

N°753 / PC

TOPIC(s) : Alternative solvents

Deep eutectic solvents as medium for recycling organometallic complexes in a hydroformylation reaction

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PURPOSE OF THE ABSTRACT

1. Motivation

Hydroformylation of olefins is the most common pathway to yield linear aldehydes, of great interest as intermediates of perfumes, fine chemicals and certain pharmaceutical products [1,2]. This reaction has been performed employing homogeneous catalysts based on organometallic complexes containing costly transition metals like Rh [3,4], which makes necessary to develop strategies for recycling.

Deep eutectic solvents (DESs) are mixtures formed by Lewis or Brønsted acids and bases that consist of a wide array of anionic and cationic species, whose main characteristic is the collapse of the melting point with respect to their pure components [5]. A common type of DES consists of quaternary ammonium salts with halide anions as hydrogen bond acceptors (HBA) and a hydrogen bond donor (HBD) in different proportions. DESs have great advantages, such as high biodegradability and low volatility, which make them ideal to substitute volatile organic compounds.

Here the hydroformylation of 1-decene (non-polar phase) was conducted using Rh(acac)(CO)₂ with phosphine-based ligands (Biphephos, Sulfoxantphos and TPPMS) in a liquid-liquid biphasic system to enable catalyst recycling. The polar phase consisted of DESs based on choline chloride as HBA as well as urea (U), glycerol (Gly), 1,2-propanediol (1,2-PD), ethylene glycol (EG) and glycerol carbonate (GC) as HBD. The selected ratio of HBD:HBA was in all cases 2:1.

2. Screening of deep eutectic solvents in the hydroformylation of 1-decene

An assessment of the performance of three ligands (a) Biphephos, (b) Sulfoxantphos and (c) TPPMS was made in five different DESs, as shown in Fig. 1. The best operation could be achieved with (a) Biphephos as ligand using ChCl:U as solvent reaching a value for the conversion of 1-decene of 54%, with a yield to aldehydes of 41%, leading to a TOF of 54.3 h⁻¹. In the case of (b) Sulfoxantphos, ChCl:Gly performed better than the others, obtaining conversion of 47%, with a yield to aldehydes of 35%, leading to a TOF of 46.7 h⁻¹. Biphephos has higher catalytic activity and a slightly better selectivity towards linear aldehydes than Sulfoxantphos (97:3 compared to 90:10). Finally, (c) TPPMS gave much lower catalytic performances (TOF=25-6 h⁻¹) without much difference among the solvents. In this case, not only did the overall activity decline remarkably compared to systems (a) and (b), but also the selectivity to the linear aldehyde is far lower, reaching only a value of 62:38.

Fig. 1(d) shows the leaching of Rh into the product phase relative to the initial concentration as measured by ICP-OES. Greater leaching is observed with Biphephos as ligand, with Rh losses ranging from 16 to 24% compared to TPPMS and Sulfoxantphos. In the case of TPPMS and Sulfoxantphos, leaching between 5 and 7% and from 1 to 4% were measured, respectively. This capacity to immobilize the Rh is due to the presence of sulphonic groups in Sulfoxantphos and TPPMS [6], which makes them more polar for interaction with the HBA and HBD of the DESs compared to Biphephos.

3. Catalyst recycling

Fig. 2 features the catalytic results after a total of 5 cycles for each of the systems together with the amount of Rh leached and the calculated TOFs. First, with Biphephos in ChCl:U, Rh shows a much higher trend to leach throughout the cycles into the product phase. This has a subsequent effect on the important decline of the observed TOFs. On the contrary, for Sulfoxantphos, ChCl:Gly appears to immobilize the Rh catalyst much better, leading to losses of only between 1 and 2 % per cycle, with the TOF showing less decrease with the number of cycles. Thus, using Biphephos in ChCl:U shows a higher performance in the first cycles, but Sulfoxantphos in ChCl:Gly appears to outperform it upon reutilization, thus being a much more stable system for the catalyst. Finally, TPPMS in ChCl:U shows lower leaching than Biphephos, thus leading to a higher stability of the catalytic activity throughout.

FIGURES

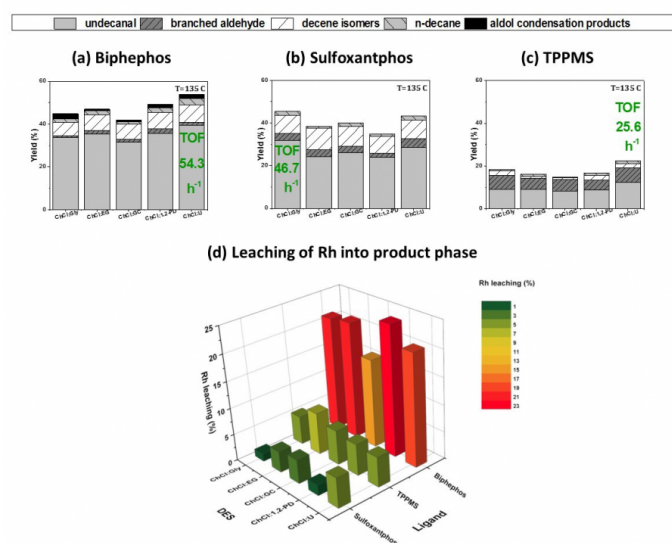


FIGURE 1

Figure 1. Screening of solvents for each of the ligands tested in the hydroformylation of 1-decene with (a) Biphephos, (b) Sulfoxantphos and (c) TPPMS. (d) Leaching of Rh as measured by ICP-OES

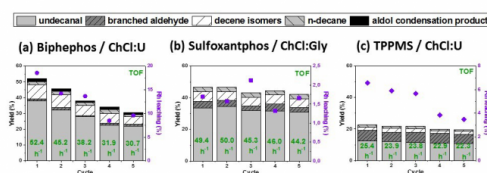


FIGURE 2

Figure 2. Yield to products, leaching and TOFs in recycling experiments using the best performing ligand and DESs couples: (a) Biphephos in ChCl:U, (b) Sulfoxantphos in ChCl:Gly and (c) TPPMS in ChCl:U.

KEYWORDS

deep eutectic solvent | hydroformylation | catalyst recycling | phosphine ligands

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