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The action of onium salts and other modifiers on Pt/C, Pd/C, and Raney–Ni catalysts in the multiphase reduction system

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Abstract

In the presence of a catalyst modifier (an onium salt, an amine, or a polyethylene glycol), in a biphasic aqueous–organic mixture, the reactivity of Pt/C, Pd/C, and Raney–Ni changes significantly. Hydrodehalogenation reactions of halo aromatics, reductions of functional groups on the aromatic ring, benzyl hydrogenolysis, can be conducted under mild conditions, and with interesting rates and regio-, chemo-, and stereoselectivities. The modifier coats the catalyst, and forms 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 substrate–catalyst interactions, and by providing a hydrogen reservoir in the vicinity of the active sites.
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1. Introduction

It is possible to conduct a variety of reduction reactions under mild conditions ($T = 50\,°C$, $pH_2 = 1$ atm) in a multiphase catalytic reduction system. For example, the hydrodehalogenation (HDX) of halo aromatics [1–5], the selective hydrogenation of aromatic carbonyls [6], the hydrogenolysis of benzyl ethers [7], up to aromatic hydrogenation [6,8], proceed smoothly in a system made by five different phases: aqueous, organic, a heterogeneous catalyst (e.g. Pd/C, Pt/C, Raney–Ni), hydrogen, and an insoluble modifier. The modifier is usually an onium salt such as Aliquat 336® (A336), or an

amine, or a polyethylene glycol (Table 1). Its presence, combined with the other components of the system, allows to achieve interesting yields, rates, along with chemo-, regio-, and stereoselectivities [9–12].

Two examples of reactions that proceed in the multiphase system are shown in Eqs. (1) and (2). Tetrachlorbenzene can be rapidly (1 h) and selectively (100%) reduced to benzene (Eq. (1). *p*-Chloroacetophenone can be selectively reduced either to acetophenone, or to phenyl-ethanol, by an appropriate choice of catalyst, modifier and aqueous base concentration (Eq. (2).

In the absence of one or more of the components, the reduction reactions are often slow and not selective. In particular, the modifier seems to be the key ingredient of the mixture, because of the way it interacts with the catalyst,

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Table 1
Types of modifiers used in the multiphase catalytic reduction

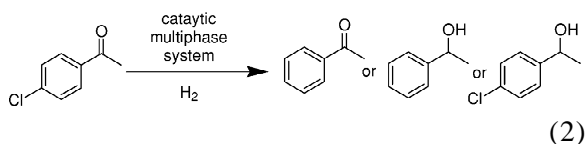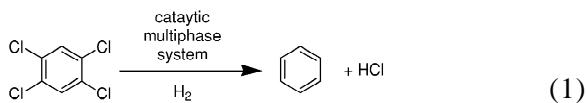|	Modifier	Ref.
1	Aliquat 336® (A336)	[1–11]
2	$C_{16}H_{33}(C_{18}H_{37})_3N^+Br^-$	[2,4]
3	$C_{16}H_{33}(n\text{-}Bu)_3P^+Br^-$	[1–4]
4	$C_{16}H_{33}(py)^+Br^-$	[1]
5	$PhCH_2(C_2H_5)_3N^+Br^-$	[2]
6	$(n\text{-}Bu)_4N^+HSO_4^-$	[2]
7	$MeO(CH_2CH_2O)_nH_{n\sim15}$	[2,3]
8	PEG 6000	[2]
9	PPG 2000	[2]
10	Brij 35	[8]
11	Brij 52	[8]
12	Brij 58	[8]
13	Brij 56	[8]
14	$PhCH_2(CH_3CH_2)_3N^+Cl^-$	[8,9]
15	$PhCH_2(n\text{-}Bu)_3N^+Cl^-$	[8]
16	Et_2NH	[9]
17	Et_3N	[9]
18	$n\text{-}Bu_3N$	[9]
19	$(PhCH_2)_3N$	[9]
20	$n\text{-}C_8H_{17}NH_2$	[9]
21	Cinchonidine	[12]
22	Cinchonine	[12]

apparently by coating it [3,9,11]. The question of how the modifiers act in promoting these effects has been addressed periodically, and has allowed to collect a number of pieces of evidence. The scope of this paper is to describe some conclusions on the study of the mechanism for the catalytic multiphase reduction system, and to propose a mode of action for the catalyst modifier.

