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Chemically modified β-cyclodextrins in biphasic catalysis: a fruitful contribution of the host–guest chemistry to the transition-metal catalyzed reactions

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Abstract

Biphasic hydroformylation, Wacker oxidation and hydrocarboxylation of water insoluble olefins have been investigated in the presence of chemically modified β-cyclodextrins. In all cases, cyclodextrins appear more efficient than common mass transfer promoters to increase the activity and the selectivity of reactions. Most of the results are interpreted from the molecular recognition between the host cavity of modified cyclodextrins and substrate. The stability of the chemically modified cyclodextrins is also reported.

Keywords: Hydroformylation; Wacker; Hydrocarboxylation; Cyclodextrin; Biphasic catalysis

1. Introduction

The major disadvantage of the homogeneous catalysis versus heterogeneous catalysis is the recycling of the catalyst. To solve this problem, the two-phase systems where the catalyst is dissolved in a phase which contains neither the substrate nor the products are of great interest. Indeed, the catalyst can be recovered at the end of the reaction by simple decantation of the two layers and reused several times without impairment of the catalyst properties. Among the various two-phase systems described in the literature (aqueous [1,2]-, alcohol [3]-, ionic salt [4]-, or fluorous [5–7]-organic two-phase system), the aqueous–organic two-phase system is the more attractive from an economical and environmental point of view. Furthermore, its industrial feasibility has been demonstrated by Hoechst in the case of the hydroformylation of propene (Rhurchemie/Rhône–Poulenc process) [8,9]. In the aqueous–organic two-phase system, the water solubility of the substrate is considered as a crucial parameter. Indeed, with water insoluble substrates, the activities dramatically decrease due to the low mass transfer between the two layers [1].

In this context, we have developed a new and versatile approach which allows to extend the scope of biphasic catalysis to water insoluble substrates. Our approach is based on the use of supramolecular receptors such as chemically modified β-cyclodextrins (Fig. 1).

The cyclodextrins which are cyclic oligosaccharides composed of seven glucopyranose units linked by α(1–4)-glycosyl bonds are schematically represented

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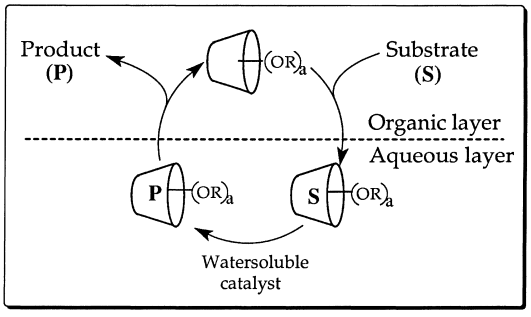

Fig. 1. Inverse phase transfer catalysis with chemically modified cyclodextrins.

by a truncated cone where (*a*) and R correspond, respectively, to average number of substituted hydroxyl group and to functional group of the β-cyclodextrin [10,11]. The functional group in the place of the primary or secondary hydroxyl group can be $-CH_3$; $-C(O)CH_3$, $-CH_2CH(OH)CH_3$, $-CH_2CH_2OH$ or $-SO_3Na$. Owing to the formation of inclusion complexes between the cyclodextrin and the water insoluble substrate, the cyclodextrins can transfer the substrate into aqueous phase, and therefore improve the mass transfer between aqueous and organic layers (Fig. 1). So, chemically modified cyclodextrins can be considered as inverse phase transfer catalysts.

The feasibility and the scope of this approach have been investigated through three well-known transition-metal catalyzed reactions: the hydroformylation [12], the hydrocarboxylation [13,14] and the oxidation of olefins [15]. (Fig. 2).

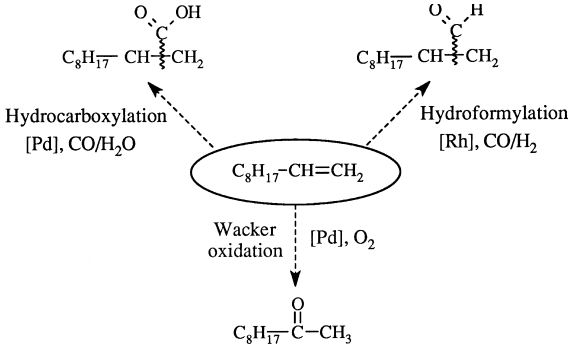

Fig. 2. Transition metal catalyzed reactions in the presence of chemically modified cyclodextrins.

