

Catalytic hydrogenolysis of aromatic ketones by a sol–gel entrapped combined Pd-[Rh(cod)Cl]₂ catalyst

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Abstract

Co-entrapment of palladium nanoparticles and soluble [Rh(cod)(μ-Cl)]₂ in a silica sol–gel matrix forms a catalyst that promotes exhaustive hydrogenation and hydrogenolysis of various aromatic ketones. While the hydrogenation of acetophenone may proceed by initial formation of α-phenylethanol followed by dehydration to styrene and further reduction of the olefinic and aromatic C–C bonds, the reaction of benzophenone and related compounds does not involve the intermediary of a carbinol. The immobilized combined catalyst is leach-proof and perfectly recyclable in at least five consecutive runs. Its unique catalytic activity is attributed to a synergistic effect between the different metal atoms.

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Keywords: Ketones; Hydrogenation; Palladium; Rhodium; Sol–gel

1. Introduction

Although the direct conversion of carbonyl compounds into hydrocarbons can be accomplished by alkali metals in liquid ammonia, by Lewis acid promoted metal-hydride reduction, by the classical Clemmensen and Wolff-Kishner type reactions and by electrochemical transformations [1,2], only a few cases have been reported on catalytic hydrogenolysis of C=O to CH₂ groups [3]. Recently [4], we have shown that the catalytic activity of the combined system composed of metallic palladium and soluble [Rh(cod)Cl]₂ is considerably increased upon entrapment in a silica sol–gel matrix, and consequently the ceramic material promotes exhaustive hydrogenation

of polycyclic aromatic compounds. We have now found that this immobilized combined catalyst promotes the total hydrogenation and hydrogenolysis of aromatic ketones in many cases to give the corresponding oxygen-free hydrocarbons.

2. Experimental

2.1. General procedure for hydrogenation of ketones

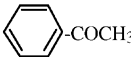
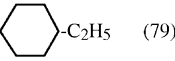
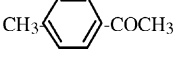
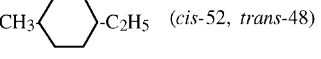
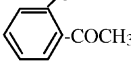
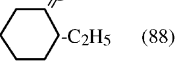
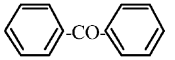
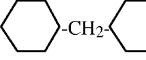
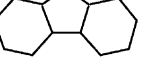
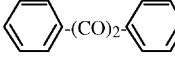
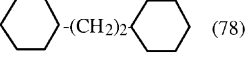
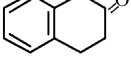
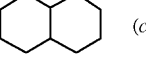
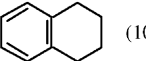
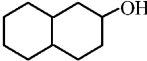
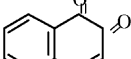
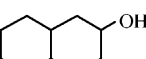
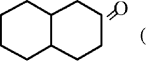
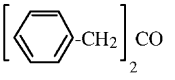
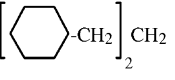
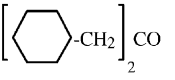
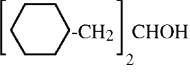
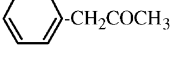
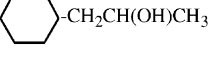
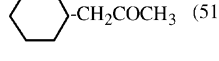
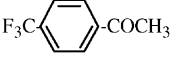
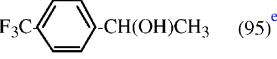

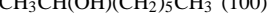
The sol–gel encapsulated combined Pd-[Rh(cod)Cl]₂, prepared by co-entrapment of metallic palladium particles [from 95 mg Na₂PdCl₄, 67 mg NaBH₄ and 0.8 ml H₂N(CH₂)₃Si(OCH₃)₃] and 30 mg (0.06 mmol) [Rh(cod)Cl]₂ in a silica matrix from 5 ml of Si(OCH₃)₄ [4] was introduced into a mini-autoclave together with 6 mmol of the ketonic substrate and 10 ml of *n*-heptane. The sealed reaction vessel was flushed (three times) with hydrogen and pressurized to 400 psi. The reaction mixture was

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Table 1
Hydrogenation of some ketones in the presence of the sol-gel entrapped combined Pd-[Rh(cod)(μ-Cl)]₂ catalyst^a

Entry	Substrate	Reaction time (h)	Product (yield, %) ^b
1		24	 (79)
2		24	 (<i>cis</i> -52, <i>trans</i> -48)
3		24	 (88)
4		72	 (69)  (30) ^c
5		48	 (78)
6		36	 (<i>cis</i> -46, <i>trans</i> -9)
			 (10)  (<i>cis,cis-form</i> -32)
7 ^d		36	 (<i>cis,cis-form</i> -27, <i>cis,trans-form</i> -12)
			 (<i>trans</i> -60)
8		36	 (21)  (32)
			 CHO
9		24	 (47)  (51)
10		36	 (95) ^e
11		4	 (100)

^a Reaction conditions: 6 mmol substrate, catalyst containing 0.06 mmol Rh and 0.32 mmol Pd, 10 ml heptane, 400 psi H₂, 80 °C.

