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Oxidative “reverse-esterification” of ethanol with benzyl/alkyl alcohols or aldehydes catalyzed by supported rhodium nanoparticles

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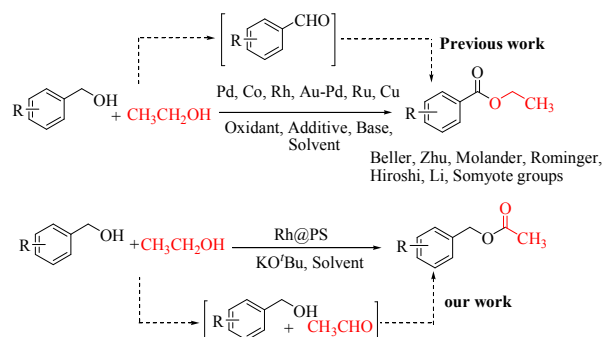
A very unusual role of polystyrene stabilized rhodium (Rh@PS) nanoparticles as supported catalyst was described for “reverse-esterification” of ethanol with benzyl/alkyl alcohols or aldehydes. Faster and selective oxidation of ethanol to acetaldehyde and H₂ under Rh@PS catalyzed condition which restricted further oxidation of benzyl/alkyl alcohols and their *in situ* reaction gave corresponding acetate esters following dehydrogenative-coupling approach. A hitherto redox dehydrogenative-coupling of ethanol and aldehydes has also been explored for the same acetate esters synthesis under Rh@PS catalyzed conditions.

Introduction

Esters are important precursors and intermediates for fine chemicals, fragrances, natural products and polymers.¹ Among esters, acetate esters such as hexyl acetate, isoamyl acetate and 2-phenylethyl acetate act as a solvent in synthesis of resins, plastic, polishes, and ink; contribute to the aroma of fruits like those of banana, strawberry, pear and apple and are thus widely recognized as substantial flavor compounds in wine and other grape-derived alcoholic beverages.² Conventional protocols for the synthesis of acetate esters are Fischer esterification of alcohols, acylation of alcohols with activated acid derivatives (acyl chlorides and anhydrides), the acetylation of aromatic alcohols catalyzed by alcohol acetyltransferase,³ lipase catalyzed enzymatic trans esterification,⁴ ketene addition to alcohols and the condensation of acetaldehyde in the presence of aluminium ethoxide catalyst.⁵ Transition metal catalyzed oxidative esterification/dehydrogenation of alcohols via “hydrogen auto-transfer process” has emerged as a fundamental research

area in the synthetic organic chemistry over the past few years.⁶ For primary alcohols, most attention have been devoted to the direct synthesis of benzoates from the oxidative esterification of benzyl alcohols with small aliphatic alcohols such as methanol, ethanol, butanol etc.⁷ Of all the reported esterifications, benzyl alcohols by β -hydride elimination are first oxidized to the respective benzaldehydes and are then participated in coupling with alkyl alcohol to produce benzoate esters.

However, despite the advantage of using ethanol as quasi-renewable energy source, very few work has been carried out on similar oxidative transformations.⁸ But in all of the reactions, much more attention has been devoted either to the direct synthesis of ethyl acetate from the oxidative dimerisation of ethanol only, in which stoichiometric quantity of metal oxides as additives at high temperature have to be used⁹ or to the synthesis of ethyl benzoates as esterification products.¹⁰ Due to high oxidation potential, higher pKa of the hydroxyl group and the stronger α -C-H bond, the oxidation of ethanol is generally hindered relative to benzylic alcohols¹¹ and hence require photocatalytic or electrolytic conditions for its oxidation.¹² The inherent challenge of oxidizing aliphatic alcohols relative to benzyl alcohols encouraged us to use ethanol as primary coupling partner in the present catalyst



Scheme 1. Comparison of oxidative coupling of ethanol with benzyl alcohols

development efforts. Inspired by recent investigations of oxidative esterification of alcohols¹⁰ herein, we demonstrate

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application of Rh@PS catalyst system that promotes selective oxidative esterification of ethanol and benzyl/alkyl alcohols or aldehydes following a very unusual and unexplored pathway to the corresponding acetate esters synthesis.

