



# Modifier effects on Pt/C, Pd/C, and Raney-Ni catalysts in multiphase catalytic hydrogenation systems

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Dedicated to Professor Renato Ugo on the occasion of his 65th birthday

## Abstract

In the presence of a catalyst modifier (an onium salt, an amine, or a polyethylene glycol (PEG)), in a biphasic aqueous–organic mixture, the activity and the selectivity of hydrogenation reactions conducted using catalysts such as Pt/C, Pd/C or Raney-Ni, can change significantly. Hydrodehalogenation of haloaromatics, reduction of functional groups on the aromatic ring and of the aromatic ring itself, benzyl group hydrogenolysis, can be conducted under mild conditions, with high rates and interesting regio-, chemo- or stereoselectivities. The modifier coats the catalyst, thereby forming an interfacial film, wherein the reactions take place. This film partitions the catalyst at the aqueous–organic interface and influences the outcome of the reactions by mediating the substrate–catalyst interactions.

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## 1. Introduction

Catalytic hydrogenolysis of aromatic halides represents a viable, low-cost, and green methodology with an environmental value since it can be applied for the degradation of hazardous halogenated organic substances, such as polychlorinated benzenes, phenols, Cl–C3 halocarbons, and of more toxic PCB, pesticides, dioxins, etc. This methodology is a promising detoxification tool for a number of environmental objects, such as contaminated soils, municipal waste incinerator fly-ashes, hazardous organochlorine wastes, etc. There are a number of examples in the literature [1–10] that exemplify applications of the catalytic hy-

drodehalogenation (HDX), in particular, hydrodechlorination (HDCl), and point at the advantages of the catalytic reductive treatment before combustion for waste disposal.

As a rule, supported palladium [1–12] is the most active catalyst for the HDCl reaction, especially for the exhaustive dechlorination of polychlorinated substrates, which are known to be the harder to reduce as the number of chlorine atoms present on the aromatic ring grows. There are examples using supported Ni catalysts as well [13–16], and other metals, such as Pt, Ru, Rh, etc. However, for HDCl with H<sub>2</sub> in most cases high pressures and/or temperatures are required in both gas- and liquid-phase systems.

Herein, we report the use of catalyst modifiers in multiphase catalytic systems, which allow to

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conduct a variety of reduction reactions under mild conditions: at 50 °C, 1 atm of H<sub>2</sub> pressure and in moderate reaction times. For example HDX of haloaromatics [17–21], selective hydrogenation of aromatic carbonyls [22], hydrogenolysis of benzyl ethers [23], up to aromatic hydrogenation [22,24] proceed smoothly in a system made by four immiscible phases: aqueous and organic ones, a solid heterogeneous catalyst (e.g. Pd/C, Pt/C, Raney-Ni), and gaseous hydrogen. The presence of the modifier, combined with the other components of the system, allows to achieve higher reduction rates, e.g. in the case of HDCl, and to optimize chemo-, regio-, and stereoselectivities of the reaction when competing reduction of other functional groups is possible [25–28].

In particular, the modifier seems to be the key ingredient of the mixture, because of the way it interacts with the catalyst [29]. The question of how the modifiers acts in promoting these effects has been addressed periodically, and has allowed to collect a number of pieces of evidence. Scope of this paper is to report some recent results and to gather some conclusions on the mechanism, or on the mode of action, of catalyst modifiers in the multiphase system.

## 2. Results and discussion

### 2.1. Nature of the modifier

The modifier has to be a molecule with a relatively polar head group, and one or more lipophilic chains, e.g. a phase-transfer agent, like Aliquat<sup>®</sup> 336 (A336, tricaprilmethylammonium chloride), or a surfactant, like polyethylene glycols (PEG) (see Table 1). Various onium salts, amines, and PEGs have been found to behave similarly.

