

Selective oxidation of alcohols using ferrocene-labeled Merrifield resin-supported ionic liquid phase catalysts

Rajanikant Kurane¹ · Prakash Bansode¹ · Sharanabasappa Khanapure¹ · Rajashri Salunkhe¹ · Gajanan Rashinkar¹

Received: 30 January 2016/Accepted: 26 April 2016 © Springer Science+Business Media Dordrecht 2016

Abstract A novel ferrocene-labeled Merrifield resin-supported ionic liquid phase catalysts has been synthesized and successfully utilized for the selective oxidation of primary alcohols into corresponding aldehydes. The catalysts were recovered by simple filtration which greatly simplified the purification step and allowed successive reuse for multiple times without significant loss in activity.

Graphical Abstract



Gajanan Rashinkar gsr_chem@unishivaji.ac.in

¹ Department of Chemistry, Shivaji University, Kolhapur, M.S. 416004, India

Keywords Merrifield resin · Selective oxidation · Alcohols · Ferrocene · Reusability

Introduction

Selective oxidation of alcohols into aldehydes is a ubiquitous and pivotal process in organic chemistry [1-4]. Traditionally, high-valent metal oxides of chromium, manganese and ruthenium are widely employed for this purpose [5-8]. Insights into these homogeneous catalytic systems have revealed some serious problems, such as over-oxidation of aldehydes to carboxylic acid, the use of hazardous terminal oxidants, drastic reaction conditions, tedious work-up procedures and generation of significant amounts of toxic waste products. The covalent immobilization of these reagents on solid supports has been carried out to alleviate aforementioned problems and provide an attractive alternative in organic synthesis in view of the selectivity and associated ease of manipulation [9-14]. A variety of other reagents, such as oxone [15], calcium hypochlorite [16], 2-hydroperoxyhexafluoro-2-propanol [17], vanadium [18], Cu-NHC-TEMPO [19], nano structured rutile TiO₂ [20], palladium [21], choline peroxydisulphate [22], nickel phosphine complexes [23], In(NO₃)₃ in [C₁₂mim][FeBr₄] [24], derivatives of 1-acetoxy-1,2-benziodoxole-3(1*H*)-one [25], sym-collidinium chlorochromate (S-COCC) [26], Ag-NHC complex [27], etc. have been used for selective oxidation of alcohols to aldehydes. However, despite of impressive progress, a mild protocol using a highly robust heterogeneous catalyst still represents a considerable synthetic challenge.

Environmental and economic concerns have recently raised much attention in redesigning synthetic processes using green chemistry principles so that the use of hazardous reagents and the use of toxic waste can be minimized. In this regard, considerable attention has been focused on the contemporary concept of supported ionic liquid phase (SILP) catalysis involving covalent immobilization of ionic liquid-like units onto a surface of a porous high area support material, as it provides an elegant approach for designing advanced materials for sustainable synthesis [28]. The noteworthy features of this novel class of environmentally benign reagents include high activity and selectivity along with the ease of separation from the reaction mixture by simple filtration. The development of novel SILP catalysts for various organic transformations has dramatically advanced in recent years [29–35].

In continuation of our work related to SILP catalysis [36–38], we report here the synthesis of ferrocene-labeled Merrifield resin-supported ionic liquid phase catalysts containing perruthenate, permanganate and perchromate anions for the selective oxidation of primary alcohols into corresponding aldehydes. Our interest in incorporating the ferrocene moiety into the backbone of SILP catalysts stem from the bulk of the ferrocenyl group which causes substantial improvements in the permeability of the substrate into the catalyst matrix, thereby improving the accessibility of reactants to the active sites which ultimately facilitates the catalyst performance of such catalysts [39–44].

Experimental

General

All reactions were carried out under air atmosphere in dried glassware. Infrared spectra were measured with a Perkin-Elmer one FTIR spectrophotometer. The samples were examined as KBr discs ~5 % w/w. ¹H NMR and ¹³C NMR spectra were recorded on a Bruker AC (300 MHz for ¹H NMR and 75 MHz for ¹³C NMR) spectrometer using CDCl₃ as solvent and tetramethylsilane (TMS) as an internal standard. Chemical shifts are expressed in δ parts per million (ppm) values with tetramethylsilane (TMS) as the internal reference, and coupling constants are expressed in hertz (Hz). Mass spectra were recorded on a Shimadzu QP2010 GCMS. The materials were analyzed by SEM using a JEOL model JSM with 5 and 20 kV accelerating voltage. Elemental analyses were performed on the EURO EA3000 vector model. Melting points were determined on a MEL-TEMP capillary melting point apparatus and are uncorrected. *N*,*N*-Dimethylaminomethyl ferrocene was synthesized using a previously reported procedure [70]. The various aryl alcohols (Spectrochem) and Merrifield resin (2 % cross linked, 200–400 mesh, ca 2–3 mmol/g; Alfa Aesar) were used as received.

