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Asymmetric hydrogenation of the C=O bond with the recycling of an organometal catalyst deposited on a solid organic polyelectrolyte

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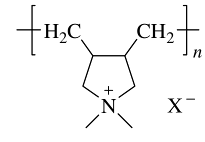
The asymmetric hydrogenation of methyl levulinate to chiral γ-valerolactone has been performed with the recycling of a Ru^{II}–BINAP catalyst deposited on a solid organic polyelectrolyte; enantioselectivity up to 99% *ee* has been achieved at high conversion of substrate after three recycles of the catalyst.

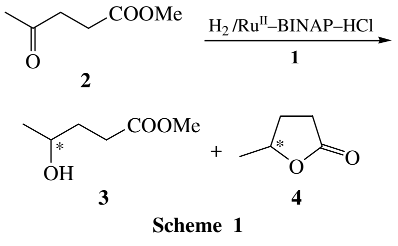
The recycling of expensive transition metal chiral catalysts (TMCCs) is of considerable current interest. An approach to solve the problem of the catalyst recovery is the immobilization of TMCCs on mineral or polymer carriers.[1–6] However, it often gives rise to a decrease in catalytic reaction rate. Recently, a method of TMCC recycling by 'immobilization' in organic salt solutions including ionic liquids has attracted considerable attention.[7–14] Another promising approach to TMCC recycling is based on the use of ionic polymers, polyelectrolytes (PEs), as catalyst carriers. In particular, an efficient catalyst system for asymmetric aldol reaction between aldehydes and ketones based on L-proline supported on organic PE, poly(diallyldimethylammonium salt) **1**, has been recently elaborated.[15] This heterogeneous system retained high activity after several reaction cycles without decreasing enantioselectivity.



a X = Cl, *n* = 1800–2250
b X = BF_4, *n* = 1800–2250
c X = PF_6, *n* = 1800–2250
d X = PF_6, *n* = 450–900

1a–d

Here, we report on the first use of solid organic PEs bearing no additional components[†] for TMCC recycling. The asymmetric hydrogenation of methyl levulinate **2** to γ-hydroxyvaleric acid methyl ester **3** in the presence of the Ru^{II}–BINAP–HCl–PE catalyst system was used as a model reaction. The cyclization of hydroxyester **3** under reaction conditions afforded chiral γ-valerolactone **4**, a versatile building block that can be used for the synthesis of medications and other useful products (Scheme 1).



Scheme 1

Table 1 Asymmetric catalytic hydrogenation of ketoester **2** with the recycling of the catalyst deposited on PE **1a–c**.[a]

Series of runs	PE	Reaction cycle	Conversion of **2** (%)	Composition of the reaction products (mol%)		
				3[b]	**4**[b]	*ee* (*S*) (%)[c]
I	—	1	72	0	100	99
	1a	1	63	19	81	98.5
	1b	1	74	12	88	98.5
	1c	1	72	0	100	99
II	**1b**	1	99	1	99	97.5
	1b	2	12	21	79	98
	1b	3	14	20	80	98.5
III	**1c**	1	100	0	100	99
	1c	2	98	1	99	99
	1c	3	94	1	98	98.5
	1c	4	52	2	98	98
	1c	5	22	24	76	98

[a] Solvent: abs. MeOH, [**2**] = 1.6 M, catalyst system: Ru^{II}–(*S*)-BINAP–HCl; PE, 100 mg, [**2**]:[Ru] = 200; 40 atm. (H_2), 40 °C, 2 h (series of runs I); 60 atm (H_2), 60 °C, 3 h (series of runs II and III). [b] NMR data. [c] GLC data.

It was found that the use of PE **1b** or **1c** did not reduce substrate **2** conversion compared with a control experiment performed under homogeneous conditions, whereas in the case of PE **1a** the conversion of **2** decreased by ~10% (Table 1, series I). The **4**:**3** product ratio depended on the PE anion nature increasing in the order: **1a** (81:19) < **1b** (88:12) < **1c** (> 99:1).

