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Co-immobilization of transition-metal complexes and ionic liquids in a polymeric support for liquid-phase hydrogenations

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Abstract—A new recyclable heterogeneous system is reported for reactions with a transition-metal catalyst in ionic liquid medium. It consists of a polymeric phase in which both the ionic liquid and the transition-metal catalyst are incorporated. The system is readily prepared by simple mixing of the components. In hydrogenations, the polymeric system always outperformed the 'classical' biphasic systems with ionic liquids and it could be re-used successfully without loss of activity. © 2003 Elsevier Science Ltd. All rights reserved.

1. Introduction

Transition-metal complexes (TMCs) are widely known to be active and selective catalysts in various homogeneous reactions[1,2]. However, their recycling and separation from the formed products often remains problematic. Numerous methods have been developed already to heterogenize the complexes for this purpose, but leaching of the complexes during reaction and lowered activities or selectivities are often troublesome.[2–4]

An increasingly popular and attractive way to achieve heterogenization is by dissolving the TMCs in an ionic liquid (IL) phase, which is then applied in biphasic catalysis[5–8]. In addition to the heterogenization, the IL sometimes even stabilizes the complex or acts as a modifier that accelerates the reaction and enhances the selectivity. On the other hand, IL-biphasic reactions can not simply be run continuously and activities are often lowered due to mass transfer limitations. Furthermore, in spite of the biphasic nature of the system, the product work-up might be complicated when numerous extractions steps are required to obtain reasonable product yields.

Supporting the IL on a solid-phase could solve these problems. Pd/C and Rh-complexes were thus already mixed with ILs and subsequently supported on poly(vinylidene fluoride)-based membranes[9]. They were used in gas-phase hydrogenations only, where their stability towards leaching could not be evaluated. Other types of ILs, functioning as Lewis acid catalysts, were immobilized by impregnation on inorganic supports[10] or charcoal[11] and applied in Friedel–Crafts liquid-phase alkylations and acylations, respectively.

We report here the preparation of a new type of supported IL-phase (SILP) for TMC-catalyzed reactions, made by simple mixing of the TMC and the IL with poly(diallyldimethylammonium chloride) (Fig. 1). The thus formed polymeric phase simultaneously heterogenizes the TMC and the IL. For two classical catalysts, this will be proven to form an active and selective leach-free system in liquid-phase hydrogenations.

2. Results and discussion

First, the leaching of both the IL (1-butyl-3-methylimidazolium hexafluorophosphate, bmimPF$_6$) and the

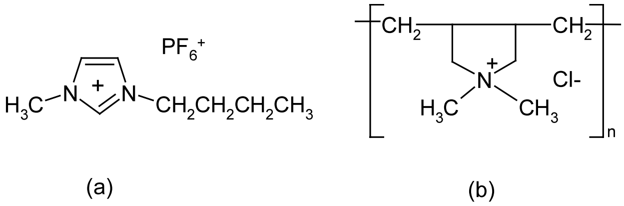

Figure 1. The 1-butyl-3-methylimidazolium hexafluorophosphate (bmimPF$_6$) IL (a) and the poly(diallyldimethylammonium chloride) support (b).

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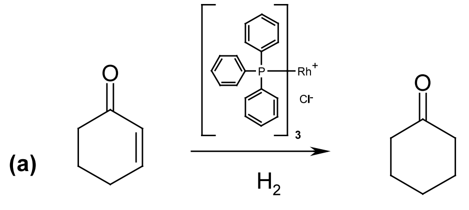
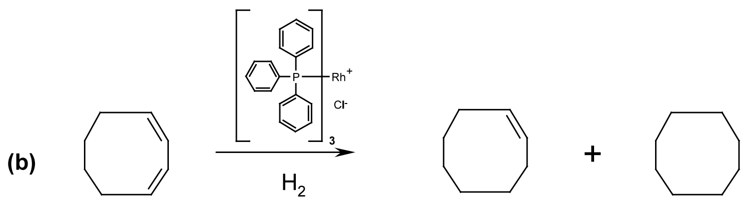
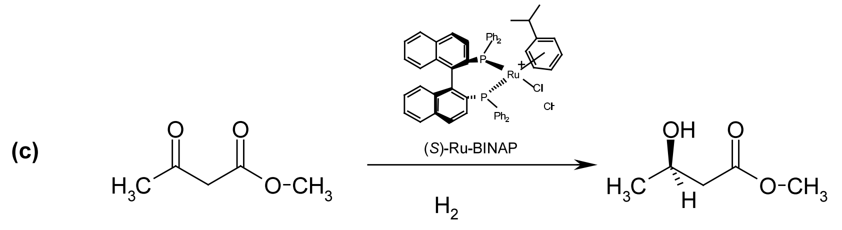


Hydrogenation of 2-cyclohexen-1-one



Hydrogenation of 1,3 cyclooctadiene



Asymmetric hydrogenation of methyl acetoacetate

Figure 2. Representative hydrogenation reactions.

