Short communication

Rhodium catalyzed hydroformylation of 1-decene in low melting mixtures based on various cyclodextrins and N,N′-dimethylurea

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ABSTRACT

Different low melting mixtures (LMMs) based on N,N′-dimethylurea (DMU) and various cyclodextrin (CD) derivatives were synthetized. The melting point was weakly affected by the size and the chemical modification of CD. By contrast, the chemical modification of CD led to a decrease in viscosity of the LMMs. These mixtures were evaluated as solvent in rhodium-catalyzed hydroformylation reaction of 1-decene. The LMM based on DMU/RAME-β-CD (70/30) allowed reaching the highest catalytic activity (1980 h^{-1}). The influence of several factors was studied and it was established that the conversion increased with the 1-decene solubility and decreased with the LMM viscosity.

1. Introduction

Low melting mixtures (LMMs) have recently emerged in the current literature as new reaction media for organometallic catalytic process. A LMM is a fluid generally composed of two or three components that are capable of self-association, often through hydrogen bond interactions, to form a mixture with a melting point lower than that of each individual component. LMMs are generally liquid at temperatures lower than 100 °C [1–5]. These solvents can be formed by simply mixing the commercial starting materials. Additionally, their synthesis is 100% atom economic and no purification is required, thus making their large-scale use feasible. They can be prepared from cheap, readily available and toxicologically well characterized starting materials. Despite these advantages, the use of LMMs in the field of organometallic catalysis was barely described. Different LMM mixtures based on carbohydrate/urea (or its derivatives) have been used as reaction medium for organometallic catalytic processes in the cases of palladium-catalyzed Suzuki coupling [6], rhodium-catalyzed hydrogenation reaction [6], palladium-catalyzed Stille cross-coupling [7], palladium-catalyzed Heck and Sonogashira coupling [8] while ruthenium-catalyzed isomerization reaction was performed in choline chloride/glycerol mixture [9]. Very recently, our group has published new LMMs based on β-cyclodextrin (β-CD) series and N,N′-dimethylurea (DMU) to perform palladium-

catalyzed Tsuji-Trost and rhodium-catalyzed hydroformylation reactions [10]. These LMMs were simply prepared by mixing DMU and different β-CDs at a weight ratio of 70/30. The best result was obtained for the mixture between DMU and randomly methylated-β-CD (RAME-β-CD) and this combination allowed reaching higher catalytic activity than those reported for classical systems based on CD in water as solvent. In order to extent the scope of the LMMs based on CD, we synthetized new LMMs by varying the size of CD, the nature and the number of the CD substituents (Fig. 1) and also the amount of CD in the mixture DMU/CD. The effects of these different solvents on the catalytic activity during rhodium catalyzed hydroformylation reaction of 1-decene were studied. Finally, the influence of several factors was discussed to rationalize the catalytic results.

2. Experimental

All chemicals were used as supplied without further purification. The LMM melting points were determined by using an apparatus PerkinElmer DSC Pyris 1. A Brookfield Model LVDVII + Pro viscometer was used to determine the LMM viscosity. Other information relative to the determination of LMM melting points by DSC (and also the thermograms), the LMMS viscosity, and the solubility of 1-decene in LMMs are gathered in the supplementary data.

In a typical hydroformylation experiment, [Rh(acac)(CO)$_2$] (5.5 mg; 21 μmol; 1 eq.), TPPTS (60 mg; 105 μmol; 5 eq.) and solvent constituents at solid state (4.2 g of N,N′-dimethylurea and 1.8 g of RAME-β-CD (w/w

