RESEARCH NOTE

New Method to Recycle Homogeneous Catalysts from Monophasic Reaction Mixtures by Using an Ionic Liquid Exemplified for the Rh-Catalysed Hydroformylation of Methyl-3-pentenoate

Wilhelm Keim, Dieter Vogt, Horst Waffenschmidt, and Peter Wasserscheid[1]

Institut für Technische Chemie und Makromolekulare, Chemie der RWTH-Aachen, Templergraben 55, 52056 Aachen, Germany

In general, homogeneously catalysed reactions suffer from complicated and expensive catalyst separation from the product. Therefore, the technical application of homogeneous catalysis with an expensive metal complex is only reasonable if the catalyst loss is minimised or if its regeneration is feasible (1). In the case of homogeneous Rh-catalysed hydroformylation for example, several methods have been published to recover the catalyst after reaction using additional extractive methods with subsequent precipitation steps (2–4).

Alternatively, a biphasic reaction mode can be used for effective catalyst separation and recycling. In the case of Rh-catalysed hydroformylations this principle was technically realised in the Ruhrchemie–Rhône–Poulenc-process, where water is used as the catalyst phase (5–7). Unfortunately, the use of water as polar catalyst phase limits this process to C_2-C_5-olefins due to the low water solubility of higher olefins. As an alternative polar medium for biphasic hydroformylation, Chauvin *et al.* suggested novel solvents known as ionic liquids (8–11). These authors described in detail the biphasic hydroformylation of pentene-1 with $Rh(acac)(CO)_2$ in 1-Butyl-3-methylimidazolium hexafluorophosphat (BMIM PF_6) and 1-Butyl-3-methylimidazolium tertafluoroborat (BMIM BF_4) (12, 13).

In extension of Chauvin's work, we chose the Rh-catalysed hydroformylation of methyl-3-pentenoate (M3P) to demonstrate the great potential of ionic liquids as solvents for homogeneous catalysis even in cases where the reaction mixture is monophasic. The use of an ionic liquid solvent results in the almost complete retention of the regioselectivity which is influenced by the ligand and in significant enhancement of the catalyst's lifetime and overall productivity. The latter is achieved by a distillation process under reaction conditions. The immobilised catalyst is sta-

bilised by the ionic liquid under the thermal stress of the distillation. The catalyst can be reused several times without additional regeneration process and without loss in activity and selectivity. We consider the method described here as a very general way to recycle homogeneous catalysts from monophasic reaction mixtures.

Methyl-3-pentenoate is an interesting model feedstock for hydroformylation experiments: First, the reaction has some industrial relevance as part of a possible new reaction pathway to produce adipinic acid from butadiene (Fig. 1). Second, the reaction is a model for the technically interesting hydroformylation of fatty esters.

Obviously, the control of the reaction's selectivity towards the product carrying the new functionality in the end-position is highly desirable. Figure 2 shows all possible reaction pathways of the Rh-catalysed reaction of M3P with CO/H_2. The formation of the desired product, 5-FMP (Fig. 2), requires an isomerisation step followed by hydroformylation at the end-position (14).

We have been especially interested in the hydroformylation of M3P because this feedstock is an example of technically important olefins which do not form biphasic reaction mixtures with ionic liquids, e.g., BMIM PF_6.

All reactions were performed under argon using standard Schlenk techniques. Solids were dried under reduced pressure and liquids were distilled over appropriate desiccating agents prior to use (15). BMIM Cl (ELEMENTIS SPECIALITIES), PPh$_3$ (Sigma-Aldrich), and Rh(acac)(CO)$_2$ (Degussa) were used without further purification. All NMR-spectra were recorded with a Bruker DPX-300FT-spectrometer.

BMIM PF_6 was synthesised by reacting 1 mol BMIM Cl with 1.1 mol HPF$_6$ (60% aqueous solution, Sigma-Aldrich) in cold water, analogous to a method described by Carlin *et al.* (16). The formed BMIM PF_6 phase was separated and washed with water to neutrality. The ionic liquid was dried under reduced pressure at 60°C.

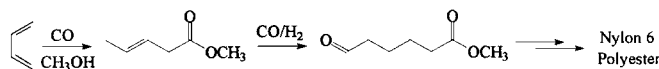[1] Fax: ++49241-8888177. E-mail: Wasserscheidp@itc.rwth-aachen.de.

FIG. 1. Alternative route to produce adipinic acid from butadiene.

