

Entrapment of metallic palladium and a rhodium(I) complex in a silica sol–gel matrix

Formation of a highly active recyclable arene hydrogenation catalyst

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Abstract

A combined palladium–rhodium catalyst, generated by silica sol–gel-co-entrapment of metallic palladium and [Rh(cod)(μ -Cl)]₂, catalyzes under ambient conditions the hydrogenation of toluene and other simple benzene derivatives. The catalyst is perfectly recyclable and promotes at 80 °C and 400 psi, also the hydrogenation of polycyclic and sterically hindered arenes that are capable of penetrating the matrix pores. A synergistic effect is assumed to exist between the two metals, as either of the entrapped metallic components is a less active catalyst than the combination of both. © 2002 Elsevier Science B.V. All rights reserved.

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1. Introduction

Many sol–gel-entrapped catalysts have proven to be versatile, efficient and user friendly [1]. Practically all previous studies with these heterogeneous catalysts focused on the engagement of single species. We now take one step forward by co-entrapment of two catalytic functionalities within the same matrix. The motivation for this study is based on the observation that synergism may exist between two metal atoms

that are located in close proximity [2]. The synergistic effect can show up in the chemical performances of the pair of metals which differ from the chemical behavior of each of the metallic components alone [2]. A most interesting bimetallic catalyst system composed of native palladium adsorbed on a silica surface, and a soluble rhodium complex tethered to the same support, has been reported in 1997 by Gao and Angelici [3] (cf. an earlier related example [4]). This unique catalyst and some similar supported “homogeneous–heterogeneous” hybrid materials, proved to be very efficient for reduction of cyclohexanone to cyclohexanol, for hydrogenation of naphthalene and benzene derivatives to the corresponding alicyclic compounds [5–10], for hydrodehalogenation of fluorobenzenes [9] and for hydro-formylation of

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terminal olefins [6,11]. In this study we show that the efficiency of these catalysts can be further increased by entrapment of both metallic components within a sol–gel matrix rather than their attachment to the silica surface. By this technique we obtained a recyclable catalyst that promotes not only the reduction of simple arenes to cyclohexanes but also the exhaustive hydrogenation of some polycyclic aromatic hydrocarbons that, so far, could be achieved either via synthetic routes or by high pressure and high temperature catalytic processes.

2. Experimental

2.1. General

^1H and ^{13}C NMR spectra were recorded on Bruker AMX-200 and AMX-400 instruments. MS measurements were performed on a Hewlett-Packard model 4989A mass spectrometer equipped with an HP gas chromatograph model 5890 series II. Gas chromatographic separation and analyses were carried out with the aid of a Hewlett-Packard GC Model 417. IR spectra were recorded on a Bruker Model Vector 22 FT-IR instrument.

2.2. Preparation of the combined catalyst

2.2.1. Method A

To a solution of 95 mg (0.323 mmol) of Na_2PdCl_4 in 100 ml MeOH was added under N_2 , a solution of 0.8 ml (4.55 mmol) of $\text{H}_2\text{NCH}_2\text{CH}_2\text{CH}_2\text{Si}(\text{OMe})_3$. To the resulting colorless solution was then added 67 mg (1.77 mmol) of NaBH_4 . After the evolution of hydrogen had ceased the black reaction mixture was allowed to settle for 15 h in a sealed vessel. The liquid was removed by careful decantation and the fine palladium precipitate was suspended in 12 ml of THF. To the suspension was added 5 ml (33.6 mmol) of tetramethoxysilane followed by a solution of 30 mg (0.06 mmol) of $[\text{Rh}(\text{cod})(\mu\text{-Cl})_2]$ in 2 ml of the same solvent. To the stirred reaction mixture was added 3.8 ml of triply distilled water and the stirring was continued until gelation occurred (approximately 2 days). After aging at room temperature for additional 24 h, the gel was dried at 0.1 mm until constant weight of 2.6 g was reached. In order to

avoid leaching of the rhodium complex the material was heated for 1 h under 400 psi H_2 at 80°C , sonicated for 30 min with CH_2Cl_2 , dried again and stored under N_2 .