These reactions present a great interest for the valorization of higher olefins, into carboxylic acids, aldehydes and ketones which are important chemical intermediates.

2. Experimental

2.1. Materials and apparatus

The chemically modified cyclodextrins were supplied by Cyclolab (Budapest, Hungary) and Aldrich Chemical and were used as received without further purification. In particular, the commercially available per(2,6-di-*O*-methyl)-β-cyclodextrin is a mixture of methylated β-cyclodextrin. Indeed, electrospray mass spectrum of this modified cyclodextrin exhibits signals at *m/z*: 1311, 1325, 1339, 1353, 1367 and 1381 corresponding to different degrees of methylation. In the case of this cyclodextrin, the average number of substituted hydroxyl group was equal to 14. Palladium chloride, palladium sulfate, copper sulfate, dicarbonylacetylacetonato rhodium (I) and organic compounds were purchased from Strem Chemicals, Aldrich Chemical and Acros Organics in their highest purity and used without further purification. Trisodium tris(*m*-sulfonatophenyl)phosphine (TPPTS) was synthesized as reported by Gärtner et al. [16]. The purity of the TPPTS was carefully controlled. In particular, ^{31}P solution NMR indicated that the product was a mixture of TPPTS (ca. 98%) and its oxide (ca. 2%). Oxygen, carbon monoxide and carbon monoxide/hydrogen mixture were used directly from cylinders (>99.9% pure; Air Liquide). Distilled deionized water was used in all the experiments. All the catalytic reactions were performed under nitrogen using standard Schlenk techniques. All the solvents and liquid reagents were degassed by bubbling nitrogen for 15 min before each use or by two freeze-pump-thaw cycles before use.

All the high pressure experiments were carried out in a 100 or 25 ml stainless steel autoclave. The autoclave supplied by autoclave engineer was equipped with arrangements for automatic temperature control, pressure regulation, and variable stirred speed. A safety rupture disk was also fitted to the reactor. Gas–liquid chromatography analyses were carried out on a Chrompack 9001 apparatus

equipped with a CP Sil 5-CB column (25 m× 0.32 mm).

Electrospray mass spectroscopy experiments were performed on a Micromass Quattro II. In order to obtain a concentration of about 20 pmol/μl, the sample was diluted in a mixture of ammonium acetate (0.06 mM), water and acetonitrile (50/50) and was introduced through the fused silica inlet capillary at a flow rate of 3 μl/min. Except where other stated in the text, the ion spray needle potential and the orifice potential were set at 3100 and 40 V, respectively. The temperature of the interface was set at 80°C. Positive ion detection mode was used. Calibration was performed with polypropylene glycol.

2.2. Typical experiment for the wacker oxidation of olefins

$PdSO_4$,$2H_2O$ (0.86 mmol), $CuSO_4$ (10 mmol) and chemically modified-β-cyclodextrin (1 mmol) were introduced into an aqueous solution (30 ml) of phosphomolybdovanadic acid (10 mmol of phosphorus) adjusted to pH 1 with concentrated sulfuric acid. The resulting solution and the organic phase (olefin (40 mmol) and undecane (5 mmol – GC internal standard)) were then introduced in a 250 ml flask. Oxygen was bubbled through the solution which was vigorously stirred at 80°C. At the end of the reaction, the solution was then cooled and the organic layer was analyzed.

2.3. Typical experiment for hydroformylation of olefins

$Rh(acac)(CO)_2$ (0.16 mmol), TPPTS (0.8 mmol) and chemically modified cyclodextrin (1.12 mmol) were dissolved in 45 ml of water. The resulting aqueous phase and an organic phase composed of olefin (80 mmol) and undecane (4 mmol – GC internal standard) were charged under an atmosphere of N_2 into a 100 ml stainless steel autoclave, then heated at 80°C, and pressurized with 50 atm of CO/H_2 (1/1). Mechanical stirring (1000 rpm) equipped with a multipaddle unit was then started. The pressure was kept constant throughout the whole reaction by using a gas reservoir along with a pressure regulator and the reaction was analyzed.