Preparation of [FemDMMerA]Cl (3)

A mixture of *N*,*N*-dimethylaminomethyl ferrocene (1) (3.03 gm, 10 mmol) Merrifield resin (2) (3.0 g) and in 25 mL of DMF was heated at 80 °C in an oil bath. After 72 h, the polymer was filtered, washed with DMF (3 × 50 mL), MeOH (3 × 50 mL), CH₂Cl₂ (3 × 50 mL), and dried under vacuum at 50 °C for 24 h to afford [FemDMMerA]Cl (3). The loading was found to be 1.40 mmol/g of matrix. FT-IR (KBr, thin film): v = 3408, 3053, 3019, 2918, 2851, 2689, 1602, 1510, 1448, 1420, 1317, 1219, 1160, 1104, 939, 830, 805, 758, 696, 556, 464 cm⁻¹; FT-RAMAN (KBr, thin film): v = 2253, 2155, 2088, 2043, 1552, 1399, 1251, 1110, 904, 675, 580 cm⁻¹; Elemental analysis observed: %C 70.12, %H 5.62, %N 3.02.

Preparation of [FemDMMerA]RuO₄ (4a)

The suspension of **3** (3.0 g) and KRuO₄ (1.84 g, 9 mmol) in a distilled water (25 mL) was stirred for 24 h. Afterward the polymer was filtered and washed with distilled water (3 × 20 ml), as well as washed under Soxhlet and dried under vacuum at 50 °C for 48 h to afford [FemDMMerA]RuO₄ (**4a**). The loading was found to be 1.7 mmol/g of matrix. FT-IR (KBr, thin film): v = 3409, 2922, 2854, 1615, 1507, 1404, 1320, 1258, 1160, 1099, 1017, 840, 808, 699, 668, 558, 464 cm⁻¹; FT-RAMAN (KBr, thin film): v = 2900, 2472, 2303, 2243, 2162, 2102, 2053, 2021, 1912, 1754, 1699, 1596, 1216, 1145, 1101, 1031, 922, 841, 737, 694, 580, 531 cm⁻¹; Elemental analysis observed: %C 51.73, %Fe 11.66, %Ru 16.78.

Preparation of [FemDMMerA]MnO₄ (4b)

The suspension of **3** (3.0 g) and KMnO₄ (1.42 g, 9 mmol) in a distilled water (25 mL) was stirred for 24 h. Afterward the polymer was filtered and washed with distilled water (3 × 20 ml) as well as washed under Soxhlet and dried under vacuum at 50 °C for 48 h to afford [FemDMMerA]MnO₄ **4b**. The loading was found to be 8.0 mmol/g of matrix. FT-IR (KBr, thin film): v = 3365, 2924, 2851, 1601, 1508, 1485, 1396, 1253, 1158, 1104, 1018, 853, 702, 567, 464 cm⁻¹; FT-RAMAN (KBr, thin film): v = 2298, 2162, 2059, 1829, 1792, 1401, 1210, 1009, 917, 807, 574 cm⁻¹; Elemental analysis observed: %C 30.80, %Fe 11.67, %Mn 44.10.

Preparation of [FemDMMerA]CrO₄ (4c)

The suspension of **3** (3.0 g) and CrO₃ (0.9 g, 9 mmol) in a distilled water (25 mL) was stirred for 24 h. Afterward the polymer was filtered and washed with distilled water (3 × 20 ml) as well as washed under Soxhlet and dried under vacuum at 50 °C for 48 h to afford [FemDMMerA]CrO₄ **4c**. The loading was found to be 4.2 mmol/g of matrix. FT-IR (KBr, thin film): v = 3425, 2924, 2851, 1620, 1507, 1454, 1398, 1261, 1099, 1019, 942, 802, 702, 537, 464 cm⁻¹; FT-RAMAN (KBr, thin film): v = 2591, 2287, 2156, 2086, 2048, 2004, 1917, 1868, 1765, 1640, 1531, 1428, 1199, 1096, 955, 754, 585 cm⁻¹; Elemental analysis observed: %C 52.94, %Fe 17.91, %Cr 21.93.

General procedure for the oxidation of alcohols

A mixture of aryl alcohol (1 mmol) and [FemDMMerA]Y (100 mg) in solvent (5 mL) was refluxed in oil bath. After completion of the reaction as monitored by TLC, the reaction mixture was filtered to remove insoluble SILP catalyst. Evaporation of solvent in vacuuo followed by column chromatography over silica gel using petroleum ether/ethyl acetate (95:5 v/v) afforded pure aldehydes.

