

Substrate selectivity in biphasic Wacker-oxidation of alkenes in the presence of water-soluble calixarenes

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Abstract

Biphasic Wacker-oxidation of higher olefins, catalyzed by palladium complexes with water-soluble sulfonated calix[4]arene- and calix[6]arene-derived ligands have been studied. Complexes showed high catalytic activity under mild conditions and can be multiply reused. Catalysts display substrate selectivity in oxidation of C₆ and C₈ olefins—internal cavity of calixarenes recognizes the size of the substrates. The correlation between binding constants of inclusion complexes and selectivity has been established. © 2002 Elsevier Science B.V. All rights reserved.

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1. Introduction

One of the main problems of applying water-soluble metal complex catalysts in reactions of higher alkenes is to ensure the transfer of substrates into the aqueous phase. This problem can be solved by using various surfactants or compounds capable of forming host–guest complexes [1–3]. Of special interest are cyclodextrin and calixarene ligands which can be used as matrices for the construction of transition metal complexes [4,5]. In the case of such complexes, cooperative substrate binding could be achieved which, on one hand, can increase the catalyst activity and, on the other hand, can enable one to control the process selectivity.

A number of previous works on two-phase catalysis showed that cyclodextrins and also their based supramolecular catalysts, which combine the proper-

ties of phase transfer agent and metal complex with the function of molecular recognition, can change the reaction selectivity and can increase the activity of catalysts. For example, a study of hydroformylation of alkenes has demonstrated that the cyclodextrin-containing metal complexes substantially increase the styrene hydroformylation rate as compared with the rates of hydroformylation of other alkenes [6,7]. Cyclodextrin–palladium complexes modified by propionitrile groups exhibited a high activity in the Wacker-oxidation of 1-octene [8,9]. Hydroformylation has also been performed in the presence of another class of compounds capable of forming host–guest complexes, specifically, water-soluble calixarenes modified by phosphine-containing groups [10,11].

In this work, we have studied the Wacker-oxidation of olefins with the use of water-soluble calixarene-derived ligands as components of catalytic systems. Water-soluble ligands capable of molecular recognition were produced from calix[4]arene-*p*-tetrasulfonic acid, calix[6]arene-*p*-hexasulfonic acid, and calix[4]arene-*p*-tetrasulfonic acid, modified by alkyl and

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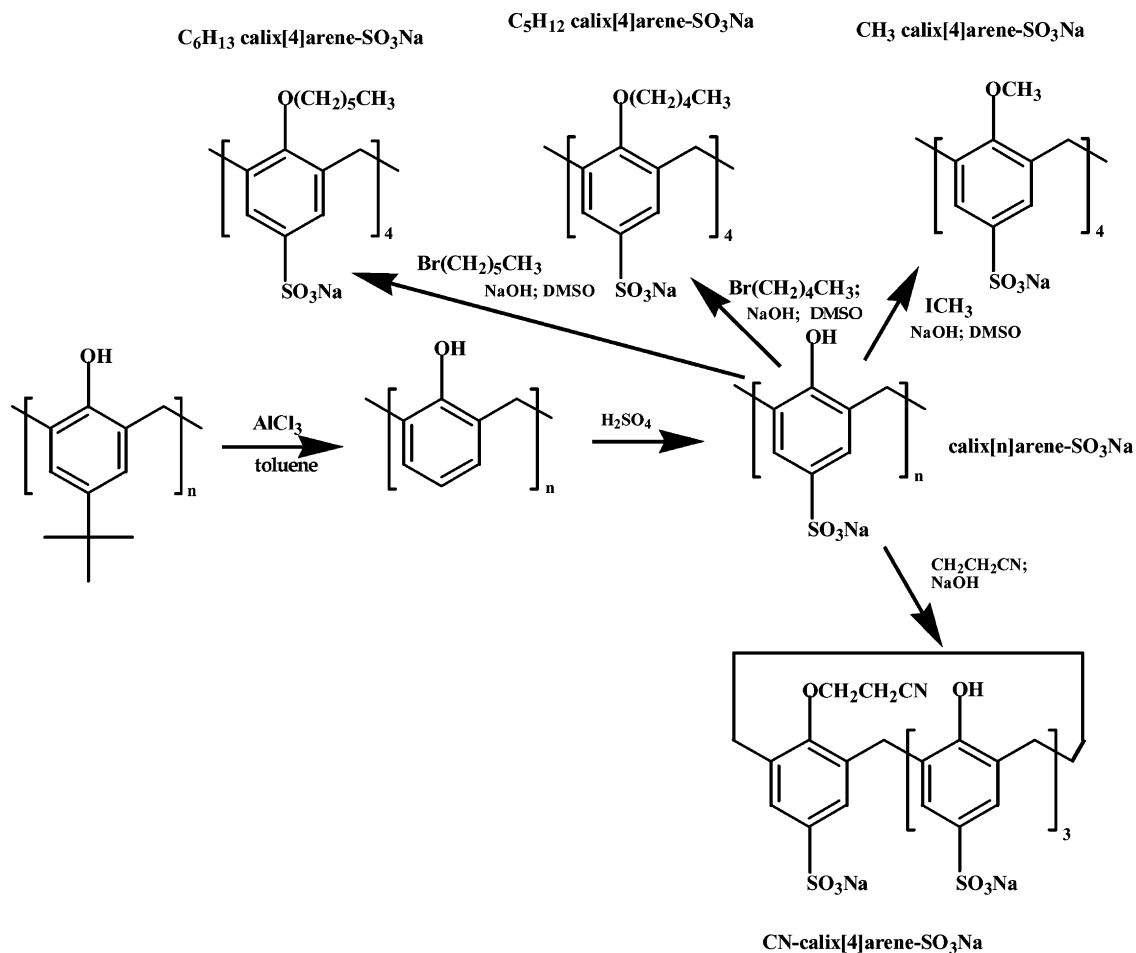


