DOI: 10.1002/chem.200900763

# Thermoregulated Microemulsions by Cyclodextrin Sequestration: A New Approach to Efficient Catalyst Recovery

**Loïc Leclercq, Matthieu Lacour, Samantha H. Sanon, and Andreea R. Schmitzer*[a]**

The separation of homogeneous hydroformylation catalysts from reaction mixtures has been a tremendous challenge and continues to be the focus of intense research.[1] Over the last three decades, several elegant approaches have been explored to overcome this limitation including aqueous[2] and fluorous biphasic catalysis,[3] reactions in supercritical media[4] and catalyst immobilization onto solid-support materials.[5] Although some of these novel concepts have successfully been developed into commercial processes, such as the Ruhr Chemie Rhône Poulenc process used in the production of butyraldehyde,[2] catalyst recovery continues to be one of the key issues of homogeneous catalysis. More recently, imidazolium ionic liquids have been used as alternative reaction media for homogeneous catalysis.[6] Based on their highly charged nature, ionic liquids are well suited for biphasic reactions with organic substrates. While the first hydroformylation reaction in an ionic liquid (at that time referred to as a molten salt) was performed by Parshall[7] as early as 1972, it was not until 1995 that Chauvin et al.[8] used water-soluble phosphine ligands such as the tri(*m*-sulfonyl)triphenyl phosphine sodium salt (TPPTS)[9] to retain active rhodium complexes in the ionic-liquid phases and used them successfully in biphasic hydroformylation catalysis. Since then, a variety of different metal complexes have been investigated for liquid–liquid biphasic hydroformylation reactions in ionic liquid media.[10] Alkylmethylimidazolium salts have also been applied as additives for the aqueous-biphasic hydroformylation of higher linear olefins. Cole-Hamilton et al. described the use of 1-octyl-3-methylimidazolium bromide for classical aqueous biphasic hydroformylation with good reaction rates and catalytic activity.[11] The influence of surfactants and micelle forming agents on the rate of the hydroformylation reaction may arise from two sources. Due to the decreased surface tension at the boundary of the aqueous and organic phases a larger interphase area is produced which facilitates mass transport. Perhaps more important is the effect which can be linked to the appearance of micelles. Water-insoluble olefins show increased concentration in the aqueous phase in the presence of surfactants above the critical micelle forming concentration (CMC). The solubilized olefin is preferentially located in the hydrophobic region of micelles and if the catalyst can also be concentrated into that region then a very efficient catalytic reaction can occur. In such micro-heterogeneous systems metal-complex catalysis and micellar catalysis jointly contribute to fast hydroformylation. However, in order to achieve high conversions and good selectivities, fine-tuning is required between the size and the charge of the micelle and those of the catalyst and substrate molecules.[12] The surfactant should be able to produce a sufficiently large interfacial area to promote mass transfer. Despite all advantages brought by micellar catalysis, the presence of surfactants complicates the phase separation and in some cases a kinetically stable emulsion is obtained instead of a biphasic system, after cooling down the reaction mixture. The emulsification must be reversible so that the products can be separated by phase separation. Another advantage in using dialkylimidazolium salts as surfactants in the hydroformylation reaction is the possibility to vary their physico-chemical properties by changing the alkyl groups and/or the anion.

It is well known that cyclodextrins (CDs) can form inclusion complexes with various hydrophobic residues such as linear alkyls, aromatics.[13] Upon addition of CD to a surfactant solution, a considerable change in the physicochemical properties can be observed, that is, the surface tension of the surfactant changes.[14] The CD's presence results in the dissociation of the micelle to form inclusion complexes[15] and thus controllable self-aggregating systems can be obtained (Figure 1). We report here the winning combination of imidazolium surfactants with CDs as a control element in the thermoregulated olefin hydroformylation.

[a] Dr. L. Leclercq, M. Lacour, S. H. Sanon, Prof. Dr. A. R. Schmitzer
Department of Chemistry, Université de Montréal
C.P. 6128 Succursale Centre-ville
Montréal, Québec, H3C 3J7 (Canada)
Fax: (+1) 514-343-7586
E-mail: ar.schmitzer@umontreal.ca

Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/chem.200900763.

