

Supported Ionic Liquid Catalysis – A New Concept for Homogeneous Hydroformylation Catalysis

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Homogeneous hydroformylation catalysis is one of the largest volume processes in the chemical industry with a worldwide oxo-aldehyde production of 7.8×10^6 t/a (1997).¹ Although the catalysis is well established, catalyst separation still remains a big challenge and continues to be the focus of intense research. Over the last three decades, several elegant approaches have been explored to overcome these limitations, for example, aqueous and fluororous biphasic catalysis,^{2a–c} reactions in supercritical media,^{2d} and catalyst immobilization onto solid supports.^{2e–g}

More recently, ionic liquids have attracted significant attention as an alternative reaction medium for homogeneous catalysis.³ On the basis of their highly charged nature, ionic liquids are well suited for biphasic reactions with organic substrates. In this respect, Chauvin et al.^{4a} utilized water-soluble phosphine ligands [tri(*m*-sulfonyl)triphenylphosphine trisodium salt (tppts)] to retain active rhodium complexes in ionic liquid phases and used them successfully in biphasic hydroformylation reactions. Following this novel approach, a variety of metal complexes have been recently investigated for hydroformylation catalysis in ionic liquid media.^{4b–h}

Although the ability of biphasic hydroformylation catalysis in ionic liquid media has successfully been demonstrated, the chemical industry still prefers heterogeneous catalyst systems. Because of the ease of separation and the possibility to use a fixed-bed reactor, a solid catalyst is highly advantageous for the production of aldehyde. Furthermore, the use of a biphasic reaction system requires a large amount of ionic liquid. On the basis of economic criteria and possible toxicological concerns, it is desirable to minimize the amount of utilized ionic liquid in a potential process. Inspired by the early work of Davis et al.^{2b} on the support of aqueous catalyst systems, we became interested in the immobilization of ionic liquid phases onto solid supports.⁵ Herein, we report a new concept for the immobilization of homogeneous catalyst systems and our initial findings for hydroformylation reactions.

The new concept of supported ionic liquid catalysis (silc) (Figure 1) involves the surface of a support material that is modified with a monolayer of covalently attached ionic liquid fragments. Treatment of this surface with additional ionic liquid results in the formation of a multiple layer of free ionic liquid on the support. These layers serve as the reaction phase in which the homogeneous catalyst is dissolved. Although the resulting material is a solid, the active species is dissolved in the ionic liquid phase and performs as a homogeneous catalyst.

In the preparation of a surface modified silica gel with a covalently anchored ionic liquid fragment (Scheme 1), the complex

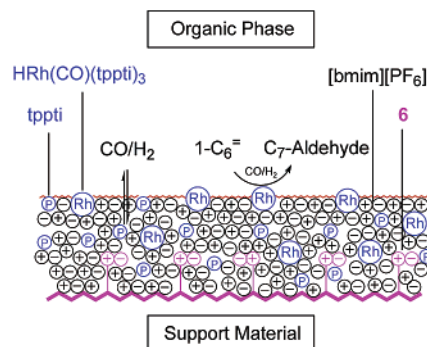
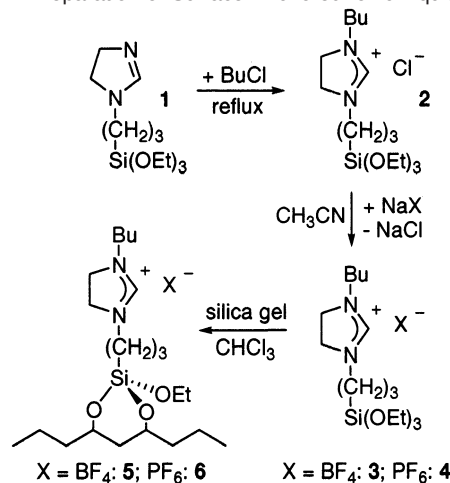


Figure 1. Supported ionic liquid catalysis used in the hydroformylation reaction of 1-hexene to form *n*,*i*-heptanal. The ionic liquid phase [bmim][PF₆] containing the active catalyst HRh(CO)(tppti)₃ and excess of the free ligand (tppti) is immobilized on the surface of the modified support materials 6.

Scheme 1. Preparation of Surface Anchored Ionic Liquid Phases



N-3-(3-triethoxysilylpropyl)-4,5-dihydroimidazol-1-ium chloride **1** was reacted with 1-chlorobutane to give the complex 1-butyl-3-(3-triethoxysilylpropyl)-4,5-dihydroimidazolium chloride **2**. The resulting compound was further treated with either sodium tetrafluoroborate or sodium hexafluorophosphate in acetonitrile to form the corresponding derivatives **3** and **4**. In the immobilization step, pretreated silica gel was refluxed with a chloroform solution of complex **3** and **4** to undergo a condensation reaction giving the modified support materials **5** and **6**, respectively. Analysis of the surface coverage revealed an average of 0.4 ionic liquid fragments per nm², which corresponds to approximately 35% of all the hydroxyl groups based on a hydroxyl content of 2.4 per nm² for the pretreated silica gel.