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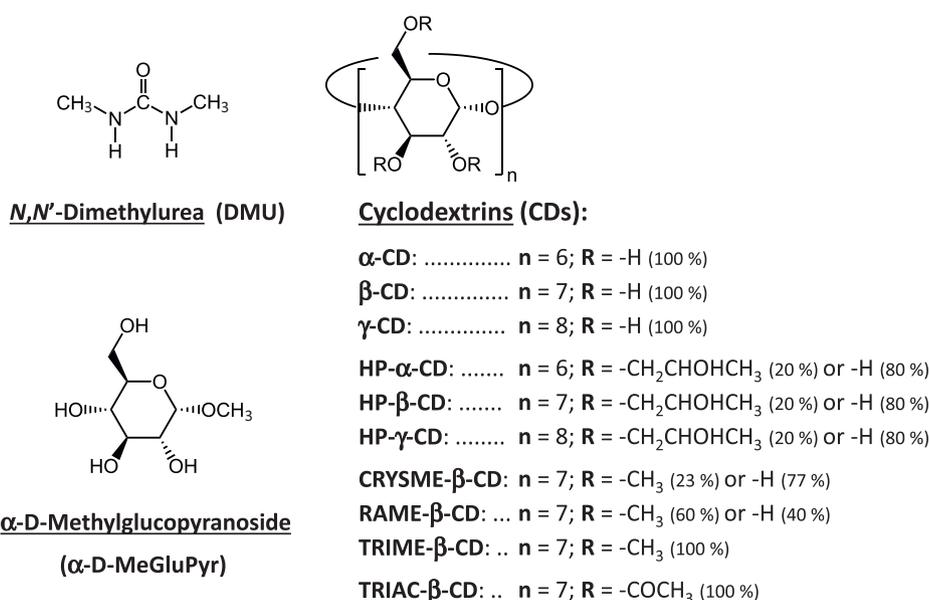
Fig. 1. Structure of compounds used for the preparation of LMMs.

(%) = 70/30) for example) were charged into a 25 mL autoclave. Air was replaced by 20 bar of CO/H₂ (1/1) and after heating at 90 °C, the mixture was stirred using a multipaddle unit (1500 rpm) for 1 h for an incubation period. The stirring was then stopped and after cooling and depressurization, 1-Decene (6 g; 42 mmol; 2000 eq.) was introduced under nitrogen in the autoclave. The medium was heated at 90 °C and then stirred (1500 rpm) for 1 h at this temperature under 50 bar of CO/H₂ (1/1).

3. Results and discussion

Different mixtures were prepared by grinding at different ratios DMU and CD in a mortar. Then, this preparation was gradually heated until the melting of the mixture. Table 1 summarized the melting temperature of these mixtures determined visually and by differential scanning calorimetry (DSC — see supplementary data). The temperatures obtained by the two ways are in accordance (Table 1).

The first determinations of melting temperatures were realized at a ratio DMU/CD (70/30) since it was previously described that a melt was observed for DMU/α-CD [11] or DMU/β-CD [10] mixture at this ratio. For the three native CDs and the three hydroxypropylated CDs, the melting points were around 90 °C and these latter were not significantly modified by the size of the cavity (i.e. the number of glucopyranose units; 6, 7 and 8 for α-, β- and γ-CD) (entries 1–6). The permodified CDs, TRIME-β-CD and TRIAC-β-CD, did not form LMMs, probably because of the absence of hydroxyl groups on these CD preventing from the formation of hydrogen bonds. In the case of β-CD series and at the ratio DMU/CD (70/30), the hydroxypropylation or methylation of

Table 1
Melting points and viscosities of the various mixtures[a].

Entry	Mixture	% weight of CD in the mixture	Melting point (°C) (visually)	Melting point (°C) (DSC)	Viscosity (cP) at 90 °C
1	DMU/α-CD	30	90	86	1436
2	DMU/β-CD	30	90	91	1165
3	DMU/γ-CD	30	90	91	1096
4	DMU/HP-α-CD	30	90	87	163
5	DMU/HP-β-CD	30	85	91	205
6	DMU/HP-γ-CD	30	90	94	208
7[b]	DMU/TRIME-β-CD	30	–	–	–
8[b]	DMU/TRIAC-β-CD	30	–	–	–
9	DMU/CRYSME-β-CD	30	90	92	445
10	DMU/RAME-β-CD	30	90	91	235
11[b]	DMU/β-CD	20	–	–	–
12	DMU/β-CD	50	75	67	434
13[b]	DMU/β-CD	70	–	–	–
14[b]	DMU/CRYSME-β-CD	20	–	–	–
15	DMU/CRYSME-β-CD	50	77	79	103
16	DMU/CRYSME-β-CD	70	69	71	45500[c]
17[b]	DMU/CRYSME-β-CD	80	–	–	–
18[b]	DMU/RAME-β-CD	20	–	–	–
19	DMU/RAME-β-CD	50	71	71	196
20	DMU/RAME-β-CD	70	50	51	834
21[b]	DMU/RAME-β-CD	80	–	–	–
22[d]	DMU/α-D-MeGluPyr	30	79	82	459