BMIM PF$_6$ (Fig. 3) NMR data: ^{1}**H** (CDCl$_3$), $\delta = 8.3$ ppm (*s*, 1H, H$_a$), 7.2 ppm (*d*, $^3J_{cd} = 10$ Hz, 2H, H$_c$, H$_d$), 4.0 ppm (*t*, $^3J_{ef} = 7.4$ Hz, 2H, H$_e$), 3.8 ppm (*s*, 3H, H$_b$), 1.7 ppm (*m*, 2H, H$_f$), 1.2 ppm (*m*, 2H, H$_g$), 0.8 ppm (*t*, $^3J_{hg} = 7.4$ Hz, 3H, H$_h$); ^{13}**C** (CDCl$_3$), $\delta = 136$ ppm (Cl), 124–123 ppm (C3, C4), 50 ppm (C5), 32 ppm (C6), 19 ppm (C7), 13 ppm (C8) ppm; ^{31}**P** (CDCl$_3$), $\delta = 143$ ppm (septett, PF$_6^-$); ^{19}**F** (CDCl$_3$), $\delta = -72.5$ ppm (dublett, $J = 710$ Hz).

Ligand **1**, 2,2'-Bis{((2,2'-bis(4-methoxy-6-^{t}butyl)phenoxy)phosphino)-oxy}-1,1'-binaphtyl (Fig. 4) was synthesised by reacting binaphthol and 2,2'-bis(4-methoxy-6-^{t}butyl) phenyl-chlorophosphite, analogous to methods described by Takaya *et al.* and van Leeuwen *et al.* (17, 18). NMR data: ^{1}**H** (CDCl$_3$), $\delta = 7.8$–7.1 (4*m*, 12H, binaphthyl), 6.9–6.5 (4*d*, 8H, bisphenoxy), 3.75 (*s*, 6H, OCH$_3$), 3.8 (*s*, 6H, OCH$_3$), 1.1 (*s*, 18H, ^{t}butyl), 1.0 (*s*, 18H, ^{t}butyl) ppm; ^{31}**P** (CDCl$_3$), $\delta = 134.8$ (*s*, P(OR)$_3$) ppm.

Batch experiments were carried out in a stirred 75-ml steel autoclave equipped with a dropping funnel. The catalyst-precursor, the ligand, and the ionic liquid were stirred under syngas pressure for 1 h at reaction temperature to form the active catalyst species. The starting material was then added to the ionic catalyst solution by opening the dropping funnel. After the reaction, the organic compounds were distilled out of the autoclave at reaction temperature (usually 110°C) and under reduced pressure (<0.01 mbar). The products were collected in a cooling trap.

Recycling experiments were carried out in an apparatus as shown in Fig. 5. In a stirred 75-ml steel autoclave equipped with a dropping funnel, the catalyst-precursor, the ligand, and the ionic liquid were stirred under syngas pressure for 1 h at reaction temperature to form the active catalyst species. The starting material was added to the ionic catalyst solution by opening the dropping funnel. After the re-
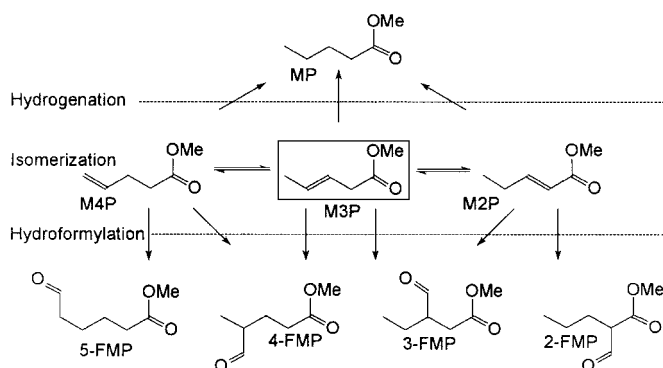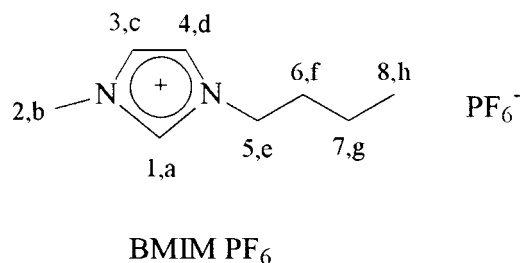

FIG. 3. 1-Butyl-3-methylimidazolium hexafluorophosphate.

action, the organic compounds (boiling point: M3P, 155°C; MP, 128°C; n-FMP, 190–210°C) were distilled out of the autoclave at reaction temperature (usually 110°C) and under reduced pressure (<0.01 mbar) and the products were collected in a cooling trap. The ionic catalyst solution remained in the hot autoclave during the distillation step. After complete distillation, new starting material was added and a new catalytic reaction was started.

The catalytic reaction products were analysed by GC on a Siemens Sichromat, with 50-m Pona HP column. The temperature programme was 5 min isotherm at 50°C and then 8°C min^{-1} up to 250°C. The He pressure was 1.5 bar. The selectivities in hydroformylation and hydrogenation products were obtained from these data using correction factors. The retention time of the products was determined by comparison with authentic samples. A complete mass balance of M3P and all detected products was calculated using dibutylether as internal standard to ensure the almost quantitative recovery of feedstock, product, or byproduct during the distillation step for complete GC analysis.

