyst obtained for the liquid-phase chemoselective acetalization of carbonyl compound with alcohol. We should add that the Co(II) anchored mesoporous silica catalyzes the acetalization of aldehydes to the corresponding acetals in high yields.

## EXPERIMENTAL

### General Remarks

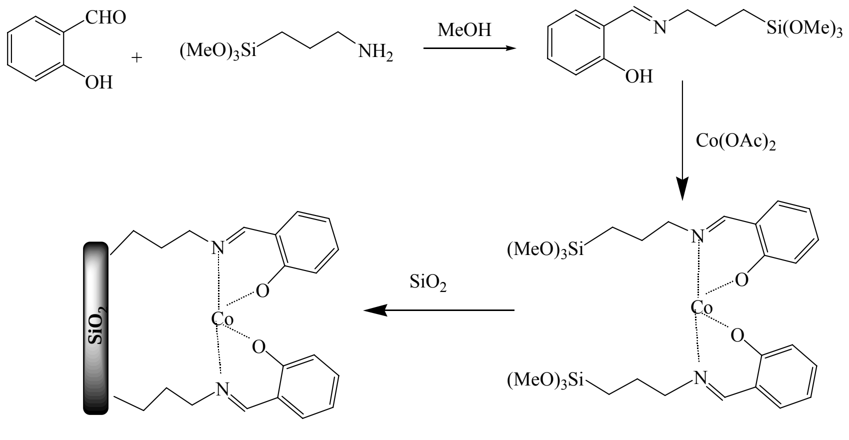
All chemicals were obtained from Aldrich. DRIFT spectra were performed in a Bruker Equinox 55 FTIR instrument. Nitrogen adsorption/desorption experiments were carried out using a Coulter SA3100 surface area analyser. Prior to the analysis, samples were degassed at 130 °C for 5 h. Surface areas were determined using the BET equation. Thermogravimetric analysis was performed using a Polymer Laboratories STA 625, using a heating rate of 10 K $min^{-1}$ under flowing nitrogen. Atomic absorption spectroscopy was performed using a Philips PU 9200 instrument. $^1H$ NMR spectra were recorded on a 500 MHz BRUKER NMR spectrometer in $CDCl_3$ solution.

### Supported Cobalt(II) Catalyst Preparation

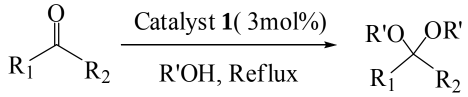
The supported cobalt(II) catalyst was prepared using some known literature procedure with a slight modification [48]. Salicylaldehyde (2 mmol, 0.244 g) was added to excess absolute MeOH, to which 3-aminopropyl (trimethoxy) silane (2 mmol, 0.352 g) was further added. The solution instantly turned yellow due to imine formation. After 3 h, 1 mmol, 0.248 g cobalt(II) acetate, $Co(OAc)_2.2H_2O$ was added to the solution, and the mixture was stirred for a further 3 h to allow the new ligands to complex the cobalt. A colour change from pink to olive green was observed. Mesoporous silica (average pore diameter 60 Å, 3 g) was activated by refluxing in concentrated hydrochloric acid (6 M) and then washed thoroughly with the deionized water and dried before undergoing chemical surface modification. Hydrated mesoporous silica was then added, and the mixture was stirred overnight. The solvent was removed using a rotary evaporator. The final product was washed with MeOH and water. Further drying of the solid product was carried out in an oven at 80 °C for 8 h (Scheme 1).

### General Procedure for Acetalization of Carbonyl Compounds Catalysed by Silica Supported Cobalt(II) Catalyst

A typical procedure for the acetalization of carbonyl compounds was adopted. Supported cobalt(II) catalyst (0.03 mmol, 0.01 g) was added to a solution of aldehyde (1 mmol)



*Scheme 1.* Preparation of supported Cobalt(II) catalyst **1**



*Scheme 2.* Acetalization of carbonyl compounds supported Cobalt(II) catalyst **1**

in methanol or ethanol (5 ml), and the resulting mixture was stirred at reflux conditions. After completion of the reaction monitored by TLC, the reaction mixture was filtrated, washed with methanol, and the supported catalyst was recovered. The filtrate was concentrated under vacuum to afford crude product, which was purified by distillation under reduced pressure to give the pure acetal characterized by 500 MHZ NMR and IR analysis (Scheme 2).