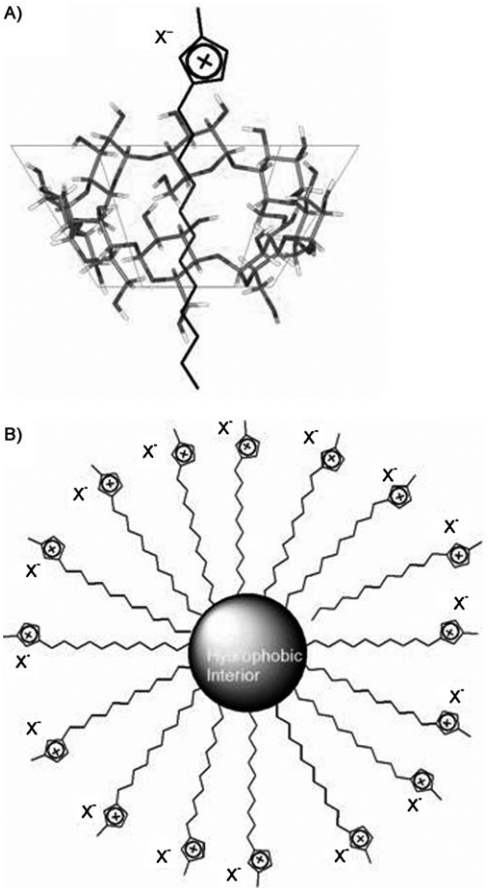
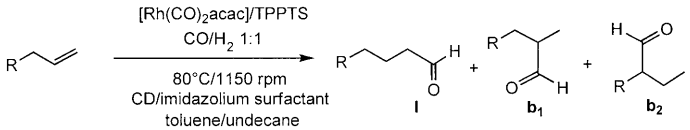


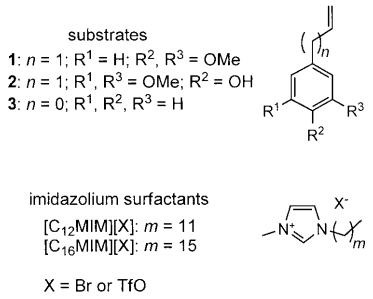

Figure 1. Representation of the imidazolium surfactant/α-CD organization. A) The majority inclusion complex at room temperature; B) at high temperature the majority self organization is the micellar aggregation.

We used the 1-alkyl-3-methylimidazolium salts (in which 1-alkyl represents the 1-dodecyl and the 1-decahexyl residues, called [$C_{12}$MIM] and [$C_{16}$MIM], respectively) as surfactants for the rhodium-catalyzed hydroformylation reaction of water insoluble olefins. In this process, the CD can form inclusion complexes with the alkyl residue of the imidazolium surfactant at room temperature. However, during the reaction (at 80 °C) only micelles of 1-alkyl-3-methylimidazolium salts are present in the bulk reaction. The use of the CD/imidazolium surfactant combination in this reaction results in good activity, an increase of the regioselectivity and an important reduction of the decantation time (Scheme 1). Our choice of CD was dictated by the nature of the imidazolium salt and the substrate's nature. The imidazolium salt can be complexed by the CD with the inclusion of the alkyl chain into its hydrophobic cavity. In our case, α-CD is a good choice because the cavity can accommodate the alkyl chain more easily than native aromatic groups and far more than *ortho*- and *meta*-substituted aromatics.[13]




Scheme 1. Biphasic aqueous hydroformylation reaction performed in the presence of Rh/TPPTS and a combination of CD/imidazolium surfactant.

The substrates used are allyl-substituted aromatics and styrene as a native aromatic olefin. The bromide and the triflate anions were used in combination with [$C_{12}$MIM] and [$C_{16}$MIM] (Scheme 2).




Scheme 2. Biphasic substrates and imidazolium surfactants used in the aqueous hydroformylation reaction.

As mentioned by many authors, the purity of imidazolium salts is essential for a catalytic process in order to avoid undesirable modifications of the active species.[16] Thus, we have used imidazolium salts with high purity, which we prepared according to a reported procedure.[17] Before each analysis, the imidazolium surfactant was dehydrated by water extraction under vacuum.[18]