[a] All these CDs are commercially available and are used without drying (see supplementary data) at normal pressure in air; the melting points of all the CDs are superior to 200 °C and that of DMU is equal to 104 °C.
[b] For these mixtures, no melt was observed.
[c] This high value was confirmed by several measurements and cannot be attributed to a decomposition of the CRYSME-β-CD. Indeed, the integrity of this CD was preserved as checked by NMR analysis.
[d] α-D-methylglucopyranoside (α-D-MeGluPyr) was used as CD building block.

β-CD was also without notable effect on the melting point (compare entries 2, 5, 9 and 10). So, the modification of the size or the chemical modification of CDs had no major impact on the melting points. By contrast, the chemical modification of CD seemed to be a crucial factor for the viscosity since the values decreased when CD was hydroxypropylated (Table 1 — compare entries 1–3 with 4–6) [12]. This tendency was confirmed in the case of the methylated β-CDs. Indeed, the values of viscosity were lower for the mixtures DMU/CRYSME-β-CD and DMU/RAME-β-CD compared to DMU/β-CD (compare entries 9 and 10 with 2). Concerning the size of CDs, the number of glucopyranose units did not significantly modify the viscosities of the LMMs inside a series (for native series, compare entries 1–3 and for hydroxypropyl series, compare entries 4–6). The influence of the CD amount was also explored by varying the ratios DMU/β-CD, DMU/CRYSME-β-CD and DMU/RAME-β-CD from 80/20 to 20/80. For the ratios 80/20 and 20/80, no melt was observed (entries 11, 14, 17, 18 and 21). A melt was observed for the ratios DMU/CD comprised between 70/30 and 30/70 except for the mixture DMU/β-CD (30/70). This exception could be due to the well-known strong intramolecular hydrogen bonds observed for β-CD decreasing the formation of hydrogen bonds with DMU [13]. The melting points decreased with the increasing CD amount (for β-CD, entries 2, 12; for CRYSME-β-CD, entries 9, 15, 16; for RAME-β-CD, entries 10, 19, 20). For example in the case of DMU/RAME-β-CD, the melting point was equal to 90 °C, 71 °C and 50 °C for the mixtures 70/30, 50/50 and 30/70, respectively. The viscosities firstly decreased from the DMU/CD ratio 70/30 to 50/50 and secondly increased from the ratio 50/50 to 30/70 (entries 9, 15, 16 and 10, 19, 20). As comparison, both measurements were performed with a mixture of 70% of DMU and 30% of α-D-methylglucopyranoside (α-D-MeGluPyr – CD building block – entry 22). The melting point was in the same order of magnitude than the three natives CD whereas the viscosity was lower (compare entries 1–3 and 22).

To evaluate the potentiality of these new solvents, the rhodium-catalyzed hydroformylation reaction was selected as a model reaction and 1-decene was chosen as a non-miscible substrate in order to obtain a biphasic system. Tris(m-sulfonatophenyl)phosphine trisodium salt (TPPTS) was used as ligand to maintain rhodium in the LMMs. This polar ligand is well soluble in all the LMMs used (up to 3% w/w). The reaction was performed at 90 °C and stopped after 1 h (Table 2).