Fig. 1. Synthesis of calixarenes.

propionitrile groups at the phenolic hydroxyls (Fig. 1). Such molecules combining a catalytic center with a calixarene cavity can be exploited for the shape selectivity catalysis. The use of calixarenes with the different size of cavity suggests the dependence of selectivity on the size of guest molecule. The use of calixarenes modified by complex-forming groups enabled one to expect an increase in the activity of the catalysts owing to the cooperative effect.

2. Experimental

Calix[4]arene-*p*-tetrasulfonate and calix[6]arene-*p*-hexasulfonate have been synthesized according to

a literature procedures [12,13]. The modification of calix[4]arene-*p*-tetrasulfonic acid by alkyl groups was carried out by a previously reported methods using the corresponding alkyl bromides [14].

The modification of calixarenes by propionitrile groups was performed as follows. To a paste prepared from 0.3 mmol sodium calix[*n*]arene-*p*-sulfonate and 0.25 ml of a 10% sodium hydroxide solution, acrylonitrile was added during intense agitation at 55 °C. The obtained mixture was kept at this temperature for 3 h, and then cooled and placed into 15 ml of methanol, which led to the formation of a white precipitate. The precipitate was filtered off and dried. The yields of sodium calix[4]arene-*p*-tetrasulfonate and sodium calix[6]arene-*p*-hexasulfonate

modified by propionitrile groups were 78 and 25%, respectively.

Modified calixarenes and palladium complexes of calixarene modified by propionitrile groups were studied by ^1H NMR spectroscopy with a Varian VXR-400. The spectrum of sodium calix[4]arene-*p*-tetrasulfonate modified by propionitrile groups contained the following signals (ppm): ArCH_2Ar , 3.1 and 4.2; ArH , 7.2; CH_2CN , 2.78; OCH_2 , 3.525. The spectrum of sodium calix[6]arene-*p*-hexasulfonate modified by propionitrile groups contained the following signals (ppm): ArCH_2Ar , 4.4; ArH , 7.9; $\text{CH}_2\text{CH}_2\text{CN}$, 2.9 and 3.9.

The Wacker-oxidation of 1-alkenes was carried out in a steel autoclave under an oxygen pressure of 0.5 MPa for 2–8 h in a temperature range 50–80 °C. After completion of experiment, the autoclave was cooled, and diethyl ether and an internal standard (hexadecane) were added. The organic layer was separated and analyzed by GC. The accuracy and the reproducibility of the results were checked by performing several experiments under identical conditions.