2.4. Typical experiment for hydrocarboxylation of olefins

$PdCl_2$ (0.2 mmol), TPPTS (1.2 mmol) and the chemically modified β-cyclodextrin (1.4 mmol) were dissolved in 11 ml of water. The pH value of the resulting aqueous phase was then adjusted to 1.8 with diluted HCl solution. The final aqueous solution and an organic phase composed of olefin (20 mmol) and undecane (2 mmol – GC internal standard) were charged under N_2 into a 25 ml stainless steel autoclave, then heated at 100°C, and pressurized with 40 atm of CO. The pressure was kept constant throughout the whole reaction by using a gas reservoir along with a pressure regulator and the reaction was monitored by gas chromatographic analysis.

2.5. Recycling experiments

The first batch was carried out as described above. After 1 h (hydroformylation) or 2 h (hydrocarboxylation) of reaction, the autoclave was cooled to room temperature and the CO/H_2 or CO pressure was evacuated. After a 15 min time of decantation, the bulk organic solution was then removed under CO/H_2 or CO atmosphere, leaving the aqueous phase in the bottom of the reactor. The latter was washed with toluene, and a new reaction mixture containing olefin and internal standard was introduced. The second batch was carried out using the same procedure as described above. The overall recycling procedure was then repeated.

3. Results and discussion

In our preliminary works, dec-1-ene has been chosen as model substrate. Typical results obtained in the presence of various functionalized cyclodextrins are given in Figs. 3–5, where the values in brackets correspond to the average number of substituted hydroxyl group.

Figs. 3–5 show that the β-cyclodextrin is an efficient mass transfer promoter for the three reactions and that its catalytic properties can be greatly improved when it contains a suitable functional group. The extent of conversion of dec-1-ene depends

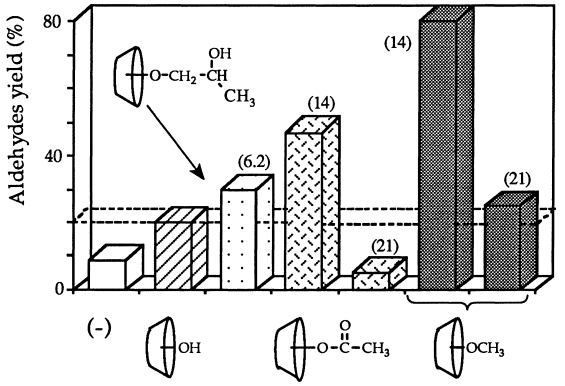

Fig. 3. Biphasic hydroformylation of dec-1-ene in the presence of various chemically modified cyclodextrins. Experimental conditions: [Dec-1-ene]/[Rh]: 500; [β-cyclodextrin]/[Rh]: 7; $[P(C_6H_4SO_3Na)_3]$/[Rh]: 5; *T*: 80°C; *P*(CO/H_2): 50 bar; 6 h.

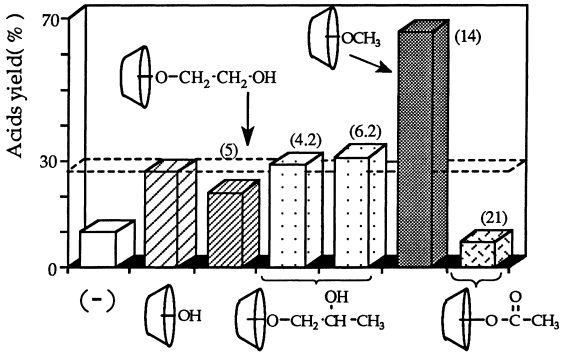

Fig. 5. Biphasic hydrocarboxylation of dec-1-ene in the presence of various chemically modified cyclodextrins. Experimental conditions: [Dec-1-ene]/[$PdCl_2$]: 100; [β-cyclodextrin]/[$PdCl_2$]: 7; $[P(C_6H_4SO_3Na)_3]$/[Pd]: 6; pH: 1.8 (HCl); *T*: 100°C; *P*(CO): 40 bar; 6 h.

strongly on the nature of the functional group and on the degree of substitution of the cyclodextrin [17–20]. For instance, the 2-hydroxyethyl-β-cyclodextrin, the 2-hydroxypropyl-β-cyclodextrin and the per(2,6-di-*O*-acetyl)-β-cyclodextrin (R: $C(O)CH_3$; a: 14) exhibited always a much lower activity than the per(2,6-di-*O*-methyl)-β-cyclodextrin (R: CH_3; a: 14) and no increase in activity is observed with the sulfated cyclodextrin and the perfunctionalized cyclodextrins such as the permethylated-β-cyclodextrin (R: CH_3; a: 21) and the peracetyl-β-cyclodextrin (R: $C(O)CH_3$; a: 21).