2.2.2. Method B

To a solution of 6 ml (26.9 mmol) of tetraethoxysilane in 10 ml of THF was added under N_2 , 2 ml of triply distilled water and 0.3 ml of triethoxysilane (1.6 mmol). The mixture was stirred at room temperature for 15 min and a solution of 94 mg (0.32 mmol) of Na_2PdCl_4 in 2 ml of water was added. After additional 15 min, 30 mg (0.06 mmol) of $[\text{Rh}(\text{cod})(\mu\text{-Cl})_2]$ was added in 2 ml of THF, and the mixture heated at 60°C until gelation was completed (2–3 days). The gel was dried for 24 h at 0.1 mm, sonicated with CH_2Cl_2 , dried again and stored under N_2 . Pretreatment of the material with H_2 was unnecessary as no rhodium leaching was observed when the catalyst was prepared by this method.

2.3. Blank experiments

For the rhodium-deficient blank experiments the matrix was prepared according to method A without $[\text{Rh}(\text{cod})\text{Cl}]_2$. Entrapment of the rhodium complex without metallic palladium was accomplished by the general method for bimetallic rhodium complexes described previously [12].

2.4. General procedure for hydrogenation of benzene derivatives

Typically, a glass lined preheated mini-autoclave, equipped with a mechanical stirrer, a sampler and a temperature controller was charged with 5 ml (46.7 mmol) of toluene, 70 ml of hexane and sol–gel-entrapped combined catalyst (prepared by method A) that contained 90 mg (0.18 mmol) of $[\text{Rh}(\text{cod})(\mu\text{-Cl})_2]$ and 0.9 mmol of palladium. The sealed reaction vessel was flushed with H_2 , and then pressurized to 400 psi. Stirring was operated at 150 rpm and the heating was tuned to 81°C . Samples of 20 μl were withdrawn and analyzed periodically. After 42 min the entire toluene was converted into methylcyclohexane. The used catalyst was filtered, sonicated and washed with CH_2Cl_2 , dried and reused in a second run.

2.5. Hydrogenation of polycyclic arenes

The same procedure as in Section 2.4, was applied to the hydrogenation of the polycyclic compounds, except that a molar ratio of the encapsulated rhodium complex in the catalyst to substrate was increased to 1:50, and the solvent and reaction time were as indicated in Table 1. The reaction mixture was first analyzed on a 25 m × 0.25 mm CP-Sil capillary column by GC and then separated on preparative columns. The resulting compounds were either compared directly with authentic samples or their IR, MS and NMR spectra compared with the data given in the literature [13–24].

3. Results and discussion

Unlike the silica-supported catalyst system in which the soluble complex had to be modified with silyloxy groups for covalent binding to the support, we used a non-modified metallic complex for *physical* entrapment in the sol–gel matrix. The catalyst of choice was composed of $[\text{Rh}(\text{cod})(\mu\text{-Cl})_2]$ which was encapsulated without modification in silica sol–gel material predoped with nanoparticles of palladium. Two of the following methods for the dispersion of the metal and the formation of the combined encaged “homogeneous–heterogeneous” materials gave active hydrogenation catalysts. In the first method we used a modification of the procedure of Bharathi et al. [25] for the formation of palladium nanoparticles by reduction of a methanolic solution of Na_2PdCl_4 with NaBH_4 in the presence of $\text{H}_2\text{NCH}_2\text{CH}_2\text{Si}(\text{OMe})_3$. The free palladium and $[\text{Rh}(\text{cod})(\mu\text{-Cl})_2]$ were co-entrapped in a sol–gel matrix. A second method was based on the work of Tour et al. [26] in which Na_2PdCl_4 was reduced under neutral conditions by $\text{HSi}(\text{OEt})_3$, and the palladium dispersion so formed, added together with the rhodium complex to a polycondensation reaction mixture of $\text{Si}(\text{OEt})_4$. In a third method the metallic palladium was generated in the presence of a thiol [27]. Either $\text{Pd}(\text{OAc})_2$ or Na_2PdCl_4 in THF was reduced in the presence of one-half equivalent of $(\text{MeO})_3\text{Si}(\text{CH}_2)_2\text{SH}$ by excess NaBH_4 . The thiol-stabilized palladium colloid was then added, together with a THF solution of $[\text{Rh}(\text{cod})(\mu\text{-Cl})_2]$ to $\text{Si}(\text{OEt})_4$ during hydrolytic polycondensation.