The interaction of water-soluble calixarenes with unsaturated compounds has been studied by HPLC with a Gilson chromatograph with a Silasorb C18 column (250 mm in length and 4 mm in diameter) and a Gilson Model 113 refractometer as a detector. As eluents, solutions of calixarenes *p*-sulfonates of various concentrations in an 80:20 acetonitrile–water mixture were used. At each of the calixarene *p*-sulfonates concentrations, the retention times for 1-hexene, 1-octene, styrene, and acetophenone were determined. The constants of stability of complexes were calculated by a published method [15–17].

3. Results and discussion

Ligands and components of catalytic systems were synthesized according to the scheme shown in Fig. 1. All the synthesized compounds were characterized by FTIR, ^1H NMR, and ^{13}C NMR spectroscopy.

The degree of modification was computed as the average of the values obtained by comparing the theoretical and calculated ratios of the integral intensity of the signal of CH_2 protons of alkyl or propionitrile groups to the integral intensity of the signal of an ensemble of identical methylene protons

of calixarene. These ratios for sodium calix[4]arene-*p*-tetrasulfonate modified by amyl bromide and hexyl bromide were 4:1 and 5:1, respectively. This counts in favor of the hypothesis of the exhaustive alkylation of sodium calix[4]arene-*p*-tetrasulfonate. For sodium calix[4]arene-*p*-tetrasulfonate modified by acrylonitrile, the ratio of the integral intensity of the signal of protons of acrylonitrile group to the intensity of the signal of protons of aromatic residue was about 1:4, which suggested that the degree of modification was close to 1. The modification of sodium calix[6]arene-*p*-hexasulfonate at any acrylonitrile–calixarene ratios yielded a product where acrylonitrile groups were bound to all the oxygen atoms, and molecule contained six nitrile groups per one calixarene fragment. The presence of nitrile groups in acrylonitrile-modified calix[4]arene-*p*-tetrasulfonate and calix[6]arene-*p*-hexasulfonate was also proven by FTIR spectroscopy. In the spectra of modified calixarenes, there emerged an absorption band corresponding to vibrations of nitrile groups at 2255 cm^{-1} .

The Wacker-oxidation was carried out at pH 8. As substrates, 1-alkenes (1-hexene, 1-octene, 1-heptene, and 1-dodecene), and also diallyl and styrene were chosen.

Catalytic systems consisted of palladium compounds (palladium sulfate and bis(benzonitrile)palladium (II) dichloride), copper chloride (as a co-catalyst), and water-soluble calixarenes (sodium calix[4]arene-*p*-tetrasulfonate and sodium calix[6]arene-*p*-hexasulfonate). The main products of oxidation of 1-alkenes in the presence of any of the studied catalytic systems were methylketones. The selectivity with respect to ketone was from 85 to 97%.

Note that the oxidation rate was substantially dependent on the number of carbon atoms in alkene. The activity of the calix[4]arene-based catalysts was maximum in the 1-hexene oxidation: under optimum conditions, the quantitative yields were reached in 3 h. The activity in the oxidation of substrates containing more carbon atoms was considerably lower. For comparison, we have also studied catalytic systems that involved no supramolecular groups and consisted of palladium sulfate and the surfactant—sodium dodecyl sulfonate. It proved that, in the 1-hexene oxidation, the activity of the catalyst involving soluble calix[4]arenes was substantially higher than the activity of the catalytic systems based on sodium dodecyl

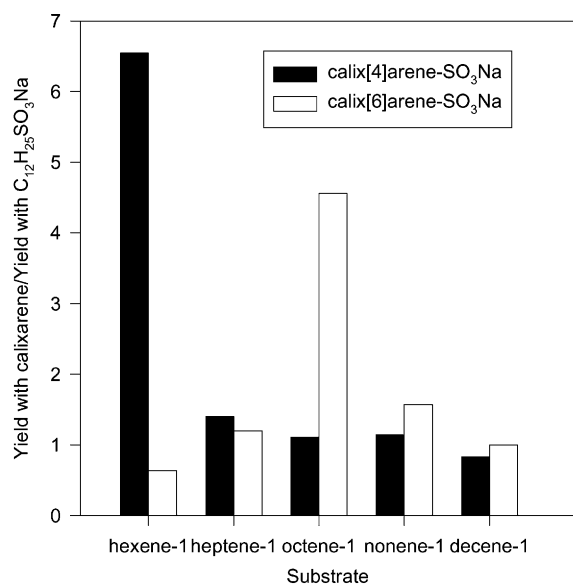


Fig. 2. Activity of calixarene-based catalytic systems in oxidation of different 1-alkenes: $P_{O_2} = 0.5$ MPa; $T = 50^\circ\text{C}$, 2 h; $[Pd^{2+}]/[calixarene]/[Cu^{2+}]/[C_8H_{14}] = 1/1/10/40$.

sulfonate. Note that the calix[6]arene-based catalysts exhibited no such a considerable difference in activity in the 1-hexene oxidation (Fig. 2, Table 1).