The aforementioned differences in catalytic activity arise mainly from the different solubility of the modified cyclodextrins in both the aqueous and organic layers. Indeed, contrary to the β-cyclodextrin and the 2-hydroxypropyl-β-cyclodextrins which are, respectively, totally insoluble and sparingly soluble in the organic phase, the per(2,6-di-*O*-methyl)-β-cyclodextrin is well soluble in water and partly in the organic

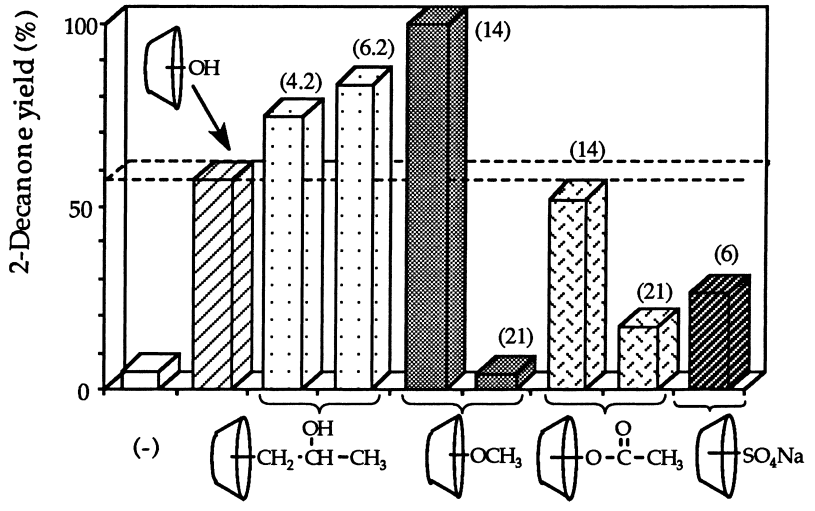

Fig. 4. Biphasic Wacker oxidation of dec-1-ene in the presence of various chemically modified cyclodextrins. Experimental conditions: [Dec-1-ene]/[$PdSO_4$]: 50; [β-cyclodextrin]/[$PdSO_4$]: 1; [$CuSO_4$]/[$PdSO_4$]: 10; $[H_9PV_6Mo_6O_{40}]$/[$PdSO_4$]: 10; *T*: 80°C; *P*(O_2): 1 bar; 6 h.

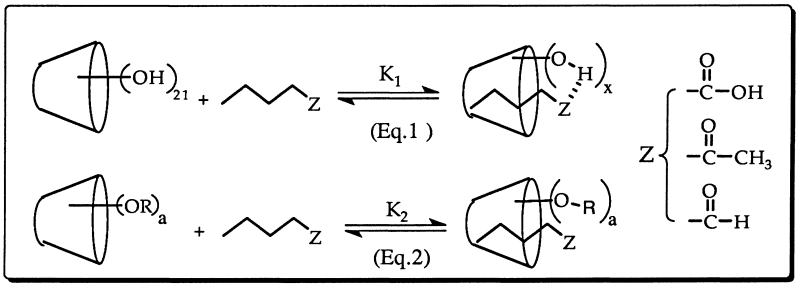

Fig. 6. Formation of inclusion complexes between cyclodextrin and various substrates.

layer. This remarkable property allows to transfer rapidly the olefin into the aqueous phase. This hypothesis is in agreement with the results obtained with the peracetylated and the permethylated-β-cyclodextrins. Indeed, as these cyclodextrins are weakly soluble in water and preferably localized in the organic layer, the transfer of substrate into the aqueous layer is unlikely.