Spectral data of representative compounds

Table 2, entry d: White solid, M.p.: 103 °C, FT-IR (neat, thin film): $\upsilon = 2970$, 2850, 2229, 1701, 1680, 1608, 1571, 1530, 1460, 1430, 1410, 1383, 1296, 1201, 1171, 1011, 980, 827, 780, 765 cm⁻¹; ¹H NMR (300 MHz, CDCl₃) δ : 10.11 (s, 1H, –CHO), 8.00-8.03 (q, 2H, Ar–H), 7.86 (d, 2H, J = 10.2 Hz, Ar–H) ppm; ¹³C NMR (75 Hz, CDCl₃) δ : 191.3, 138.7, 132.9, 129.9, 117.7, 117.6 ppm; MS (EI): m/z 131[M]⁺; Elemental analysis observed: %C: 73.13, %H: 3.82, %N: 10.65.

Table 2, entry o: Lusterous red solid, M.p.: 122 °C, FT-IR (neat, thin film): $\upsilon = 3093$, 2827, 2761, 1682, 1662, 1586, 1510, 1452, 1409, 1371, 1268, 1243, 1201, 1136, 1106, 1023, 1001, 821, 762 cm⁻¹; ¹H NMR (300 MHz, CDCl₃) δ : 9.98 (s, 1H, –CHO), 4.81 (s, 2H, Cp–H), 4.63 (s, 2H, Cp–H), 4.29 (s, 5H, Cp–H) ppm; ¹³C NMR (75 Hz, CDCl₃) δ : 193.4, 73.2, 69.7 ppm; MS (EI): *m/z* 214 [M]⁺; Elemental analysis observed: %C: 61.48, %H: 4.57, %Fe: 26.05.

Results and discussion

Our initial studies were focused on the synthesis of SILP catalysts. They were readily prepared through a two-step procedure (Scheme 1). First, N,N-dimethy-laminomethyl ferrocene (1) was quaternized with Merrifield resin (2) to afford [FemDMMerA]Cl (3). The anion metathesis reaction of 3 with KRuO₄, KMnO₄ and



Scheme 1 Synthesis of ferrocene labeled Merrifield resin supported ionic liquid phase catalysts

 CrO_3 resulted in the formation of the desired ferrocene-labeled Merrifield resinsupported ionic liquid phase catalysts containing perruthenate, permanganese and perchromate anion acronymed as [FemDMMerA]RuO₄ (4a), [FemDMMerA]MnO₄ (4b) and [FemDMMerA]CrO₄ (4c).

Due to insolubility of **4a–c** in common organic solvents, their structure elucidation was limited to FT-IR and FT-Raman spectroscopy. The quaternization reaction was examined by using FT-IR spectroscopy. The negative bands at 669 cm⁻¹ (C–Cl stretching band) and 1260 cm⁻¹ (wagging bands of CH₂–Cl) [45] almost disappeared while the peaks at 464 cm⁻¹ (Fe–Cp stretching band), 1105 and 1160 (stretching modes of C–N), 3019, 2918 and 2851 cm⁻¹ (C–H stretching of Cp rings) increased in intensity after 72 h, reflecting the substantial degree of quaternization. Anion metathesis reaction was monitored using FT-IR as well as FT-Raman spectroscopy. In the FT-IR spectra, the appearance of a peak at 840 cm⁻¹ (for [FemDMMerA]RuO₄), 853 cm⁻¹ (for [FemDMMerA]MnO₄), 942 cm⁻¹ (for [FemDMMerA]CrO₄), which are characteristic peaks of RuO₄⁻, MnO₄⁻, and CrO₄⁻, confirmed the formation of **4a–c**. In addition, the FT-Raman spectra of **4a–c** displayed characteristic peaks of RuO₄⁻, MnO₄⁻ and CrO₄⁻ at 1031, 1009 and 1096 cm⁻¹, respectively, confirming the proposed structures of the desired SILP catalysts.

The Ru, Mn, and Cr contents were mapped by EDX analysis (Fig. 1). The results that indicated about 1.7, 8.0, and 4.2 mmol of ruthenium, manganese and chromium g^{-1} were present in 4a, 4b and 4c, respectively.