Results and discussion

In our continuous thirst to develop solid supported transition metal nanoparticles (NPs) as heterogeneous catalysts¹⁴ and

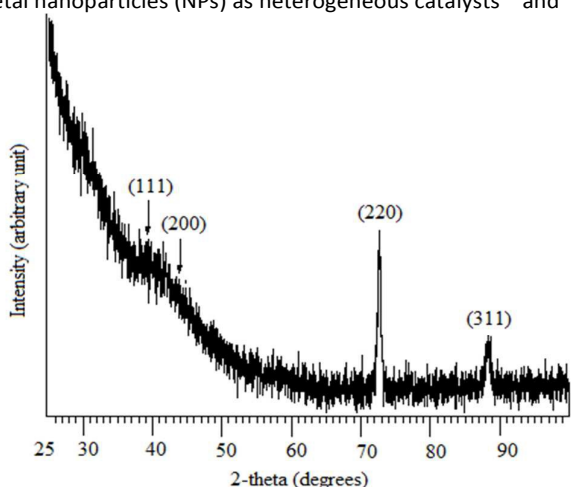


Fig. 1 Powder X-ray diffraction (XRD) patterns for Rh@PS catalyst

their applications in different area of organic transformations, Rh@PS was synthesized following our previously reported procedure^{15,13} and before application the morphological feature of the catalytic surface was investigated by XRD (Fig. 1), transmission electron microscopy (TEM) and selected area electron diffraction (SAED) (Fig 2) analysis.

The presence of metallic Rh particles in power XRD spectra is indicated by four characteristic reflections originating from the (111), (200), (220) and (311) crystallographic planes of the fcc lattice.¹⁶ However, during XRD study low intense peaks were observed due to rigidity of solid support as well as low concentration of Rh per gram of the support (Fig. 1).

The low field TEM images confirmed the impregnation of spherical Rh-nanoparticles in the polystyrene matrix (Fig. 2(a-b)). High resolution TEM (HR-TEM) bright field image of Rh@PS representing the crystallographic orientation of the Rh NPs was shown in Fig. 2c. The histogram representing the particle size distribution was drawn from Fig. 2b by measuring the size of 493 NPs with the help of Image-J software. The distribution curve indicated that the average size of Rh NPs was approximately 1-2 nm (Fig. 2d). SAED pattern was presented in Fig. 2e contains diffraction rings corresponding to (111), (200), (220) and (311) crystallographic planes confirming the existence of crystallites of Rh NPs, which is consistent with the d-spacing observed in XRD measurements (Fig. 1). HR-TEM with FEG (field emission gun) source reveals the crystalline feature of a single Rh NPs having d-spacing 0.23 nm which corresponds to the (111) reflection plane (Fig. 2f). The electron diffractogram pattern of the marked region in Fig. 2f (shown in

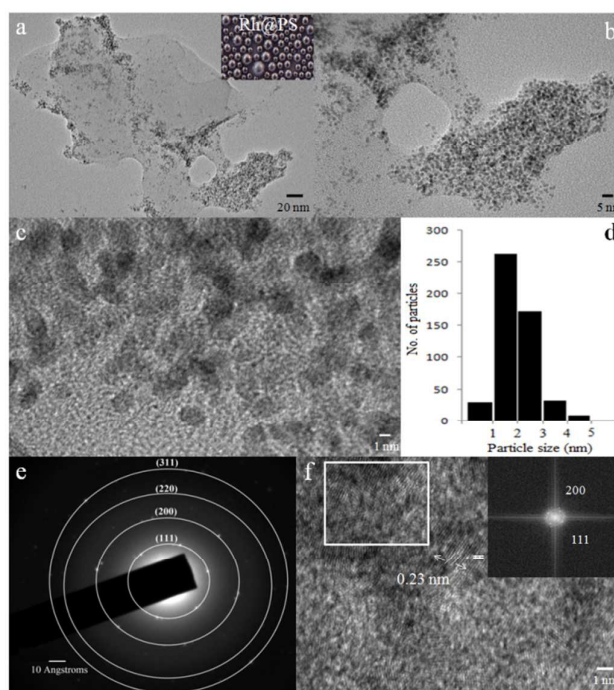


Fig. 2 (a–b) TEM images of Rh nanoparticles supported on polystyrene resin at different magnifications. (c) HRTEM bright field image of Rh@PS. (d) Particle size distribution curve based on statistical analysis of TEM images; (e) SAED image of Rh@PS. (f) HRTEM image indicating lattice fringe spacing corresponding to the plane [111] and fast Fourier transformation (FFT) image (right inset).