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Table 1. Evaluation of the Hydroformylation Reaction of 1-Hexene To Form *n,i*-Heptanal Using Supported Ionic Liquid Catalysis, Biphasic Catalysis, and Homogeneous Catalysis

entry	condition ^a / ligand	solvent	time, min	yield, %	<i>n/i</i>	tof, ^b min ⁻¹
1	silc/tppti	[bmim][BF ₄]	300	33	2.4	65
2	silc/tppts	[bmim][BF ₄]	240	40	2.4	56
3	silc/tppti	[bmim][PF ₆]	270	46	2.4	60
4	silc/no ligand	[bmim][PF ₆]	180	85	0.4	190
5	biphasic/tppti	[bmim][BF ₄]	230	58	2.2	23
6	biphasic/tppti	[bmim][PF ₆]	180	70	2.5	22
7	biphasic/tppts	H ₂ O	360	11	23	2.4
8	homog/PPh ₃	toluene	120	95	2.6	400

^a Reaction conditions: All runs were conducted at 100 °C with a Rh/P ratio of 1:10, silc runs were evaluated in a 70 mL autoclave at 1500 psi, and biphasic and homogeneous catalyst systems were evaluated in a 300 mL autoclave at 600 psi. ^b tof defined as mol(aldehyde) per mol(rhodium) per min (full reaction time).

In the next step of the catalyst preparation, an acetonitrile solution of the precursor, dicarbonylacetylacetonate rhodium, was treated with either the ligand tri(*m*-sulfonyl)triphenyl phosphine trisodium salt (tppts) or the ligand tri(*m*-sulfonyl)triphenyl phosphine tris(1-butyl-3-methyl-imidazolium) salt (tppti) (Rh/P ratio of 1:10). The ligand tppti dissolved in both ionic media, [bmim][BF₄] and [bmim][PF₆], while the ligand tppts only exhibited solubility in [bmim][BF₄].⁶ The resulting acetonitrile solutions were combined with the ionic liquid phases⁷ (25 wt % loading) and added to the corresponding support materials 5 and 6. After the solvent was removed under reduced pressure, a slightly yellow-colored, free-flowing powder was obtained.

In our catalyst investigation, the substrate 1-hexene was reacted with syngas (CO/H₂ ratio of 1:1) to produce *n,i*-heptanal (Table 1). The comparison study between the supported ionic liquid catalyst and the biphasic ionic liquid reaction showed that the supported system exhibited a slightly enhanced activity with comparable selectivity (*n/i* ratio). The supported system containing the ionic liquid [bmim][BF₄] (entry 1) produced *n,i*-heptanal with a tof of 65 min⁻¹, while the biphasic ionic liquid system (entry 5) showed a value of 23 min⁻¹. This improved activity might be attributed to a higher concentration of the active rhodium species at the interface and the generally larger interface area of the solid support in comparison to the biphasic system. If the reaction was carried out without a ligand (entry 4), the rhodium precursor leaches from the ionic liquid layer and forms an active hydroformylation species in the organic phase which is responsible for the conversion of the olefin. For further comparison, we also evaluated the aqueous biphasic reaction (entry 7) and the conventional homogeneous catalyst in toluene (entry 8). As expected, the aqueous system was significantly less active due to the low solubility of 1-hexene in the water phase. With respect to the homogeneous catalyst system, a tof of 400 min⁻¹ was recorded. Although the homogeneous system is clearly favored due to its high activity, the supported ionic liquid system is attractive on the basis of its convenient product separation.

Both the supported and the biphasic ionic liquid systems exhibit similar metal leaching behavior. On the basis of the comparable aldehyde concentration in the reactor (~60 wt %), the ionic liquid [bmim][BF₄] and [bmim][PF₆] exhibited a rhodium metal loss (metal concentration in the reactor *c*(Rh) = 100 μmol) of 2.10 μmol and 0.07 μmol, respectively. Although the active rhodium species,

[HRh(CO)(tppts)₃] and [HRh(CO)(tppti)₃], are insoluble in the organic medium, the ionic liquid [bmim][BF₄] partially dissolved in the organic phase at high aldehyde concentrations and facilitated the leaching of the rhodium complex. In addition, high aldehyde concentrations resulted in the depletion of the supported ionic liquid layer and shortened the catalyst lifetime. To reduce the metal loss and the depletion of the ionic liquid layer to an acceptable level, the aldehyde concentration was usually kept below 50 wt % in the reaction mixtures. In addition, the loss of rhodium complex can be even further suppressed through an increase of the phosphine ligand concentration.

Supported ionic liquid catalysis combines the advantages of ionic liquid media with solid support materials which enables the application of fixed-bed technology and the usage of significantly reduced amounts of the ionic liquid. In summary, the concept of supported ionic liquid catalysis has successfully been used for hydroformylation reactions and can be further expanded into other catalysis areas.

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Supporting Information Available: Experimental details and analysis data (PDF). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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- (6) On the basis of high-pressure ³¹P NMR investigation under elevated reaction conditions (up to 2000 psi CO/H₂ and 150 °C), neither free nor coordinated tppts ligand was observed in the ionic liquid [bmim][PF₆]. To increase solubility of the ligand tppts, the sodium cation was exchanged with 1-butyl-3-methyl-imidazolium chloride to form tppti.
- (7) Small-angle X-ray scattering (SAXS) investigations of supported ionic liquid phases (loading 25 wt %) on defined silica spheres with a diameter of 0.1 μm and a surface area of 30 m²/g showed a layer thickness of 80 Å. Accordingly, an average ionic liquid layer thickness of 6 Å can be approximated for silica gel with a surface area of 400 m²/g.

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