^b The missing percentage reflects usually on the unreacted starting material.

^c The mixture of the six isomers was separated on a 30 m × 0.3 mm DB-5 GC column operated between 50 and 300 °C (4 °C/min) into 28.5% *cis, syn, cis*-perhydrofluorene, 58% *cis, anti, cis*-perhydrofluorene, 3.2% *trans, anti, cis*-perhydrofluorene, 2.1% *cis, syn, trans*-perhydrofluorene, 6% *trans, syn, trans*-perhydrofluorene and 2.2% *trans, anti, trans*-perhydrofluorene.

^d In 1,2-dichloroethane.

^e Contaminated with traces of an alicyclic compound.

stirred magnetically at a rate of 150 rpm at 80 °C for the required length of time. After cooling to room temperature, the catalyst was filtered, sonicated and washed with CH₂Cl₂, dried and reused in a second run. The filtrate was concentrated and the reaction products separated if necessary by GC, and either compared with authentic samples, or their IR, MS and NMR spectra compared with the data given in the literature. Hydrogenation, experiments of representative carbonyl compounds are summarized in Table 1.

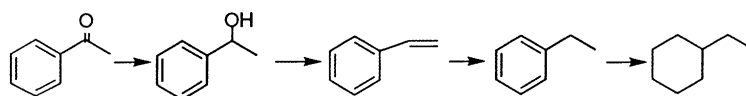
3. Results and discussion

The catalyst system was composed of sol–gel co-entrapped palladium nanoparticles (prepared by reduction of methanolic Na₂PdCl₄ with NaBH₄ in the presence of H₂N(CH₂)₂Si(OCH₃)₃ [5]) and [Rh(cod)(μ-Cl)]₂. IR analysis revealed that during the entrapment process, the rhodium complex retains its original structure. The major peaks are not shifted by more than 1–2 cm⁻¹. However, the COD bands disappear gradually during the hydrogenation.

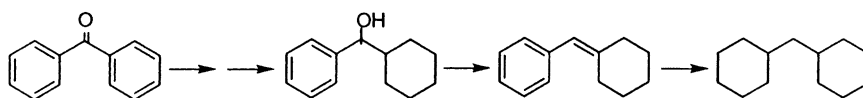
In the presence of the entrapped combined catalyst, a heptane solution of acetophenone was hydrogenated at 80 °C and 400 psi H₂ to give within 24 h 79% of ethylcyclohexane (see Table 1, entry 1). Likewise, alkyl-substituted acetophenones, such as 4-methylacetophenone (entry 2) gave exclusively the fully hydrogenated hydrocarbon. Non-entrapped Pd-Rh combined catalysts with similar structures promoted the conversion of these acetophenones mainly into cyclohexyl methyl carbinols [6]. Partially hydrogenated products were not formed in experiments 1 and 2. However, ketones derived from phenols were transferred into the keto-tautomers of 1-cyclohexenols. Thus, 2-hydroxyacetophenone after 24 h gave 2-ethylcyclohexanone in 88% yield (entry 3). After a prolonged reaction period, benzophenone formed both dicyclohexylmethane and the isomeric perhydrofluorenes (entry 4). (Separation of the six isomers of perhydrofluorene was accomplished by GC on

a capillary DB-5 column under the conditions given in Table 1 [7].) Introduction of a second carbonyl function as in benzil gave upon hydrogenation solely bibenzyl derivatives. The cyclic ketone, 2-tetralone (entry 6), was converted under the conditions of Table 1 into *cis*- and *trans*-decaline, tetraline and 2-tetralol. The latter was formed as the *cis, cis*-form as a single isomer, as evidenced by the IR spectrum [8]. No other oxygen-containing compounds were traced in this reaction. 1,2-Naphthalenequinone, which is sparingly soluble in heptane, was hydrogenated in 1,2-dichloroethane. The oxygen in the benzylic (α) position underwent complete hydrogenolysis, but the carbonyl group in the β position remained partly unchanged and partly became a carbinol function of *cis, cis*- and *cis, trans*-2-decalol (entry 7). The hydrogenation of dibenzyl ketone, in which the carbonyl group is in the homobenzyl position, gave only 21% of the fully hydrogenated 1,3-dicyclohexylpropane, along with 77% of oxygenated products (entry 8) and the reduction of benzyl methyl ketone (entry 9) did not furnish oxygen-free products at all. Oxygen-containing products were also obtained in the hydrogenation of acetophenone derivatives with electron-attracting substituents (e.g. 4-trifluoromethylacetophenone, entry 10) as well as in the reduction of non-cyclic aliphatic ketones (entry 11). It is worth noting that in experiment 10, the CF₃ group prevents not only the direct reduction of the carbonyl to a CH₂ moiety, but interferes also with the hydrogenation of the aromatic C–C bonds. Thus, in this experiment 1-(4-trifluoromethylphenyl)ethanol [9] is practically the only product.

