Journal of Organometallic Chemistry, 240 (1982) 441–445
Elsevier Sequoia S.A., Lausanne – Printed in The Netherlands

CATALYTIC HYDROGENATION OF 1,3-*trans*-PENTADIENE OVER $Rh_4(CO)_{12}$ SUPPORTED ON γ-Al_2O_3 *

P. MICHELIN LAUSAROT **, G.A. VAGLIO and M. VALLE

Istituto di Chimica Generale ed Inorganica, Università di Torino, Corso Massimo d'Azeglio 48, 10125 Torino (Italy)

(Received July 1st, 1982)

Summary

$Rh_4(CO)_{12}$ anchored on γ-Al_2O_3 ($Rh_4(CO)_{12}/Al_2O_3$) has been studied as a catalyst for the hydrogenation of 1,3-*trans*-pentadiene. Under mild conditions (1 atm H_2 and temperatures between 60°C and 80°C) hydrogenation occurs at only one of the double bonds of the diene, and analysis of the products shows that the terminal double bond is preferentially hydrogenated. Hydrogenation of the second double bond of the conjugated diene occurring only after all the 1,3-*trans*-pentadiene has been consumed. In this respect $Rh_4(CO)_{12}/Al_2O_3$ behaves like toluene solutions of $Rh_4(CO)_{12}$. Anchoring of $Rh_4(CO)_{12}$ on the solid support gives a catalyst which is less active but more stable than toluene solutions of $Rh_4(CO)_{12}$. The effects of CO and of triphenylphosphine on catalytic activity and on specificity of $Rh_4(CO)_{12}/Al_2O_3$ have also been investigated and both shown to cause a reduction of the rate of hydrogenation of 1,3-*trans*-pentadiene.

Introduction

Transition metal clusters are receiving much attention for their possible use as catalysts since they reproduce some of the features of multinuclear metal centers of homogeneous catalysts and are more amenable to designed modifications [1–4]. The limited thermal stability of metal clusters, however, constitutes a drawback whenever moderately high reaction temperatures are required. The thermal stability of metal cluster compounds has in some cases been improved by anchoring them on solid supports [5,6].

As part of our studies on the influence which the anchoring of metal clusters on inorganic oxides has on their stability as well as their catalytic activity and

---

* Work supported by the Italian CNR, contract No. 81.00727.95 (Progetto finalizzato Chimica fine e secondaria).

** To whom correspondence should be addressed.

0022-328X/82/0000–0000/$02.75

specificity [7,8], we report below the results of a study of the hydrogenation of 1,3-*trans*-pentadiene catalysed by $Rh_4(CO)_{12}$ anchored on γ-Al_2O_3. A detailed consideration of the active species present in the catalytic systems investigated is beyond the scope of this paper, and the emphasis is placed on comparisons of their specificities and stabilities.

Results and discussion

Toluene solutions of $Rh_4(CO)_{12}$ readily catalyse hydrogenation of 1,3-*trans*-pentadiene under mild reaction conditions. In Figs. 1a, b and c are shown the distributions of the products during reactions at 60, 70 and 80°C, respectively, and with 1 atm H_2. Change in temperature considerably influences the reaction rates but has no effect on the nature of the products nor on their order of formation. The first product appearing in the reaction mixture is 2-*trans*-pentene, and this remains the most abundant throughout the reaction. Smaller amounts of 1-pentene and of 2-*cis*-pentene are also present, whilst no pentane can be detected as long as 1,3-*trans*-pentadiene is present. These results are consistent with a preferential hydrogenation of the terminal double bound of the diene. Hydrogenation of the internal double bond, which can be determined from the amount of 1-pentene in the products, is disfavored by a factor of 4.5–5.0. Moreover, the catalyst preferentially activates the diene compared with the pentenes, since there is no extensive isomerisation of the pentenes and no further hydrogenation of pentenes to pentane occurs as long as the diene is present. After all the pentadiene has been consumed, active sites on the catalyst become available for pentenes, and isomerisation as well as further hydrogenation can take place (see Fig. 1c). Both of these processes mainly involve 1-pentene, since it has been shown previously [7] that isomerisation and hydrogenation of 2-*trans*-pentene catalysed by $Rh_4(CO)_{12}$ are very slow processes. Anchoring of $Rh_4(CO)_{12}$ on γ-Al_2O_3 does not alter the order of appearance nor the relative amounts of the products (Figs. 2a, b and c), and the same features observed for