If the solubility of the cyclodextrin in the aqueous and organic phase is a crucial parameter, the stability of the host–guest complexes must also be considered. Indeed, an efficient mass transfer between aqueous and organic layers requires fast dissociation–association reactions between the organic compounds and the cyclodextrin. In other terms, the poisoning of the cyclodextrin by the reaction product must be avoided. As intermolecular hydrogen bonds between hydroxyl groups of the cyclodextrin and the carbonyl group of the product play an important role in the stabilization of host–guest complexes, the decrease in number of free hydroxyl groups in chemically modified cyclodextrins lead to decrease the intermolecular interactions and the K_2 stability constant of product-functionalized cyclodextrin complex (Eq. (2) in Fig. 6) is probably weaker than the K_1 stability constant of product-cyclodextrin complex (Eq. (1) in Fig. 6). This contribute to increase undoubtedly the mass transfer proprieties of modified cyclodextrin [21].

However, reversible and partial "poisoning" of the cyclodextrins by some particular substrates such as the carboxylic acids can still occur when the cyclodextrin is chemically modified. This phenomenon was confirmed by carrying out, under the same reaction conditions, the hydrocarboxylation of a 50:50 mixture of decene and undecanoic acid and the hydrocarboxylation of 50:50 mixtures of decene and organic compound. As organic compounds, 1,3,5-triethylbenzene and cumene have been chosen because of their different ability to form inclusion complexes with cyclodextrins. Indeed, it is known that cumene fits very well in the host cavity of the cyclodextrin (stability constant with the β-cyclodextrin: 1200 M^{-1}), and that the 1,3,5-triethylbenzene is a too large molecule to form stable inclusion complexes (stability constant with the β-cyclodextrin $<60\ M^{-1}$) [10,11]. The results obtained with these different mixtures are presented in Fig. 7.

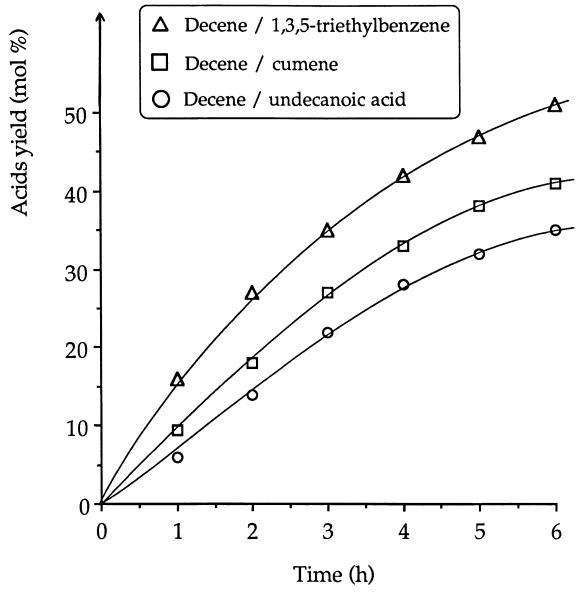

Fig. 7. Hydrocarboxylation of different mixtures. Experimental conditions: Dec-1-ene: 10 mmol; organic compound: 10 mmol; [Dec-1-ene]/[$PdCl_2$]: 50; [β-cyclodextrin]/[$PdCl_2$]: 7; [$P(C_6H_4SO_3Na)_3$]/[Pd]: 6; pH: 1.8 (HCl); *T*: 100°C; *P*(CO): 40 bar.

Best results are obtained with 1,3,5-triethylbenzene. With cumene, the conversion is lower and reached 42%. In the case of decene/undecanoic acid mixture, only 35% of decene initially present was hydrocarboxylated. The effect of organic compound on the rate hydrocarboxylation can be interpreted by considering a competitive binding of the decene and organic compound to cyclodextrin. Indeed, as cumene forms stable inclusion complexes with cyclodextrin, the available amount of cyclodextrin to transfer decene into aqueous layer is probably lower in the presence of cumene and the hydrocarboxylation rate decreases. A similar phenomenon can also be invoked to account for the low activity observed with the decene/undecanoic acid mixture. To conclude this section the three separate experiments presented in Fig. 7 show clearly that the product of the reaction, namely undecanoic acid can inhibit the reaction. So, the stability of host–guest complexes and the solubility of these complexes in both phases appear as the main parameters which affect the catalytic properties of cyclodextrins.

In our opinion, the most interesting feature of cyclodextrin is the beneficial effect of these compounds on the chemio-selectivity of the reaction [17–20]. Fig. 8 illustrates clearly the increase in selectivity observed with cyclodextrins during the oxidation, hydroformylation or hydrocarboxylation of dec-1-ene.