TMC from the SILP was screened. It was found that the strong interactions between the IL-containing TMC-phase and the support prevented their leaching to the contacting solvent. Indeed, while solvents that dissolve the IL induced leaching from the SILP, leaching was absent in solvents that form a biphasic system with the IL. In general, every solvent that can be used in a biphasic IL-system can thus also be used with the SILP. The only exception is water, a solvent that would dissolve the polymer. In protic solvents that form two-phase systems with IL, the SILP was found to swell, but no IL-leaching was observed.

The hydrogenations of 2-cyclohexen-1-one and 1,3-cyclooctadiene (Fig. 2a and 2b, Tables 1 and 2) with Wilkinson's catalyst were tested under three different conditions: homogeneous, biphasic IL and SILP. The homogeneous hydrogenation of 2-cyclohexen-1-one (Table 1, entries 1 and 2) was successfully performed in dichloromethane and tetrahydrofuran (THF). Joo et al.[12] found that water could enhance the activity of Wilkinson's catalyst. Indeed, the reaction rate of the THF-system was doubled when water was added (entry 3). The presence of the polymer in solution did not influence catalytic performances (entry 4). As expected, performing reference reaction in biphasic IL-systems yielded substantially lower activities than the homogeneous reactions, but the TMC could now be re-used successfully (entries 5 and 6). The heterogeneous SILPs were tested in several solvents (entries 7–9). All activities were clearly higher than for the biphasic IL-systems and about as high as for the best water-free homogeneous reactions. Homogeneous reference reactions could not be done in diethyl ether, toluene and hexane due to the poor solubility of the complex in these solvents. In addition, as mentioned before, the solubility of the polymer in water prevented the use of water in the SILP-system. Moreover, attempts to prepare a leach-free heterogeneous polymeric system without the addition of IL failed.

Table 1. Homogeneous, biphasic and heterogeneous hydrogenations of 2-cyclohexen-1-one with Wilkinson's catalyst in different solvents[a]

Entry	Reaction	Solvent	TOF[b] (h^{-1}) (re-use)
1	Homogeneous	Dichloromethane	8
2		THF	3
3		THF+water[c]	15
4		THF+water +polymer[c,d]	15
5	Biphasic IL	Diethyl ether	2.7 (3.1)
6		Toluene	1.1 (0.9)
7	SILP	Diethyl ether	9.0 (9.3)
8		Toluene	7.0 (7.1)
9		Hexane	7.7 (7.9)

[a] *Reaction conditions*: 1 μmol complex, S/C=140, 5 bar H_2, 30°C, 3 h. Homogeneous: 2 mL solvent. Biphasic: 1 g bmimPF_6, 4 mL solvent. Heterogeneous: 0.2 g polymer, 1 g bmimPF_6, 4 mL solvent.

[b] TOF=turn-over frequency.

[c] 1 mL of each solvent.

[d] Addition of 0.2 g polymer.

Table 2. Homogeneous, biphasic and heterogeneous hydrogenations of 1,3-cyclooctadiene with Wilkinson's catalyst in different solvents[a]

Entry	Reaction	Solvent	TOF (h^{-1}) (re-use)	Selectivity[b]
1	Homogeneous	Dichloromethane	13	66
2	Biphasic	Diethyl ether	5.9 (6.2)	65
3	SILP	Diethyl ether	14.1 (14.6)	67
4		Hexane	15.0 (15.2)	64

[a] *Reaction conditions*: 1 μmol complex, S/C = 100, 5 bar H_2, 30°C, 35% conversion. Homogeneous: 2 mL solvent. Biphasic: 1 g bmimPF_6, 4 mL solvent. Heterogeneous: 0.2 g polymer, 1 g bmimPF_6, 4 mL solvent.

[b] Selectivity to cyclooctene.

The enhanced activity of the SILP-system compared to the biphasic IL-system, is believed to be due to improved mass transfer between the supported IL-phase and the substrate containing solvent phase. Upon re-use, activities of both the biphasic IL and the SILP-systems surprisingly increased slightly. The homogeneous reaction also showed such a somewhat increasing activity in time, but this phenomenon was not further studied. Atomic absorption spectroscopy was done on the extractant phases, but metal traces were never detected.

The reduction of 1,3-cyclooctadiene to cyclooctene and cyclooctane with Wilkinson's catalyst (Fig. 2b) under homogeneous, biphasic IL and SILP-conditions was also investigated (Table 2). At similar conversion levels, the selectivities were comparable for all systems. Here again, the traditional biphasic IL-system showed a lower activity than both the homogeneous and the SILP-catalyzed reaction, due to the quality of the mixing. The SILP-system was now even slightly faster than the homogenous reference reaction. Re-use of both recyclable systems showed again a slightly increased activity with unchanged selectivity.