Studies on the activity of the entrapped combined metal compounds as hydrogenation catalysts revealed that while the sol–gel materials prepared in the presence of either $\text{H}_2\text{NCH}_2\text{CH}_2\text{Si}(\text{OMe})_3$ or $\text{HSi}(\text{OEt})_3$ are highly active arene hydrogenation catalysts, the material obtained by the third method proved practically inactive. The catalyst prepared by the first method requires careful removal of the amine, as the latter is, in large quantities a hydrogenation inhibitor. Toluene could be converted exclusively into methylcyclohexane under a wide range of experimental conditions starting from room temperature (30 °C) and atmospheric pressure of H_2 . The best results were obtained however when the arene was reacted at 80 °C under 400 psi H_2 in the presence of the heterogenized $\text{Pd}-[\text{Rh}(\text{cod})\text{Cl}]_2$ catalyst containing 1/259 equiv. of rhodium and 1/50 equiv. of palladium per each mole of substrate. The progress of the reaction was shown to depend strongly on the stirring, e.g. at a stirring rate of 150 rpm, 5 ml of toluene was completely hydrogenated within 42 min (vide infra). In our initial experiments we noticed that during the hydrogenation process up to 10% of the rhodium complex leached from the catalyst prepared by the first method in which $\text{H}_2\text{NCH}_2\text{CH}_2\text{Si}(\text{OMe})_3$ was used. This leaching could be stopped completely when the ceramic material was treated with H_2 under 400 psi at 80 °C for 1 h prior to the addition of the aromatic substrate. The heterogenized catalyst prepared in the presence of $\text{HSi}(\text{OEt})_3$ was leach-proof and did not require pretreatment with hydrogen. Nevertheless, it gave practically the same results as the catalyst prepared with NaBH_4 and $\text{H}_2\text{NCH}_2\text{CH}_2\text{Si}(\text{OMe})_3$.

Upon termination of the hydrogenation, the filtered and CH_2Cl_2 -washed catalyst could be reused. No change whatsoever in the catalytic activity was observed upon recycling of the catalyst for five consecutive runs. Control experiments which included studies on the catalytic activity of $[\text{Rh}(\text{cod})\text{Cl}]_2$ -free sol–gel-entrapped palladium dispersion, and of palladium-free sol–gel encaged $[\text{Rh}(\text{cod})(\mu\text{-Cl})_2]$ revealed that the entrapped palladium catalyst is only able to promote hydrogenation of olefins (it catalyzed, e.g. the conversion of styrene to ethylbenzene), but does not affect aromatic C–C bonds. The encapsulated $[\text{Rh}(\text{cod})(\mu\text{-Cl})_2]$ does promote the transformation of toluene to methylcyclohexane, but at a lower rate than the combined encapsulated $\text{Pd}-[\text{Rh}(\text{cod})\text{Cl}]_2$

Table 1

Hydrogenation of representative arenes by the sol-gel encapsulated Pd-[Rh(cod)(μ-Cl)]₂ catalyst^a