The unexpected high selectivities (70–99%) observed with cyclodextrins compared to these

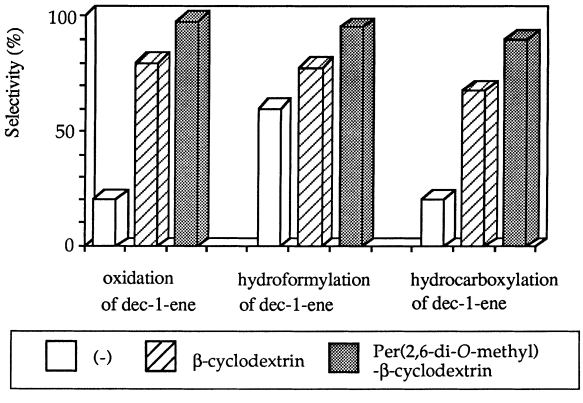

Fig. 8. Effect of cyclodextrins on the ketone, aldehyde or acids selectivity. Experimental conditions: see Figs. 3–5. The main side products are isomeric decene.

obtained without cyclodextrin result from the formation of inclusion complexes. Indeed, when olefin is inside the hydrophobic host cavity of the cyclodextrin, internal double bonds are not accessible and the effect of bulking isomerizing species is considerably reduced. This is in total agreement with the fact that we could not observe any improvement of the selectivity with acyclic oligosaccarides composed of glucopyranose units such as methyl-α-glucopyranoside, maltose and maltoheptaose. These compounds have the same subunits as the cyclodextrins but do not posses a lipophilic host cavity, and so cannot form inclusion complex. The unusually high selectivity observed with per(2,6-di-*O*-methyl)cyclodextrin could be explained by the deeper cavity of this cyclodextrin which would wrap the olefin more efficiently. Finally, two points must be highlighted:

1. Such an increase in the selectivity is a peculiarity of the cyclodextrin. Indeed, under comparable experimental conditions, no increase of the selectivity was observed with common mass transfer promoters like cosolvents or surfactants [19].
2. The protective effect of cyclodextrin is an undeniable advantage for the functionalization of terminal olefins but a major obstacle for the functionalization of internal olefins. For instance, hydroformylation of cyclohexene or dec-5-ene did not occur in the presence of modified cyclodextrins [22]. It must be pointed out that the lack of reactivity of the olefin cannot be attributed to the well-known low reactivity of internal olefins as these olefins can be hydroformylated very slowly in the presence of cosolvent.

Interestingly, the shape selectivity phenomenon has been observed with chemically modified cyclodextrins [23]. For instance, in Wacker oxidation conditions, dec-1-ene reacted more rapidly than other straight higher α-olefins (Fig. 9).

This result is due to subtle molecular recognitions between olefin and chemically modified-β-cyclodextrin. The olefin optimal size and shape are reached with dec-1-ene; with other olefins, the molecular recognition is too weak and the cyclodextrin becomes inefficient [23]. One possible fruitful application of this property could be the selective functionalization of an olefin mixture. Obviously, this functionalization

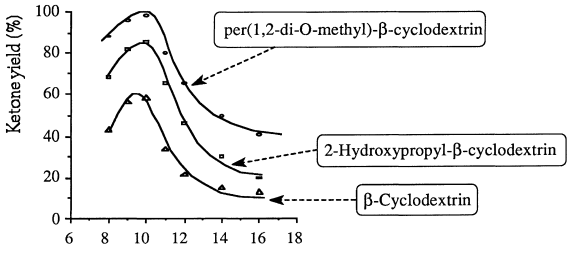

Fig. 9. Effect of chain length of olefin on 2-ketone yield after 6 h of reaction in the presence of various cyclodextrins. Experimental conditions: see Fig. 3.

would be also most unlikely with the common mass transfer promoters.

As emphasized in Section 1 the most important aspect of the aqueous organic two-phase catalysis is the possibility to separate easily the catalyst from the reaction medium and to recycle it in further experiments. The possibility to recycle the catalytic phase and the stability of the inverse phase transfer catalyst have been investigated via the hydroformylation and the hydrocarboxylation of dec-1-ene. Fig. 10 shows that the catalytic systems can be recovered at least five times without any significant loss of catalytic activity.