In general, surfactants, e.g. an anionic surfactant, such as sodium dodecylsulfate have no or little effect on the reaction kinetics and selectivity. This suggests that the action of the modifier is not a micellar effect and involves an interaction of the positively charged site of the modifier molecule (e.g. of nitrogen in ammonium salts or amines) with the catalyst. On the other hand, this action cannot be ascribed to simple phase-transfer catalysis.

Table 1

Types of modifiers used in the multiphase catalytic reduction

No.	Modifier	Refs.
1	Aliquat <sup>®</sup> 336 (A336)	[17–27]
2	C <sub>16</sub> H <sub>33</sub> (C <sub>18</sub> H <sub>37</sub> ) <sub>3</sub> N <sup>+</sup> Br <sup>-</sup>	[18]
3	C <sub>16</sub> H <sub>33</sub> ( <i>n</i> -Bu) <sub>3</sub> P <sup>+</sup> Br <sup>-</sup>	[17–19]
4	C <sub>16</sub> H <sub>33</sub> (py) <sup>+</sup> Br <sup>-</sup>	[17,18]
5	PhCH <sub>2</sub> (C <sub>2</sub> H <sub>5</sub> ) <sub>3</sub> N <sup>+</sup> Br <sup>-</sup>	[18]
6	( <i>n</i> -Bu) <sub>4</sub> N <sup>+</sup> HSO <sub>4</sub> <sup>-</sup>	[18]
7	MeO(CH <sub>2</sub> CH <sub>2</sub> O) <sub><i>n</i></sub> H <sub><i>n</i>-15</sub>	[18,19]
8	PEG 6000	[18]
9	PPG 2000	[18]
10	Brij 35, 52, 56, 58	[24]
11	PhCH <sub>2</sub> (CH <sub>3</sub> CH <sub>2</sub> ) <sub>3</sub> N <sup>+</sup> Cl <sup>-</sup>	[24,25]
12	PhCH <sub>2</sub> ( <i>n</i> -Bu) <sub>3</sub> N <sup>+</sup> Cl <sup>-</sup>	[24]
13	Et <sub>2</sub> NH	[25]
14	Et <sub>3</sub> N	[25]
15	<i>n</i> -Bu <sub>3</sub> N	[25]
16	(PhCH <sub>2</sub> ) <sub>3</sub> N	[25]
17	<i>n</i> -C <sub>8</sub> H <sub>17</sub> NH <sub>2</sub>	[25]
18	Cinchonidine	[28]
19	Cinchonine	[28]

### 2.2. Catalyst partitioning

It is assumed that the modifier forms a nano-layer, adsorbed over the particles of heterogeneous catalyst, therefore constituting an environment, where the reaction proceeds. The onium salt (A336) in such a system forms a separate liquid-phase between the aqueous and organic ones [30–33]. This phase can be visually recognized in a system where water, iso-octane and A336 are present together: with addition of the heterogeneous catalyst, the latter resides preferably in this third phase. The readily apparent effect of the modifier is therefore macroscopic and appears to be connected with a better dispersion of the catalyst particles in the organic phase. It is visually evident that the modifier-catalyst assembly is in better contact with the organic than it is with the aqueous phase, which may be responsible for a prompt access of the organic substrate to the active sites of the catalyst. In a system with only water and iso-octane the catalyst tends to reside mainly at the phase boundary and in the aqueous phase (Fig. 1A), while with the addition of A336, this pattern reverses and the catalyst is partitioned between the interface and the organic phase (Fig. 1B). Interestingly, the addition of base in the aqueous phase, such as KOH, used

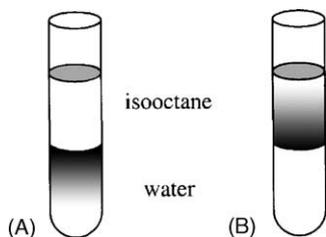


Fig. 1. Distribution of metal catalyst in a biphasic isooctane–water system: (A) without, and (B) with the modifier (A336).

in the HDX reactions, seems to favor transfer of the catalyst to the organic phase as well. In the presence of base (even if no A336 is present) the catalyst is also distributed between the interface and the organic phases, while the aqueous base solution stays transparent.