The activity of the catalytic systems varied in the order:

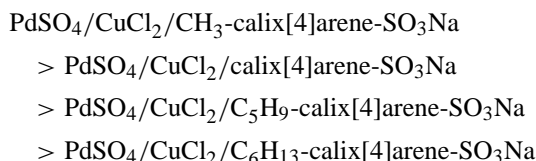


Table 1

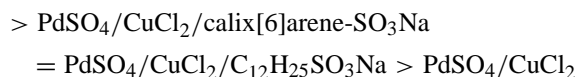
Wacker-oxidation of 1-hexene ($P_{O_2} = 0.5$ MPa; $T = 50^\circ\text{C}$, 2 h; $[Pd^{2+}]/[calixarene]/[Cu^{2+}]/[C_6H_{12}] = 1/1/10/50$)

Catalytic system	2-Hexanone yield (%)
$PdSO_4/CuCl_2$	<5
$PdSO_4/CuCl_2/C_{12}H_{25}SO_3Na$	11
$PdSO_4/CuCl_2/C_6H_{13}\text{-calix[4]arene-SO}_3Na$	48
$PdSO_4/CuCl_2/C_5H_9\text{-calix[4]arene-SO}_3Na$	61
$PdSO_4/CuCl_2/CH_3\text{-calix[4]arene-SO}_3Na$	95
$PdSO_4/CuCl_2/calix[4]arene-SO}_3Na$	82
$PdSO_4/CuCl_2/calix[6]arene-SO}_3Na$	10

Table 2

Wacker-oxidation of 1-octene ($P_{O_2} = 0.5$ MPa; $T = 50^\circ\text{C}$, 2 h; $[Pd^{2+}]/[calixarene]/[Cu^{2+}]/[C_8H_{14}] = 1/1/10/40$)

Catalytic system	2-Octanone yield (%)
$PdSO_4/CuCl_2$	7
$PdSO_4/CuCl_2/C_{12}H_{25}SO_3Na$	9
$PdSO_4/CuCl_2/CH_3\text{-calix[4]arene-SO}_3Na$	5
$PdSO_4/CuCl_2/C_6H_{13}\text{-calix[4]arene-SO}_3Na$	7
$PdSO_4/CuCl_2/C_5H_{11}\text{-calix[4]arene-SO}_3Na$	12
$PdSO_4/CuCl_2/calix[6]arene-SO}_3Na$	41



Unlike the Wacker-oxidation of 1-hexene, the reaction of 1-octene in the presence of the calix[4]arene-based catalysts occurred at a low rate (Table 2). In the 1-octene oxidation, the maximum activity was exhibited by calix[6]arenes.

In our opinion, this dependence of the activity is related to the specificity of the reaction in the presence of water-soluble calixarenes with the formation of host-guest complexes in aqueous medium. In this case, the rate of the reaction in the two-phase system should correlate with the constants of formation of such complexes (binding constants).

The constant is maximal when there is a structural correspondence between the cavity of water-soluble calixarene and the substrate molecule. The sizes of the cavities of calix[4]arene and calix[6]arene correspond to the sizes of 1-hexene and 1-octene molecules, respectively. This inference was also suggested by the results of studying the diallyl oxidation—yield of ketones was quantitative (ketone to diketone 2 to 1). In this reaction, the activity of the calix[4]arene-based catalyst was much higher than the activity of the catalyst based on calix[6]arene.

For testing the validity of this assumption, the formation constants of 1-hexene and 1-octene complexes (K) were found by HPLC in a water-acetonitrile mixture. The capacity factors were measured at various concentrations of water-soluble calixarenes. The measurement results were processed by the equation [15]

$$\frac{1}{k} = \frac{1}{k_0} + K^* \frac{C_i}{k_0},$$

Table 3
Formation constants (K , mol⁻¹) for inclusion complexes

Calixarene	1-Hexene ^a	1-Octene ^a	Styrene ^b	Acetophenone ^b
Calix[4]arene tetrasulfonate	840	95	1400	800
Calix[6]arene hexasulfonate	18	220	10000	12000

^a CH₃CN/H₂O = 4.