In a first time, we have determined the critical micellar concentration (CMC) values for each imidazolium surfactant used in this work with and without α-CD (Table S1, see Supporting Information). The CMC at 25 °C found for [$C_{12}$MIM][Br] is in agreement with the data reported by Inoue et al.[19] The CMC values decrease for the same anion with longer alkyl chain, which reflects the influence of the hydrophobic character of the alkyl chain to the self-assembly process. It is also important to note that the counterion has a great influence on the CMC: for example, in the case of [$C_{12}$MIM] a decrease from 8.4 mM for the bromide to 2.1 mM for the triflate salts can be observed. For higher α-CD concentration the CMC increases from 8.4 to 9.9 mM (Table S1, entry 2, Supporting Information), as previously reported.[20] For the other imidazolium surfactants, the CMC values increase in the presence of α-CD (Table S1, entries 3 and 4, Supporting Information).[14,15] The CMC value for [$C_{12}$MIM][Br] at 60 °C is 2.5 mM, which demonstrates that the temperature increase favors the micelle formation. At this temperature, the addition of **α-CD** has no consequence on the CMC value, which suggests that at 60 °C no inclusion complexes are formed (Table S1).

The results described above were used to set the parameters of the catalytic hydroformylation. For each reaction, the concentration of imidazolium surfactant was fixed at 8 mM and the α-CD concentration was fixed at 5 mM, except for [$C_{12}$MIM][Br], where two concentrations were used: 5 and 25 mM (Table 1).

Table 1. Conversion (C; %), Selectivity (S; %), linear/branched ratio (l/b) for the hydroformylation of various substrates in the presence of imidazolium surfactants with or without α-CD additives[a].

| Entry | Substrate | Surfactant | α-CD[a] | C[b] | S[c] | l/b[d] | |
|---|---|---|---|---|---|---|---|
| 1 | **1** | – | – | 3 | | 30 | 3.1 |
| 2 | **1** | – | + | 10 | | 49 | 3.6 |
| 3 | **1** | $[C_{12}MIM][Br]$ | – | 78 | | 86 | 4.0 |
| 4 | **1** | $[C_{12}MIM][Br]$ | + | 87 | | 80 | 3.9 |
| 5 | **1** | $[C_{12}MIM][Br]$ | +[e] | 41 | | 87 | 4.6 |
| 6 | **1** | $[C_{16}MIM][Br]$ | + | 100 | | 96 | 5.2 |
| 7 | **2** | – | – | 74 | | 49 | 3.3 |
| 8 | **2** | – | +[e] | 25 | | 89 | 4.9 |
| 9 | **2** | $[C_{12}MIM][Br]$ | – | 51 | | 79 | 1.4 |
| 10 | **2** | $[C_{12}MIM][Br]$ | +[e] | 73 | | 85 | 2.0 |
| 11 | **2** | $[C_{16}MIM][Br]$ | +[e] | 47 | | 91 | 2.3 |
| 12 | **3** | – | – | 21 | | 87 | 0.3 |
| 13 | **3** | – | +[e] | 38 | | 93 | 0.3 |
| 14 | **3** | $[C_{12}MIM][Br]$ | – | 99 | | 94 | 0.3 |
| 15 | **3** | $[C_{12}MIM][Br]$ | +[e] | 69 | | 94 | 2.1 |
| 16 | **3** | $[C_{16}MIM][Br]$ | +[e] | 100 | | 89 | 0.2 |

[a] $[Rh(acac)(CO)_2]$ (3.5 mM), TPPTS (18 mM), $H_2O$ (11.5 mL), substrate (2.91 mmol), α-CD (5 mM, except for [e]), imidazolium surfactant (8 mM), *n*-undecane (4 mmol, GC internal standard), 1150 rpm, $T=80\,°C$, $CO/H_2$ 1:1: 50 atm. [b] Conversion calculated with respect to the starting olefin. [c] S: % of the converted olefins. The side product was mainly internal olefins. [d] l/b: linear/branched ratio (GC). [e] α-CD (25 mM). In all cases the b1/b2 ratio was smaller than 1. All reported values were the mean of at least three runs. The standard deviation of the mean never deviated ±1.5 %. For the calculation methods see the Supporting Information.

