

Sol–gel entrapped $\text{Rh}_2\text{Co}_2(\text{CO})_{12}$: a catalyst precursor for efficient arene hydrogenation

Faina Gelman^a, David Avnir^{a,*}, Herbert Schumann^{b,1}, Jochanan Blum^{a,2}

^a Department of Organic Chemistry, The Hebrew University of Jerusalem, Jerusalem 91904, Israel

^b Institut für Anorganische und Analytische Chemie, Technische Universität Berlin, D-10623 Berlin, Germany

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Abstract

Heating of sol–gel entrapped $\text{Rh}_2\text{Co}_2(\text{CO})_{12}$ at 100°C and 0.02 mm for 16 h, results in the elimination of CO and the formation of immobilized metallic nanoparticles that efficiently catalyze hydrogenation of aromatic C–C bonds. The catalytic activity can be further increased by pretreatment of the sol–gel material with molecular hydrogen. The resulting immobilized catalyst can be used repeatedly in a variety of different hydrogenation processes. Carbon monoxide reacts with the encapsulated metallic particles to give catalytically inactive metal carbonyls. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Arene hydrogenation; Heteronuclear catalyst; Sol–gel matrix; Cobalt; Rhodium

1. Introduction

The arsenal of useful, heterogeneous, sol–gel entrapped metal complexes is growing steadily covering by now many of the major families of catalytic reactions [1–3]. Thus, we recently reported [4] that $\text{Rh}_2\text{Co}_2(\text{CO})_{12}$, [(Co–Co)(4Co–Rh)(Rh–Rh)tri- μ -carbonyltetracarbonyl(pentacarbonyldicobalt)dirhodium], which is known to disproportionate in DME solution in the presence of CO or other additives [5,6], can be stabilized by physical entrapment in a silica sol–gel

matrix. The immobilized mixed-metal complex was found to act as a recyclable catalyst that converts styrene into ethylbenzene at 30°C and 3 atm H_2 . Nitrobenzene could be hydrogenated only above 50°C to give aniline. However, upon recycling of the catalyst from the latter reaction, gradual changes were found to take place in the nature of the products as well as in the structure of the entrapped Rh–Co complex. Consequently, encaged nanoparticles of 2–3 nm of a Rh–Co alloy were formed [4]. Unlike the original entrapped $\text{Rh}_2\text{Co}_2(\text{CO})_{12}$ complex these metal particles promote not only the hydrogenation of olefinic double bonds and nitro groups, but also the reduction of the aromatic skeleton. Thus, after the fourth run of 22 h, when the decarbonylation of the immobilized Rh–Co cluster was completed, the hydrogenation of nitrobenzene yielded solely aniline-free aminocyclohexane. We have now extended this study and worked out conditions under which the metallic Rh–Co particles catalyze hydrogenation of aromatic C–C

* Corresponding author. Tel.: +972-2-6585332;

fax: +972-2-6520099.

E-mail addresses: david@chem.ch.huji.ac.il (D. Avnir), schumann@tu-berlin.de (H. Schumann), jblum@chem.ch.huji.ac.il (J. Blum).

¹ Co-corresponding author. Tel.: +49-30-31423984;

fax: +40-30-31422168.

² Co-corresponding author. Tel.: +972-2-6585329;

fax: +972-2-6513832.

bonds as well as ketonic carbonyl functions right away from the first run.

2. Experimental

2.1. Preparation of active sol–gel entrapped $Rh_2Co_2(CO)_{12}$

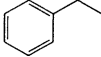
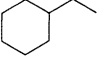
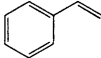
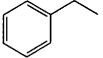
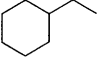
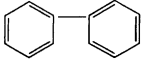
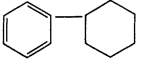
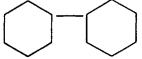
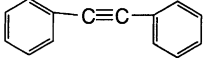
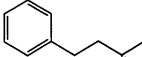
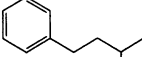
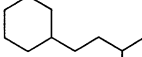
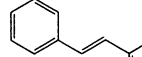
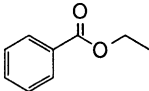
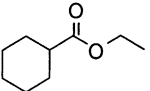
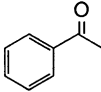
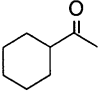
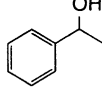
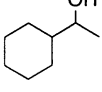
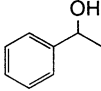
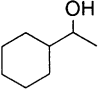
To a stirred solution of 20 mg of $Rh_2Co_2(CO)_{12}$ in 1 ml of benzene was added under N_2 atmosphere at 28°C, 2.5 ml of MeOH. After 5 min, the mixture was treated with 2.4 ml of H_2O , stirring was continued for further 20 min and then 3.5 ml of $Si(OMe)_4$ was added. Gelation started right away and was completed after 2–3 h. The resulting material was dried at 0.1 mm

for 20 h at room temperature, washed and sonicated twice in CH_2Cl_2 and dried again for 16 h at 100°C and 0.02 mm.