### 2.3. Catalyst coating by the modifier

There is a high affinity of the modifier for the catalyst particles, which are coated by a thin film of modifier. One proposed way by which this film is formed may involve the carboxyl groups present on the charcoal support, which act as anchoring points for the modifier (in this case an onium ion) [25]. In a certain sense, this film represents an example of an immobilized ionic liquid. The ionic liquids are known as a class of compounds, mainly various ammonium salts liquid at room temperature that have been widely used as alternative reaction media for the recent years. Aliquat<sup>®</sup> 336, which is usually used in our systems, is liquid at room temperature.

The supported catalyst is made more lipophilic by this surface membrane of modifier, which explains why it resides preferentially in the organic phase or at the phase boundary, or inside the phase formed by the modifier. On the contrary, if ethanol is used as a solvent, where the modifier (e.g. A336) is soluble, its affinity for the catalyst fails, and its effect is not felt any longer.

However, not all phenomena of the multiphase catalytic systems can be explained by a macroscopic mode of action of the modifier. In fact, some reactions in the presence of the modifier proceed with increased rates even if no good dispersion of catalyst particles is attained. On the other hand, in certain cases the reac-

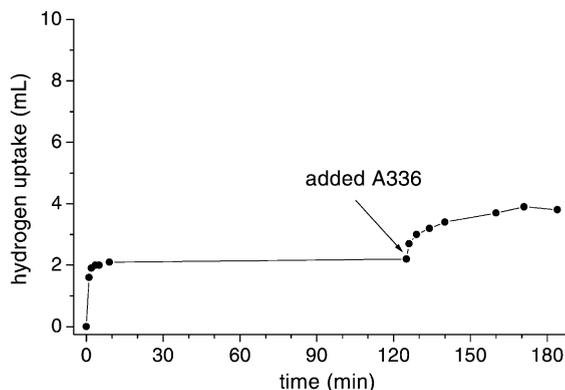


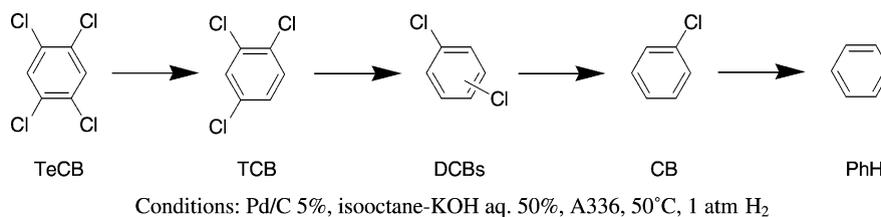
Fig. 2. Hydrogen uptake by Pt/C in suspension. Conditions: 50 °C, H<sub>2</sub> at atmospheric pressure connected to constant pressure reservoir, containing a suspension of 61 mg of 5% Pt on carbon in 10 ml of isooctane and 5 ml of aqueous phase in which 3 mg of 5% (v/v) solution in isooctane of Aliquat<sup>®</sup> 336 was added after 125 min.

tion may be completely inhibited in the absence of the modifier, even if the dispersion of the catalyst is satisfactory. In other cases the peculiarity of the modifier lies in a possibility to change the regio- or chemoselectivity of the reactions, while the rates of certain reaction steps can stay unchanged or be even lower in its presence. Taking these facts into account, we cannot exclude also a molecular-scale mode of action of the modifier, that is present on the catalyst active sites and may therefore affect the processes of adsorption of the reagents or their reaction on the active sites.

### 2.4. Uptake of hydrogen

We have found that the modifier plays a subtle role on the uptake of hydrogen as well. In fact, the amount of hydrogen adsorbed by the system appears larger when the modifier is present. This was observed by bubbling hydrogen, and measuring its uptake using a graduated burette in a isooctane–aqueous KOH–catalyst mixture, where A336 was added after the mixture had been already saturated with H<sub>2</sub> (Fig. 2) [34].