Scanning electron micrographs (SEM) at various stages of preparation of **4a–c** were recorded to understand the morphological changes on the surface of the Merrifield resin. Scanning was done across the entire length of the polymeric resin



Fig. 1 EDX of a [FemDMMerA]RuO₄, b [FemDMMerA]MnO₄, c [FemDMMerA]CrO₄

beads. Comparison of images taken at a magnification of $\sim 3 \times 10^3$ indicated that the spherical beads of Merrifield resin with smooth surfaces (Fig. 2A) were tainted upon functionalization. After functionalization, the resin beads in **4a–c** were not spherical like the original Merrifield resin beads (Fig. 2A). In fact, bead degradation was observed which may be plausibly due to stress generated during quaternization and the subsequent anion metathesis reaction (Fig. 2B–D) [46]. High ratios of covalently anchored quaternary ammonium group mass to bead volume leads to a situation where most of the beads experience enormous tension. These points of



Fig. 2 Scanning electron micrographs of A Merrifield resin, B [FemDMMerA]RuO₄, C [FemDMMerA]MnO₄ and D [FemDMMerA]CrO₄

🖄 Springer

tension evolve and give rise to stress in the bead which eventually bursts. Although the morphology of SILP catalysts was not that of the original Merrifield resin, there was no effect on their catalytic potential.

The thermogravimetric analysis (TGA) of **4a–c** was performed in the temperature range of 25–1000 °C in air to support their stability and robustness (Fig. 3A–C). The initial weight losses of 5.31, 7.69 and 5.90 % in the respective TGA curves of **4a**, **4b** and **4c** from room temperature to 100 °C are mainly due to evaporation of physically absorbed water. The second weight loss in the range 100–290 °C for **4a–c** is attributed primarily due to the decomposition of organics including the ferrocenyl group. An abrupt weight loss between 300–420 °C suggests the breakdown of the Merrifield resin backbone. Finally, the residual weights of around 19.35 % (in **4a**), 26.21 % (in **4b**) and 34.94 % (in **4c**) in the thermograms correspond to the formation of non-volatile oxides of Ru, Mn and Cr, respectively, and carbonaceous matter like graphitic carbon and carbonates due to incomplete combustion of polymers because of the high ramping rate used in TGA analysis.

Our next task was to assess the catalytic activity of the synthesized SILP catalysts. The oxidation of benzyl alcohol was chosen as a model reaction to optimize the reaction conditions in terms of the catalyst loading and solvent. Initially, the effect of various solvents on the model reaction was studied. The model reaction was performed under reflux conditions in various solvents including nonpolar toluene, 1,4-dioxane and dichloromethane, polar aprotic acetonitrile, THF, DMF and DMSO and polar protic methanol and ethanol. The experimental procedure for the reaction was trouble-free and straightforward. A mixture of benzyl alcohol (1 mmol) in each solvent (5 mL) was heated to reflux in the presence of 4a**c** (100 mg) until the completion of the reaction as monitored by TLC. The reaction was sluggish in dichloromethane, methanol and ethanol (Table 1, entries 1–3) while the use of the toluene, 1,4-dioxane and acetonitrile afforded the anticipated products in moderate yields (Table 1, entries 10-12). The reaction could not be initiated to a synthetically useful degree in solvents such as DMF and DMSO (Table 1, entries 4 and 5). It was observed that THF is the most effective in providing the highest conversion (Table 1, entry 7). The enhanced oxidation rate in THF is accounted for on the basis of the swelling factor of resin which is a crucial factor in solid phase organic synthesis. It is well established that a greater degree of swelling leads to a higher degree of diffusion rate of the reactant onto the surface of the resin, causing the accessing of the more reactive sites. This results in shorter reaction time and high chemical conversion [47-49]. Griffith et al. have extensively investigated the swelling properties of Merrifield resin in various solvents and proved that the resin has a very high degree of swelling in THF [50]. In our case, measurements of the swelling degree of SILP catalysts (4a-c) and Merrifield resin were carried out according to a previously reported procedure [51]: to a known weight of 4a-c and Merrifield resin in a separate 1 mL syringe, a known amount of THF was added and allowed to swell to full capacity. The swelling degree was determined by the measurement of bead diameter using fluorescence microscopy. An approximately 30 % increase in the size of 4a-c and Merrifield resin was observed compared with untreated materials. Overall, this proves that the highest activity of oxidation in THF is reasonably due to the high degree of swelling of the SILP catalysts in THF.



Fig. 3 Thermograms of A [FemDMMerA]RuO₄, B [FemDMMerA]MnO₄ and C [FemDMMerA]CrO₄

Next, the effect of catalyst loading on the model reaction was investigated. As shown in Table 1, the yield of benzaldehyde increased by increasing the quantity of the catalysts from 50 to 100 mg (Table 1, entries 6–7). However, a further increase in the amount of the catalysts did not have a significant effect on the product yield and reaction time (Table 1, entries 8–9).

It is also worth mentioning that **4a** was found to be a very efficient catalyst compared with **4b** and **4c** in terms of both reaction time and the yield of product. The excellent oxidation performance of **4a** may be rationalized on the basis of the stabilization of RuO_4^- anion by alcohol solvation [52]. As better results were obtained with **4a**, it was used in further studies.