^b CH₃CN/H₂O = 3.

where k_0 is the capacity factor in the absence of calixarene and k_i is the capacity factor in the presence of calixarene at concentration C_i .

The calculated formation constants of 1-hexene and 1-octene complexes differed substantially for different calixarenes: in the presence of calix[4]arene, the constant for 1-hexene complex was more than twice as large as that for 1-octene complex; and in the presence of calix[6]arene, the constant for 1-octene complex exceeded the constant for 1-octene complex more than twofold (Table 3). Note that the difference between the constants under the conditions of catalysis experiment should be larger because of the hydrophobic effect in aqueous solutions (e.g. the constants for cyclodextrins can increase by two orders of magnitude [17]).

A metal complex with the ability of producing host-guest complexes owing to the cooperative effect of the additional binding to the metal ion (similar to the double recognition for cyclodextrins) has a higher stability and a higher catalytic activity [3,6,8]. In view of this fact, in the Wacker-oxidation of 1-alkenes, we studied the activity of in situ synthesized palladium complexes of calixarenes modified by nitrile groups. The catalytic activity of complexes of tetrasulfocalix[4]arene modified by propionitrile groups (on the average, to a ratio of one nitrile group per one calixarene molecule) proved to be higher than the activities of the catalytic systems based on unmodified tetrasulfocalix[4]arene, with the substrate selectivity being the same. In the presence of this catalyst, the quantitative yields were attained in 2 h (Table 4). The activity of complexes of poly-substituted calixarenes modified by several nitrile groups per one calixarene molecule was substantially lower.

This was likely to be due to the low liability of several nitrile groups coordinated to the palladium ion in such complexes.

We have also explored the styrene oxidation in the presence of catalytic systems based on water-soluble

Table 4
Wacker-oxidation in the presence of PdSO₄/CuCl₂/CN-calix[4]arene-SO₃Na (P_{O_2} = 0.5 MPa; T = 50 °C, 2 h; [Pd²⁺]/[calixarene]/[Cu²⁺]/[alkene] = 1/1/10/50)

Substrate	Ketone yield (%)
1-Hexene	90
1-Heptene	15
1-Octene	20
1-Dodecene	3

calixarenes. The main product of the styrene oxidation was acetophenone, which formed at an yield to 45% in 10 h (Table 5, Fig. 3). In this reaction, there was no significant difference in activity between the calixarene-based systems. The maximum activity was exhibited by palladium complexes with calix[4]arene modified by acrylonitrile. Of importance is the fact that, in this case, the difference in formation constants of the product and the initial substance was small, and despite the high stability of host-guest complex with styrene, quite a rapid catalyst deactivation took place (Fig. 3).

We have also studied the possibility of catalyst recycling. However, the activity of recycled sulfocalixarene-based catalysts was dramatically lower, which

Table 5
Wacker-oxidation of styrene (P_{O_2} = 0.5 MPa; T = 50 °C, 2 h; [Pd²⁺]/[calixarene]/[Cu²⁺]/[styrene] = 1/1/10/40)

Catalytic system	Styrene conversion (%)
PdSO ₄ /CuCl ₂	<5
PdSO ₄ /CuCl ₂ /C ₁₂ H ₂₅ SO ₃ Na	12
PdSO ₄ /CuCl ₂ /C ₆ H ₁₃ -calix[4]arene-SO ₃ Na	25
PdSO ₄ /CuCl ₂ /C ₅ H ₉ -calix[4]arene-SO ₃ Na	30
PdSO ₄ /CuCl ₂ /calix[4]arene-SO ₃ Na	35
PdSO ₄ /CuCl ₂ /CN-calix[4]arene-SO ₃ Na	46
PdSO ₄ /CuCl ₂ /calix[6]arene-SO ₃ Na	44