This observation provides an additional rationale for higher reaction rates under the multiphase conditions (i.e. with A336); where the rate acceleration of the HDX reaction in the presence of the modifier can be ascribed to the increased concentration of H<sub>2</sub> available in proximity of the catalyst.



Scheme 1.

### 2.5. Effect of modifier in the hydrodechlorination of chloroaromatics

For simplicity, as a model reaction one can consider the HDCl of 1,2,4,5-tetrachlorobenzene to benzene (Scheme 1) in a system made by isooctane, aqueous KOH, hydrogen, charcoal supported Pd catalyst, and a modifier among the ones in Table 1. The catalyst and modifier are approximately 5 and 20% molar respect to the substrate, respectively.

In the absence of phase-transfer catalyst the reaction is very slow and practically inhibited in the absence of base (Table 2) [18], but in a system with concentrated base solution coupled with the presence of an onium salt (A336 or others) the HDCl of 1,2,4,5-tetrachlorobenzene, as well as that of other polychlorinated and -brominated benzenes proceeds rapidly in quantitative yields. Other than this, Pd catalyzed reactions require increased temperatures and longer reaction times, if using conventional reaction systems [35–37].

### 2.6. HCl removal from the catalyst

A role of the modifier in the HDCl reaction is ascribed to its phase-transfer nature, since it can prevent

catalyst poisoning by transporting the HCl produced by the reaction into the aqueous phase or to the phase boundary, where it is scavenged by KOH. The poisoning of the catalyst by HCl in the HDCl reactions is one of the main drawbacks in most HDCl systems [38–40]; however, under the multiphase conditions in the presence of onium salt (e.g. A336) we have not observed any pronounced rate inhibition due to this effect. The poisoning by HCl becomes readily obvious either with no PT agent or when insufficient base is present. The onium salt prevents HCl poisoning of the catalyst by removing chloride from its surface via a phase-transfer mechanism.

As far as KOH is concerned, it is apparent that, not only does it neutralize HCl, but it also acts synergistically with the modifier, providing the salification of the –COOH groups present on the carbon support, thereby allowing substitution of H<sup>+</sup> by the quaternary ammonium cation [25].

In addition, it is known that KOH may interact (as inhibitor/promoter) with the catalytic metal sites [41]. We have also noted that an excess of KOH might be detrimental to the reaction, particularly in the HDCl of chlorobenzenes over Raney-Ni. In this case, the reaction is strongly inhibited in the presence of the concentrated base (see below).

Table 2

Effects of system composition in the HDCl of 1,2,4,5-tetrachlorobenzene over Pd/C<sup>a</sup>

No.	Aqueous phase	A336	Time (h)	Conversion (%)	Yields (% GC)			
					TCB	DCBs	PhCl	PhH
1	No	No	2.0	29	16	5	–	–
2	KOH (50%)	No	0.5	100	4	19	4	73
3	KOH (50%)	Yes	0.5	100	–	4	–	96

<sup>a</sup> Reaction conditions: 50 °C, 5 ml/min H<sub>2</sub> at atmospheric pressure, 4.0 ml of aqueous phase, 7.0 ml of a 0.7 M solution of substrate in isooctane, 0.032 g of 5% Pd on carbon (0.015 mmol of Pd), and 0.085 g of Aliquat<sup>®</sup> 336 (0.2 mmol) were indicated.