2. Results and discussion

There is plenty of flexibility in the choice of the modifier. Essentially it has to be a phase transfer agent (PTA), i.e. a molecule with a relatively polar head group, and one or more lipophylic chains (Table 1). One constraint is that it must be insoluble both in the organic and in the aqueous phases.

For simplicity, as model reactions one can consider indifferently either the hydrodechlorination (HDCl) reaction of 1,2,4,5-tetrachlorobenzene to benzene (Eq. (1), or the HDCl and carbonyl reduction of *p*-chloroacetophenone

(Eq. (2), in a system made by *iso*-octane, aqueous KOH, hydrogen, charcoal supported Pt or Pd catalyst, and a modifier among the ones in Table 1.

(1)

(2)

The metal catalyst is used approximately 5% molar with respect to the substrate, the modifier in a 20% molar ratio. The following points describe the modifier–catalyst interactions and how they affect reactivity, selectivity, and the outcome of typical reactions.

2.1. Catalyst partitioning

The readily apparent effect of the modifier is macroscopic. By adding it to the aqueous–organic–catalyst mixture (Fig. 1a) the latter visibly changes its partitioning. Generally, either the catalyst distributes itself preferentially in the organic phase (Fig. 1b), or, at higher concentrations of modifier, this tends to separate out between the aqueous–organic phases, to form a third liquid phase [13], and to incorporate the catalyst (Fig. 1c). Either way, the modifier has a high affinity for the catalyst; and, in both cases the modifier–catalyst assembly is in better contact with the organic than it is with the aqueous phase, hereby allowing efficient diffusion of the organic substrate to the reactive site of the catalyst.

2.2. Catalyst coating by the modifier

There is a high affinity of the modifier for the catalyst particles, which are coated by a thin film, a kind of membrane, of modifier. One proposed mechanism by which this film is formed may be analogous to the one sketched out in Scheme 1, where the carboxy groups
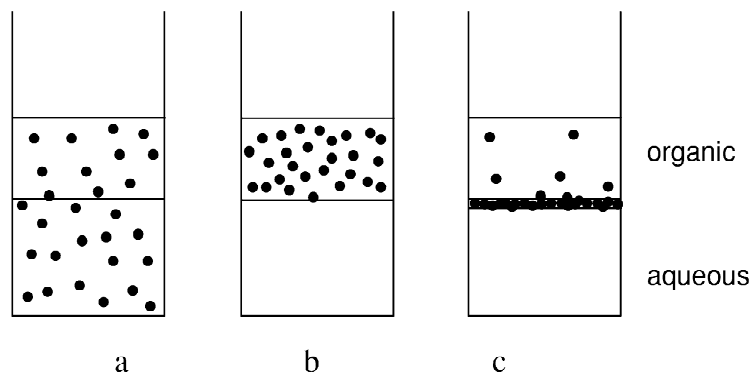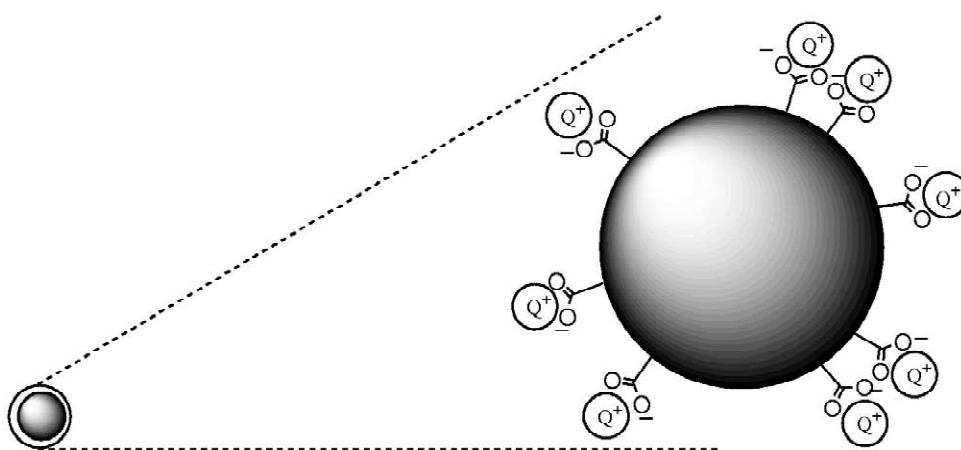
Fig. 1. Partitioning of the catalyst between the phases as a function of the modifier: a: organic phase + aqueous phase + supported catalyst; b: organic phase + aqueous phase + supported catalyst + modifier; c: organic phase + aqueous phase + supported catalyst + excess modifier.

