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# Co-immobilized formate anion and palladium on a polymer surface: a novel heterogeneous combination for transfer hydrogenation

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Dedicated to Professor Debabrata Mukherjee on the occasion of his 65th birthday

**Abstract**—A novel heterogeneous combination of a formate reagent and palladium catalyst co-immobilized on a resin support has been developed and shown to be highly efficient and recyclable for transfer hydrogenation of alkenes, imines, nitroarenes and 1,2-dicarbonyl compounds.

Catalytic transfer hydrogenation (CTH) with the aid of a stable hydrogen donor is a useful alternative method for catalytic hydrogenation by molecular hydrogen.[1] In transfer hydrogenation, organic molecules such as hydrocarbons,[2] primary and secondary alcohols[3] and formic acid and its salts[4] have been employed as the hydrogen source. The use of a hydrogen donor has some advantages over the use of molecular hydrogen since it avoids the risks and the constraints associated with hydrogen gas as well as the necessity for pressure vessels and other equipment. Although metal-catalyzed transfer hydrogenation using a stable H-donor has been found to be reliable, the current emphasis on cleaner methods for chemical transformations requires high selectivity, low cost, easy separation and the production of minimum waste. From a practical point of view, a more attractive approach is to develop a heterogeneous catalyst that is efficient for this transformation. Immobilized reagents and immobilized catalysts can afford clean transformations for laboratory to large-scale operations. While several immobilized reagents or immobilized catalysts have been demonstrated for numerous organic transformations,[5] we envisaged that both the reagent and the catalyst could be bound on the same polymer surface and employed for suitable transformations. Such an approach would provide further operational simplicity and economic control.

As a part of a continuous effort to develop solid phase organic reactions, we recently reported that polymer-supported formate (PSF) could be used as a potential H-donor in palladium-catalyzed transfer hydrogenation of alkenes, imines and aromatic nitro compounds.[6] The conditions appeared to be mild and selective for many functional groups such as ketones, esters, halogens and nitriles. The reactions were performed using catalytic palladium acetate (2 mol %) in DMF and it was assumed that the palladium catalyst worked as a homogeneous catalyst. The high degree of chemoselectivity in palladium-catalyzed transfer hydrogenation using HCOOH or its salts has been explained on the basis that the hydrogen is delivered directly from a Pd formate species which has much stronger hydridic nature compared to that of a Pd hydride species.[7] The combination of formic acid and palladium acetate is known to undergo anionic ligand exchange to form a palladium diformate complex, eventually producing Pd(0) through decarboxylation and loss of molecular hydrogen.[8] In CTH, either a source of palladium is required for each operation or it may be supported by a polymer framework and reused several times. We reasoned that the palladium catalyst might be anchored to the PSF so that it could be used and recycled. Palladium is usually attached to a solid surface either by adsorption on the polymeric surface, by

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*Keywords*: Transfer hydrogenation; Polymer-supported formate; Supported palladium catalyst; Alkenes; Imine; Nitroarenes; 1,2-Diketones.

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coordination through the ligand or by the relatively new technique of microencapsulation.[9] In this letter, we report that palladium can be immobilized on the PSF and used effectively in the CTH of a variety of functional groups. Furthermore, the formate (the H-donor) and palladium (the catalyst) supported on a polymeric surface (PSF-Pd) can be recycled at least four-times without any appreciable loss of activity. To the best of our knowledge, this approach, where both the reagent and the catalyst are co-immobilized on same polymeric backbone, has not previously been reported.

The overall procedure is simple and straightforward. The polymer-supported formate (PSF) was prepared using Amberlyst resin (IRA® 420), the chloride form being exchanged with formic acid, according to our previously reported procedure.[6] To a suspension of PSF (1 g) in DMF (5 ml) was added palladium acetate (10 mg) and the mixture magnetically stirred under nitrogen at room temperature for 2 h. The PSF beads turned black indicating that the Pd(II) species may have been reduced to Pd(0), and the solvent became colourless. The resulting mixture was filtered, washed with DMF and dried under vacuum overnight. The resulting black PSF beads of the resin supporting both the reagent and palladium catalyst (PSF-Pd) were used for the reduction.[10]