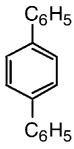
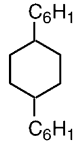
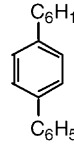
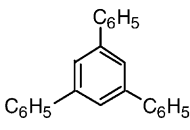
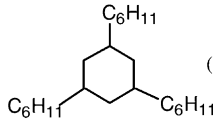
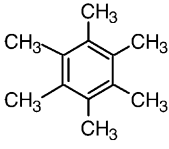
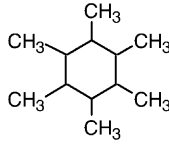
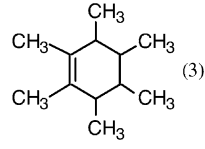
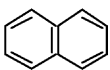
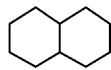
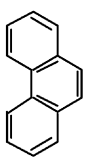
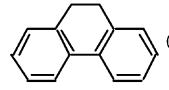
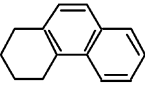
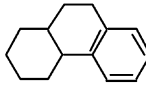
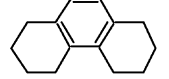
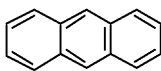
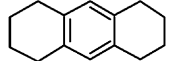
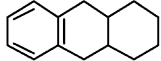
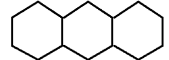
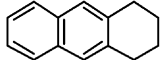
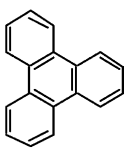
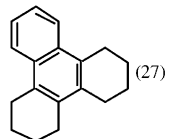
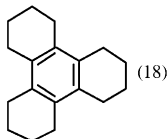
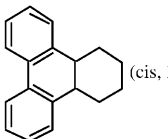
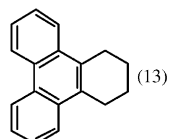
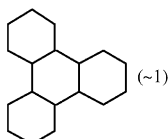
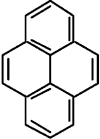
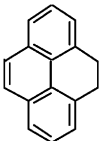
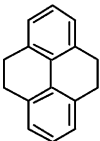
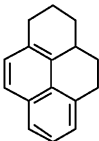
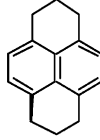
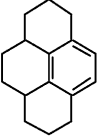
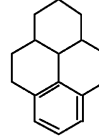
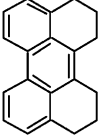
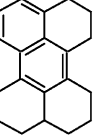
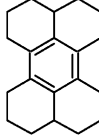
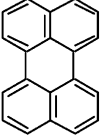
| Substrate | Solvent ^b | Product (yield, %) ^c |
|---|----------------------|--|
|  | A |  (2 isomers, 95)  (5) |
|  | A |  (100) |
|  | A ^d |  (3 isomers, 68)  (3) |
|  | B ^e |  (cis, 78; trans, 22) |
|  | C |  (37)  (20)  (cis, 5)  (2) |
|  | D |  (60)  (cis, 20)  (2 isomers, 14)  (6) |
|  | C |  (27)  (18)  (cis, 15)  (13)  (~1) |

Table 1 (Continued)

| Substrate | Solvent ^b | Product (yield, %) ^c | | |
|---|----------------------|--|---|--|
|  | B |  (27) |  (27) |  (20) |
| | |  (17) |  (3) |  (1) |
| | |  (18) |  (31) |  (37) |
|  | E | | | |

^a Reaction conditions: 3 mmol substrate, hydrogen pretreated sol-gel-entrapped combined catalyst containing 0.06 mmol Rh, 8–12 ml solvent, 80 ± 0.5 °C, 400 psi H₂, 40 h and no stirring unless otherwise stated.

^b A: ClCH₂CH₂Cl; B: *n*-heptane; C: MeOH; D: acetic acid:heptane 1:6; E: acetic acid.

^c The missing percentage reflect on the unreacted starting material.

^d 60 h.