The value of conversion varied from 41% for the mixture DMU/CRYSME-β-CD (30/70) to 99% for the mixture DMU/RAME-β-CD (70/30). The potential effect of cavity size was investigated by performing six experiments with the three natives CD (α-CD, β-CD and γ-CD; entries 1, 2 and 3) and the three hydroxypropylated CD (HP-α-CD, HP-β-CD and HP-γ-CD; entries 4, 5 and 6). For the native series, the conversions depended on the cavity size since the best results were obtained in the case of β-CD and γ-CD whereas in the case of HP series, the three CDs allowed reaching similar conversions (between 75% and 79%). So, the values of conversion did not follow the size of the cavity. The effect of chemical modification was also explored in the case of the β-CD series. The conversions were increased in the case of LMMs based on DMU and hydroxypropylated CDs compared to those based on DMU and native CDs (compare entries 1, 2 and 3 with 4, 5 and 6, respectively). The methylation of β-CD (CRYSME-β-CD and RAME-β-CD) also had a beneficial effect and it can be noticed that a higher methylation degree led to a better conversion (compare entries 2 with 7 and 8). The highest catalytic activity was obtained in the case of DMU/RAME-β-CD (70/30) and was equal to 1980 h^{-1}. The influence of the proportion of CD was also studied in the case of LMMs based on DMU and β-CD, CRYSME-β-CD or RAME-β-CD at DMU/CD ratios varying from 70/30 to 30/70. Unexpectedly, when the CD amount in the LMMs increased, the conversion decreased. Indeed, one would think that an increase in CD amount would lead to an increase in conversion. Indeed in aqueous biphasic hydroformylation reaction, CDs are known to play the role of mass transfer agents by forming inclusion complexes with hydrophobic substrates at the interface [14–16]. As comparison, LMM based on DMU and α-D-methylglucopyranoside (70/30) was used and a conversion of 66% was reached. Although α-D-methylglucopyranose did not possess a cavity, this conversion was equal to those obtained with β-CD or γ-CD, demonstrating that the formation of inclusion complexes was not necessary to obtain high catalytic activities.

In order to rationalize these results, the 1-decene conversion was plotted versus the viscosity (Fig. 2). The broader trend showed a decrease in the conversion when the viscosity increased with nevertheless

Table 2
Rhodium-catalyzed hydroformylation of 1-decene in the various LMMs[a].

Entry	Solvent	% weight of CD in the solvent	Conversion of 1-decene (%)[b]	Selectivity in aldehydes (%)[b]	l/b[b,c]
1	DMU/α-CD	30	45	96	2.3
2	DMU/β-CD	30	66	94	2.3
3	DMU/γ-CD	30	68	95	2.4
4	DMU/HP-α-CD	30	78	96	2.3
5	DMU/HP-β-CD	30	75	92	2.3
6	DMU/HP-γ-CD	30	79	94	2.3
7	DMU/CRYSME-β-CD	30	76	94	2.3
8	DMU/RAME-β-CD	30	99	90	2.2
9[d]	DMU/RAME-β-CD	30	95	90	2.2
10[e]	DMU/RAME-β-CD	30	98	90	2.2
11	DMU/β-CD	50	53	93	2.2
12	DMU/CRYSME-β-CD	50	51	94	2.1
13	DMU/CRYSME-β-CD	70	41	91	2.0
14	DMU/RAME-β-CD	50	89	94	2.2
15	DMU/RAME-β-CD	70	63	94	2.2
16[f]	DMU/α-D-MeGluPyr	30	66	94	2.4

[a] *Experimental conditions*: [Rh(acac)(CO)$_2$] = 21 μmol (1 eq.), TPPTS = 105 μmol (5 eq.), 1-decene = 42 mmol (2000 eq.), solvent (DMU/CD) = 6 g, 90 °C, 50 bar CO/H$_2$ (1/1), 1500 rpm, reaction time = 1 h.
[b] Conversion, selectivity and linear to branched aldehydes ratio (l/b) determined by ^{1}H NMR and GC.
[c] Branched aldehyde (b) is racemic.
[d] Catalyst recycle test performed using the catalytic phase recovered from run 8.
[e] Catalyst recycle test performed using the catalytic phase recovered from run 9.
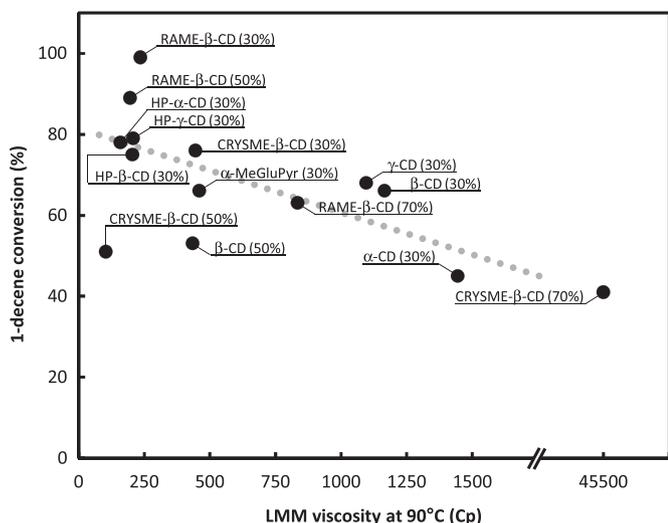[f] α-D-methylglucopyranoside (α-D-MeGluPyr) was used as CD building block.