Scheme 1. Catalyst particle in the multiphase system: magnified view of a possible coating arrangement by an onium salt.

present on the charcoal support act as anchoring points for the modifier (in this case an onium ion) [9].

The catalyst is made more lypophilic by this surface membrane of modifier, which explains why it resides preferentially in the organic (Fig. 1b) or modifier phase (Fig. 1c). On the contrary, if ethanol is used as the solvent, where the modifier dissolves, and its affinity for the supported catalyst fails, its effect is not felt any longer.

The hydrodehalogenation rate constants, plotted versus the modifier concentration, follow Langmuir adsorption type curves. For example, it was shown that the rate constants for hydro-dehalogenation of chloroethylbenzenes increase with increasing concentration of modifier, until they reach a plateau above which no further increase was detected (Fig. 2) [3]. A similar behavior was observed using Raney–Ni as the catalyst [11].

The concentration threshold, above which additional modifier is non-influential, may have a two-fold explanation: (a) it constitutes 'monolayer' formation, such as in Langmuir type adsorption; and (b) when the modifier reaches the amount on the catalyst surface where a constant concentration of reactants is maintained in proximity of the catalyst, the mass-transfer limit is effectively eliminated, and the intrinsic reaction rate is attained. This observation is substantiated by the order of the reaction,
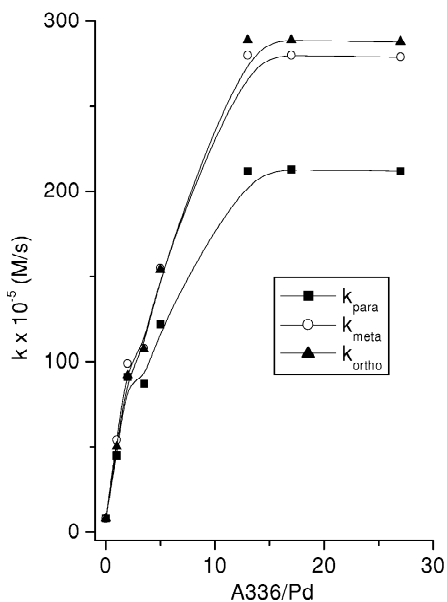
Fig. 2. HDX rate constants as a function of A336 concentration, for *o*-, *m*-, *p*-chloroethylbenzene.

Fig. 3. Effect of varying amounts of CD on the conversion (A) and ee (B) of the reduction of acetophenone.

zero in the substrate, which indicates that when a steady-state concentration of substrate is obtained in proximity of the catalyst, then bulk concentration becomes non-influential. On the other hand the reaction rate is first order in the catalyst [10].

Some support for the latter observation is given by the fact that, while in the case of Pd/C the modifier has scarce effect on the rates; in the case of Raney–Ni the modifier is indispensable for the reaction to proceed at all [11]. There must therefore be some relation between the modifier on the catalyst and substrate adsorption.