^e 8 h, stirring at a rate of 150 rpm.

catalyst. Under comparable conditions quantitative conversion of toluene to methylcyclohexane lasted 42 min in the presence of the combined catalyst, and 93 min in the palladium deficient entrapped rhodium complex. Furthermore, while the hydrogenation by the combined catalyst started right away at an initial rate of $15 \text{ mmol l}^{-1} \text{ s}^{-1}$, the reaction by the other system was preceded by a 7 min induction period and the maximum rate thereafter was $7.6 \text{ mmol l}^{-1} \text{ s}^{-1}$.

In analogy to toluene also other benzene derivatives could readily be converted in nearly quantitative yield into cyclohexane or into its derivatives. Thus, benzene and chlorobenzene formed cyclohexane, styrene gave ethylcyclohexane and nitrobenzene, as well as aniline afforded cyclohexylamine. Unlike many other typical arene hydrogenation catalysts, our system was found to promote, under relatively mild conditions, the hydrogenation of multi-substituted benzenes, as well as polycyclic aromatic hydrocarbons, to a high degree or to complete ring saturation. Several representative examples are listed in Table 1.

While the hydrogenation of mono-substituted benzene derivatives and naphthalenes is known to take

place by a variety of catalysts under mild conditions, the reduction of polysubstituted arenes require usually high temperature and pressure (see, e.g. [28]). In contrast to our study, the conversion of terphenyl and 1,3,5-triphenylbenzene into the corresponding alicyclic products required approximately 100 atm H₂ and 130–200 °C [29,30]. The transformation of hexamethylbenzene to isomers of hexamethylcyclohexanes at a reasonable rate was accomplished in the past by hydrogenation with a nickel–alumina catalyst at 200 °C and 200 atm H₂ [31]. Hexamethylcyclohexene has been prepared previously by sensitized photolysis of *exo*- and *endo*-1,2,3,4,5,6-hexamethylbicyclo[2.2.0]hexane [32]. Naphthalene has been hydrogenated in the presence of a variety of catalysts. However, most of them lead, under the reaction conditions, employed in this study to tetralin or mixtures of tetralin and decalines [13]. In a control experiment in which we hydrogenated naphthalene by palladium-free sol-gel-encaged [Rh(cod)Cl]₂ instead of the combined catalyst, we obtained only tetralin. Catalytic hydrogenation of phenanthrene under mild conditions gives in general 9,10-dihydrophenanthrene as the

sole product [14]. Catalytic saturation of the terminal rings requires more drastic reaction conditions [15], even when special catalysts of group 5 metals are used [16]. 1,2,3,4-Tetrahydroanthracene and 1,2,3,4,5,6,7,8-octahydroanthracene have been obtained under mild conditions from anthracene in the presence of $[(C_8H_{17})_3NMe][RhCl_4(H_2O)_n]$ or similar ion pairs [14]. However, 1,2,3,4,4a,9,9a,10-octahydroanthracene, as well as the isomeric perhydroanthracene required either elevated temperatures and high H_2 pressure [17], or the application of non-catalytic synthetic methods (e.g. [18]). Under the standard conditions of Table 1, the higher polycyclic arenes did not undergo exhaustive hydrogenation. Triphenylene yielded at $80^\circ C$ after 40 h mainly a mixture of 1,2,3,4-tetrahydro- [19], *trans*-1,2,3,4,4a,12b-hexahydro- [20], 1,2,3,4,5,6,7,8-octahydro- [21] and 1,2,3,4,5,6,7,8,9,10,11,12-dodecahydrotriphenylene [19], and only traces of the perhydro-derivative [22]. However, when the reaction temperature was raised to $148^\circ C$ and the time extended to 7 days, the entire aromatic hydrocarbon was converted into a mixture of the dodecahydro- and perhydrotriphenylene [22]. Pyrene afforded at $80^\circ C$ only the partially hydrogenated 4,5-dihydro- [19], 4,5,9,10-tetrahydro- [19], 1,2,3,3a,4,5-hexahydro- [15], 1,2,3,6,7,8-hexahydro- [23], 1,2,3,3a,4,5,9,10,10a,10b-decahydro- [15] and 1,2,3,4a,4,5,5a,6,7,8-decahydro-pyrene [15]. Likewise, the five-membered ring, perylene, yielded under these conditions 4,5,6,7,8,9-hexahydro- [15], 1,2,3,3a,4,5,6,7,8,9-decahydro- [24] and 1,2,3,3a,4,5,6,7,8,-9,9a,10,11,12-quaterdecahydroperylene [15].