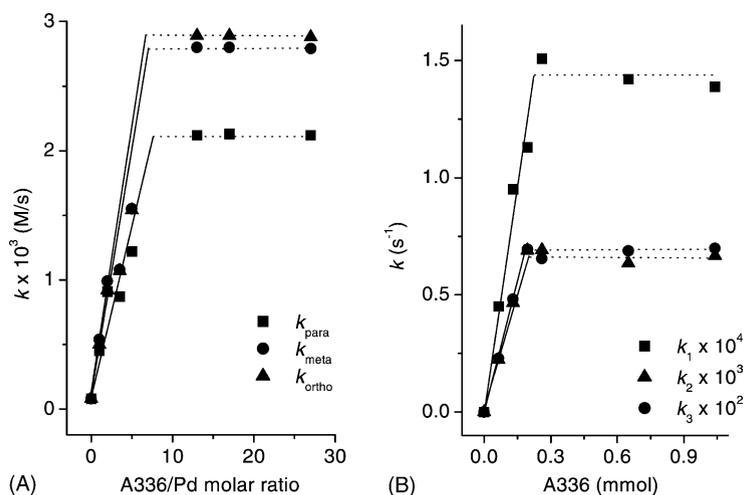


Fig. 3. HDCI rate constants as a function of A336 amount, for the reactions of *o*-, *m*-, and *p*-chloroethylbenzenes over Pd/C 5% (A) and for the consecutive HDCI steps of 1,3,5-trichlorobenzene over Raney-Ni (B). Conditions: (A) 50 °C, 1 ml/min H<sub>2</sub> at atmospheric pressure, 4.0 ml of 50% (w/w) aqueous KOH, 7.0 ml of a 0.7 M solution of substrate in isooctane, 0.032 g of 5% Pd on carbon (0.015 mmol of Pd). (B) 50 °C, 10 ml/min H<sub>2</sub> at atmospheric pressure, 5.7 ml of 7.5% aqueous K<sub>2</sub>CO<sub>3</sub>, 10.0 ml of a 0.7 M solution of substrate in isooctane, 0.25 g of 50% suspension in water of Raney-Ni (2.0 mmol of Ni, Actimet M<sup>TM</sup> from Engelhard).

### 2.7. Kinetics of hydrodechlorination of chlorobenzenes

The HDCI rate constants, plotted versus the modifier concentration, resemble the Langmuir adsorption

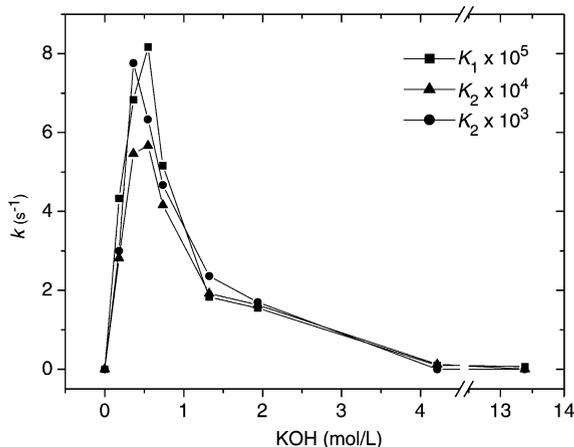


Fig. 4. Effect of aqueous KOH concentration on the rate constants of 1,3,5-trichlorobenzene HDCI over Raney-Ni in the presence of A336. Conditions: 50 °C, 10 ml/min H<sub>2</sub> at atmospheric pressure, 5.7 ml of aqueous phase, 10.0 ml of a 0.7 M solution of substrate in isooctane, 0.103 g of Aliquat<sup>®</sup> 336 (0.26 mmol), 0.25 g of 50% suspension in water of Raney-Ni (2.0 mmol of Ni, Actimet M<sup>TM</sup> from Engelhard).