Further support for the formation of a layer of modifier comes by using a chiral modifier, and by observing that, under appropriate conditions, stereospecific reactions can be conducted using this system [12,14]. By covering the supported catalyst and forming chiral pockets, which stereo-recognize the substrate, the modifier promotes enantioselectivity. The achievable ee's depend on the concentration of modifier used: too little gives high rates but poor ee's, while too much means slow rates and poor ee's (Fig.
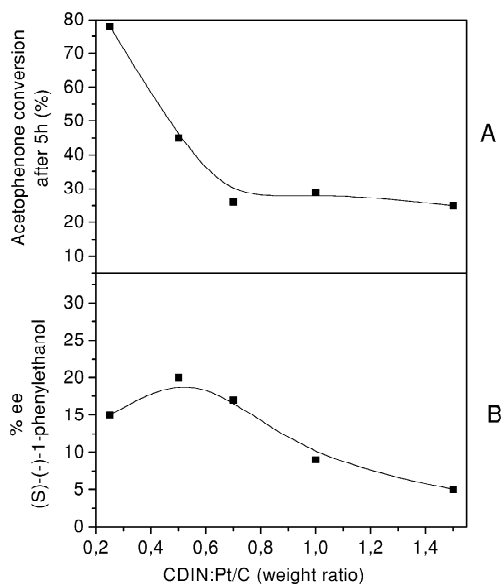
3). The right tradeoff is the concentration where tight chiral pockets are formed on the catalyst. Other similar observations [15,16], and calculations [17], support this (Fig. 4).

It has been demonstrated that the modifier does not act as a surfactant, i.e. it does not
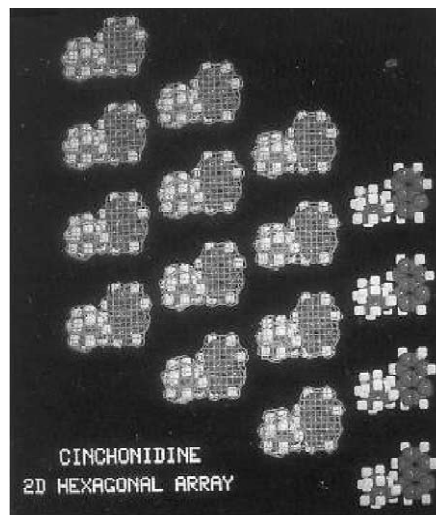

Fig. 4. Representation of how cinchonidine may form prochiral cavities on a Pt surface (reproduced by permission of Wiley–VCH) [17].

improve dispersion of the reactants or catalysts, and does not act via micellar catalysis [18].

2.3. HCl removal from the catalyst

Another role of the modifier is due to its phase transfer nature: it prevents catalyst poisoning, by transporting the HCl produced by the reaction into the aqueous phase, where it is neutralized by the KOH. The mechanism is the classical phase-transfer one (Scheme 2). The poisoning effect of HCl on the catalyst [19] becomes readily obvious either with no PT agent or when insufficient base is present: the reaction becomes inhibited.

2.4. Uptake of hydrogen

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, first in mixtures made by isooctane–KOH(aq)–catalyst, and then in identical mixtures where A336 was added. The latter mixture was able to adsorb a larger amount of hydrogen than the former. Analogously, the fact that an additional quantity of H_2 was adsorbed, when A336 was added to a mixture of isooctane–KOH(aq)–catalyst, after it had been already saturated with H_2, confirms this effect (Fig. 5) [18].

This observation is significant because it implies that the rate acceleration of the hydrodehalogenation reaction in the presence of the
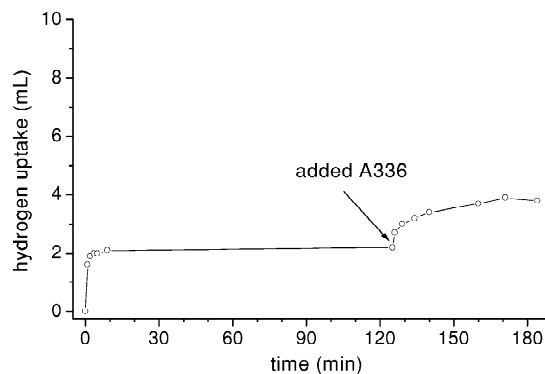

Fig. 5. Hydrogen uptake by Pt/C in solution and in the presence of A336.

modifier can perhaps be ascribed to increased and constant concentration of hydrogen, a reservoir, held in proximity of the catalyst.

2.5. Chemoselectivity

It can be tuned by varying a number of reaction parameters. Mainly modifier type and amount [3,4,6], and base concentration [8–10]. The major effect of the modifier is to induce chemoselectivity in many of the reactions. Significantly, the reaction of *p*-chloropropiophenone goes all the way to ethyl benzene with Pt/C and no modifier; while in the presence of A336 100% selectivity towards hydrodechlorination (Pd/C) or the benzyl alcohol (Pt/C) can be obtained [8]. The modifier is therefore somehow mediating between the substrate and the catalytic sites. The question is how the modifier does that.