The pretreatment of the immobilized catalyst (obtained by the first method) with hydrogen, raises the question whether this operation influences to a significant extent the toluene hydrogenation process. A possibility that during the pretreatment the entrapped palladium becomes saturated with hydrogen, which could later be transferred to the substrate (via the rhodium complex) by a spillover process, seems unlikely. The uptake of H_2 by the entrapped combined Pd-[Rh(cod)Cl]₂ catalyst in toluene and heptane at $80^\circ C$ under atmospheric pressure was compared with the H_2 uptake by the rhodium-deficient sol-gel encapsulated palladium under identical conditions. During the first hour, the H_2 uptake by the entrapped palladium was 1.5 ml. It decreased gradually and practically stopped after 5 h. During this period the absorption by

the combined catalyst was at a rate of 7–8 ml/h. As the palladium-absorbed H_2 can at most account only for the hydrogenation of 0.12 of the 19.5 mmol of toluene employed in the specific experiment, we assume that the catalytic transformation of most of the substrate to methylcyclohexane involves the action of *both* metals, between which a kind of synergism exists. We believe that such an effect, which requires close proximity of the Rh and Pd, is feasible because the physically entrapped rhodium complex may approach the palladium atoms (which are in a fivefold excess as compared to the rhodium) by diffusion.

Initial rates of hydrogenation (400 psi H_2) of toluene in hexane by the combined catalyst for several substrate concentrations (0.5–0.7 M) were recorded between 61 and $92^\circ C$. Typical rates at 61, 72, 81 and $92^\circ C$ were 7.6, 12.3, 15.0 and $19.5 \text{ mmol l}^{-1} \text{ s}^{-1}$, respectively. From the Arrhenius plot of $\ln(\text{rate})$ vs $1/T$ the observed activation energy $E_a = 7.22 \pm 0.5 \text{ kcal mol}^{-1}$ was deduced. This value clearly indicates that the hydrogenation of toluene by the entrapped combined catalyst is diffusion controlled [33]. This is supported by the observation that the process strongly depends on the stirring rate.

Finally, we compared the catalytic activity of the sol-gel-entrapped combined catalyst with that of RhCl(cod)[H₂NCH₂CH₂NH(CH₂)₃Si(OMe)₃] tethered to Pd-SiO₂, prepared according to Gao and Angelici [8]. Under identical experimental conditions, using the same quantities of palladium and the same molar ratio of rhodium complexes, the sol-gel engaged catalyst lead to quantitative hydrogenation of toluene within 42 min, while the silica-supported version gave during this period only 15% of methylcyclohexane. The differences in activity between the two versions of combined catalysts were even larger in the hydrogenation of the polycyclic arenes. For example, when the non-encaged catalyst was used for hydrogenation of pyrene under the conditions of Table 1, only 16% of 4,5-dihydro-pyrene and 1% of 4,5,9,10-tetrahydro-pyrene were obtained after 40 h. Despite the very high efficiency of our sol-gel-entrapped combined catalyst, one should take into consideration that this catalyst is applicable only to substrates that can penetrate the matrix pores of 15–20 Å. Polycyclic arenes with more than five conjugated rings cannot usually be used with our catalyst system (see [34]).

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