inset) give a lattice spacing $d = 0.23$ nm and $d = 0.19$ nm, thus, indicating only (111) and (200) reflections were visible in Fast Fourier Transformation (FFT) graph (Fig. 2f). The heterogeneity of the active Rh species in Rh@PS was confirmed by Hg(0) poisoning test (supporting information) and hot filtration test (Fig. 3). After addition of mercury to the reaction mixture, no

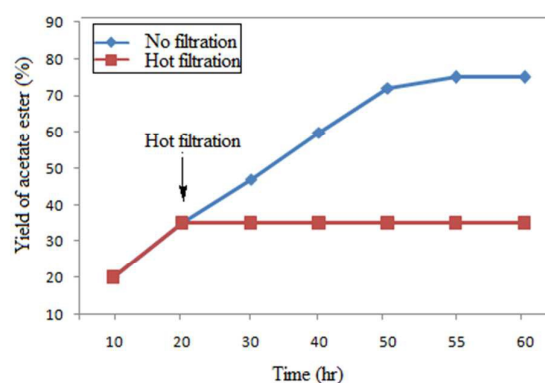
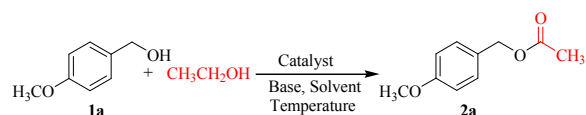


Fig. 3 Hot filtration test for the Rh@PS catalyzed oxidative reverse esterification of ethanol with *p*-OMe benzyl alcohol

conversion of reactant was observed during the Hg(0) test. Similarly, the hot filtration test showed that no extra yield of acetate **2a** was noticed after the solid catalyst was filtered off (Fig. 3). These findings revealed that the catalysis of esterification took place in a true heterogeneous manner as negligible quantity of rhodium, which is too few to react, was leached during the esterification reaction.

To begin with, 4-methoxy benzyl alcohol and ethanol were chosen as benchmark substrates to optimize the condition of oxidative coupling under Rh@PS catalyst, and the results are summarized in Table 1. Different metal loadings such as 0.5 mol%, 1 mol%, 2 mol% and 3 mol% of Rh respectively (Table 1, entries 2, 3, 9 and 10) was examined and 2 mol% Rh@PS were used as optimal catalyst loading. Base and solvent screening indicated that 4 equiv of KO^tBu in 1,4-dioxane or toluene gave

Table 1. Screen of reaction conditions for acetate esters synthesis from ethanol and *p*-OMe benzyl alcohol^a