Batch experiments. Table 1 shows the influence of an ionic liquid solvent on the Rh-catalysed M3P-hydroformylation with different ligand systems. For better comparison, the experiments with toluene as solvent were carried out under identical conditions.
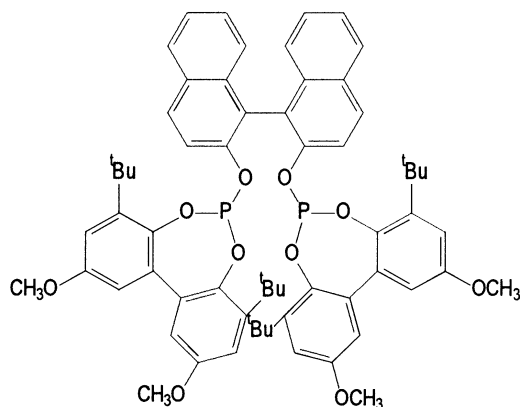

FIG. 2. Reaction pathways of methyl-3-pentenoate (M3P).

FIG. 4. Ligand **1**, 2,2'-Bis{((2,2'-bis(4-methoxy-6-^{t}butyl)phenoxy) phosphino)-oxy}-1,1'-binaphtyl.
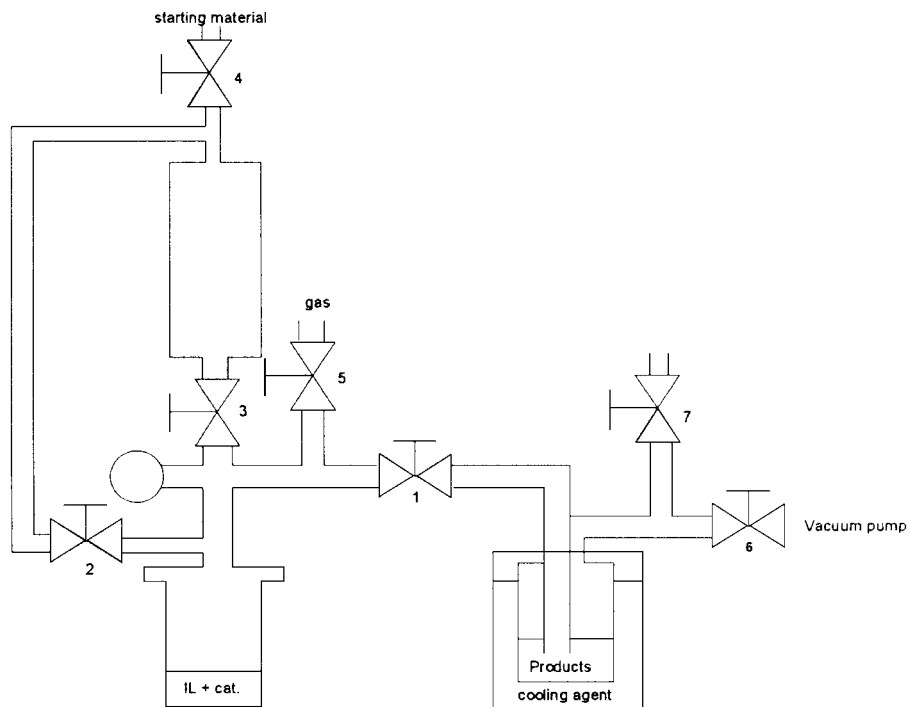
FIG. 5. Scheme of recycling process.

A comparison of the results shows that the ionic liquid solvent has a significant effect on the catalyst activity, when **1** is used as ligand. The regioselectivity of the reaction is ligand controlled and rather independent on the solvent used. In both cases, the reaction takes place in a monophasic system wherein the feedstock/products represents a certain part of the reaction medium.

Recycling experiments. The real advantage of working with an ionic liquids solvent in monophasic homogeneous catalysis comes from the ease with which effective product separation can be carried out and the possibility of catalyst recycling which results from the ionic liquid's nonvolatile nature (apparatus as described in Fig. 5).

Table 2 shows the results of the recycling experiments in the hydroformylation of M3P with $Rh(acac)(CO)_2$ and PPh$_3$ as ligand. For better comparison, the same procedure was carried out with methylenechloride, toluene, or BMIM PF$_6$ as solvent (Table 2).

Table 2 illustrates that the use of an organic solvent leads to a complete deactivation of the catalyst after the first distillative product separation. However, in the case of BMIM PF$_6$, the remaining ionic catalyst phase is still active after the product separation and can be successfully reused for catalysis.