With a reliable set of conditions to hand, we probed the generality of the protocol by oxidizing structurally diverse aryl alcohols with **4a** in THF. The results are summarized in Table 2. In all cases, corresponding aldehydes were obtained as sole products without any over-oxidation. In general, alcohols with electron-donating

Table 1 Optimization of reaction conditions



| Entry | Solvent | Amount of catalyst (mg) | Time (h) FcMerY ⁻ | | | Yield ^a (%) FcMerY ⁻ | | |
|-------|-------------------|-------------------------|------------------------------|-----------------|-----------------|--|-----------------|-----------------|
| | | | Ya ⁻ | Yb ⁻ | Yc ⁻ | Ya ⁻ | Yb ⁻ | Yc ⁻ |
| 1 | Dichloromethane | 100 ^b | 24 | 24 | 24 | 35 | 25 | 26 |
| 2 | Methanol | 100 ^b | 18 | 20 | 24 | 45 | 35 | 30 |
| 3 | Ethanol | 100 ^b | 19 | 22 | 26 | 46 | 32 | 29 |
| 4 | DMSO | 100 ^b | 29 | 32 | 35 | Trace | Trace | Trace |
| 5 | DMF | 100 ^b | 32 | 29 | 35 | Trace | Trace | Trace |
| 6 | THF | 50 ^c | 8 | 10 | 11 | 71 | 65 | 61 |
| 7 | THF | 100 ^b | 3 | 7 | 8 | 95 | 72 | 71 |
| 8 | THF | 150 ^d | 3 | 7 | 8 | 96 | 73 | 73 |
| 9 | THF | 200 ^e | 3 | 7 | 8 | 96 | 72 | 72 |
| 10 | Toluene | 100 ^b | 15 | 19 | 22 | 65 | 61 | 59 |
| 11 | 1,4-Dioxane | 100 ^b | 18 | 22 | 20 | 68 | 58 | 62 |
| 12 | Acetonitrile | 100 ^b | 13 | 18 | 15 | 65 | 55 | 52 |
| 13 | KRuO ₄ | 20.4 (0.1 mmol) | 9 | _ | _ | 69 | _ | _ |
| 14 | KMnO ₄ | 15.8 (0.1 mmol) | _ | 15 | _ | _ | 68 | _ |
| 15 | CrO ₃ | 10 (0.1 mmol) | _ | _ | 18 | _ | _ | 65 |

Optimal reaction conditions: 5a (1 mmol.), solvent (5 ml), SILP (100 mg), and reflux

^a Isolated yields after column chromatography

 $^{\rm b}\,$ %Loading of catalyst per 100 mg: (0.17 mmol of 4a), (0.8 mmol of 4b) and (0.42 mmol of 4c)

^c %Loading of catalyst per 50 mg (0.085 mmol of **4a**), (0.4 mmol of **4b**) and (0.21 mmol of **4c**)

^d %Loading of catalyst per 150 mg (0.25 mmol of **4a**), (1.2 mmol of **4b**) and (0.63 mmol of **4c**)

^e %Loading of catalyst per 200 mg (0.34 mmol of **4a**), (1.6 mmol of **4b**) and (0.84 mmol of **4c**)

substituents on the aryl ring gave good yields (Table 2, entries b, e, h–k and p) as compared with those with electron-withdrawing substituents (Table 2, entries d, f and g). In addition, heterocyclic alcohols such as furfuryl alcohol and thenyl alcohol could also be oxidized into corresponding aldehydes in excellent yields (Table 2, entries 1 and m). Moreover, organometallic alcohol such as ferrocenyl methanol could also serve as a substrate in this reaction (Table 2, entry o). In addition, the protocol tolerated the presence of functional groups in the *ortho* position of the primary alcohols (Table 2, entries b, c and i). The reaction of the sterically hindered 2-naphthyl alcohol even gave a yield of 87 %. In addition, the oxidation of cinnamyl alcohol resulted in selective oxidation, yielding corresponding cinnamaldehyde in modest yield highlighting the general applicability of the protocol. The identity of all the compounds was ascertained on the basis of IR, ¹H NMR, ¹³C NMR spectroscopy as well as by mass spectrometry. The physical and spectroscopic data are consistent with the proposed structures and are in harmony with the literature values [19, 53–60].

| | [FemDMMerA]RuO ₄ | | | |
|-----------------------------------|-----------------------------|--|----------|--|
| R — CH ₂ OH Alcohol | THF, Reflux | | Aldehyde | |
| 5 | | | 6 | |