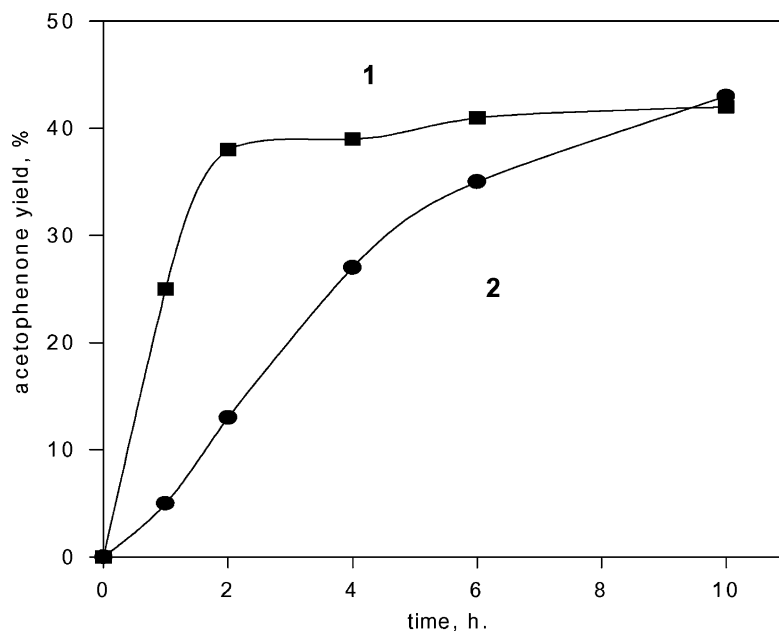


Fig. 3. Wacker-oxidation of styrene: (1) CN-calix[4]arene-SO₃Na; (2) C₁₂H₂₅SO₃Na; P_{O₂} = 0.5 MPa; T = 50 °C, 2 h; [Pd²⁺]/[calixarene]/[Cu²⁺]/[C₈H₁₄] = 1/1/10/40.

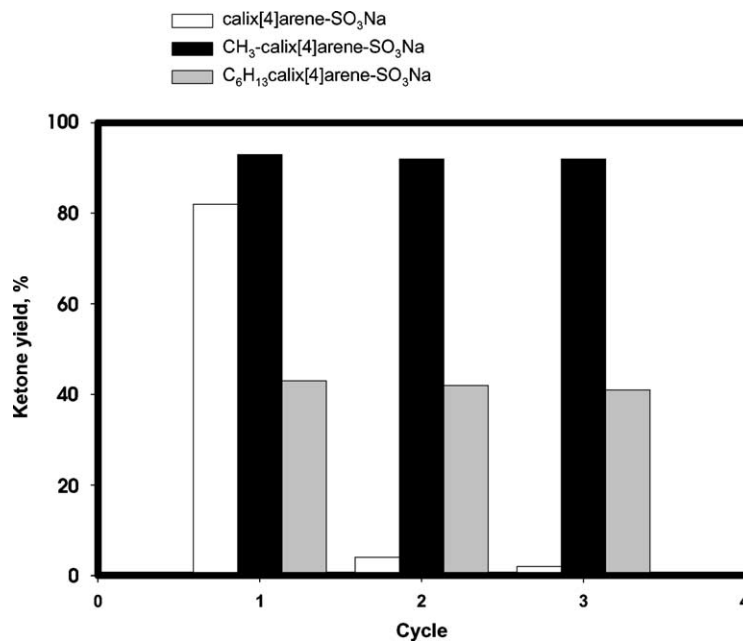


Fig. 4. Catalyst recycling: P_{O₂} = 0.5 MPa; T = 50 °C, 2 h; [Pd²⁺]/[calixarene]/[Cu²⁺]/[C₆H₁₂] = 1/1/10/40.

was probably related to the ready oxidizability of phenolic hydroxyls. An analysis of the reaction mixture by HPLC showed that the calixarene concentration after the reaction was substantially lower, and UV spectroscopy revealed that species with the quinoid structures were formed. This can be obviated by using catalysts based on calixarenes obtained by alkylation of phenolic groups. Such catalysts retain their activity after multiple recycling (Fig. 4).

4. Conclusion

The present results show that a significant selectivity improvement in biphasic catalysis can be achieved by using receptor molecules (calixarenes, cyclodextrins, etc.), which can recognize various types of organic molecules, for design of very attractive catalysts. Their use can be extended to many organic reactions, including hydroformylation, carbonylation, different types of oxidations and enantioselective syntheses.

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