2.2. General hydrogenation procedure

In a typical experiment, the dried immobilized catalyst was placed together with 20 ml of hexane and the appropriate substrate (metal-atom: substrate ratio, 1:200) in a glass-lined mini autoclave. The reaction vessel was charged with 200 psi H_2 and the reaction mixture heated at 60°C for the desired length of time. The products were analyzed by GC, GCMS and NMR spectroscopy and compared with authentic samples. Representative results are summarized in Table 1.

Table 1
Hydrogenation of some arenes by H_2 -pretreated and preheated sol–gel encapsulated $Rh_2Co_2(CO)_{12}$ under comparable conditions^a

	Substrate	Products (yield, %) ^b
1		 (92)
2		 (11)  (89)
3 ^c		 (84)  (15)
4		 (83)  (16)
		 (1)  (0.5)
5 ^c		 (97)
6 ^c		 (38)  (5)  (34)
7 ^d		 (99)

^a Reaction conditions: 2 mmol substrate; catalyst containing 1×10^{-2} mmol of each Rh and Co; 200 psi H_2 ; 20 ml benzene; 60°C, 4 h. The catalyst for the various hydrogenation experiments was one and the same unless stated otherwise. Between the experiments the catalyst was just washed and sonicated in CH_2Cl_2 .

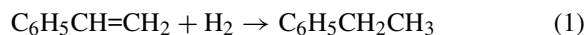
^b The yields are the average of at least two runs that did not differ by more than $\pm 3\%$.

^c New catalyst pretreated with H_2 for 8 h at 60°C.

^d Reaction time 2 h.

3. Results and discussion

The physical entrapment of $\text{Rh}_2\text{Co}_2(\text{CO})_{12}$ in the sol–gel matrix hardly changed the structural features of the tetranuclear cluster and the nine distinguishable infrared carbonyl bands of the non-entrapped complex at 1855, 1871, 1885, 1910, 1920, 2038, 2059, 2064 and 2074 cm^{-1} were shifted only slightly [4]. The TEM measurements revealed that the doped sol–gel material, so formed, does not contain any free metallic particles. The heterogenized complex was also found to retain its structure after application as catalyst in double bond hydrogenation of styrene (Eq. (1)) even after recycling



The structure did change, however, when the doped sol–gel was heated at 100°C and 0.02 mm for 16 h. During this process, the entrapped complex lost CO with the formation of metallic nanoparticles as clearly seen in Fig. 1. When the carbonyl-free catalyst has now been used in the hydrogenation of styrene, the initial product reacted further to give ethylcyclohexane (Eq. (2)). This catalyst which proved perfectly recyclable promoted also the hydrogenation of the aromatic C–C bonds in ethyl benzoate (Eq. (3)) and in nitrobenzene (Eqs. (4) and (5)) right away from the first run

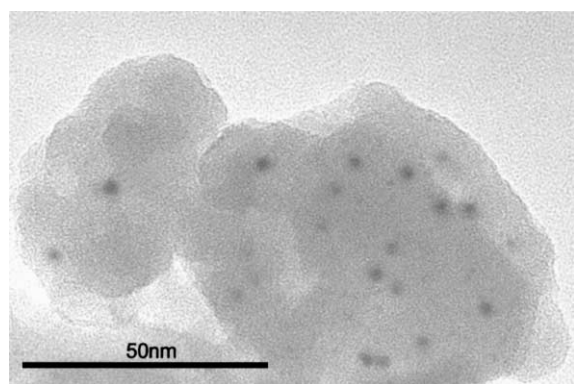
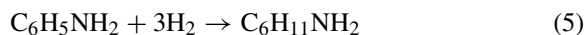
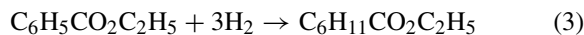


Fig. 1. Transmission electron micrograph of sol–gel entrapped $\text{Rh}_2\text{Co}_2(\text{CO})_{12}$ after heating for 16 h at 100°C in vacuum of 0.02 mm.