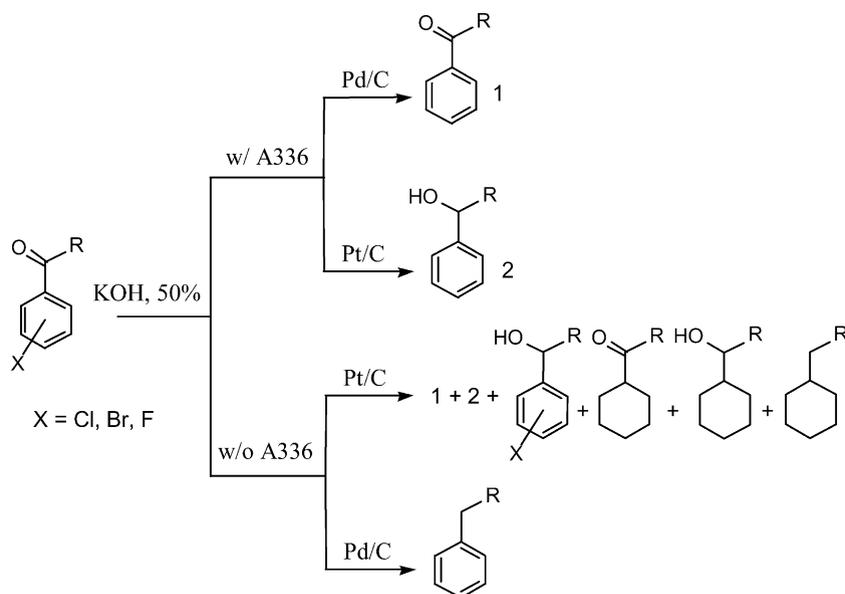
curves. The rate constants for HDCI of chloroethylbenzenes increase with the concentration of modifier, until they reach a plateau above which no further increase was detected (Fig. 3A) [19].

A similar behavior was observed using Raney-Ni as the catalyst in the HDCI of 1,3,5-trichlorobenzene [27] (Fig. 3B). These observations suggest that the role of modifier is tightly connected with its adsorption on the catalyst surface. Presumably, after a monolayer of the modifier is completed the latter has no longer an influence over the reaction rates.

Interestingly, in the HDCI of 1,3,5-trichlorobenzene over Raney-Ni, both the modifier (A336) and the aqueous base (KOH or carbonates) are indispensable for the reaction to proceed at all (Figs. 3B and 4). While in the case of Pd/C the modifier and aqueous KOH act just as promoters, and slow reaction occurs also in their absence.

### 3. Chemoselectivity

*p*-Chloroacetophenone can be selectively reduced either to acetophenone, or to phenyl ethanol, or to ethyl benzene or cyclohexyl ethane by an appropriate choice of catalyst, modifier, and aqueous base concentration. Actually, the selectivity of this reaction (or



Scheme 2.

that of *p*-chloropropiophenone or other halogenated aromatic ketones, see Scheme 2) over Pd/C [19,20,22], Pt/C [24–26] or Raney-Ni [27] can be tuned by varying the modifier type, and the amount of base.

The reaction of chlorinated aromatic ketones with Pt/C and no modifier is not selective and proceeds to a mixture of reduction products, while in the presence of A336 (or other onium salts) and aqueous KOH, a selectivity of up to 100% towards benzyl alcohol can be obtained [24]. In such a system, the respective dechlorinated aromatic ketones can also be obtained with very high yields by stopping the reaction after a few minutes, since the HDCl step proceeds with a very high rate with respect to the reduction of carbonyl function.

The reaction of non-chlorinated aromatic ketones (acetophenone or propiophenone) over Pt/C in the absence of KOH (it can be omitted since no HCl is produced) and with A336, gives selectively cyclohexyl alcohols, while in the absence of A336 the reaction proceeds towards the full reduction products, ethyl benzene and ethyl cyclohexane.

Similarly, with Pd/C the presence of the modifier (A336) also allows the reaction to proceed selectively towards the products of partial reduction. For example the reaction of various halogenated aromatic ketones

in the presence of KOH but without A336 proceeds to the alkyl benzenes, whereas in the presence of A336 only the HDCl step takes place and the respective ketones are formed [22].

The possibility to vary the selectivity of the reduction reactions towards groups different than halogen, e.g. carbonyl, hydroxyl, and aromatic ring, suggests that in such cases the roles of the modifier and base are more profound than just neutralization of HCl by a phase-transfer mechanism, or an increase in the capability of hydrogen adsorption, as was discussed earlier for the HDCl reaction. A possible explanation is that the modifier membrane (or immobilized ionic liquid) comes into play by mediating adsorption of the substrate on the catalyst surface, in a way that favors, for example C–Cl, bond cleavage over C=O hydrogenation, to give HDCl rather than carbonyl reduction.