As a control experiment, we performed the hydroformylation of each substrate in the presence of $[Rh(CO)_2(acac)]$/TPPTS without imidazolium surfactant and without α-CD (Table 1). A second control experiment was realized in the presence of imidazolium surfactant without the α-CD. For **1**, the two control experiments gave similar results: 3 and 10% conversion and an l/b ratio of 3.1 and 3.6, respectively (entries 1 and 2). The weak conversion increase in the presence of α-CD is probably due to the formation of a weak inclusion complex between the α-CD and **1**. This observation is also corroborated by the increase of the l/b ratio. In both control experiments the selectivities are in the same range (about 40%) due, generally, to the formation of the hydrogenated products. The use of $[C_{12}MIM][Br]$ without α-CD gives higher conversion (78%) and enhances greatly the selectivity of the reaction (86%), as well the l/b ratio (4.0), due to the constraint of the rhodium catalyst at the micelle's interface (i.e., anion exchange between the TPPTS ligand and the bromide; $\Delta H=-36\,kcal\,mol^{-1}$ for PM3 calculation of the anionic metathesis see Supporting Information).[21] The decrease of the conversion in the presence of α-CD may be due to the partial complexation of the imidazolium surfactant by α-CD which results in a decrease of the number of micelle ($\Delta H=-45\,kcal\,mol^{-1}$ for 2:1 complex between $[C_{12}MIM][Br]$/α-CD, see Table S2, Supporting Information).[21] The selectivity and the l/b ratio is the same with or without α-CD. If the α-CD concentration is increased, the conversion and the selectivity are in the same range, but the l/b ratio increase to 4.6 (Table 1, entry 5). We believe that this can be attributed to a α-CD effect, that is, the modification of the micelle's environment due to the rhodium sequestration by the imidazolium charge and the partial inclusion of the olefin in the CD's cavity ($\Delta H=-15\,kcal\,mol^{-1}$ for the complex **1**/α-CD).[21] The modification of the bromide anion give similar conversions and selectivities, but the l/b ratio decrease up to 2.7 in the case of the triflate anion (see Supporting Information). This is due to a lack of exchange between the TPPTS ligand and the triflate compared with the bromide salt. The use of $[C_{16}MIM][Br]$ with or without α-CD gives a quantitative conversion of **1** with very high selectivities. Moreover, a high regioselectivity is obtained with the couple **α**-CD/$[C_{16}MIM][Br]$ surfactant and the l/b ratio enhances from 4.6 to 5.2.

For substrate **2**, the control experiment without imidazolium surfactant or CD, gives a better conversion, due to the more hydrophilic character of this olefin (entry 7). The selectivity is not high (49%) and the l/b ratio is in the same range as **1** (entries 7 and 1). In the presence of α-CD, the conversion decreases strongly to 25% but the selectivity, as well as the l/b ratio, increase (entries 8 and 9). We believe that in the presence of α-CD, the formation of inclusion complexes occurs by complexation of the allyl side chain in the hydrophobic cavity. The encapsulation of the olefin inhibits the hydroformylation reaction. In the presence of $[C_{12}MIM][Br]$ the conversion increases to 51%, the selectivity is good, but the l/b ratio decreases to 1.4 (entry 9). The combination of $[C_{12}MIM][Br]$ and α-CD gives a better conversion (73%) and a good selectivity (85%; entry 10), but the l/b ratio is smaller (2.0). The higher l/b ratio is obtained for this substrate by using $[C_{12}MIM][Br]$ and α-CD, even if the conversion is smaller (entry 15).

For substrate **3**, the use of $[C_{12}MIM][Br]$ increases the reaction selectivity, but the combination of α-CD/$[C_{12}MIM][Br]$ results in the decrease of the conversion due to the competition between the incorporation of the substrate into the micelle and its complexation by the CD (entries 13–15). Previously, Monflier et al. have described the biphasic hydroformylation of styrene by a per(2,6-di-*O*-methyl)-α-CD as mass transfer promoter, where the reaction rates were good (100% conversion after 2 h vs. 65% without CD).[22] In our study the enhancement of the reaction rate is due to micelle formation and styrene transfer, as in the case of the use of CD. However, when $[C_{16}MIM][Br]$ is used in combination with the α-CD, a complete conversion of the olefin is obtained but the l/b ratio is still low. The reaction may take place in the case of the styrene, both at the micelle interface and in the CD's cavity.

