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# Chemically Modified β-Cyclodextrins: Efficient Supramolecular Carriers for the Biphasic Hydrogenation of Water-Insoluble Aldehydes

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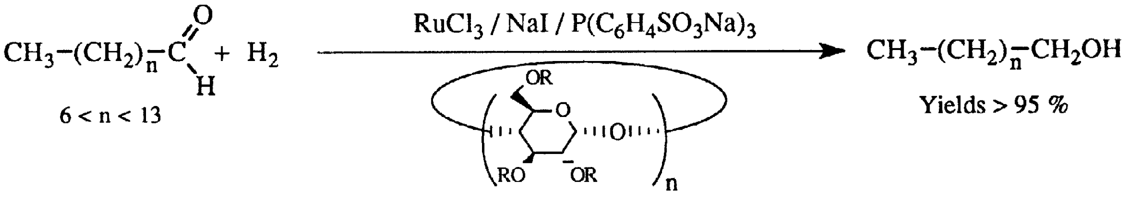
**Abstract:** Hydrogenation of water-insoluble aldehydes can be achieved in high yields in a genuine two-phase system by using a recoverable catalytic system composed of a water-soluble ruthenium/triphenylphosphine trisulfonate complex and a suitable chemically modified β-cyclodextrin.

*Keywords:* Hydrogenation; Aldehydes; Ruthenium; Cyclodextrins.

Aqueous-organic biphasic catalysis has recently become a well-established research field of catalysis [1]. At the present time, the main efforts in this area are directed to the synthesis of new water-soluble ligands and to the development of mass transfer promoters to permit the reaction of water-insoluble substrates.

In this context, we have recently described a new approach based on the use of chemically modified β-cyclodextrins to perform efficiently the functionalization of water-insoluble olefins in a two-phase system [2]. These compounds behave as inverse phase transfer catalysts, i.e. that they transfer olefins into the aqueous phase via the formation of inclusion complexes. Our continuing interest in the use of such supramolecular compounds led us to explore further catalytic applications, namely the hydrogenation of water insoluble aldehydes. The ruthenium catalyzed hydrogenation of aldehydes with short carbon chains is readily achieved in biphasic system whereas hydrogenation of higher aldehydes remains a challenging problem because of the low solubility of these reactants [3]. We would like report hereby that our approach is valuable to carry out the hydrogenation of such aldehydes.



The results obtained with undecanal as water-insoluble model substrate are presented in figure 1. As expected, the undecanal conversion is very low in the absence of mass transfer promoters. Obviously, the use of unmodified cyclodextrins like α-, β-, γ-cyclodextrin (CD) allows to increase greatly the conversion. It must pointed out that the conversion strongly depends on the magnitude of the angular aperture of the CD. Actually, the optimal size for the cavity seems to be obtained with β-CD. A larger aperture such as in γ-CD or a smaller aperture such in α-CD resulted in a decrease in conversion. These results constitute the proof of a subtle molecular recognition between

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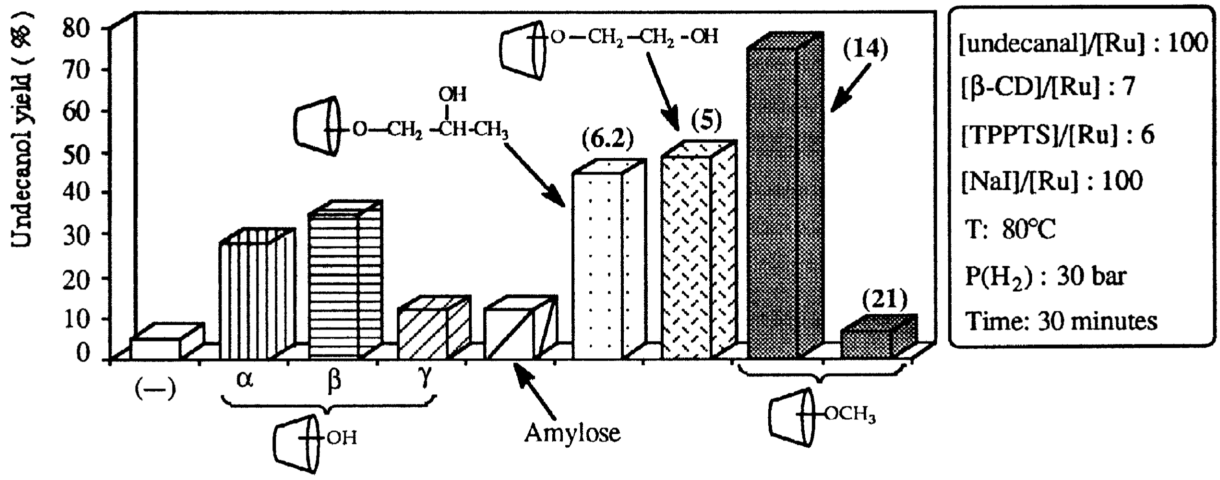
host cavity of CD and undecanal. The low conversion enhancement observed with amylose (a linear polymer of D-glucose which possess helical conformations with six glucose units per turn) reveals the low ability of this compound to form inclusion complexes. Interestingly, modified β-CDs allows to improve still more the undecanal conversion. However, the activities of these CDs are strikingly dependent on the nature of the substituent group and on the degree of substitution of the CD. For instance, whereas the permethyl-β-CD exhibits a very poor catalytic activity (20 $h^{-1}$), the hydrogenation in the presence of heptakis(2,6-di-*O*-methyl)-β-cyclodextrin (DMCD) proceeds with an high initial turnover frequency of 400 $h^{-1}$. The outstanding activity of this CD can also be turned to good account to hydrogenate other aldehydes. Indeed, conversion of nonanal, tridecanal and pentadecanal into the corresponding alcohol was completed after 0.5, 2.5, 6 hours, respectively. The effectiveness of this peculiar CD arises mainly from its high solubility in both the aqueous and organic layers [2]. Finally, it is worth mentioning that the reaction mixture is strictly biphasic with the DMCD, the aqueous phase being reddish and the organic layer colorless (Ru content < 1 ppm). The two phases separate readily, allowing five recycling of the aqueous catalytic phase without loss of catalytic activity.

In conclusion, this work demonstrates again the potentiality of chemically modified CDs in biphasic catalysis though a new application. High catalytic activities, simplicity in work-up and the quantitative recovery of the catalytic system are the most important advantages of such an approach over conventional methods.

Figure 1. Ruthenium Catalyzed Hydrogenation of Undecanal in Two-Phase System[a,b]



[a] *Experimental procedure.* $RuCl_3$ (0.1 mmol), TPPTS (0.6 mmol), NaI (10 mmol) and cyclodextrin (0.7 mmol) were dissolved in 14 ml of water. The resulting aqueous solution and an organic phase composed of aldehyde (10 mmol), toluene (8 ml) and undecane (1.5 mmol - GC internal standard) were charged under $N_2$ into a 50 mL stainless steel autoclave, then heated at 80°C, and pressurized with 30 atm of $H_2$. The pressure was kept constant throughout the whole reaction by using a gas reservoir along with a pressure regulator. The reaction was monitored by quantitative gas chromatographic analysis (CP Sil 5-CB, 25 m x 0.32 mm). Products were identified by comparison of retention times and spectral properties with authentic samples.

[b] The chemically modified β-cyclodextrins are schematically represented by a hollow truncated cone. The values in brackets correspond to the average number of substituted hydroxyl group of the cyclodextrin.

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