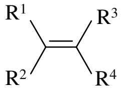
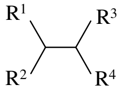
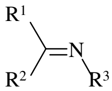
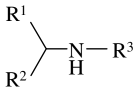
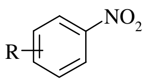
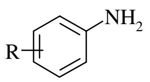
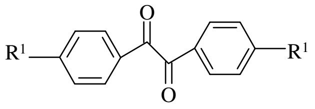
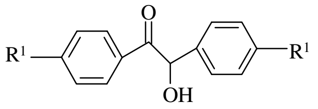
**Table 1.** FT-IR data (KBr) for the carboxylate anion

| Formate | Stretching vibration ($\nu_{max}$) cm$^{-1}$ | Anti-symmetrical/symmetrical vibration ($\nu_{max}$) cm$^{-1}$ |
|---|---|---|
| $HCOONH_4$ | 1354 | 1595 |
| HCOOK | 1348 | 1593 |
| PSF | 1344 | 1593 |
| PSF-Pd | 1404 | 1653 |

The PSF-Pd was characterized by IR spectroscopy. The FT-IR spectral data for the carboxylate anion of different formate salts, PSF and PSF-Pd are given in Table 1. The FT-IR spectrum of PSF-Pd was compared with those of ammonium formate, potassium formate and the PSF. The absorptions of the carboxylate anions of $HCOONH_4$, HCOOK and PSF were observed at 1595, 1593 and 1593 cm$^{-1}$, respectively, while that of PSF-Pd occurred at 1653 cm$^{-1}$. The significant increase of $\nu_{max}$ for PSF-Pd clearly indicated binding of the palladium metal through complexation with PSF.[11]

The efficiency and stability of this newly developed PSF-Pd was first examined in the reduction of electron-deficient alkenes conjugated with ketones, nitriles and carboxylate esters (entries 1–5 in Table 2). An excess of the polymer-supported formate/palladium catalyst (0.5 g of PSF-Pd per mmol of the substrate) was em-

**Table 2.** Catalytic transfer reduction using PSF-Pd

| Entry | Substrate | Conditions[a] temperature (°C)/time (h) | Product | Yield (%)[b] |
|---|---|---|---|---|
| |  | |  | |
| 1. | $R^1 = Ph$; $R^2 = H$; $R^3 = CN$; $R^4 = COOEt$ | 65/8 | **1** | 82 |
| 2. | $R^1 = 4\text{-}MeOC_6H_4$; $R^2 = H$; $R^3 = CN$; $R^4 = COOEt$ | 70/8 | **2** | 80 |
| 3. | $R^1 = 4\text{-}MeOC_6H_4$; $R^2 = H$; $R^3 = R^4 = CN$ | 50/6 | **3** | 86 |
| 4. | $R^1 = Ph$; $R^2 = Me$; $R^3 = CN$; $R^4 = COOEt$ | 70/7 | **4** | 78 |
| 5. | $R^1 = 4\text{-}ClC_6H_4$; $R^2 = H$; $R^3 = H$; $R^4 = CO(3\text{-}C_4H_3O)$ | 80/12 | **5** | 75 |
| |  | |  | |
| 6. | $R^1 = 3\text{-}NO_2$; $R^2 = H$; $R^3 = Ph$ | 70/7 | **6** | 80 |
| 7. | $R^1 = 4\text{-}C_5H_4N$; $R^2 = H$; $R^3 = Ph$ | 50/6 | **7** | 87 |
| 8. | $R^1 = 3\text{-}C_4H_3O$; $R^2 = H$; $R^3 = Ph$ | 60/6 | **8** | 78 |
| |  | |  | |
| 9. | R = 4-Cl | 110/11 | **9** | 76 |
| 10. | R = 4-COOMe | 100/10 | **10** | 85 |
| 11. | R = 3-COMe | 100/10 | **11** | 81 |
| 12. | 1-Nitronaphthalene | 100/10 | **12** | 75 |
| |  | |  | |
| 13. | $R^1 = H$ | 100/10 | **13** | 85 |
| 14. | $R^1 = Me$ | 110/12 | **14** | 77 |
| 15. | $R^1 = OMe$ | 110/10 | **15** | 88 |

[a] 0.5 g of PSF-Pd per 1 mmol of the substrate in DMF (1 cm$^3$).