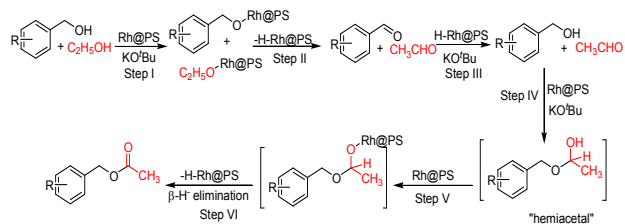


Entry	Catalyst (2 mol% Rh)	Base	Solvent	Temp. (°C)	Yield (%) ^b
1	Rh@PS	KOH	1,4-dioxane	125	60
2 ^c	Rh@PS	KO ^t Bu	1,4-dioxane	125	27
3 ^d	Rh@PS	KO ^t Bu	1,4-dioxane	125	53
4	Rh@PS	KO ^t Bu	DMF	125	n.d
5	Rh@PS	KF	1,4-dioxane	125	n.r
6	Rh@PS	DABCO	1,4-dioxane	125	n.r
7	Rh@PS	Na ₂ CO ₃	1,4-dioxane	125	n.d
8	Rh@PS	K ₂ CO ₃	1,4-dioxane	125	n.d
9	Rh@PS	KO^tBu	1,4-dioxane	125	75
10 ^e	Rh@PS	KO ^t Bu	1,4-dioxane	125	75
11	Rh@PS	KO ^t Bu	Acetonitrile	125	15
12	Rh@PS	KO ^t Bu	PEG-400	125	n.d
13	Rh@PS	KO ^t Bu	1,4-dioxane	110	32
14	Rh@PS	KO ^t Bu	1,4-dioxane	135	40
15	Rh@PS	KO ^t Bu	Toluene	125	70
16 ^f	Rh@PS	KO ^t Bu	1,4-dioxane	125	n.d
17	Rh/C	KO ^t Bu	1,4-dioxane	125	n.r
18	RhCl ₃	KO ^t Bu	1,4-dioxane	125	n.r
19	[RhCp*Cl ₂] ₂	KO ^t Bu	1,4-dioxane	125	n.r

^aAll reactions were carried out with *p*-OMe benzyl alcohol (1 equiv.), ethanol (2 mL), base (4 equiv.), solvent (1.2 mL) and time 55 h. ^b Isolated yields (**2a**); n.r = no reaction; n.d = not detected; traces of *p*-OMe benzaldehyde were formed. ^c 0.5 mol% catalyst was taken. ^d 1 mol% catalyst was used. ^e 3 mol% catalyst was charged. ^f Reaction conducted at N₂ atmosphere.

the comparable results, but due to environmental concern toluene was discarded as reaction media. The quantity of ethanol was found to be crucial for selective conversion of acetate esters. While employing variable quantity of ethanol including 0.5 mL, 1 mL and 1.5 mL separately, a mixture of acetate ester and aldehyde were detected by GCMS in each case, although the yield of benzaldehyde is diminished in that order. However, use of 2 mL of ethanol exclusively formed the acetate ester, the aldehyde could not be observed. Subsequently, different Rh-catalyst precursors were investigated and the results indicated that Rh@PS was found to be the most active and selective redox reagent for the synthesis of acetate ester **2a**. Finally, Rh@PS (2 mol%), KO^tBu (4 equiv.), and ethanol (2 mL) at 125 °C was found to be the

best optimized condition to give highest yield (75%) of the acetate ester **2a** (Table 1, entry 9). The presence of minute quantity of air in the reaction system was sufficient for the



Scheme 2. Possible redox pathway for the oxidative esterification of alcohols

oxidation reaction and no product was detected under N₂ atmosphere (Table 1, entry 16).

Under this study considering GCMS data for intermediate

Table 2. Rh@PS catalyzed reaction of substituted benzyl alcohols with ethanol for acetate esters synthesis.^a

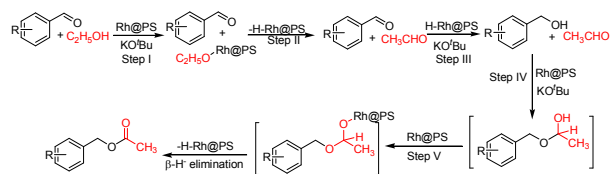
Entry	Substrate	Temp/Time (°C/hr)	Product	Yield (%) ^b
1	1b	120/53	2b	61
2	1c	120/53	2c	65
3	1d	125/55	2d	57
4	1e	125/55	2e	66
5	1f	120/50	2f	70
6	1g	122/55	2g	50
7	1h	125/55	2h	53
8	1i	120/50	2i	58
9	1j	120/50	2j	60
10	1k	120/50	2k	60
11	CH ₃ (CH ₂) ₁₀ CH ₂ OH 1l	125/55	CH ₃ (CH ₂) ₁₀ CH ₂ O 2l	57