In order to expand the application of the new heterogeneous system to other catalytic systems, the asymmetric reduction of methyl acetoacetate with Ru-BINAP was selected (Fig. 2c). It was previously found that the presence of high amounts of water decreased the enantioselectivity of homogeneous hydrogenations with Ru-BINAP, probably due to dissociation of the chloro ligand[13]. Hence, in the preparation of the Ru-BINAP/SILP-system, the aqueous polymer solution was first evaporated, followed by a re-dissolution of the crystalline polymer in methanol. Since the solvent also functions as proton donor in this type of reaction,[14] protic solvents are usually required. In the alcoholic solvents, formation of the corresponding acetals was observed throughout, explaining the lower selectivities in Table 3. Changing from methanol to isopropanol induced a lower activity, but a higher selectivity to methyl hydroxybutyrate at constant enantioselectivity (entries 1 and 2). The biphasic IL-system in isopropanol yielded lower activity and selectivity when compared to the isopropanol homogeneous reaction (entry 3). Again, the SILP-reaction in isopropanol showed higher activity (entry 4) than the biphasic IL-reaction, but the performances of the homogeneous reactions this time could not be reached. It is evident that mass transfer in the polymeric system becomes more critical for this fast reaction. A more profound characterization and optimization of the supporting polymeric phase could possibly solve this problem. Here as well, the SILP-system could be re-used without significant loss of activity, selectivity or enantioselectivity and no traces of complex were detected in the liquid phases.

3. Conclusion

The poly(diallyldimethylammonium chloride) based SILP provides an easy way to heterogenize both the IL and the TMC. This new, leach-free system was successfully tested and re-used in a selection of liquid-phase hydrogenations. It thus offers the potential to use ILs under continuous reaction conditions and to facilitate the separation of the products from the reaction liquid.

For all reactions studied, the activity of the SILP was higher than for the 'classical' biphasic IL-system, as ascribed to improved mass transfer between the IL-

Table 3. Homogeneous, biphasic and heterogeneous enantioselective hydrogenations of methyl acetoacetate with Ru-BINAP[a]

Entry	Reaction	Solvent	TOF (h^{-1}) (re-use)	Ee (%)	Selectivity[b]
1	Homogeneous	Methanol	103	99	85
2		Isopropanol	74	99	93
3		Methanol[c]	88	99	91
4	Biphasic	Isopropanol	16 (15)	97	83
5	SILP	Isopropanol	29 (29)	97	87

[a] *Reaction conditions*: 2 μmol complex, S/C = 140, 40 bar H_2, 60°C, 1 h. Homogeneous: 4 mL solvent. Biphasic: 1 g bmimPF_6, 4 mL solvent. Heterogeneous: 0.2 g polymer, 1 g bmimPF_6, 4 mL solvent.

[b] Selectivity to methyl hydroxybutyrate due to the formation of the corresponding acetal.

[c] Addition of 0.2 g polymer.

phase and the solvent. The selectivities equaled those of the homogeneous reference reactions. Whereas the recyclable system based on Ru-BINAP was slower than the homogeneous reference system, the Wilkinson-SILP showed activities that were comparable to those of the homogeneous reaction.

4. Experimental

4.1. Materials

Complexes, substrates and ionic liquid were purchased from Fluka. Solvents were obtained from Across. An aqueous 20 wt% solution of poly(diallyldimethylammonium chloride) (average molecular weight 200,000–350,000 Da) was purchased from Aldrich.

4.2. General procedures

The homogeneous, the biphasic and the SILP-reactions were done in 10 mL stainless steel pressure reactors with magnetic stirring.

In the IL-biphasic reactions, the TMC was added to the bmimPF_6-phase before addition of the reactant mixture.

The SILP-systems were prepared as follows. The TMC was dissolved in 1 g of bmimPF_6 and then mixed with 1 g of a 20 wt% aqueous or methanolic polymer solution. This solution was dried by means of a nitrogen flow at 80°C. The air sensitive Ru-BINAP complex was handled under nitrogen atmosphere. After the first run, all reactants were extracted from the IL-phase by adding 3×4 mL of the organic solvent. The catalyst was re-used by adding a fresh substrate solution to the SILP.

4.3. Reactions with Wilkinson's catalyst

For the reduction of 2-cyclohexenone with Wilkinson's catalyst, 1 μmol of complex was used with 13.4 mg of substrate and 4 mL of solvent at a hydrogen pressure of 5 bar. Before heating to 30°C, nitrogen was used to flush the air from the reactor, followed by flushing with hydrogen.

The reduction of 1,3-cyclooctadiene with Wilkinson's catalyst was performed under the same conditions.

Samples were taken after 3 h for the reduction of 2-cyclohexenone, while samples were withdrawn as a function of time for the reduction of 1,3-cyclooctadiene in order to compare the performances at similar conversion levels. Both, conversion and selectivity were determined via GC-analysis with a capillary column, type CP-Wax-58 CB, after extraction of substrate and product from the IL-phase. Atomic absorption spectroscopy was done on the collected extractant phases, but metal traces were never detected.

4.4. Reactions with Ru-BINAP

For the enantioselective hydrogenation of methyl acetoacetate with Ru-BINAP, 2 μmol of complex was used with 32.5 mg of substrate and 4 mL of solvent at 40 bar hydrogen pressure at a temperature of 60°C.

Conversion, selectivity and enantioselectivity were determined via GC-analysis with a chiral column, Chiraldex G-TA, after extraction of substrate and product from the IL-phase. Atomic absorption spectroscopy was done on the collected extractant phases, but metal traces were never detected.

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