 Table 2
 [FemDMMerA]RuO₄ catalyzed oxidation of alcohols

| Entry | Alcohol (5) R | Product (6) | Time (h) | Yield ^a (%) | Conversion % | |
|-------|--|-------------|----------|------------------------|--------------|--|
| a | C ₆ H ₅ - | 6a | 3 | 95 | >99 | |
| b | 2-OH-C ₆ H ₄ - | 6b | 3 | 89 | >99 | |
| c | 2-NO ₂ -C ₆ H ₄ - | 6c | 4 | 92 | >99 | |
| d | $4-CN-C_6H_4-$ | 6d | 3 | 96 | >99 | |
| e | 4-MeO-C ₆ H ₄ - | 6e | 4 | 89 | >95 | |
| f | 3-NO ₂ -C ₆ H ₄ - | 6f | 3 | 95 | >99 | |
| g | 4-NO2-C6H4- | 6g | 3 | 94 | >99 | |
| h | 3-MeO-C ₆ H ₄ - | 6h | 4 | 91 | >99 | |
| i | 2-CH ₃ -C ₆ H ₄ - | 6i | 5 | 88 | >99 | |
| j | 3-CH ₃ -C ₆ H ₄ - | 6j | 4 | 89 | >99 | |
| k | 4-CH3-C6H4- | 6k | 5 | 86 | >99 | |
| 1 | 2-Furyl- | 61 | 4 | 92 | >99 | |
| m | 2-Thenyl- | 6m | 4 | 89 | >99 | |
| n | Naphthyl- | 6n | 5 | 87 | >96 | |
| 0 | Ferrocenyl- | 60 | 4 | 92 | >99 | |
| р | 3,4-Di-MeO–C ₆ H ₄ – | 6р | 5 | 86 | >94 | |
| q | Cinnamyl- | 6q | 7 | 72 | >96 | |

Optimal reaction conditions: 5 (1 mmol.), THF (5 ml), SILP (100 mg.) and reflux

^a Isolated yields after column chromatography

On the basis of the literature, a tentative mechanistic rationale for the oxidation of aryl alcohols using **4a** is formulated in Scheme 2. The mechanism is likely to proceed via a free radical-like transition state, in which the metal alcoholate complex is formed [61–63] by the attack of alcohol on the oxometallate ion, as shown in Scheme 2. Finally, the alcoholate species undergoes the usual β -hydride elimination to afford the respective aldehyde along with metal hydride species which can be reoxidised by means of filtration and subsequent washing of the spent SILP catalyst for the next catalytic cycle. The reoxidation step is usually initiated by the action of electron-proton mediators such as quinone [64–66] and 2,2,6,6tetramethylpiperidin-1-yloxy (TEMPO) [67, 68]. It is noteworthy that no such mediators are required for the oxidation reaction [69].

In order to explore whether the catalyst is truly heterogeneous, we have performed a number of heterogeneity tests. A hot filtration test was performed with







Fig. 4 Reusability of [FemDMMerA]RuO₄

the model reaction. After 50 % of completion of the reaction (GC), the catalyst was removed by filtration. The resulting filtrate was subjected to heating for a further 10 h. Gas chromatographic analysis revealed no corresponding enhancement in the product beyond 50 %, confirming the heterogeneity of **4a**. Further, no evidence of leaching was observed during the catalytic reaction as no ruthenium was detected by ICP-AES analysis of the filtrate after removal of the catalyst. This indicates that the catalyst is predominantly covalently attached in the Merrifield resin matrix, thus making this SILP catalyst leaching-resistant.

The recovery and recyclability of the heterogeneous catalyst must be focused before any catalytic operation, as it is an obvious parameter for industrial and commercial scale as well as an essential aspect of green chemistry. The reusability of **4a** was tested for the model reaction. After the reaction, the catalyst was separated by simple filtration, washed with bountiful amounts of THF, dried in an oven at 60 °C for 12 h and reused for the next cycle. We were delighted to note that **4a** could be reused for six runs for the model reaction without significant loss in the product yield, conversion and catalytic activity without prolonged reaction time (Fig. 4). The slight reduction in the conversion observed on successive recycles is thought to be due to attrition during filtration and recovery of the catalyst. Another phenomenal feature of **4a** was its sturdiness. The catalytic activity of **4a** did not alter after 1 week of air exposure at room temperature, indicating its remarkable constancy.

Conclusion

In conclusion, we have demonstrated a simple and efficient strategy for the oxidation of primary alcohols into corresponding aldehydes using ferrocene-labeled Merrifield resin-supported ionic liquid phase catalysts. The protocol offers a number

of significant key features, such as excellent product yields, relatively shorter reaction times, ease of recovery and reuse of the catalyst, which make this method financially viable, liberal and a waste-free chemical process for the oxidation of alcohols.

Acknowledgments The authors thank UGC, New Delhi for financial assistance [F. No. 40-96/2011 (SR)].