In an attempt to determine whether these arene hydrogenations in the presence of the entrapped Co–Rh catalyst follow the “unsaturated” or the “hydride” pathway, we conducted three comparative experiments. In the first experiment, ethylbenzene was hydrogenated in the presence of the activated catalyst (i.e. the doped sol–gel material that had been heated for 16 h at 100°C and 0.02 mm) under the conditions described in the Section 2. The yields of ethylcyclohexane after 1, 2 and 3 h were 32, 54 and 74%, respectively. In the second experiment, the activated catalyst and ethylbenzene were heated together at 60°C for 8 h prior to the addition of H_2 (200 psi) to the reaction mixture. The corresponding yields of the cyclohexane derivative after 1, 2 and 3 h were 63, 82 and 96%. In the third experiment, the activated sol–gel material was heated for 8 h under 200 psi H_2 before the addition of ethylbenzene. In this experiment, 94% of the fully hydrogenated product was obtained already within 1 h. Thus, it is clear that although pretreatment of the catalyst with the aromatic substrate is beneficial, the “hydride” pathway, is the preferred mechanism.

The hydrogenation by the activated Rh–Co catalyst proved applicable to a variety of aromatic and other unsaturated compounds. Some representative substrates are shown in Table 1.

The table indicates that styrene and diphenylacetylene which could be hydrogenated only at their double and triple bonds, respectively, by the non-preheated entrapped $\text{Rh}_2\text{Co}_2(\text{CO})_{12}$ catalyst [4], form cyclohexane derivatives in presence of the activated sol–gel material. Substrates with more than one aromatic ring are hydrogenated stepwise. For example, biphenyl yields after 4 h mainly phenylcyclohexane, but gives solely bicyclohexane upon extension of the reaction time to 20 h. Carbonyl groups of carboxylic esters are not affected during the hydrogenation of the aromatic C–C bonds, although aromatic ketones form a mixture of the alicyclic ketones, alicyclic carbinols and aromatic alcohols. When an aromatic alcohol is used as substrate it is rapidly reduced to give the corresponding alkyl cyclohexyl carbinol. In contrast to aromatic ketones, benzaldehyde undergoes

only slow hydrogenation forming benzyl alcohol free of cyclohexane-methanol. Moreover, while the recovered catalyst from the hydrogenation of acetophenone (as well as from the reduction experiments of the other substrates listed in Table 1), could be reused repeatedly in the same as well as in other hydrogenation processes, the used sol-gel material after benzaldehyde hydrogenation proved inactive. We explain this phenomenon by the fact that part of the aldehyde is decarbonylated according to Eq. (6) and the liberated CO forms an inactive carbonyl complex



In fact, when the immobilized (carbonyl-free) Rh-Co catalyst is treated with CO (200 psi at 60°C) for 16 h, an immobilized complex with strong bridging and metal-carbonyl bands at 1846, 2061 and 2080 cm^{-1} is formed. It should be recalled, that such reversible conversion of metallic nanoparticles to complexes with covalent chemical bonds by treatment with CO gas, have already been reported in a few other cases [8–10].

The potent catalytic power of the entrapped Rh-Co cluster is attributed to a synergistic effect between the different metallic nuclei. None of the sol-gel entrapped precursors of $\text{Rh}_2\text{Co}_2(\text{CO})_{12}$ (i.e. $\text{Co}_2(\text{CO})_8$ and $\text{RhCl}_3 + \text{CO}$ [7]) catalyze arene hydrogenation under our experimental conditions (not even when heated at 100°C or pretreated with molecular hydrogen). Similar negative results were obtained when other carbonyl complexes or salts of cobalt and rhodium [11] were examined. Only when a mixture of 6.4×10^{-6} mmol of $\text{Co}_2(\text{CO})_8$ and 1.14×10^{-5} mmol of $[\text{Rh}(\text{CO})_2\text{Cl}]_2$ was entrapped in a sol-gel matrix it gave, after heating at 100°C and treatment with hydrogen, a hydrogenation catalyst of low activity. For example, hydrogenation experiments of anisole with the immobilized mixture of the cobalt and rhodium complexes, and with the original heterogenized cluster under the same conditions, gave after 22 h, 30 and 100% methoxycyclohexane, respectively. With other substrates listed in Table 1 the difference in yield was even larger.

4. Conclusions

Sol-gel entrapped Rh-Co nanoparticles, formed by thermal decarbonylation of encaged $\text{Rh}_2\text{Co}_2(\text{CO})_{12}$, are a powerful arene hydrogenation catalyst, especially after pretreatment with H_2 . The hydrogenation was shown to take place via the “hydride” rather than the “unsaturated” pathway. The immobilized Rh-Co nanoparticles were found to react with CO to reform an entrapped metal-carbonyl cluster. Complex formation from the metallic particles seems to occur also upon their treatment with aromatic substrates.

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