Fig. 2. 1-Decene conversion (%) vs. viscosity of DMU/CD low melting mixtures at 90 °C.
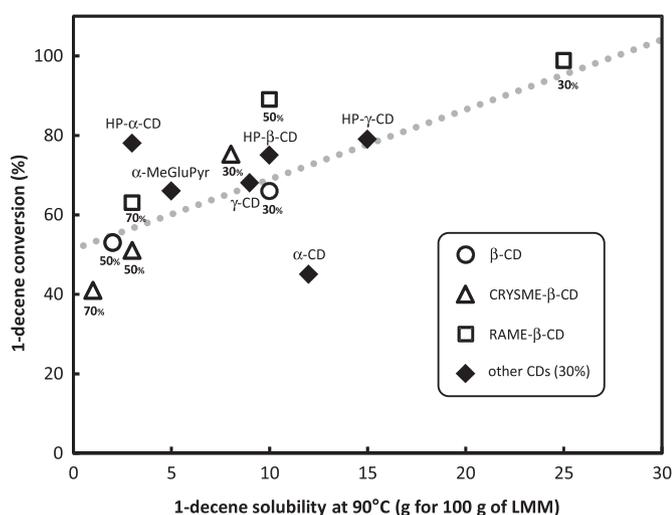

Fig. 3. 1-Decene conversion (%) vs. 1-decene solubility at 90 °C in the DMU/CD LMMs.

a high dispersion of the points around the regression line (gray dotted line).

As the catalytic activity in a two-phase system was generally connected to the solubility of the substrate in the catalytic layer, the solubility of 1-decene was determined at 90 °C in the various LMMs (see supplementary data). From these data, it was possible to plot the conversion versus the solubility of 1-decene in the LMMs (Fig. 3). Even if all the points were not regularly distributed around the regression line (gray dotted line), there appeared to be an overall increase in the conversion when the 1-decene solubility increased. This behavior was more marked inside a same series. Indeed, for the DMU/CRYSME-β-CD (70/30, 50/50 and 30/70) LMMs, the three points were perfectly aligned (triangle). This tendency was also evidenced for the LMMs based on β-CD (circle) and on RAME-β-CD (square).

So, Figs. 2 and 3 globally showed that the conversion increased with the 1-decene solubility and decreased with the LMM viscosity. Nevertheless, it seems evident that the conversion can be also influenced by other parameters since all the values of viscosity or solubility were not perfectly distributed on the regression lines. These other parameters could be

the interfacial tension or the interactions between the LMM constituents and the catalytic species. All these parameters were intimately linked leading to a very complex medium. So, other physicochemical analyses have to be realized to better understand the behavior of CDs.

Finally, the selectivity in aldehydes was high (90–95%) in each case and the linear to branched aldehydes ratio (l/b) varied from 2.0 to 2.4. Note that these values of selectivity were similar to those reported for hydroformylation experiments performed in water and showed the integrity of the organometallic catalytic species based on rhodium and TPPTS. The stability of the catalytic system was also confirmed in the case of the best LMM (DMU/RAME-β-CD: 70/30) since two recycling experiments showed no loss of activity and selectivity (entries 9 and 10 in table 2).

4. Conclusion

In summary, we have reported the use of LMMs based on DMU and various CDs as solvents for hydroformylation reaction. The LMM based on DMU/RAME-β-CD (70/30) allowed reaching the highest catalytic activity. The influence of several factors such as the size and the nature of the CDs, the proportion of CDs, the viscosity or the solubility of 1-decene was studied. It was established that the conversion increased with the 1-decene solubility and decreased with the LMM viscosity. Finally, experiments are currently underway to perform hydrogenation of pro-chiral substrates as this new reaction medium has high potential of application in asymmetric catalysis due to the chirality of CD.

Appendix A. Supplementary data

Supplementary data to this article can be found online at http://dx.doi.org/10.1016/j.catcom.2014.11.001.

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