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A highly efficient and reusable mesoporous supported Co(II) catalyst for chemoselective deprotection of aryl acetates

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ABSTRACT

Chemoselective deprotection of aryl acetates is successfully carried out in excellent yield using a mesoporous silica-supported (Salen) Co(II) catalyst. The catalyst shows high thermal stability and also can be recovered and reused at least 10 times without any significant loss of its catalytic activity. The present process is environmentally benign and economical.

Phenol derivatives are a class of organic compounds which has attracted attention regarding their various biological and pharmaceutical activities.[1] Thus, selective protection and subsequent deprotection of phenol groups is important in multi-step organic syntheses. Generally, protection of phenolic compounds as their acetates is preferred due to their ease of formation and cleavage. Removal of an acetyl group can be achieved either using either acidic or basic conditions. Commonly employed deprotection methods include acid or base hydrolysis. Several acids and bases have been reported to be effective in promoting selective deprotection of acetates such as NaOMe,[2] micelles,[3] Zn–MeOH,[4] cyclodextrin,[5] enzymes,[6] metallo-enzymes,[7] metal complexes,[8] and antibodies,[9] Montmorillonite K-10,[10] I_2,[11] $NaBO_3$,[12] and $HCOONH_4–SiO_2$,[13] These methods, while useful, suffer from limitations including harsh reaction conditions, the use of unrecoverable and expensive catalysts, long reaction times, large amounts of reagents, tedious work-up procedures, and difficulty in separation of the catalyst, poor atom efficiency, and limited practical application on a large scale. Therefore, the development of new and recoverable heterogeneous catalysts for selective deprotection of aromatic acetates which work efficiently under economically and environmentally appropriate conditions are highly desirable.

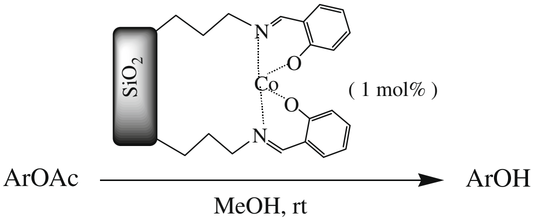
Recently, solid-supported catalysts have gained increased consideration for organic transformations due to their ease of separation from the reaction mixture and the possibility of reuse as well as for economical and environmental reasons.[14] Among solid-supported catalysts, silica-based catalysts have attracted significant attention due to their interesting properties including thermal stability and their commercial availability for liquid phase reactions. It is believed that mesoporous silicas with tunable pore sizes are able to facilitate reactions by localizing reactants in their pores and providing a high local concentration of active centers (typically acidic or basic).[15]

During our recent research program on the development of organic transformations employing efficient and recyclable solid-based catalysts, an immobilized cobalt(II) Schiff base on mesoporous silica showed good stability and activity in aerobic oxidation and protection reactions.[16] In this Letter, a convenient and efficient procedure for the chemoselective deprotection of aromatic acetates in the presence of aliphatic acetates using a catalytic amount of supported cobalt(II) catalyst is developed (Scheme 1).

Previously, we reported the chemoselective acetylation of alcohols and phenols catalyzed by the supported Co(II) catalyst in excellent yield.[17] However, to the best of our knowledge, there is no report on the use of this catalyst for the selective deprotection of aryl acetates. In this regard, deprotection of phenyl acetate in the presence of solid-supported cobalt(II) in MeOH was investigated under various conditions. The optimized conditions required phenyl acetate (1 mmol), heterogeneous cobalt(II) catalyst (0.01 mmol), and MeOH (5 mL) at room temperature (Scheme 1, Table 1, entry 2).

To prove that the immobilized Co(II) catalyst was required for the deprotection of phenyl acetate, we examined the reaction in the absence of the supported catalyst. However, no appreciable deprotection was observed under similar reaction conditions even after 12 h (Table 1, entry 1).

To test the catalytic activity and heterogeneity of the supported cobalt(II) catalyst, the reaction was conducted with phenyl acetate in the presence of supported cobalt(II) catalyst for 20 min which



Scheme 1. Deprotection of aromatic acetates using a supported cobalt(II) catalyst.

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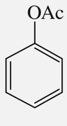
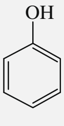
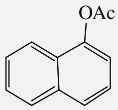
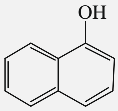
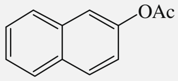
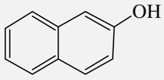
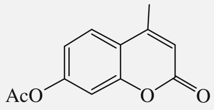
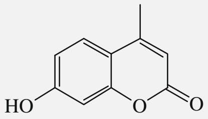
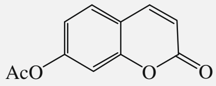
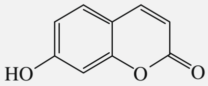
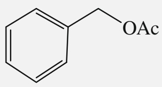
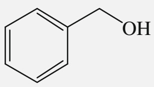
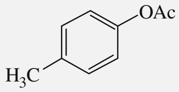
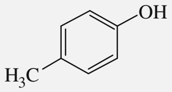
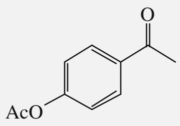
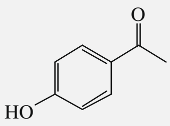
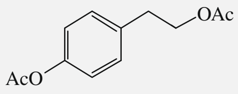
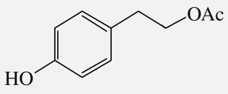
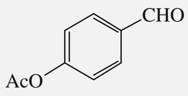
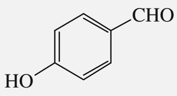
Table 1
Deprotection of aromatic acetates with a supported cobalt(II) catalyst in MeOH at room temperature