To summarize the catalytic process, the imidazolium surfactants can exchange their bromides by the TPPTS sulfonates. This exchange creates a high rhodium micro-concentration in direct micelle proximity.[23] The aldehydes selectivities observed in the reaction are lower than in the case of the previous use of the cyclodextrins as mass promoter. When the olefin is inside the hydrophobic interior of the micelle, the formation of the isomerization species leading to internal olefins by β-hydride elimination is less prohibited by the steric hindrance, as in the case of CDs.[24] This obser-

vation leaves us to suppose that the inclusion complex formed by the CD and the substrate is present during the reaction only in a very low amount. The substrate is transferred in the aqueous media into the micelle. For substrates **1** and **3** a competition may occur between the micelle self-assembly and the substrate complexation into the α-CD. As a general observation we can underline that the combination of imidazolium surfactant and CD provides an increased l/b ratio, compared to the case where only imidazolium salts were used. This fact can be seen as a synergistic participation of the inclusion complex and the micellar catalysis; even a weak complexation of the substrate inside the α-CD's cavity provides a different reaction environment (as in the case of styrene).

The most important parameter of this biphasic system has not been discussed until now: the decantation process. The emulsion type and time of phase separation are reported in Table 2 for each catalytic system.

Table 2. Effect of α-CD (5 mM, except for [a]) on the time for phase separation after hydroformylation of various substrates in the presence of imidazolium surfactants.

| Entry | Substrate | Surfactant | α-CD | Type[b] | Phase sep. [h][c] |
|---|---|---|---|---|---|
| 1 | **1** | $[C_{12}MIM][Br]$ | – | o/w | 15 |
| 2 | **1** | $[C_{12}MIM][Br]$ | + | o/w | 2 |
| 3 | **1** | $[C_{12}MIM][Br]$ | +[a] | o/w | 1 |
| 4 | **1** | $[C_{12}MIM][TfO]$ | – | w/o | 6 |
| 5 | **1** | $[C_{12}MIM][TfO]$ | + | w/o | 3 |
| 6 | **1** | $[C_{16}MIM][Br]$ | – | w/o | 28 |
| 7 | **1** | $[C_{16}MIM][Br]$ | + | w/o | 16 |
| 8 | **2** | $[C_{12}MIM][Br]$ | – | o/w | 3 |
| 9 | **2** | $[C_{12}MIM][Br]$ | +[a] | o/w | 2 |
| 10 | **3** | $[C_{12}MIM][Br]$ | – | o/w | 3 |
| 11 | **3** | $[C_{12}MIM][Br]$ | +[a] | o/w | 2 |

[a] α-CD (25 mM). [b] Emulsion type: w/o water in oil, o/w oil in water.

A drastic decrease of the decantation time is observed when the α-CD is present in the bulk solution. The best results in terms of emulsion break process are obtained when the reaction is performed in the presence of $[C_{12}MIM][Br]$: α-CD in a 1:2 stoichiometry (entry 3). The decantation process of $[C_{16}MIM][Br]$ is presented in Figure 2 as an example. It is obvious that from the beginning the decantation process is faster in the presence of the α-CD. This rapid break of the aqueous phase emulsion, containing the rhodium catalyst and the imidazolium salt allows facile separation of the catalyst and its reuse. The same aqueous phase was submitted to several rounds of catalytic reactions, without modification of the conversion or the selectivity (the recycling of the aqueous phase for **1** is presented in Table 3).

In conclusion, we have demonstrated that imidazolium surfactants can be used as "micellar promoters" in hydroformylation reactions. Furthermore, the combination of these surfactants with α-CDs underpins a novel and efficient separation strategy. The modification of the aggregation properties of the surfactants is only due to their complexation by the α-CD. The supramolecular interactions of the imidazolium surfactants favor the micellization process at high temperatures and by decreasing the temperature CDs destabilize the micelles by complexing the surfactant monomers more strongly than they are bound in self-association process. The temperature control of these equilibria provides a valuable element for further developments in organometallic catalysis as well as for various organic reactions. The most important feature of our system is the decrease of the decantation time and the perfect phase separation. This represents a nice example of the use of the supramolecular assistance to thermoregulate a microemulsion catalytic process. This parameter is of valuable interest for the recycling of the rhodium catalyst without decrease in conversion or selectivity. The catalytic mechanism and its extension to other micellar catalysis is under study in our group.

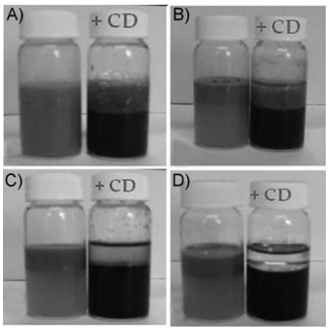



Figure 2. First steps of the decantation process at the end of the catalytic reaction: A) initial time; B) after 15 min; C) after 1 h; and D) after 16 h. In each panel the left vial corresponds to the reaction performed only with the imidazolium surfactant and the right vial represents the imidazolium surfactant/cyclodextrin reaction mixture.