Under our conditions the reduction mechanism presumably does not involve radical
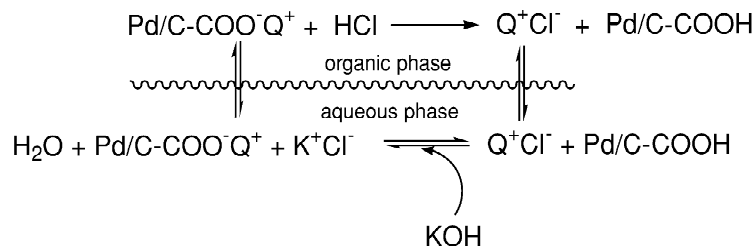
Scheme 2. Phase-transfer mechanism.

species, but rather oxidative addition of the substrate to the catalyst, followed by hydrogen insertion, and elimination of the products. The modifier membrane must therefore come 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 hydrodechlorination rather than carbonyl reduction.

There is a dependence of chemoselectivity on the hydrophilicity of the modifier. Higher hydrophilicity, causes the reaction of Eq. (2) to yield chemoselectively acetophenone, the hydrodechlorination product. In this case perhaps, the modifier–catalyst ensemble, by hindering approach causes a less positive interaction between substrate and the catalyst. This, in turn, could favor reaction of the more polarized C–Cl bond with respect to the C=O one, i.e. higher chemoselectivity.

This explains, for example, why hydrodechlorination is generally the fastest reaction: approach and reaction of the aromatic chlorine would be favored initially with respect to carbonyl.

2.6. Kinetics

Kinetic studies show that certain reaction parameters (KOH concentration, nature of the metal, nature of the modifier) play a role on the reaction outcome. As far as KOH is concerned, for example, it is apparent that, not only does it neutralize HX, it also acts synergistically with the modifier in determining kinetics and selectivities. Part of its role may be in the salification of the COOH groups present on the support, thereby allowing substitution of H^+ by the onium cation (Schemes 1–2) [9]. In addition, KOH may interact (as inhibitor/promoter) with the catalytic metal sites [20]. It was also noted that an excess of KOH is detrimental to the reaction selectivity, perhaps too much KOH wipes the catalyst clean and decreases chemoselectivity.

3. Conclusions

At this stage 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 this interaction is largely responsible for the selectivity features of the system.
2. The modifier membrane forms the nanoenvironment wherein the reaction takes place.
3. The modifier is adsorbed on the surface of the catalyst and behaves like a hydrogen reservoir for the reaction.
4. The reaction itself occurs at the interface between modified-catalyst, aqueous and organic phases, in a tight nanostructured environment where transfers between the phases are favored. The substrate, H_2, KOH, HCl, the product, and the modified-catalyst are in close contact with one another, allowing efficient transfer of the reactants between
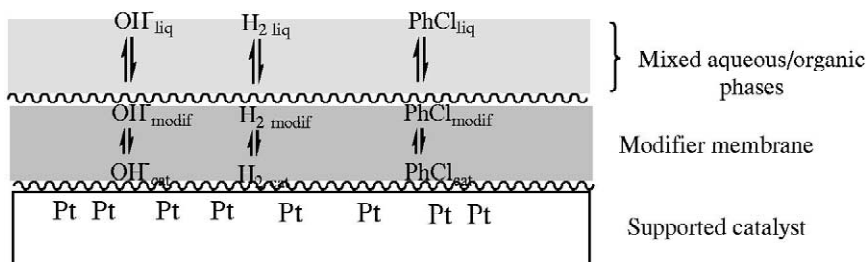

Fig. 6. Equilibria of the reactants at the catalyst–modifier–aqueous/organic interfaces.

the phases. Reagent, and product selectivity are determined by the equilibria which are established by these species between the phases. Fig. 6 shows the membrane formed by the modifier on the catalyst, the liquid phase made by the aqueous and organic solvents, and the equilibria of some of the involved species.

Acknowledgements

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