^aReaction conditions: substituted benzyl alcohols, **1b-l** (1 equiv.), KO^tBu (4 equiv.), ethanol (2 mL) and Rh@PS (2 mol% Rh) in 1,4-dioxane (1.2 mL). ^b Isolated yields

molecules, both benzyl and ethyl alcohols coordinates to the Rh and through β-hydride elimination generate aldehydes (step I to II) and formal hydrogen. The liberated formal H₂ further reduces benzaldehyde/ benzylalcohol coordinated Rh to benzyl alcohol (step III) which directly reacts with

acetaldehyde to produce corresponding hemiacetal (Step IV). Finally, acetate ester was formed through Rh-catalyzed β -hydride elimination of the hemiacetal (step VI) (Scheme 2). This indicates that a formal “H₂” release takes place (steps I-II and V-VI) but the nature of compound (H₂ or H₂O) released is still uncertain.

The Rh@PS catalyst system exhibits a slow and sustainable process with broader substrate scope for the oxidative esterification of various primary alcohols with ethanol. The results provided in Table 2 indicated a high degree of functional-group tolerance under redox reaction condition. Considering earlier reports for similar esterification reactions, it is highly undesired to restrict oxidation of benzyl alcohol but in this study a reverse order reactivity of electron rich benzyl alcohols **1b-c** was explored to produce corresponding benzyl acetates **2b-c** (61-65%) under optimized condition (Table 2, entry 1-2). Similarly, benzyl alcohols substituted with electron-withdrawing Cl atom at *o* and *p* position of the benzene ring **1d-e** produced the desired products **2d-e** in 57 and 66% yields respectively (Table 2, entries 3-4) and no dehalogenation product was observed by GCMS. Even sterically hindered α -naphthylmethanol **1f** underwent smooth transformation into the corresponding acetate **2f** exclusively in 70% yield (Table 2, entry 5). Delightfully, heterocyclic alcohols **1g-h** also reacted with



Scheme 3. Possible redox pathway for the oxidative esterification of aldehydes with ethanol following reverse order of reactivity

ethanol to afford the corresponding acetate esters **2g-h** in 50 and 53% yields respectively (Table 2, entries 6 and 7). Furthermore, geraniol **1i** containing C-C double bond was also tolerated under the redox conditions and produced the desired ester **2i** in 58% yield (Table 2, entry 8). Moreover, aliphatic alcohols are known for self oxidative esterification but interestingly aliphatic primary alcohols **1j-l** furnished anticipated esters **2j-l** in 60, 60 and 57% yields, respectively (Table 2, entries 9-11).

Over the last few years, groups of Molander,¹⁷ Rominger,¹⁸ Hiroshi,¹⁹ Li²⁰ and Somyote²¹ demonstrated the synthesis of “ethyl benzoates” through the oxidative esterification of aldehydes with ethanol using various transition metals as catalyst. But, in the present study ethanol under Rh@PS catalyzed conditions acts as a “redox reagent” and becomes oxidized into acetaldehyde with the formation of H₂. The liberated H₂ then *in situ* reduces aryl/alkyl aldehydes to their corresponding alcohols and finally coupling of these alcohols with acetaldehyde through β -H elimination resulted into the formation of acetate esters (Scheme 3).

However, to the best of our knowledge, no Rh catalyzed “reverse esterification” protocol involving the oxidation of ethanol, reduction of aryl/alkyl aldehydes and simultaneous

coupling between their intermediates in a cascade sequence has been demonstrated.

The newly developed tandem strategy was further applied to a number of aromatic and aliphatic aldehydes for “reverse esterification” reaction (Table 3). Both electron-rich and electron-deficient benzaldehydes **1m-p** were well tolerated under the optimized reaction conditions and afforded the desired acetate esters **2m-p** in substantial yields (Table 3, entries 1-4). Surprisingly, the reaction of aliphatic aldehydes

Table 3 Rh@PS catalyzed reaction of substituted aldehydes with ethanol for acetates synthesis.^a

Entry	Substrate	Temp/Time (°C/hr)	Product	Yield[%] ^b
1		120/60		55
2		120/60		51
3		120/62		50
4		125/65		57
5		125/65		66
6		120/65		40
7		120/65		45

^aReaction conditions: substituted benzaldehydes **1m-s** (1 equiv.), KO^tBu (2.5-3 equiv.), ethanol (2 mL) and Rh@PS (2 mol% Rh) in 1,4-dioxane (1.2 mL). ^bIsolated yields

1q and **1r** with ethanol also proceeded well to produce alkyl acetates **2q** and **2r** respectively in good to moderate yields (Table 3, entry 5 and 6). Moreover, naturally occurring citronellal **1s** was transformed into the desired acetate **2s** with an equal efficacy (Table 3, entry 7).