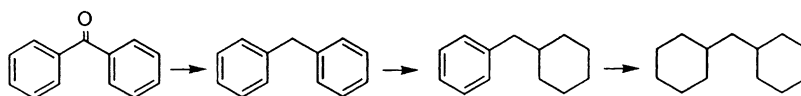
Apparently, the hydrogenolysis of the various ketones listed in entries 1–8 of Table 1 can be rationalized by initial reduction of the CO moieties to CHOH functions, followed by dehydration and addition of hydrogen to the double bond so formed. Thus, the conversion of acetophenone into ethylcyclohexane could proceed via initial formation of 1-phenylethanol, dehydration to styrene and gradual hydrogenation of the side chain and the aromatic ring as shown in Scheme 1.



Scheme 1.



Scheme 2.



Scheme 3.

The hydrogenation of benzophenone that does not have any non-aromatic hydrogen atoms, would then have to follow the route outlined in [Scheme 2](#). This pathway is in line with the formation of dicyclohexylmethane in the final stage of the process, and does not contradict the production of perhydrofluorenes, which may result from an intramolecular alkylation in a transient cyclohexenylphenylmethane intermediate. Its features are also in agreement with the fact that benzhydrol yields after 36 h the same two hydrocarbons as benzophenone in 80 and 18% yield, respectively. However, in the initial stages of the reactions, the ketone and the carbinol give different products. While the reaction mixture of benzophenone consists after 10 h of 35% of diphenylmethane, 27% of cyclohexylphenylmethane, 7% of dicyclohexylmethane, 9% of cyclohexyl phenyl ketone, 3% of perhydrofluorene and nearly 19% of unreacted starting ketone, no diphenylmethane could be traced in the hydrogenation mixture of benzhydrol under similar reaction conditions. Thus, [Scheme 2](#) cannot account for the formation of diphenylmethane from benzophenone unless there is a hydrogen transfer from cyclohexylphenylmethane or from dicyclohexylmethane to the starting material, or else some disproportionation (or dehydrogenation) of a short-lived phenylcyclohexadiene intermediate takes place [10]. Since the sol-gel entrapped Pd-Rh system proved both inactive as a transfer hydrogenation catalyst from cyclohexane, cyclohexene and cyclohexylphenylmethane, and does neither promote disproportionation nor dehydrogenation of 1,3-cyclohexadiene derivatives in the absence of H₂, the involvement of these processes in the formation of diphenylmethane from

benzophenone is unlikely. Thus, the hydrogenation of benzophenone probably takes place by the route outlined in [Scheme 3](#). In analogy to benzophenone also, fluorenone underwent direct hydrogenation and gave after 10 h under the conditions of [Table 1](#), 29% of fluorene.

The sol-gel entrapped Pd-Rh catalyst is perfectly leach-proof and can be recycled at least five times without the loss in the catalytic activity. Its unusual catalytic potency is attributed to a synergetic effect between the different metal atoms as neither the entrapped palladium nor the immobilized [Rh(cod)(μ-Cl)]₂ promote exhaustive hydrogenation and hydrogenolysis of aromatic ketones.

Acknowledgements

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References

- [1] S. Yamamura, S. Nishiyama, in: *Comprehensive Organic Synthesis*, in: B.M. Trost, I. Fleming (Eds.), Vol. 8, Pergamon Press, Oxford, UK, 1991 (Chapter 1.13).
- [2] R.O. Hutchins, M.K. Hutchins, in: *Comprehensive Organic Synthesis*, in: B.M. Trost, I. Fleming (Eds.), Vol. 8, Pergamon Press, Oxford, UK, 1991 (Chapter 1.14).
- [3] V. Kogan, Z. Aizenshtat, R. Neumann, *New J. Chem.* 26 (2002) 272 and references therein.

- [4] R. Abu-Reziq, D. Avnir, I. Miloslavski, H. Schumann, J. Blum, *J. Mol. Catal. A Chem.* 185 (2002) 177.
- [5] S. Bharathi, N. Fishelson, O. Lev, *Langmuir* 15 (1999) 1929.
- [6] H. Yang, H. Gao, R.J. Angelici, *Organometallics* 19 (2000) 622.
- [7] A.V. Kiselev, V.I. Nazarova, K.D. Shcherbakova, *Chromatographia* 18 (1984) 183.
- [8] T. Oritani, K. Tamashita, *J. Org. Chem.* 49 (1984) 3689.
- [9] A.K. Mandal, T.G. Kasar, S.W. Mahajan, D.G. Jawalkar, *Synth. Commun.* 17 (1987) 563.
- [10] A. Rosenfeld, J. Blum, D. Avnir, *J. Catal.* 164 (1997) 363.