Entry	Substrate	Product	Time (h)	Yield[a] (%)
1	C_6H_5OAc	C_6H_5OH	12	7[b]
2			1.5	98
3	4-Cl(C_6H_4)OAc	4-Cl(C_6H_4)OH	2.5	88
4	4-N0_2(C_6H_4)OAc	4-N0_2(C_6H_4)OH	2.5	90
5	4-Br(C_6H_4)OAc	4-Br(C_6H_4)OH	3	92
6	2-Br(C_6H_4)OAc	2-Br(C_6H_4)OH	3.5	94
7	2-Cl(C_6H_4)OAc	2-Cl(C_6H_4)OH OH	3.5	95
8			2	91
9			2	94
10			1.5	93
11			1.5	90
12			12	0
13			1	95
14			2.5	93
15			2	91
16			2.5	90

[a] Isolated yield.
[b] The reaction was conducted in the absence of the supported cobalt(II) catalyst.

Table 2
Recycling of the supported cobalt(II) catalyst for the deprotection of phenyl acetate according to Scheme 1

Cycle	1	2	3	4	5	6	7	8	9	10
Time (h)	1.5	1.5	1.5	2	2	2	2.5	2.5	3	3.5
Yield[a] (%)	95	97	95	93	90	91	90	90	89	85

[a] Isolated yield.

gave a conversion of 55%. The catalyst was then removed from the reaction mixture. The filtered, 'catalyst-free' reaction liquor was returned to the reaction conditions. It was observed that no further conversion of substrate occurred. The catalyst showed excellent selectivity for the deprotection of aryl acetates to the corresponding phenols. Alkyl acetates (benzyl acetate, 4-CH_3(C_6H_4)-CH_2OAc, and butyl acetate) were unaffected under similar experimental conditions even after 12 h. Furthermore, the chemoselectivity of the reaction was demonstrated. Thus, in a competitive reaction, when a mixture of benzyl acetate and phenyl acetate was treated with the mesoporous silica-supported Co(II) catalyst in methanol, benzyl acetate remained intact while phenyl acetate was easily deprotected to phenol.

In order to explore the generality of this procedure, a variety of aromatic acetates were subjected to the optimized deprotection conditions. Aromatic acetates containing electron-donating or -withdrawing groups were deprotected to the corresponding phenols in excellent yields.

The reusability of supported catalysts is an important benefit and makes them useful for commercial applications. Therefore, the reusability of the supported cobalt(II) catalyst was investigated. After the first use of the catalyst for the deprotection of phenyl acetate, it was removed from the reaction mixture via filtration and successfully used in 10 subsequent runs without any significant loss in catalytic activity under similar experimental conditions. However, the reaction time increased from 1.5 h to 3.5 h over the 10 runs (Table 2). No pretreatment step was required, although the recovered catalyst was washed with ca. 5 mL of MeOH to remove traces of the previous reaction mixture and dried before the next cycle.

In conclusion, a novel and efficient protocol for selective cleavage of aromatic acetates using a supported cobalt(II) Salen complex in methanol at room temperature is developed. The advantages of the present method are the simplicity of operation, the high yield of deprotected products, and the recyclability of the catalyst. The use of the supported cobalt(II) Salen complex catalyst provides a useful alternative to the selective deprotection of aryl acetates with the notable advantages that the work-up procedure is reduced to a simple filtration. The catalyst is very robust and shows high thermal stability (up to 480 °C). The use of a small amount of supported catalyst (1 mol %) makes this procedure an environmentally friendly chemical process. Further experiments are ongoing in our laboratory in order to investigate the catalytic activity of the mesoporous silica-supported Co(II) catalyst in various organic transformations.

General procedure: aryl acetate (1 mmol) and supported cobalt(II) catalyst (0.01 mmol, 0.033 g) were stirred in methanol (5 mL) at room temperature. After completion of the reaction (TLC), the cobalt catalyst was removed by filtration and then rinsed twice with methanol (15 mL) and reused. The filtrate was concentrated under vacuum to give the phenol in almost pure form which could be purified by flash chromatography through a short pad of silica gel using an appropriate solvent, if necessary.

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Supplementary data

Supplementary data (copies of thermogravimetric analysis, surface analysis nitrogen adsorption/desorption experiments, and diffuse reflectance fourier transform infrared spectroscopy of the supported cobalt(II) catalyst before and after recovery are available) associated with this article can be found, in the online version, at doi:10.1016/j.tetlet.2009.10.012.

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