Pergamon

Tetrahedron Letters, Vol. 35, No. 5, pp. 781-784, 1994
Elsevier Science Ltd
Printed in Great Britain
0040-4039/94 $6.00+0.00

0040-4039(93)E0305-4

Polystyrene-Supported $RhCl_3$-Quaternary Ammonium Ion pair as a Long-Lived, Efficient and Recyclable Catalyst

Merav Setty-Fichman[a], Jochanan Blum[a]* and Yoel Sasson[b]*

[a]Department of Organic Chemistry, and [b]Casali Institute of Applied Chemistry,
The Hebrew University, Jerusalem 91904, Israel

Moris Eisen

Department of Chemistry, Israel Institute of Technology, Technion City,
Haifa 32000, Israel

Abstract: *Polymer-supported ion pair, generated from $RhCl_3$ and Dowex^R 1 anion exchanger was found to be a highly stable, efficient and recyclable catalyst for isomerization of allylic compounds, disproportionation of cyclic 1,3-dienes and trimerization of alkynes.*

Under phase transfer conditions, ion pairs generated from $RhCl_3$ and quaternary ammonium salts[1] were shown to act as highly selective catalysts for hydrogenation[2] and other hydrogen transfer reactions,[1,3,4] for carbonylation[5] and for various alkyne transformation processes.[5-8] The catalyst used in some of these reactions could be recovered in part as water soluble $RhCl_4^-$ by treatment of the reaction mixture with a lipophilic anion.[1,3,4,8] In the other processes, however, this method of catalyst recovery proved non-applicable. Recently we found a more general method for the recycling of metal-onium ion pairs based on encapsulation of the catalysts in sol-gel matrices, though each catalytic run had to be preceded by reopening of blocked pores by sonication and water assisted Si-O bond rupture.

We now find that attachment of an ion pair to a commercially available polystyrene resin (by the reaction shown in eq. 1) gives an even better immobilized catalyst that does not lose its activity on recycling, and does not require any special treatment between successive runs. In a typical preparation, a mixture of 1.5

g of dried Dowex^{R} 1 (crosslinked with 4% divinylbenzene, containing 1.33 meq/g Cl^-, 200-400 mesh), 5 ml of 95% EtOH and 150 mg of $RhCl_3 \cdot 3H_2O$ was stirred at 25 °C for 24 h. The red resin was washed with EtOH until the washings were free of rhodium (checked by atomic absorption) followed by drying of the solid at 0.05 mm for 24 h. The polymer-bound ion pair was found to be leach-proof in boiling water, ethanol, butanol, toluene and dichloroethane. However, upon stirring of the resin with aq. $NaClO_4$ for 3 d it decomposed according to eq. 2 in analogy to the homogeneous ion pair.[1]

$$\begin{aligned}&[\text{polystyrene-CH}_2\text{NMe}_3]^+\text{Cl}^- + \text{RhCl}_3.(\text{H}_2\text{O})_n \rightarrow\\ &\quad[\text{polystyrene-CH}_2\text{NMe}_3]^+[\text{RhCl}_4(\text{H}_2\text{O})_2]^- + \text{n-2H}_2\text{O}\end{aligned}\tag{1}$$

$$\begin{aligned}&[\text{polystyrene-CH}_2\text{NMe}_3]^+[\text{RhCl}_4(\text{H}_2\text{O})_2]^- + \text{NaClO}_4 \rightarrow\\ &\quad[\text{polystyrene-CH}_2\text{NMe}_3]^+\text{ClO}_4^- + \text{NaRhCl}_4 + 2\text{H}_2\text{O}\end{aligned}\tag{2}$$

In aqueous EtOH, the immobilized ion pair proved to act as a recyclable catalyst for isomerization of both allylbenzene and 1-octen-3-ol, for disproportionation of 1,3-cyclohexadiene, as well as for trimerization and hydration of phenylacetylene.

Transformation of allylbenzene to an equilibrium mixture of 0.3% of the starting material, 7.7% of *cis*- and 92.0% of *trans*-3-propenylbenzene was accomplished within 20 min by heating of the olefin (1 ml) in boiling 92% aqueous EtOH (5 ml) in the presence of the supported catalyst that contained 0.57 meq of Rh. Upon completion of the reaction the beads were filtered, washed with EtOH, dried and recycled in a second run. Neither loss in activity nor change in the kinetics was observed in advanced