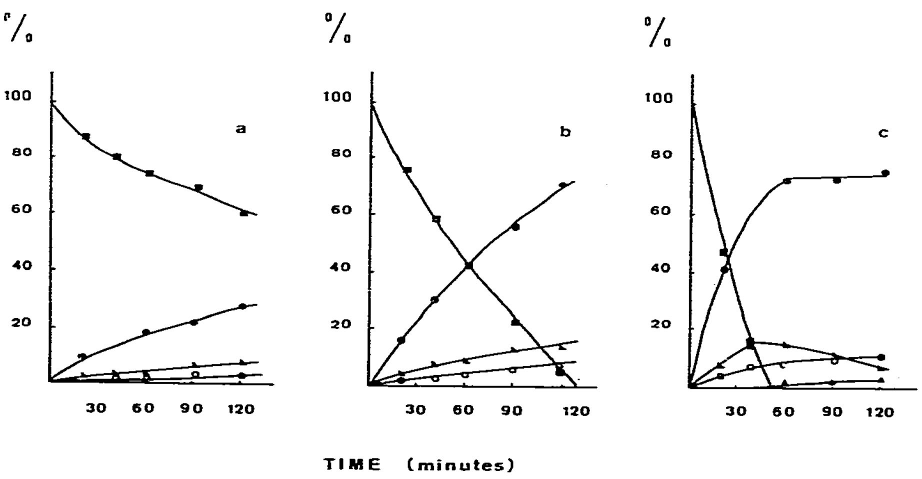

Fig. 1. Hydrogenation of 1,3-*trans*-pentadiene catalysed by $Rh_4(CO)_{12}$ at 60°C(a), 70°C(b) and 80°C(c). ■ 1,3-*trans*-pentadiene, ● 2-*trans*-pentene, 1-pentene, ○ 2-*cis*-pentene, ▲ pentane.

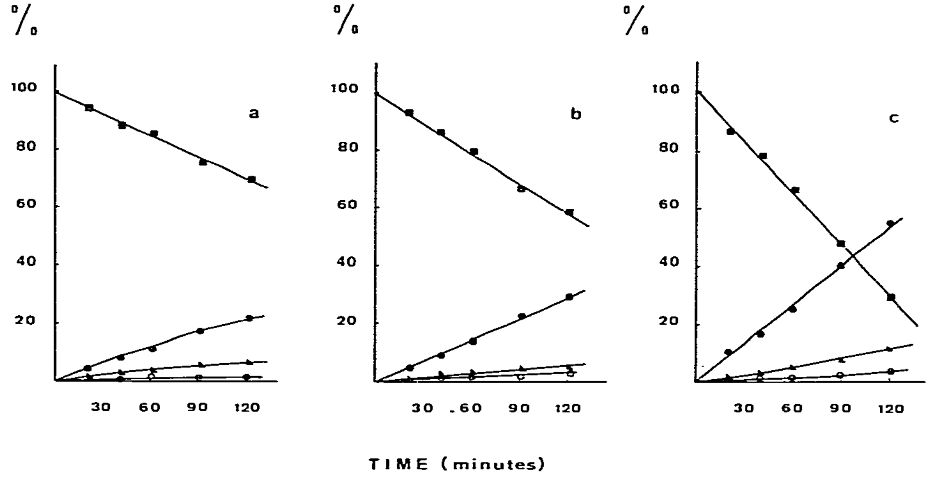

Fig. 2. Hydrogenation of 1,3-*trans*-pentadiene catalysed by $Rh_4(CO)_{12}/Al_2O_3$ at 60°C(a), 70°C(b) and 80°C(c). ■ 1,3-*trans*-pentadiene, ● 2-*trans*-pentene, 1-pentene, ○ 2-*cis*-pentene.