Elemental analyses of the organic layer arising from the hydrocarboxylation and the hydroformylation of dec-1-ene indicate that no leaching of metal and water-soluble phosphine into the organic phase occurs (hydrocarboxylation: palladium <1 ppm, phosphore <10 ppm; hydroformylation: rhodium <0.5 ppm, phosphore <2 ppm). Furthermore, in all cases, the phase separation between organic and aqueous phases is fast and excellent (<1 min; formation of stable emulsion was not observed). The stability of the cyclodextrin has been studied by electrospray mass spectroscopy. Indeed, it has been recently demonstrated that the electrospray mass spectroscopy is ideally suited to the detection of cyclodextrins and supramolecular complexes [24]. Such experiments on the reaction crudes arising from hydroformylation reactions indicate that the per(2,6-di-*O*-methyl)cyclodextrin is stable and that no degradation of the inverse phase transfer catalyst occurs. As shown in Fig. 11, the results are different in the case of the hydrocarboxylation.

Indeed, the electrospray mass spectrum of a reaction crude recycled five times displayed five groups of signals whose the middle *m/z* were 421, 629, 1353,

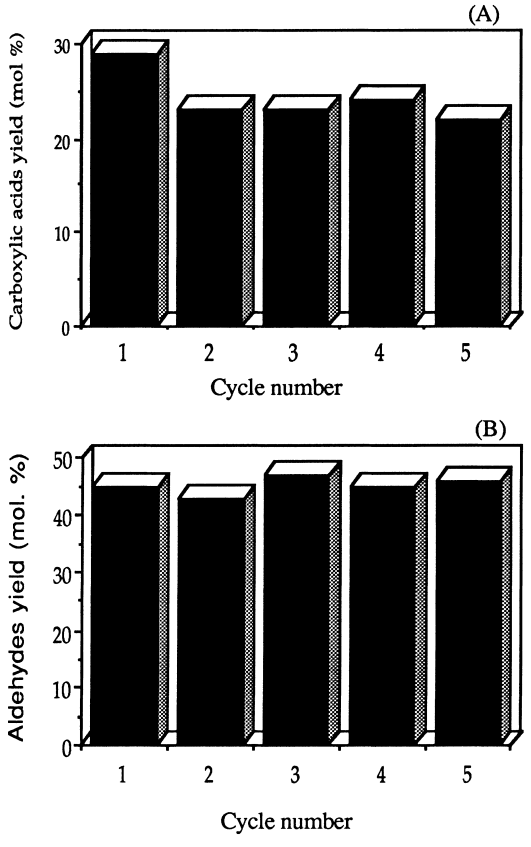

Fig. 10. (A) Carboxylic acids yield as a function of the recycling of the Pd/TPPTS/per(2,6-di-*O*-methyl)cyclodextrin catalytic system. Experimental conditions: $PdCl_2$ (0.8 mmol); TPPTS (4.8 mmol) HCl such as pH: 1.8, per(2,6-di-*O*-methyl)-β-cyclodextrin (5.6 mmol); water (44 ml); dec-1-ene (80 mmol); *T*: 100°C; *P*(CO): 40 atm; *t*: 2 h. Recycling experiments were carried out under CO atmosphere. (B) Aldehydes yield as a function of the recycling of the Rh/TPPTS/per(2,6-di-*O*-methyl)cyclodextrin catalytic system. Experimental conditions: see Fig. 4; *t*: 1 h. Recycling experiments were carried out under CO/H_2 atmosphere.

1507 and 1548. These signals have been attributed to methylated maltose (*m/z*: 407, 421, 435), to methylated maltotriose (*m/z*: 615, 629), to the per(2,6-di-*O*-methyl)cyclodextrin (*m/z*: 1325, 1339, 1353, 1367), to the (3-*O*-undecanoyl)per(2,6-di-*O*-methyl)cyclodextrin (*m/z*: 1493, 1507) and to the formation of an inclusion complex between undecanoic acid and the cyclodextrin (*m/z*: 1534, 1548, 1562). The presence of the (3-*O*-undecanoyl)per(2,6-di-*O*-methyl)cyclodextrin and an undecanoic acid/cyclodextrin complex has been confirmed by MS/MS experiments and by