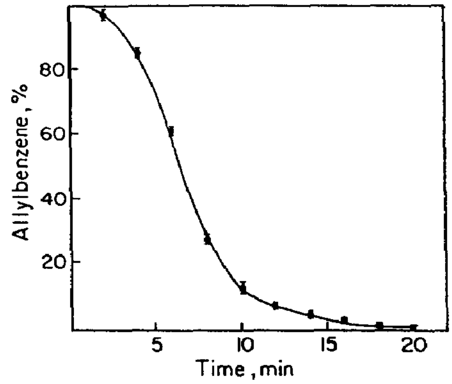

Fig. 1. Reaction profile of isomerization of allylbenzene in six consecutive runs. Reaction conditions: 1 ml allylbenzene, 5 ml 92% EtOH; polymer-bound catalyst containing 0.57 meq Rh; 78 °C.

cycles. A plot that summarizes six consecutive runs of allylbenzene isomerization is shown in Fig. 1. The figure indicates that the double bond migration by the immobilized catalyst is faster by an order of magnitude than by the homogeneous $RhCl_3$-Aliquat® 336 ion pair at 80 °C.[1] While the isomerization can be carried out successfully in polar solvents (EtOH, BuOH, THF) the addition of aromatic hydrocarbons (that are effective swelling agents for polystyrene resins and generally enhance catalyses by polymer supported transition metal complexes[10]) stalls our catalytic processes. The amount of water present in the reaction mixture is crucial for successful execution of the catalysis. Experiments in absolute EtOH failed to give any products. Comparative experiments in EtOH with 1, 5, 10 and 15% of water led to 14, 64, 94 and 90% conversion after 15 min. The decrease in activity in the presence of 15% water is due to slow deterioration of the catalyst under these conditions. The amount of 8% water was found optimal to ensure both catalyst stability and highest rate for numerous catalytic cycles. XPS studies revealed that in 92% aq. EtOH the rhodium in the recovered catalyst exists mainly as Rh(III). After several runs the measurements indicate the presence of traces of Rh(I) but not of Rh(0).[11] In 85% EtOH, however, considerable amounts of metallic rhodium was found. The formation of Rh(I) can be explained by the involvement of an oxidative addition-reductive elimination mechanism in the process. The short induction period (see Fig. 1) was found to result from an initial slow coordination of the substrate to the supported metal. Thus, when the catalyst was pretreated for 1.5-3 h with allylbenzene (before addition of the aqueous EtOH) the induction period either shortened or vanished completely. The solvent was found to take part in the reaction mechanism. Substitution of the EtOH by ethanol-d_6 led to substantial deuteriation of the products. We assume that the alcohol is involved in the formation of a metal hydride which is apparently a key intermediate in the catalytic cycle. It should be noted, however, that no kinetic isotope effecct was observed when either ethanol-d_6 or D_2O was added to the solvent.

Under the conditions described for the isomerization of allylbenzene, 1-octen-3-ol was transformed within 80 min in quantitative yield to 3-octanone, probably via the corresponding enol $C_5H_{11}C(OH)=CHCH_3$. Disproportionation of 1,3-cyclohexadiene was best carried out in 90% aq. THF. After 225 min at reflux, equimolar amounts of benzene and cyclohexene were obtained in nearly quantitative yield. It is remarkable that while the homogeneous ion pair $[(C_8H_{17})_3NMe]^+[RhCl_4(H_2O)_2]^-$ often promoted both disproportionation and dehydrogenation of the diene,[3] the immobilized catalyst gave exclusively the disproprtionation products.

Since the soluble $RhCl_3$-Aliquat® 336 catalyst could not be recycled when utilized in alkyne oligomerization, the application of the immobilized ion pair for trimerization of acetylenes is of particular interest. When, e.g., a mixture of 4.5 mmol of phenylacetylene, 5 ml of 92% EtOH and the polymer-attached catalyst (containing 0.57 meq Rh) was refluxed for 5 h, 25% of 1,2,4-, 8% of 1,3,5-triphenylbenzene and 30% of acetophenone were isolated. Exactly the same mixture of products was obtained in the following four runs in which the recovered catalyst was used. Reduction of the amount of H_2O in the reaction mixture increased the yield of the triphenylbenzenes on account of the ketone, but caused the rate to slow down.

In conclusion, it should be recalled that many conventional transition metal complexes have been attached to polymer supports. However, the applicaltion of these immobilized catalysts resulted often in metal leaching.[10] Metal salts have also been reacted previously with ion exchange resins and with other polymer-bound quaternary ammonium ions, but the immobilized ion pairs so formed, were reduced to supported metal particles in which the ammonium moiety served just to increase the polarity of the reaction medium.[13,14] The polystyrene-bound ion pair described in this communication has not been reduced during the catalytic processes. Under the described conditions it proved to be leach proof, long-lived, highly active and recyclable.

We thank the Israel Science Foundation administered by the Israel Academy of Sciences and Humanities for financial support of this study.

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(*Received in UK* 1 *November* 1993; *accepted* 26 *November* 1993)