solutions of $Rh_4(CO)_{12}$ apply also to the heterogenised $Rh_4(CO)_{12}/Al_2O_3$ system. Anchoring of $Rh_4(CO)_{12}$ on γ-Al_2O_3, however, considerably decreases the hydrogenation rate. Initial rates for the hydrogenation of 1,3-*trans*-pentadiene catalysed by $Rh_4(CO)_{12}$ and by $Rh_4(CO)_{12}/Al_2O_3$ at 60, 70 and 80°C are listed in Table 1. It can be seen that the ratio between initial rates for the homogeneous and the anchored catalyst increases with increasing temperature. The IR spectra of $Rh_4(CO)_{12}$ solutions, indicate, however, that $Rh_4(CO)_{12}$ reacts with the substrate and decomposes upon heating. After longer reaction periods Rh separates as a metallic mirror on the sides of the vials. Anchoring of $Rh_4(CO)_{12}$ on γ-Al_2O_3 results in a more stable catalytic system, as supported by the following observations: a) the IR spectrum of $Rh_4(CO)_{12}$ anchored on γ-Al_2O_3 (absorption maxima at 2080 cm^{-1} and 1997 cm^{-1} [7]) does not change following thermal treatment under 1 atm H_2 and in the

TABLE 1

INFLUENCE OF THE TEMPERATURE ON INITIAL RATES OF HYDROGENATION OF 1,3-*trans*-PENTADIENE CATALYSED BY $Rh_4(CO)_{12}$ AND BY $Rh_4(CO)_{12}/Al_2O_3$ IN THE PRESENCE OF 1 atm H_2 [a,b,c]

Catalyst	Temperature (°C)	Initial rate (mMh^{-1})
$Rh_4(CO)_{12}$	60	40
$Rh_4(CO)_{12}$	70	70
$Rh_4(CO)_{12}$	80	160
$Rh_4(CO)_{12}/Al_2O_3$	60	15
$Rh_4(CO)_{12}/Al_2O_3$	70	21
$Rh_4(CO)_{12}/Al_2O_3$	80	33

[a] $[Rh_4(CO)_{12}]/[Diene] = 1/100$. [b] Toluene solutions of $Rh_4(CO)_{12}$ were 1.04×10^{-3} M.
[c] $Rh_4(CO)_{12}/Al_2O_3$ samples were 0.46 wt.% in $Rh_4(CO)_{12}$.

presence of 1,3-*trans*-pentadiene; b) recycling experiments have shown that $Rh_4(CO)_{12}/Al_2O_3$ retains most of its catalytic activity. The loss of activity after 1 h reaction was approximately 20%; c) no metallic Rh separates under the reaction conditions since the supported catalyst is not active for hydrogenation of toluene; d) the IR spectra of $Rh_4(CO)_{12}/Al_2O_3$, treated with CO, do not display absorption bands typical of CO adsorbed on metallic rhodium [9,10]; e) when $Rh_4(CO)_{12}$ is pyrolysed on γ-Al_2O_3, the resulting catalyst differs from the anchored one both in activity and in specificity, since it promotes a rapid hydrogenation of both double bonds of 1,3-*trans*-pentadiene and shows no preferential interaction with the conjugated double bond system; thus pentane appears among the products from the beginning.

Increasing the CO pressure in the reaction vial leads to a decrease in the rate of hydrogenation of 1,3-*trans*-pentadiene catalysed by $Rh_4(CO)_{12}$ solutions and by $Rh_4(CO)_{12}/Al_2O_3$. Detachment of CO may, therefore, be a rate limiting step. Alternatively, a pre-equilibrium between the catalyst and substrate involving release of CO could explain the decrease in the reaction rate. The decrease in rate is less pronounced for $Rh_4(CO)_{12}$- than for $Rh_2Cl_2(CO)_4$-containing catalysts [8].

Addition of triphenylphosphine (PPh_3) in molar ratios to the cluster ranging from 1/1 to 4/1 was investigated. $Rh_4(CO)_{12}$ readily reacts at room temperature with PPh_3 to give a mixture of mono- and poly-substituted derivatives even at low $PPh_3/Rh_4(CO)_{12}$ ratios. Substitution of CO groups on the cluster considerably increases the time required for a complete anchoring of the cluster onto γ-Al_2O_3. With the exception of the 1/1 $[PPh_3]/[Rh_4(CO)_{12}]$ ratio, the rate of hydrogenation of 1,3-*trans*-pentadiene catalysed by $Rh_4(CO)_{12}$ and by $Rh_4(CO)_{12}/Al_2O_3$ partially substituted with PPh_3 is lower than that measured for the unsubstituted catalytic systems (Fig. 3). $Rh_4(CO)_{12}/Al_2O_3$ differs from $Rh_2Cl_2(CO)_4/Al_2O_3$ which we studied previously [8], since a more active catalyst is not obtained when PPh_3 is left in contact for several hours with γ-Al_2O_3 prior to the introduction of $Rh_4(CO)_{12}$ into the system.