[b] Yields are based on at least two runs and the products were isolated as pure compounds after column chromatography. All products showed satisfactory IR, $^1H$ NMR and $^{13}C$ NMR spectral data.

ployed, with the expectation that other functional groups would not react, to force the reaction to completion. The reduction of the C–C double bond proceeded smoothly at 50–80 °C requiring only gentle agitation; work-up was then achieved by simple filtration, extraction with diethyl ether and evaporation. The reduced product was purified by column chromatography over silica gel and isolated in 75–86% yield. Other reducible groups such as the ketone, nitrile or halogen and ester groups remained unaffected under the reaction conditions.

To extend the scope and generality of the PSF-Pd in CTH, we explored reduction of the C–N double bonds of imines. Since imines are generally derived from the corresponding aldehydes or ketones, the overall reaction in one-pot constitutes a method for 'direct reductive amination' and is an attractive synthetic route to secondary and tertiary amines. Using the PSF-Pd, the imines could be reduced efficiently at 50–70 °C (entries 6–8 in Table 2). A nitro group and heteroaromatic moiety remained unaffected under the reaction conditions.

The reduction of nitroarenes to anilines is a synthetically important transformation both in the laboratory and in industry. To broaden the scope of PSF-Pd, reduction of the nitro group was investigated with nitroarenes as the substrates. While the nitro group was not reducible at a lower temperature (70 °C) it could be reduced at 100–110 °C to yield the corresponding anilines (entries 9–12 in Table 2). Several other reducible groups such as a halogen, ester or ketone were inert to these conditions illustrating a clear advantage in terms of chemoselectivity.

Further applications of this new heterogeneous reductive system were tested with 1,2-dicarbonyl compounds. When benzil or substituted benzils were used as the substrate, the reduction of one of the carbonyl groups with PSF-Pd in DMF at 100 °C reached completion after 10–12 h to give the corresponding α-hydroxyketone (benzoin) in a 77–88% isolated yield (entries 13–15 in Table 2).

The novel combination PSF-Pd was easily used for four successive recycling runs without any significant drop of reactivity. With methyl 4-nitrobenzoate as the substrate, the reduction proceeded to completion giving excellent yields for up to four runs.

In summary, formic acid as its formate anion and a palladium catalyst from palladium acetate have been co-immobilized effectively on an inexpensive Amberlyst ion-exchange resin. This resin (PSF-Pd) proved to be a versatile and heterogeneous reductive combination for transfer hydrogenation of functionalized alkenes, imines, nitroarenes and 1,2-diketones. This new technique also demonstrates high chemoselectivity in the reduction of alkenes, imines and nitro groups, thus establishing an efficient, environmentally benign, economically friendly and sustainable process. Further studies on structural aspects and the reaction behaviour (leaching of the palladium) of PSF-Pd along with newer applications for other transformations are currently underway.

## Acknowledgements

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10. *A representative procedure for the CTH of 1,2-diketones using PSF-Pd*: To a solution of 4,4′-dimethoxybenzil (2 mmol) in freshly distilled DMF (2 $cm^3$) was added PSF-Pd (1 g) and the reaction mixture was stirred at 110 °C for 10 h. The reaction mixture was diluted with ether (15 $cm^3$) and filtered through a bed of cotton. The filtrate was extracted with ether ($2 \times 15\ cm^3$) and the combined organic layers were washed brine ($2 \times 10\ cm^3$) and dried ($Na_2SO_4$). Evaporation under reduced pressure and purification by column chromatography afforded 4,4′-dimethoxybenzoin as a pale yellow solid (88% yield); mp 111–112 °C; FT IR (Nujol): $\nu_{max}$ 3466, 1666, 1597, 1512, 1466 $cm^{-1}$; $^1H$ NMR (300 MHz, $CDCl_3$): $\delta = 7.91$ (d, $J = 9$ Hz, 2H), 7.26 (d, $J = 8.7$ Hz, 2H), 6.87 (d, $J = 9$ Hz, 2H), 6.85 (d, $J = 8.7$ Hz, 2H), 5.87 (s, 1H), 4.85–4.3 (br s, 1H), 3.82 (s, 3H), 3.76 (s, 3H); $^{13}C$ NMR (75 MHz, $CDCl_3$): $\delta = 197.3$, 163.9, 159.6, 131.8, 131.5, 129.0, 126.2, 114.5, 113.9, 75.2, 55.4, 55.2.
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