References

- 1. R.A. Sheldon, I.W.C.E. Arends, G.-J.T. Brink, A. Dijksman, Acc. Chem. Res. 35, 774 (2002)
- 2. T. Mallat, A. Baiker, Chem. Rev. 104, 3037 (2004)
- 3. T. Punniyamurthy, S. Velusamy, J. Iqbal, Chem. Rev. 105, 2329 (2005)
- 4. C.D. Pina, E. Falletta, M. Rossi, Chem. Soc. Rev. 41, 350 (2012)
- 5. R.B. Augustine, Oxidation. M. Dekker (New York, 1969)
- 6. K.B. Wiberg, Oxidation in Organic Chemistry Part A. (Academic, New York, 1965)
- 7. W.S. Trakanovsky: Oxidation in Organic Chemistry Part B. (Academic, New York, 1973)
- 8. B.M. Trost: Comprehensive Organic Synthesis (Oxidation), vol. 7. (Pergamon, New York, 1991)
- 9. P. Laszlo, Preparative Chemistry Using Supported Reagents (Academic, San Diego, 1987)
- 10. F. Xu, Z. Zhang, ChemCatChem 7, 1470 (2015)
- 11. Z. Zhang, Z. Yuan, D. Tang, Y. Ren, K. Lv, B. Liu, ChemSusChem 7, 3496 (2014)
- 12. Z. Zhang, J. Zhen, B. Liu, K. Lv, K. Deng, Green Chem. 17, 1308 (2015)
- 13. B. Liu, Y. Ren, Z. Zhang, Green Chem. 17, 1610 (2015)
- 14. L. Gao, K. Deng, J. Zheng, B. Liu, Z. Zhang, Chem. Eng. J. 270, 444 (2015)
- 15. R.T. Benjamin, M. Sivakumar, G.O. Hollist, B. Borhan, Org. Lett. 5, 1031 (2003)
- 16. S.O. Naukwa, P.M. Keehn, Tetrahedron Lett. 23, 3131 (1982)
- 17. B. Ganem, R.P. Heggs, A.J. Biloski, D.R. Schwartz, Tetrahedron Lett. 21, 685 (1980)
- 18. S. Velusamy, T. Punniyamurthy, Org. Lett. 6, 217 (2004)
- 19. X. Liu, Q. Xia, Y. Zhang, C. Chen, W. Chen, J. Org. Chem. 78, 8531 (2013)
- S. Yurdakal, G. Palmisano, V. Loddo, V. Augugliaro, L. Palmisano, J. Am. Chem. Soc. 130, 1568 (2005)
- 21. A.S. Guram, X. Bei, H.W. Turner, Org. Lett. 5, 2485 (2003)
- 22. B.L. Gadilohar, H.S. Kumbhar, G.S. Shankarling, Ind. Eng. Chem. Res. 53, 19010 (2014)
- 23. C.J. Weiss, P. Das, D.L. Miller, M.L. Helm, A.M. Appel, ACS Catal. 4, 2951 (2014)
- 24. Y.L. Hu, D. Fang, C. R. Chimie. 18, 614 (2015)
- 25. M. Iinuma, K. Moriyama, H. Tog, Eur. J. Org. Chem. 2014, 772 (2014)
- 26. L. Shiri, D. Sheikh, M. Seikhi, Rev. Roum. Chim. 59, 825 (2014)
- 27. L. Han, P. Xing, B. Jiang, Org. Lett. 16, 3428 (2014)
- 28. C.V. Doorslaer, J. Wahlen, P. Mertens, K. Binnemans, D. DE Vos, Dalton Trans. 39, 8377 (2010)
- 29. A.H. Tamboli, A.A. Chaugule, F.A. Sheikh, W.J. Chung, H. Kim, Chin. J. Catal. 36 (2015)
- 30. S. Martin, R. Porcar, E. Peris, M.I. Burguete, E.G. Verdugo, S.V. Luis, Green Chem. 16, 1639 (2014)
- 31. U. Hintermair, G. Francio, W. Leitner, Chem. Eur. J. 19, 4538 (2013)
- 32. B. Karimi, M. Vafaeezadeh, Chem. Commun. 48, 3327 (2012)
- 33. N.A. Khan, Z. Hasan, S.H. Jhung, Chem. Eur. J. 20, 376 (2014)
- 34. B. Ni, A.D. Headley, Chem. Eur. J. 16, 4426 (2010)
- 35. A. Riisager, R. Fehrmann, M. Haumann, P. Wasserscheid, Eur. J. Inorg. Chem. 695 (2006)
- 36. V. Gaikwad, R. Kurane, J. Jadhav, R. Salunkhe, G. Rashinkar, Appl. Catal. A 451, 243 (2013)
- 37. J. Jadhav, V. Gaikwad, R. Kurane, R. Salunkhe, G. Rashinkar, Tetrahedron 69, 2920 (2013)
- 38. R. Kurane, J. Jadhav, S. Khanapure, R. Salunkhe, G. Rashinkar, Green Chem. 15, 1849 (2013)
- 39. A. Togni, R.L. Halterman (Eds.), Metallocenes (Wiley-VCH, Weinheim, 1998)
- 40. A. Togni, T. Hayashi (Eds.), Ferrocenes: Homogeneous Catalysis, Organic Synthesis, Material Science (Wiley-VCH, Weinheim, 1995)
- 41. R.C.J. Atkinson, V.C. Gibson, N.J. Long, Chem. Soc. Rev. 33, 313 (2004)
- 42. P. Barbaro, C. Bianchini, G. Gianbastini, S.L. Parisel, Coord. Chem. Rev. 248, 2131 (2004)
- 43. U. Siemeling, T.C. Auch, Chem. Soc. Rev. 34, 584 (2005)