## RESULTS AND DISCUSSION

### Catalyst Characterization

Thermogravimetric analysis exhibited a high thermal stability of the supported catalyst (up to 480 °C). The loading of cobalt(II) catalyst on the support was about 0.3 mmol $g^{-1}$, as determined from the 11.5% loss in mass between 200 and 600 °C, as well as the atomic absorption analysis of the $HNO_3$-digested material. The $N_2$ adsorption isotherm of the catalyst corresponded to a type IV adsorption isotherm suggesting mesoporosity. The surface analysis showed that the surface area was 197 $m^2$ $g^{-1}$. As expected, a general decrease in the surface area was found due to the functionalization and loading of cobalt salt to mesoporous silica. The catalyst had a single point total pore volume of 0.461 $cm^3$ $g^{-1}$, compared to 0.69 $cm^3$ $g^{-1}$ for the support. This indicates that supporting the complex brings about a substantial reduction in the surface area, possibly due to pore blockage from the bulky silane limiting access to some very narrow-entrance pores in the material. The diffused reflectance infrared spectrum of the catalyst shows the expected bands, including a distinctive one at 1605 $cm^{-1}$, which could be attributed to the C=N stretching lowered in frequency on complexation to cobalt(II).

### Acetalization of Aldehydes

In order to explore the influence of the supported Co(II) catalyst on the reaction system, the reaction of benzaldehyde with methanol was chosen as a model. Initially, the reaction was performed under catalyst free condition and no product formation was observed. Then, to obtain optimized reaction conditions, the acetalization reaction was performed with benzaldehyde and using different amounts of supported cobalt(II) catalyst at different temperatures. The results are summarized in Table 1.

In order to demonstrate versatility and generality of this protocol, the acetalization reaction was extended to a various range of aromatic and aliphatic aldehydes in methanol or ethanol. The supported catalyst proved to be most highly active and effective one producing the acetal within 2-5 h of

**Table 1.** Effect of Temperature and amount of Catalyst on the Yield of Acetalization[a] of Benzaldehyd

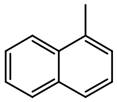
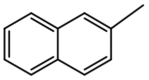
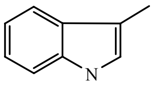
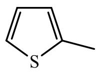
| Entry | Catalyst (mol%) | Temperature | Yield (%)[b] |
|---|---|---|---|
| 1 | none | reflux | 6 |
| 2 | 1 | reflux | 55 |
| 3 | 2 | reflux | 71 |
| 4 | 3 | reflux | 99 |
| 5 | 3 | rt | 90 |

[a]Reactions were performed reacting benzaldehyde (1 mmol) in $CH_3OH$ (5 ml) for 2 h. [b]Isolated yields.

addition (Table 2).

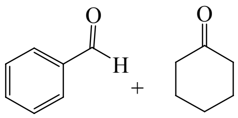
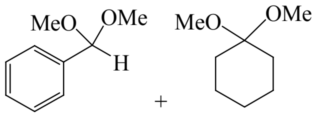
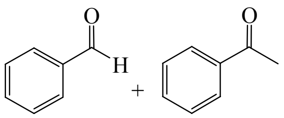
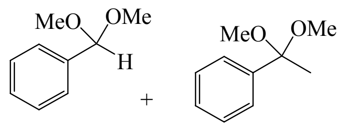
The effect of substitution of benzaldehyde on the catalyzed reaction involved electron donating or withdrawing forces of the substituting group. The nitro group, in contrast to the methoxy group, had a strong electron-withdrawing effect and therefore the expected order of reactivity for the substituted aldehydes was $NO_2$ > H > Me > OMe, which is in good agreement with the experimental results (Table 2).