Table 3. Recycling of the aqueous phase with **1**.

| Run | Surfactant | Conversion [%] | Selectivity [% ] |
|---|---|---|---|
| 1 | $[C_{12}MIM][Br]$ | 41 | 86 |
| 2 | $[C_{12}MIM][Br]$ | 41 | 85 |
| 3 | $[C_{12}MIM][Br]$ | 40 | 84 |
| 4 | $[C_{12}MIM][Br]$ | 40 | 79 |
| 5 | $[C_{12}MIM][Br]$ | 38 | 75 |
| 1 | $[C_{16}MIM][Br]$ | 100 | 96 |
| 2 | $[C_{16}MIM][Br]$ | 99 | 95 |
| 3 | $[C_{16}MIM][Br]$ | 99 | 95 |
| 4 | $[C_{16}MIM][Br]$ | 96 | 92 |
| 5 | $[C_{16}MIM][Br]$ | 92 | 92 |

## Experimental Section

**Material, methods, and synthesis**: See the Supporting Information.

**General hydroformylation experiments**: $[Rh(acac)(CO)_2]$ ($4.07\times10^{-2}$ mmol), TPPTS (0.21 mmol) and, if necessary, surfactant ($9.66\times10^{-2}$ mmol) and α-CD ($5.86\times10^{-2}$ mmol) were dissolved in water (11.5 mL). The resulting aqueous phase and an organic phase composed by the olefin (2.91 mmol) and undecane (4 mmol; GC internal standard) were charged in a glove bag into the 60 mL reactor which was sealed and heated at 80 °C. Magnetic stirring was then started (1150 rpm) and the autoclave was pressurized with 50 atm of $CO/H_2$ 1:1 from a gas reservoir connected to the reactor through a high pressure regulator valve. At the

end of the reaction the autoclave was cooled and depressurized and after the decantation process the contents were analyzed using CG for the organic products. The results presented are the average of at least three runs under each set of conditions.

## Acknowledgements

This work was supported by the Natural Sciences and Engineering Research Council of Canada, the Fonds Québécois de la Recherche sur la Nature et les Technologies, the Canada Foundation for Innovation and the Université de Montréal.

**Keywords:** cyclodextrins · hydroformylation · imidazolium salts · rhodium · supramolecular chemistry

[1] C. D. Frohning, C. W. Kohlpainter in *Applied Homogeneous Catalysis with Organometallic Compounds* (Eds.: B. Cornils, W. A. Herrmann), Wiley-VCH, Weinheim, **1996**, p. 29.

[2] a) B. Cornils, E. G. Kuntz in *Aqueous-Phase Organometallic Catalysis* (Eds.: B. Cornils, W. A. Herrmann), Wiley-VCH, Weinheim, **1998**, p. 271; b) J. P. Arhancet, M. E. Davis, J. S. Merola, B. E. Hanson, *Nature* **1989**, *339*, 454–455.

[3] I. T. Horvath, J. Rabai, *Science* **1994**, *266*, 72–75.

[4] a) P. G. Jessop, T. Ikariya, R. Noyori, *Chem. Rev.* **1999**, *99*, 475; b) P. G. Jessop, W. Leitner in *Chemical Synthesis using Supercritical Fluids* (Eds.: P. G. Jessop, W. Leitner), Wiley-VCH, Weinheim, **1999**, p. 351.

[5] a) F. R. Hartley, *Supported Metal Complexes: A New Generation of Catalysts*, Kluwer Academic, Dordrecht, **1985**; b) M. T. Reetz, G. Lohmer, R. Schwickardi, *Angew. Chem.* **1997**, *109*, 1559–1562; *Angew. Chem. Int. Ed. Engl.* **1997**, *36*, 1526–1529; c) W. Keim, B. Driessen-Hölscher in *Handbook of Heterogeneous Catalysis, Vol. 1* (Eds.: G. Ertl, H. Knözinger, J. Weitkamp), Wiley-VCH, Weinheim, **1997**.

