Dowex® 1-supported PtCl$_4$ ion pair as a recycle hydrogenation catalyst

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Abstract

Polystyrene-supported ion pairs, generated from PtCl$_4$ and Dowex® 1 anion exchangers in EtOH, were shown to be leach-proof and recyclable catalysts for hydrogenation of alkenes and for other unsaturated compounds at < 35°C. In the hydrogenation of 1-decene the intraparticle diffusion of the substrate was found to contribute to the overall rate of the process. XPS analysis revealed the presence of Pt(II) and Pt(IV) species in the reaction mixture. No detectable amount of Pt(0) could be traced even after completion of the catalytic process. © 1999 Elsevier Science B.V. All rights reserved.

1. Introduction

Commercial polystyrene-based anion and cation exchangers have been proposed long ago as suitable supports for the preparation of various transition metal catalysts. Thus, e.g., when palladium dichloride as well as K$_2$PdCl$_4$ have been reacted with the anion exchanger Amberlite® A27, supported ion pairs of general structure {[polystyrene-CH$_2$N(CH$_3$)$_3$]$_2$[PdCl$_4$]}$_n$ have been obtained [1–6]. Analogous immobilized rhodium and platinum resinous compounds were formed when the palladium salts were replaced by Rh(III) or Pt(IV) chlorides [7].

Conversion of the ion pairs into supported dispersions of the corresponding free platinoid metals, either by chemical reduction or by thermal decomposition, furnished a series of hydrogenation and isomerization catalysts of substantial activity [1–7]. Likewise, manganese and cobalt acetates were complexed with Dowex 50 to give catalysts for autooxidation of propionaldehyde to propionic acid [8], and the modified products of Cr(III) and Ce(IV) with the cation exchanger Nafion® 551 were utilized in *tert*-butylhydroperoxide oxidation of secondary alcohols to ketones [9]. Various Co, Ru, Rh, Os and bimetallic carbonyls that have been supported by commercial and non-commercial quaternary ammonium-ion containing resins have been utilized as catalysts in hydroformylation processes [10,11].

The extremely high catalytic potency of some soluble $RhCl_3$–quaternary ammonium ion pairs [12] arose our interest in heterogenizing of these compounds. We have already shown that some $RhCl_3$–Dowex 1 adducts are, in their native state, (i.e., without any modification), selective and recyclable catalysts for (i) isomerization of allylic compounds, (ii) disproportionation of 1,3-cyclohexadiene, and (iii) hydration and oligomerization of alkynes [13]. The supported rhodium-containing ion pairs proved, however, unstable under hydrogen atmosphere so that they could not be used as hydrogenation catalysts. We have now found that Dowex 1-supported $PtCl_4$ ion pairs are sufficiently stable under H_2 to function as efficient and recyclable catalysts for the hydrogenation of various alkenes and other unsaturated compounds.

2. Experimental

2.1. General

Gas chromatographic analyses were performed with the aid of a Hewlett-Packard GC model 7620A equipped with a flame ionization detector and columns packed with 10% stabilized DEGS and with 10% Apiezon L on Chromosorb W. MS measurements were carried out using an HP Model 4989A mass spectrometer equipped with an HP gas chromatograph model 5890 series II. NMR spectra were recorded on a Bruker AMX-400 instrument. Nitrogen-BET surface area measurements were obtained by using a Micrometrics ASAP 2000 instrument. Atomic absorption spectrometry was performed on a Perkin-Elmer spectrophotometer model 403 using a Juniper platinum cathode lamp. XPS experiments were carried out with a PHI AES-XPS model 555 spectrometer with a background pressure of 2×10^{-10} Torr using Al Kα radiation.

2.2. Preparation of the supported catalysts

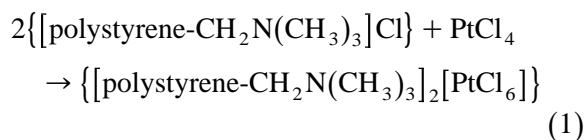Typically, 1.5 g of Dowex 1×4 (i.e., polystyrene-bound trimethylbenzylammonium chloride crosslinked with 4% divinylbenzene) of 40–80 μm diameter particles containing 1.33 meq/g Cl^- (predried overnight at 110°C) was stirred for 24 h at 25°C under N_2 with 0.6 mmol of $PtCl_4$ in 5 ml of 95% EtOH. The resin was washed with EtOH until the washings were free of Pt (checked by atomic absorption). The platinum content of the catalyst was obtained by subtraction of the amount of the metal in the washings from the initial quantity of Pt used in the process. In most cases the ion exchanger reacted with 95–100% of the $PtCl_4$ employed. The effective surface area of the catalyst was obtained by N_2-BET measurements [14].