There is a dependence of chemoselectivity on the hydrophilicity of the modifier. Higher hydrophilicity causes the reaction of Scheme 2 to yield chemoselectively acetophenone, the HDCl product.

### 3.1. Chiral modifiers under multiphase conditions

Further support for the formation of a layer of modifier comes by using a chiral modifier, and by observing

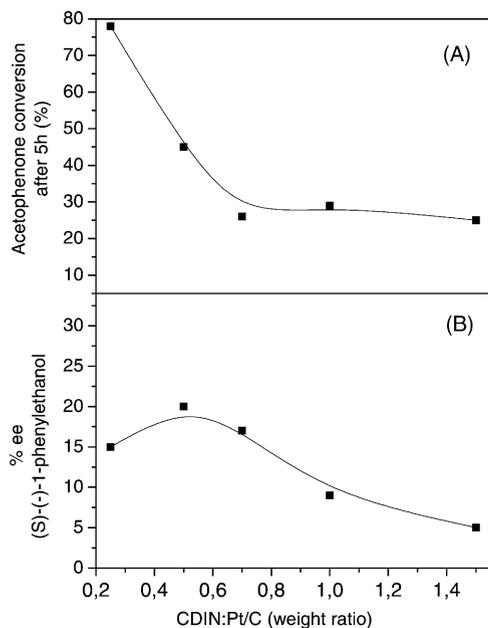


Fig. 5. Effect of varying amount of cinchonidine (CDIN) on the conversion (A) and e.e.'s (B) of the acetophenone reduction. Conditions: 50 °C, 5 ml/min H<sub>2</sub> at atmospheric pressure, 5.5 ml of water, 10.0 ml of a 0.7 M solution of substrate in isooctane, 0.085 g of 5% Pt/C (0.02 mmol of Pt).

that, under appropriate conditions, stereoselective reactions, can be conducted using this system [28,42,43]. The model reaction is the hydrogenation of acetophenone to 1-phenyl ethanol, using a Pt/C catalyst impregnated with a chiral modifier.

By covering the supported catalyst and forming chiral pockets, which stereo-recognize the substrate, the modifier promotes enantioselectivity. The achievable e.e.'s depend on the concentration of modifier used: too little gives high rates but poor e.e.'s, while too much means slow rates and poor e.e.'s (Fig. 5). The right trade-off is the concentration where tight chiral pockets are formed on the catalyst. Other similar observations [44,45], and calculations [46], support this.

#### 4. Conclusions

The conclusions that can be drawn on the mode of action of the modifier, based on experimental evidence, are the following:

1. The modifier coats the catalyst particles, and forms a “nanoenvironment”, wherein the reaction takes place. Adsorption of the modifier on the catalyst is mainly responsible for the phenomena observed, and can be either adsorption of the modifier on the metal sites or its interaction with the carbon support.
2. The effect of the modifier is co-catalytic in the case of the HDCl reaction of halobenzenes, where the presence of the modifier together with the aqueous base leads to the improvement of reaction rates and/or prevents the catalyst poisoning. This could be connected to better catalyst particle dispersion and/or increase of the organic–aqueous interface area, or phase-transfer neutralization of HCl. Some observations suggest that the co-catalytic effect of the modifier in the HDCl reaction may be also connected with the improvement of hydrogen adsorption capacity of the catalyst in the presence of the modifier.
3. The effect of the modifier (as well as that of the aqueous base) on the reaction selectivity can arise from its interactions with both the catalyst active sites and the substrate, i.e. via its interference in the reaction step on the surface or, in the mediation/restriction of substrate adsorption on the catalyst active sites. This leads to the possibility to tune regio-, chemo-, and enantioselectivity in the reductions of polyfunctional substrates.
4. The multiphase systems represent a mild and efficient detoxification tool for removal of the aromatic chlorine in chlorinated POPs, such as dioxins, PCBs, etc. and can be used for treatment of the polychlorinated waste as well as for remediation of the contaminated soils. Research is currently under way in this direction.

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