PEs **1b** and **1c**, which showed better results, were applied as carriers in the catalyst recycling experiments. We found that the use of recovered Ru^{II}–BINAP–**1b** catalyst system resulted in a decrease of the conversion of **2**; the enantioselectivity remained high even after three cycles (series II). The best results were obtained in experiments with PE **1c** having hexafluorophosphate anions (series III).[‡] The second and third hydrogenation cycles proceeded with an only slight decrease of the substrate conversion (by 2 and 6%, respectively). The activity of the catalyst deposited on PE **1c** noticably fell in the fourth reaction cycle; nevertheless, the enantioselectivity remained unchanged in at least five cycles. The length of the PE chain plays an important role. The use of shorter-chain PE **1d** with the same counter-ion (PF_6^-) led to a substantial decrease of the substrate conversion in the first hydrogenation cycle.

In each cycle, after the addition of MeOH to solid PE containing an adsorbed catalyst, the solvent grew yellow, the

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[†] Earlier,[13] the asymmetric hydrogenation of C=C and C=O bonds was studied in the presence of Rh- and Ru-containing recyclable heterogeneous systems consisting of PE in which both the ionic liquid and TMCC are incorporated.

colour typical of Ru^{II} bisphosphine dihalide complex solution.[16] Evidently, an equilibrium between adsorbed and desorbed catalysts was established in the reaction mixture, and both forms may be active in the hydrogenation reaction. The equilibrium shifted towards a supported catalyst upon MeOH removal (evaporation). No marked leaching of the catalyst deposited on PE **1c** was observed during product extraction with hexane.[‡]

We believe that the proposed approach to recycling organometal catalysts by using solid organic PE carriers may be used in other TMCC-catalysed reactions.

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[‡] *Asymmetric hydrogenation of* **2** *with the recycling of a Ru^{II}–BINAP catalyst.* Commercial (*S*)-BINAP (Fluka) and (COD)Ru(2-methylallyl)$_2$ (Acros) were used. Polymers **1a**–**c** were synthesised as described earlier;[15] PE **1d** was similarly prepared from poly(diallyldimethylammonium) chloride (Aldrich) (MM 100000–200000 Da) 20% aqueous solution by the anion exchange reaction. Methyl ester **2** was prepared from levulinic acid (Acros) according to a standard procedure. MeOH was dehydrated and distilled under argon before use. Ar was purified by passing through columns packed with a nickel–chromium catalyst, copper on Kieselguhr (80 °C), and molecular sieves (4 Å). H_2 was purified by passing through columns packed with a nickel–chromium catalyst and molecular sieves (4 Å). All manipulations with the catalyst, including its regeneration, were carried out under purified argon. The conversion of keto ester **2** and the composition of hydrogenation products were determined by ^{1}H NMR spectroscopy on a Bruker AM-300 instrument. Enantiomeric GLC analysis of lactone **4** was performed on a Biochrom-21 chromatograph, a quartz capillary column (30 m×0.25 mm×0.25 μm) coated with 2,6-dipentyl-3-trifluoroacetyl-β-cyclodextrine, He (1 ml min^{-1}), 130 °C. Retention times of the test components (min): CH_4 (unsorbed), 3.5; (*R*)-**4**, 12; (*S*)-**4**, 15.3.

PE **1c** (100 mg), (COD)Ru(2-methylallyl)$_2$ (4.8 mg, 0.015 mmol) and (*S*)-BINAP (9.4 mg, 0.15 mmol) were placed in a glass tube, which was evacuated and filled with argon three times; then, preliminary degassed solutions of methyl levulinate (490 mg, 3 mmol) in MeOH (2 ml) and 3 M HCl in anhydrous MeOH (50 μl, 0.15 mmol) were added. The tube was placed in a stainless-steel autoclave (50 ml) filled with argon; the autoclave was pressured with hydrogen up to 60 atm, and the reaction mixture was agitated with a magnetic stirrer at 60 °C for 3 h. Methanol was distilled off; the products were extracted with degassed hexane (3×5 ml), and combined extracts were passed through a 1 cm thick silica bed. The solvent was removed, and the products were analysed by NMR spectroscopy and GLC. The tube containing the catalyst deposited on PE was evacuated, filled with argon and used in subsequent hydrogenation experiments; 30 μl of 3 M methanolic HCl were added in each subsequent cycle.