2.3. Hydrogenation of unsaturated compounds

Typically, a 100 ml Teflon lined Parr autoclave, equipped with a mechanical stirrer, a sampling device and a temperature controller, was charged with 11.4 mmol of 1-decene, Dowex 1×4-$PtCl_4$ catalyst containing 0.57 mmol of platinum and 10 ml of THF. The autoclave was flushed with H_2 and pressurized to 600 psi. After stirring at 30°C for the desired length of time, the reaction vessel was cooled to 0–10°C and its content analyzed both by GC-MS and by NMR. The liquid was also checked for leached metal by atomic absorption. The used catalyst was filtered, washed with THF and dried overnight at 18 Torr. Kinetic runs were performed by withdrawal of 10–20 μl samples from the reaction mixture every 10 min followed by GC analysis on Apiezon L.

3. Results and discussion

Catalysts **1**–**3** were prepared according to Eq. (1) from Dowex 1×2, Dowex 1×4 and Dowex 1×8 and $PtCl_4$, respectively.

$$2\{[\text{polystyrene-}CH_2N(CH_3)_3]Cl\} + PtCl_4$$
$$\rightarrow \{[\text{polystyrene-}CH_2N(CH_3)_3]_2[PtCl_6]\}$$

$$(1)$$

When reaction (1) was conducted in 95% EtOH at 25°C, almost the entire platinum tetrachloride was absorbed by the resins within 24 h. N_2-BET measurements revealed that the corresponding surface areas of **1–3** were 1.88; 1.32 and 1.1 m^2/g. These values are typical for many polystyrene-bound catalysts [14]. In THF the supported ion pairs acted as hydrogenation catalysts for a variety of unsaturated substrates. Some representative results are presented in Table 1.

It is apparent that the supported ion pair is particularly active for the hydrogenation of terminal and cyclic olefins. Unsaturated ketones acetylenes and nitro compounds reacted substantially slower. In any event, if the substrates listed in Table 1 were allowed to react for a sufficiently long time, they afforded fully hydrogenated compounds in practically quantitative yield. However, some substrates that have strongly acidic functions (monosubstituted acetylenes, unsaturated carboxylic acids and alcohols) rarely gave high yields of the expected products due to gradual reduction of the platinum catalysts to inactive Pd(0).

Since atomic absorption measurements showed that no metal leaching occurred during the hydrogenation processes, we were able to recycle the recovered catalysts in several consecutive runs with practically no loss of activity. In fact, in most cases the catalytic activity increased in the first few runs. In a typical experiment of 1-decene hydrogenation by **2** (under the conditions of Table 1) the initial rates in the first 8 runs were 6.50, 6.60, 6.75, 7.20, 7.46, 7.68, 8.20 and 9.00×10^{-5} mol l^{-1} s^{-1}, and in the next two runs the rate did not change. We attribute this increase in activity to slow swelling of the catalyst (that lasted for $8 \times 4 = 32$ h) during which the beads have become more accessible to the substrate molecules. Fully swollen catalyst beads were obtained also by their pretreatment with THF for 32 h prior to the addition of the substrate and H_2. In such a case the initial rate in the first run was similar to that recorded in the 8th run with non-pretreated beads (8.87×10^{-5} mol l^{-1} s^{-1}).

Owing to the different capabilities of the various solvents to swell resinous matrices and/or to stabilize metallic catalysts, the hydrogenation processes were found to be strongly solvent dependent. Thus, while in THF the hydrogenation of 1-decene proceeded smoothly below 30°C, the initial rate and yield after 4 h decreased by ca. 70% when this solvent was replaced by toluene. In EtOH gradual reduction of the catalyst to metallic platinum took place, and in ethyl acetate the alkene did not react at all. The presence of water proved also to be important. In absolute THF the catalysis yielded exclusively the saturated hydrocarbon while the commercial solvent with 4% H_2O led to the formation of small amounts of several by-products although the rate increased by a factor of 3–4.

The diversified swelling properties due to dissimilar crosslinking (and surface areas) led to different initial reaction rates. Thus, under the conditions of Table 1, the corresponding hydrogenation rates of 1-decene by catalyst **1, 2** and **3** (that were crosslinked with 2, 4 and 8% divinylbenzene, respectively) were in the first runs 6.76, 6.50 and 3.53×10^{-5} mol l^{-1} s^{-1}.

Because of the tendency of the supported platinum catalyst to decompose above 35°C, we

Table 1
Hydrogenation of some unsaturated compounds in the presence of catalyst **2** under comparable conditions[a]

Substrate	Products (yield)
1-Decene	decane (100)
1-Octadecene	octadecane (58)
Cyclohexene	cyclohexane (100)
1,3-Cyclohexadiene	cyclohexene (33), cyclohexane (66)
Cycloheptatriene	cycloheptane (94)
Allylbenzene	1-propylbenzene (30)
4-Phenyl-3-buten-2-one	1-phenyl-3-butanone (27)
1,3-Diphenyl-2-propen-1-one	1,3-diphenyl-1-propanone (20)
Diphenylacetylene	bibenzyl (11), *cis*-stilbene (2), *trans*-stilbene (1)
Nitrobenzene	aniline (22)

[a]Reaction conditions: 11.4 mmol substrate, catalyst containing 0.57 mmol Pt, 10 ml THF, 600 psi H_2, 30°C, 4 h.