Unfortunately, the catalyst activity decreases to almost zero after four cycles. Theoretically, two different possibilities leading to the deactivation during the repeated recycling procedures have to be taken into account: either the catalyst with PPh$_3$ is not thermally stable enough during the distillation procedure or the byproducts

TABLE 1

Activity and Regioselectivity in the Monophasic Hydroformylation of M3P Performed in Toluene or in BMIM PF$_6$

Entry	Solvent	Ligand	TOF^a (1/h)	MP^b (%)	S(2-FMP)^c (%)	S(3-FMP)^c (%)	S(4-FMP)^c (%)	S(5-FMP)^c (%)	n : i^d
1	Toluene	PPh$_3$	83	4	9	42	39	3	<0.1
2	Toluene	**1**	89	12	0	12	25	50	1.3
3	BMIM PF$_6$	PPh$_3$	107	7	7	37	38	10	0.1
4	BMIM PF$_6$	**1**	180	5	0	17	29	47	1.0

^{a} Turnover frequency (TOF) in mol of M3P converted per mol of Rh per hour: P/Rh, 4; p(CO/H$_2$), 10 bar; t, 3 h; T, 110°C; M3P/Rh, 3000.
^{b} Selectivity for methylpentanoate.
^{c} Selectivity for, respectively, 2-, 3-, 4-, and 5-Formyl-methylpentanoate.
^{d} Ratio of n-hydroformylated product to iso-hydroformylated products.

TABLE 2

Recycling-Experiments with Rh(acac)(CO)$_2$ and PPh$_3$

Reusing run	CH$_2$Cl$_2$ TOF (1/h)[a]/TON[b]	Toluene TOF (1/h)[a]/TON[b]	BMIMPF$_6$ TOF (1/h)[a]/TON[b]
0	56/280	170/850	169/845
1	0	0	108/540
2	0	0	58/290
3	0	0	24/120
4	0	0	5/25
$\sum$(TON)	280	850	1820

Note. P/Rh, 10; p(CO/H$_2$), 30 bar; t, 5 h; T, 110°C; M3P/Rh, 1300.
[a] Turnover frequency (TOF) in mol of M3P converted per mol of Rh per hour.
[b] Turnover number (TON) in mol of M3P converted per mol Rh over the complete reaction time.

with higher boiling points may deactivate the Rh-catalyst.

We looked for a thermally more stable ligand system and did the same recycling experiments with Rh(acac)(CO)$_2$ and ligand **1** as catalyst system. (See Table 3.)

The comparative examples with organic solvents still show a significant loss in catalyst activity during the first product distillation even with ligand system **1** and a complete loss after the third recycling run. However, in the case in which BMIM PF$_6$ is used as solvent, the higher thermal stability of ligand **1** is of great positive influence on the Rh-catalyst's lifetime during the recycle procedure.

Obviously, the presence of the ionic liquid is essential for the successful stabilisation of the Rh-catalyst under the thermal stress of the product distillation. A catalyst regeneration step is no longer necessary. A comparison of the overall turnover number of the catalyst system with organic

TABLE 3

Recycling Experiments with Rh(acac)(CO)$_2$ and Ligand **1**

Turn	CH$_2$Cl$_2$ TOF (1/h)[a]/TON[b]	Toluene TOF (1/h)[a]/TON[b]	BMIMPF$_6$ TOF (1/h)[a]/TON[b]
0	134/630	91/455	149/745
1	45/255	25/125	159/795
2	19/95	10/50	116/580
3	0	0	92/460
4	0	0	149/745
5	0	0	127/635
6	0	0	111/555
7	0	0	150/750
8	0	0	103/515
9	0	0	80/400
10	0	0	92/460
$\sum$(TON)	980	630	6640

Note. P/Rh, 4; p(CO/H$_2$), 30 bar; t, 5 h; T, 110°C; M3P/Rh, 1300.
[a] Turnover frequency (TOF) in mol of M3P converted per mol of Rh per hour.
[b] Turnover number (TON) in mol of M3P converted per mol Rh over the complete reaction time.

and ionic solvent demonstrates that this method greatly enhances the overall productivity of the catalyst.

Using a suitable ionic liquid solvent for the heterogenisation of homogeneous catalysts during distillative product separation seems to be an attractive and cheap method of very general applicability. Of course, for some reactions, an accumulation of high-boiling byproducts in the nonvolatile catalyst layer after several distillation cycles may become a problem. However, this can be circumvented by using a regeneration method by simple extraction after a certain number of recycling runs. BMIM PF$_6$ for example, forms biphasic systems with polar solvents (e.g., water) as well as with highly nonpolar solvents (e.g., hexane). After extracting the accumulated high-boiling byproduct with suitable solvents, it should be possible to rid the ionic liquid of the extraction solvent and reuse it again.

Generally, we think that the described method can greatly enhance the lifetime of a transition metal catalyst, both in batch and in continuous homogenous reactions. It can therefore significantly contribute towards clean catalytic chemistry.

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