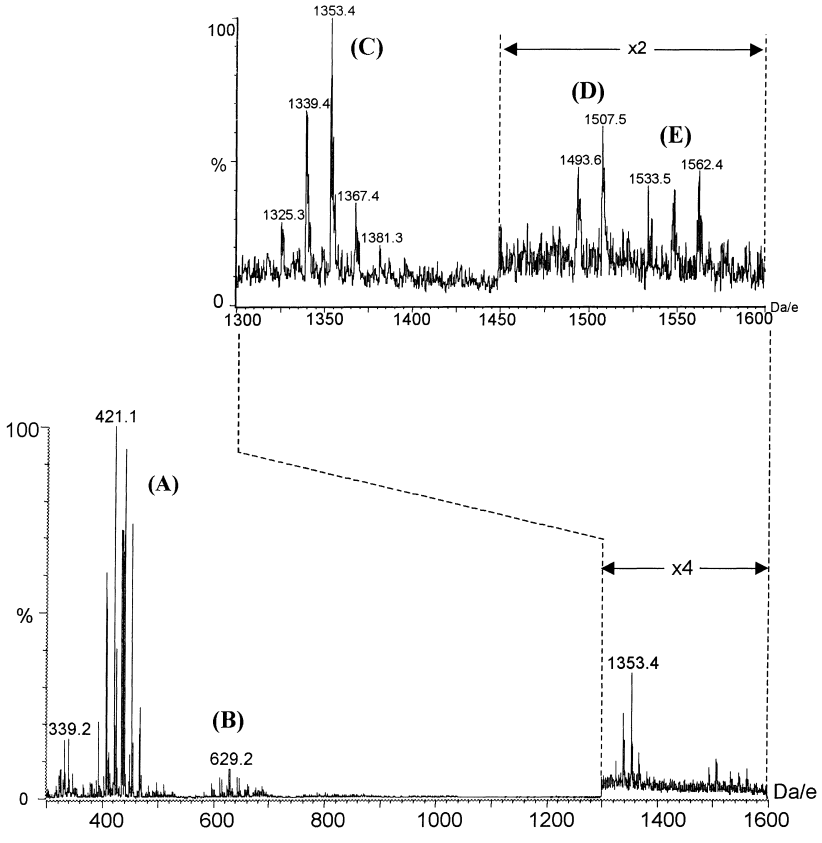

Fig. 11. Electrospray mass spectrum of a five times recycled hydrocarboxylation crude: (A) methylated maltose; (B) methylated maltotriose; (C) per(2,6-di-*O*-methyl)cyclodextrin; (D) (3-*O*-undecanoyl)per(2,6-di-*O*-methyl)cyclodextrin; (E) 1/1 inclusion complex between undecanoic acid and the cyclodextrin.

electrospray mass experiments at high orifice potentials (90 and 120 V), respectively. Experiments conducted without palladium have also shown that the (3-*O*-undecanoyl)per(2,6-di-*O*-methyl)cyclodextrin is obtained from free undecanoic acid and per(2,6-di-*O*-methyl)cyclodextrin by an acid catalyzed process. The methylated maltose and methylated maltotriose result probably from the acid catalyzed hydrolyze of the methylated cyclodextrins [25]. Although the catalytic mixture arising from the hydrocarboxylation can be recovered at least five times without any loss in catalytic performances, the partial esterification and hydrolyze of cyclodextrin constitute irreversible deactivation pathways which will prevent the recycling on a much longer period. So, the hydrocarboxylation or, more generally, the reactions where one component (substrate, product or catalyst) reacts with the cyclodextrin do not fulfil all requirements for durable recovery. Severe reaction conditions which induce degradation of the cyclodextrin (low pH values and high temperature) must also be avoided. Finally, it is worth also noting the drop in acids yield during the first recycling of hydrocarboxylation catalytic phase. This drop has been attributed to the reversible and partial ‘‘poisoning’’ of the cyclodextrin by carboxylic acid and emphasizes once again the important role played by interactions between substrate and cyclodextrin (vide supra).

4. Conclusion

The whole results demonstrate the advantages of cyclodextrins in relation to classical mass transfer

promoters and prove undoubtedly that the use of concept of supramolecular chemistry allows to extend the scope of the biphasic catalysis to water-insoluble substrates. As the functionalized cyclodextrins are nontoxic, cheap, biodegradable and bulk industrial chemicals, the use of these compounds in biphasic transition-metal catalyzed reactions should become general. Due to the molecular recognition, shape selectivity is also possible with cyclodextrins. Further works are in progress in our laboratory to investigate this practically unexplored field in homogeneous catalysis.

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