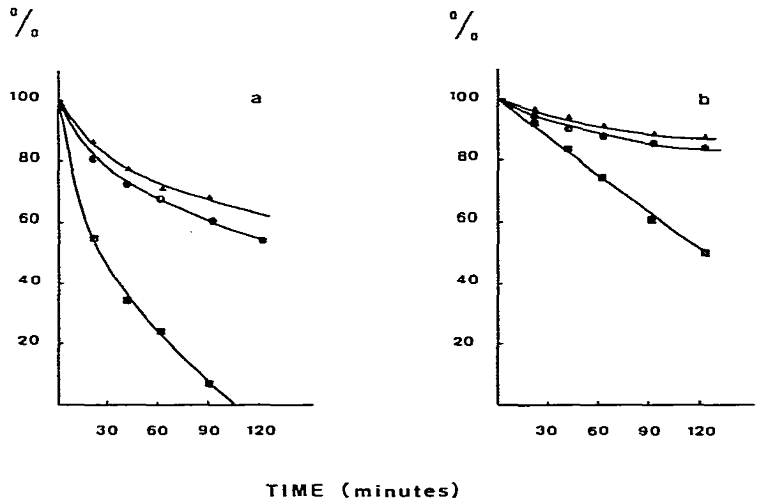

Fig. 3. Residual 1,3-*trans*-pentadiene during hydrogenation catalysed by $Rh_4(CO)_{12}$ (a) and by $Rh_4(CO)_{12}/Al_2O_3$ (b) in the presence of PPh_3. $[Catalyst]/[PPh_3] = 1$ (■), 2 (●) and 4 (▲).

On the basis of the results reported above we conclude that anchoring of $Rh_4(CO)_{12}$ on γ-Al_2O_3 is a useful means of stabilising the catalyst, although a slight reduction of initial rates results from this anchoring. However, it is noteworthy that hydrogenation of 1,3-*trans*-pentadiene proceeds with the same specificity in the presence of the homogeneous and of the supported catalysts even though the environments of the Rh atoms are presumably different.

Experimental

Details of the preparation of $Rh_4(CO)_{12}$ and its anchoring on γ-Al_2O_3 (Merck, specific area 130 m^2/g) have been described previously [7,11,12]. Hydrogenation experiments (at temperatures ranging from 60°C to 80°C) and analyses of reaction products were performed as detailed elsewhere [8,13,14]. Blank tests were carried out to show that Al_2O_3 does not catalyse hydrogenation of 1,3-*trans*-pentadiene under the conditions used, and that no transfer of catalytic activity occurs between the anchored catalyst and the solution.

References

1 R. Ugo, Catal. Rev., 11 (1975) 225.
2 E.L. Muetterties, Science, 196 (1977) 839.
3 J.M. Basset and R. Ugo in R. Ugo (Ed.), Aspects of Homogeneous Catalysis, Reidel Publ., Dordrecht, Netherlands, 1977.
4 A. Brenner and D.A. Hucul, J. Amer. Chem. Soc., 102 (1980) 2484.
5 F.R. Hartley and P.N. Vezey, Adv. Organometal. Chem., (1977) 15.
6 D.C. Bailey and S.H. Langer, Chem. Rev., 81 (1981) 109.
7 P. Michelin Lausarot, G.A. Vaglio and M. Valle, J. Organometal. Chem., 204 (1981) 249.
8 P. Michelin Lausarot, G.A. Vaglio and M. Valle, J. Organometal. Chem., 215 (1981) 111.
9 A.K. Smith, F. Hugues, A. Theolier, J.M. Basset, R. Ugo, G.M. Zanderighi, J.L. Bilhou-Bougnol and F. Graydon, Inorg. Chem., 18 (1979) 3104.
10 A. Theolier, A.K. Smith, M. Leconte, J.M. Basset, G.M. Zanderighi, R. Psaro and R. Ugo, J. Organometal. Chem., 191 (1980) 415.
11 P. Chini and S. Martinengo, J. Chem. Soc. Chem. Commun., (1968) 251.
12 P. Chini and S. Martinengo, Inorg. Chim. Acta, 3 (1969) 315.
13 P. Michelin Lausarot, G.A. Vaglio and M. Valle, Gazzetta, 109 (1979) 127.
14 P. Michelin Lausarot, G.A. Vaglio and M. Valle, Inorg. Chim. Acta, 36 (1979) 213.