**Table 2.** Chemoselective Acetalization of Carbonyl Compounds according to Scheme 1

| Entry | $R_1$ | $R_2$ | Alcohol | Time(h) | Yield(%)[a] |
|---|---|---|---|---|---|
| 1 | Ph | H | MeOH | 2 | 99 |
| 2 | Ph | H | EtOH | 2.5 | 96 |
| 3 | $4\text{-}(NO_2)C_6H_4$ | H | MeOH | 2 | 99 |
| 4 | $4\text{-}(MeO)C_6H_4$ | H | MeOH | 3 | 98 |
| 5 | $4\text{-}(Cl)C_6H_4$ | H | MeOH | 2.5 | 95 |
| 6 | $4\text{-}(Cl)C_6H_4$ | H | EtOH | 3 | 91 |
| 7 | $2,4\text{-}(Cl)_2C_6H_3$ | H | MeOH | 4 | 98 |
| 8 | $4\text{-}FC_6H_4$ | H | MeOH | 4.5 | 92 |
| 9 | $3\text{-}(NO_2)C_6H_4$ | H | MeOH | 3 | 90 |
| 10 | $CH_3CH_2CH_2$ | H | MeOH | 2.5 | 98 |
| 11 | $CH_3CH(Ph)CH_2$ | H | MeOH | 4.5 | 90 |
| 12 | $4\text{-}(Me)C_6H_4$ | H | MeOH | 2.5 | 98 |
| 13 | $C_6H_4$ | $CH_3$ | MeOH | 5 | 5 [b] |
| 14 | Cyclohexanone | | MeOH | 5 | 9[b] |
| 15 | Cyclopentanone | | MeOH | 5 | 8[b] |
| 16 |  | H | MeOH | 2 | 98 |
| 17 |  | H | MeOH | 2 | 99 |
| 18 |  | H | MeOH | 2.5 | 99 |
| 19 |  | H | MeOH | 2 | 99 |

[a]Isolated yield. [b]The yield was based on $^1H$ NMR spectra of crude reaction mixtures.

**Table 3.** Chemoselective Acetalization of Carbonyl Compounds by Catalyst **1** according to Scheme 1

| Entry | Substrate | Product (yield%)$^{a}$ |
|---|---|---|
| 1 |  | <br>$(99)^{b}$ $(99)^{c}$ + $(0)^{b}$ $(22)^{c}$ |
| 2 |  | <br>$(99)^{b}$ $(99)^{c}$ + $(0)^{b}$ $(18)^{c}$ |

$^{a}$Isolated yield. $^{b}$Reaction performed with 3 mol% of supported Co(II) catalyst for 5 h. $^{c}$Reaction performed with 5 mol% of supported Co(II) catalyst for 5 h.

Since ketones undergo acetalization considerably slower than aldehydes, it seemed plausible that this system could promote the chemoselective acetalization of aldehydes in the presence of ketones. The chemoselectivity of the reaction was demonstrated by the carbonyl groups of different compounds. Thus, in competitive reaction, ketones remained intact while benzaldehyde was easily acetalized (Table 3).

## Leaching Test and Recycling

To test the heterogeneity of the catalytic system, the leaching test was performed. The catalyst was filtered after 60 min and the filtrate was allowed to react further (60 min). It was found that after filtration of the supported cobalt catalyst, the filtration liquor reacted much more slowly and at a similar rate to the reaction taking place in the absence of the catalyst (Table 1, Entry1), indicating that no leaching of the active catalytic species occurred during the reaction. Then, the catalyst was filtered after the end of the first reaction and AAS confirmed that no cobalt existed in the solution phase (detection limit 0.5 ppm Co).

Moreover, the reusability of the catalyst was investigated by hot filtrating from the first successful run of acetalization of benzaldehyde in methanol. After filtration, the supported catalyst was washed with methanol and dried before the next cycle. The catalyst was found to be reusable for up to ten consecutive cycles without any significant loss of activity. After the first reaction run, no significant changes were observed in DRIFT spectrum of the catalyst, indicating that no catalyst or ligand decomposition was observed for the supported catalyst.

## CONCLUSIONS

In this study, a novel, simple, efficient and chemoselective procedure was developed for the acetalization of carbonyl compounds using a covalent attachment of cobalt(II) complex functionalized to mesoporous silica as a heterogeneous catalyst. The catalyst showed high thermal stability (up to 480 °C). It could also be recovered and reused for at least ten reaction cycles without any significant loss of catalytic activity. The use of a low amount of supported catalyst (3 mol%) in a nonchloronited solvent, along with the absence of additives such as dehydrating agent, make this procedure an environmentally benign chemical process. Furthermore, when compared to the reaction run in the homogeneous phase, under similar experimental conditions, an increase in the yield of products was observed for supported cobalt(II) catalyst.

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