- 44. T.J. Colacot, Platinum Met. Rev. 45, 22 (2001)
- 45. B. Altava, M.I. Burguete, E. Garcia-Verdugo, S.V. Luis, M.J. Vicent, Tetrahedron 57, 8675 (2001)
- 46. G. Sanclimens, L. Crespo, M. Pons, E. Giralt, F. Albericio, M. Royo, Tetrahedron Lett. 44, 1751 (2009)
- 47. D. Walsh, D. Wu, Y.-T. Chang, Curr. Opin. Chem. Biol. 7, 353 (2003)
- 48. S. Chen, K.D. Janda, Tetrahedron Lett. 39, 3943 (1998)
- 49. M. Collot, S. Eller, M. Wieshaupt, P.H. Seeberger, Beilstein J. Org. Chem. 9, 97 (2013)
- 50. R. Santini, M.C. Griffith, M. Qi, Tetrahedron Lett. 39, 8951 (1998)
- 51. A.R. Vaino, D.B. Goodin, K.D. Janda, J. Comb. Chem. 2, 330 (2000)
- 52. M. Hasan, M. Musawir, P.N. Davey, I.V. Kozhevnikov, J. Mol. Cat. A: Chem. 180, 77 (2002)
- N.S. Ramegowda, M.N. Modi, A.K. Koul, J.M. Bora, C.K. Narang, N.K. Mathur, Tetrahedron 29, 3985 (1973)
- 54. S. Cacchi, G. Fabrizi, A. Goggiamani, J. Comb. Chem. 6, 692 (2004)
- 55. C.O. Kangani, D.E. Kelley, B.W. Day, Tetrahedron Lett. 47, 6289 (2006)
- 56. E. Balali, A. Shameli, H. Naeimi, M.M. Ghanbari, Orient. J. Chem. 29, 1611 (2013)
- 57. J.E. Steves, S.S. Stahl, J. Am. Chem. Soc. 135, 15742 (2013)
- 58. J.M. Hoover, S.S. Stahl, J. Am. Chem. Soc. 133, 16901 (2011)
- 59. Y. Yang, S. Pan, J.-D. Xue, X. Zheng, W.-H. Fang, D.L. Phillips, J. Raman Spectrosc. 45, 105 (2014)
- 60. M.F. Daniel, A.J. Leadbetter, R.E. Meads, W.G. Parker, J. Chem. Soc., Faraday Trans. 2 74, 456 (1978)
- 61. D.G. Lee, L.N. Congson, Can. J. Chem. 68, 1774 (1990)
- 62. K.B. Sharpless, K. Akashi, K. Oshima, Tetrahedron Lett. 17, 2503 (1976)
- S. Kanemoto, S. Matsubara, K. Takai, K. Oshima, K. Utimato, H. Nozaki, Bull. Chem. Soc. Jpn 61, 3607 (1988)
- 64. J.E. Backvall, R.L. Chowdhury, U. Karlsson, J. Chem. Soc. Chem. Commun. 473 (1991)
- 65. A. Hanyu, S. Sakaguchi, E. Takezaki, Y. Ishii, Tetrahedron Lett. 39, 5557 (1998)
- 66. G. Csjernyik, A.H. Ell, L. Fadini, B. Pugin, J.E. Backvall, J. Org. Chem. 67, 1657 (2002)
- 67. A. Dijksman, I.W.C.E. Arends, R.A. Sheldon, Chem. Commun. 1591 (1999)
- A. Dijksman, A. Marino-Gonzalez, A.M.I. Payeras, I.W.C.E. Arends, R.A. Sheldon, J. Am. Chem. Soc. 123, 6826 (2001)
- 69. K. Behari, H. Narayan, R.S. Shukla, K.C. Gupta, Int. J. Chem. Kinet. 16, 195 (1984)
- 70. J.K. Lindsay, C.R. Hauser, J. Org. Chem. 22, 355 (1956)