[6] a) T. Welton, *Chem. Rev.* **1999**, *99*, 2071–2983; b) P. Wasserscheid, W. Keim, *Angew. Chem.* **2000**, *112*, 3926–3945; *Angew. Chem. Int. Ed.* **2000**, *39*, 3772–3789; c) R. Sheldon, *Chem. Commun.* **2001**, 2399–2407; d) J. Dupont, R. F. de Souza, P. A. Z. Suarez, *Chem. Rev.* **2002**, *102*, 3667–3691.

[7] G. W. Parshall, *J. Am. Chem. Soc.* **1972**, *94*, 8716–8719.

[8] Y. Chauvin, L. Mussmann, H. Olivier, *Angew. Chem.* **1995**, *107*, 2941–2943; *Angew. Chem. Int. Ed. Engl.* **1995**, *34*, 2698–2700.

[9] E. G. Kuntz, *CHEMTECH* **1987**, 570–575.

[10] a) J. F. Knifton, *J. Mol. Catal.* **1987**, *43*, 65–78; b) M. F. Sellin, P. B. Webb, D. J. Cole-Hamilton, *Chem. Commun.* **2001**, 781–782; c) R. P. J. Bronger, S. M. Silva, P. C. J. Kamer, P. W. N. M. van Leeuwen, *Chem. Commun.* **2002**, 3044–3045; d) O. Stenzel, H. G. Raubenheimer, C. Esterhuysen, *J. Chem. Soc. Dalton Trans.* **2002**, 1132–1138.

[11] S. L. Desset, D. J. Cole-Hamilton, D. F. Foster, *Chem. Commun.* **2007**, 1933–1935.

[12] a) Y. Dror, J. Manassen, *Stud. Surf. Sci. Catal.* **1981**, *7*, 887–897; b) H. Chen, Y. Li, J. Chen, P. Cheng, Y. He, X. Li, *J. Mol. Catal. A* **1999**, *149*, 1–15; c) P. J. Quinn, C. E. Taylor, *J. Mol. Catal.* **1981**, *13*, 389–396.

[13] M. V. Rekharsky, Y. Inoue, *Chem. Rev.* **1998**, *98*, 1875–1917.

[14] a) A. B. Dorrego, L. García-Río, P. Hervés, J. R. Leis, J. C. Mejuto, J. Pérez-Juste, *Angew. Chem.* **2000**, *112*, 3060–3062; *Angew. Chem. Int. Ed.* **2000**, *39*, 2945–2948; b) H. Xing, S.-S. Lin, P. Yan, J.-X. Xiao, *Langmuir* **2008**, *24*, 10654–10664.

[15] R. Palepu, V. C. Reinsborough, *Can. J. Chem.* **1988**, *66*, 325–328.

[16] a) L. Leclercq, I. Suisse, G. Nowogrocki, F. Agbossou-Niedercorn, *Green Chem.* **2007**, *9*, 1097–1103; b) C. P. Mehnert, R. A. Cook, N. C. Dispenziere, E. J. Mozeleski, *Polyhedron* **2004**, *23*, 2679–2688.

[17] L. Leclercq, I. Suisse, F. Agbossou-Niedercorn, *Chem. Commun.* **2008**, 311–313.

[18] Imidazolium surfactants were freshly purified under vacuum to remove residual water.

[19] B. Dong, N. Li, L. Zheng, L. Yu, T. Inoue, *Langmuir* **2007**, *23*, 4178–4182.

[20] J. Yun-Bao, W. Xiu-Juan, *Appl. Spectrosc.* **1994**, *48*, 1428–1431.

[21] For more information see Supporting Information and for software information: J. J. P. Stewart, Stewart Computational Chemistry, version 7.213W, http://openmopac.net/.

[22] E. Monflier, S. Tilloy, G. Fremy, Y. Castanet, A. Mortreux, *Tetrahedron Lett.* **1995**, *36*, 9481–9484.

[23] a) H. Chen, Y. Z. Li, J. R. Chen, P. M. Cheng, Y. E. He, X. J. Li, *J. Mol. Catal. A* **1999**, *149*, 1–6; b) A. Riisager, B. E. Hanson, *J. Mol. Catal. A* **2002**, *189*, 195–202; c) L. Wang, H. Chen, Y. He, Y. Li, M. Li, X. Li, *Appl. Catal. A* **2003**, *242*, 85–88.

[24] L. Leclercq, M. Sauthiert, Y. Castanet, A. Mortreux H. Bricout, E. Monflier, *Adv. Synth. Catal.* **2005**, *347*, 55–59.

Received: March 24, 2009
Published online: May 28, 2009