To understand the intermediates and reaction mechanism several cross studies were performed. Without ethanol, benzyl alcohol **1a** becomes oxidized to the respective benzaldehyde **1t** in high yield showing that ethanol plays a crucial role to prevent the oxidation of other alcohols as well to promote their facile nucleophilic attack in generating hemiacetal intermediate (Scheme 4a). In scheme 4b, ethanol reduces the benzaldehyde **1t** to the corresponding benzyl alcohol **1a** in good yield. This result clearly indicated that ethanol also serves as a reducing agent for the synthesis of acetate ester through cross-dehydrogenative coupling reaction under the present catalytic conditions. The reduction of *p*-OMebenzaldehyde **1t** by ethanol is a hydrogen transfer reaction, which follows: i) the coordination of ethanol onto the metal, ii) the deprotonation giving rise to a metal-alkoxide species, iii) the

beta-elimination to form acetaldehyde and a metal hydride, iv) the coordination of the methoxybenzaldehyde on the metal and its insertion into the metal-hydride bond, v) and finally the protonation of the corresponding metal-alkoxide and the release of the *p*-OMebenzylalcohol **1a**. The coupling reaction proceeds through the *in situ* formation of acetaldehyde **2t** as an intermediate, which was detected by infrared spectral analysis (Scheme 4c and supporting information). Finally, treatment of acetaldehyde **2t** with benzyl alcohol **1a** leads to the formation of desired ester **2a** confirming the involvement of hemiacetal generated from acetaldehyde solely (Scheme 4d).

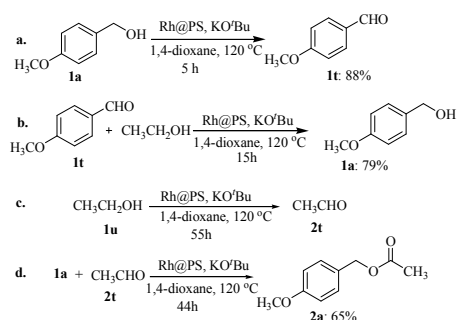
The recyclability experiment of Rh@PS was done on *p*-OMe benzyl alcohol. After completion, the reaction mixture was filtered off through a cotton bed, washed with water and acetone properly, dried over rotary evaporator. Finally, the

Table 4 Recyclability experiment of Rh@PS for oxidative esterification

No. of cycles	1 st cycle	2 nd cycle	3 rd cycle	4 th cycle	5 th cycle	6 th cycle
Yield (%)	75	73	73	72	71	71

recovered dried catalyst was repeatedly used for the same reaction. The catalyst retained its activity upto six cycles of reaction with negligible metal leaching.

During the recyclability experiment, Inductively coupled plasma atomic absorption spectra (ICP-AES) study of the



Scheme 4. Control experiments to prove the redox nature of ethanol and understanding the reaction mechanism

reaction mixture was analyzed to determine the amount of Rh-metal leached from the solid surface (Supporting information). The result of the test showed that only 0.45 ppm of Rh-metal was leached after six runs of the reaction.

Conclusions

In summary, a highly efficient nano-impregnated heterogeneous Rh(0) catalysed cross-dehydrogenating coupling of ethanol with aryl/alkyl alcohols or aldehydes under aerobic conditions has been investigated for the synthesis of acetate esters in a one pot consecutive approach. Vast range of aryl/alkyl alcohols or aldehydes has been targeted to prove *in situ* redox behaviour of ethanol and its

reactivity for esterification reaction. Unusual redox nature of ethanol in presence of Rh@PS catalyst makes the system an unprecedented for acetate ester synthesis comparing the existing advanced and traditional methods.

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