carefully checked the starting immobilized ion pair as well as its transformation compound for the existence of Pt(0) species after each run of 1-decene hydrogenation. The X-ray photo-electron spectra of the finely ground unused catalyst **2** that was taken at 25 eV pass energy (calibrated vs. the C 1s signal) showed in the 70–80 eV binding energy region, a discrete signal at 75 eV which corresponds to Pt(IV) [15]. The recovered catalyst showed an additional peak at 72.8 eV which reveals the presence of Pt(II) species. In none of the measurements (even after the 10th run) did a Pt(0) signal appear at 71 eV [15]. Thus, we are certain that no appreciable amounts of metallic platinum are formed under our experimental conditions throughout the entire catalytic process. The catalyst remains perfectly stable until in one of the advanced runs (usually between the 10th and the 20th run) the catalyst changes at once into a cotton-like material with complete loss of activity.

The reaction rate of 1-decene hydrogenation was found to increase linearly as long as the catalyst:substrate ratio did not exceed 1:50. At higher ratios this rate dependence proved to level off, so that above the ratio of 1:5 the amount of catalyst did not effect the rate anymore.

Except for highly diluted solutions of 1-decene, the dependence of the initial rate of hydrogenation on the concentration of the substrate resembles that observed in the classical Michaelis–Menten mechanism. The profile shown in Fig. 1 indicates a zero order behavior above 0.4 M, but the kinetics shift to first order in the range of 0.1–0.3 M. Upon replacement of the hydrogen gas in the hydrogenation of 1-decene by deuterium a small kinetic isotope effect of rate (H)/rate $(D) = 1.14$ was measured.

In order to appraise the role of mass transfer (intraparticle diffusion rate) in the overall catalytic process, we examined the activity of **2** of different particle sizes. Utilization of the catalyst beads with diameters, d, of (i) 40–80, (ii)
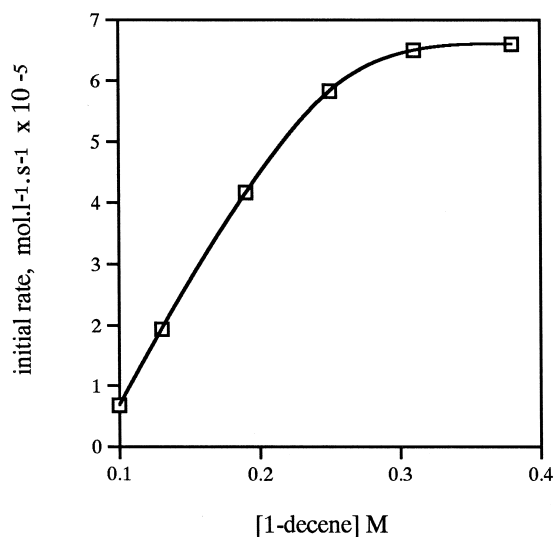

Fig. 1. Dependence of the initial rate of **2**-catalyzed hydrogenation of 1-decene on the concentration of the substrate.

150–300 and (iii) 300–840 μm (of average surface areas of 1.32, 0.72 and 0.44 m^2/g, respectively) under the conditions of Table 1 led to the respective initial rates, r, of 6.50, 4.72 and 2.77×10^{-5} mol l^{-1} s^{-1} in the first runs. Although these values do not match exactly those expected for purely diffusion controlled reactions, where $r(\text{i})/r(\text{ii}) \sim d(\text{ii})/d(\text{i})$, they are significantly remote from the value $r(\text{i})/r(\text{ii}) = r(\text{i})/r(\text{iii}) \sim 1$ that is characteristic for chemically controlled processes [16]. This suggests a major role of the intraparticle diffusion on the overall rate of the hydrogenation process. It is conceivable that the intrinsic kinetic isotope effect is amply masked by the diffusion effect and that its congenital value is significantly higher.

In view of the evidences at hand we assume that our platinum-catalyzed hydrogenation proceeds via the well established steps of oxidative addition of dihydrogen to the starting catalyst forming supported platinum dihydride. This intermediate reacts then with the alkene to form a η^2-platinum compound, that in turn undergoes migratory insertion, followed by reductive elim-

ination and release of product to complete the catalytic cycle [17]. This pathway incorporates platinum species in the oxidation state two and four as evidence by the XPS measurements.

Finally, it is notable that unlike the Dowex 1-bound $PtCl_4$ complex neither its homogeneous analog $[C_6H_5CH_2N(CH_3)_3]_2[PtCl_6]$, nor the ion pair generated from $[(C_8H_{17})_3NCH_3]Cl$ and $PtCl_4$ (see e.g., Ref. [18]) can be used as alkene hydrogenation catalyst. However, the conversion of soluble $PtCl_4$-onium ion pairs into recyclable catalysts is not restricted to the Dowex 1 derivative. The hybrid ion pair generated from $PtCl_4$ and divinylbenzene-crosslinked polystyrene-bound tributylmethylphosphonium chloride was found to be almost as active as **2**, although it proved more sensitive to oxygen and required careful exclusion of air during the recovery of the catalyst after each run.

Acknowledgements

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