

HYDROGENATION OF PENTYNES AND OF PENTADIENES CATALYSED BY $\text{Ru}_3(\text{CO})_{12}$, $\text{Fe}_3(\text{CO})_{12}$ AND MIXED METAL Ru–Fe DODECACARBONYLS SUPPORTED ON $\gamma\text{-Al}_2\text{O}_3$

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(Received May 11th, 1984)

Summary

Hydrogenation under mild conditions of 1- and 2-pentyne and of 1,3-*cis*- and 1,3-*trans*-pentadiene catalysed by $\text{Ru}_3(\text{CO})_{12}$, $\text{FeRu}_2(\text{CO})_{12}$, $\text{Fe}_2\text{Ru}(\text{CO})_{12}$ and $\text{Fe}_3(\text{CO})_{12}$ in toluene solutions or anchored on $\gamma\text{-Al}_2\text{O}_3$ has been studied. For all the systems examined, catalytic activity was highest for $\text{Ru}_3(\text{CO})_{12}$ -containing catalysts and lowest for $\text{Fe}_3(\text{CO})_{12}$ -containing ones. For mixed metal catalysts, activity decreased with increasing number of Fe atoms in the dodecacarbonyls. Anchorage of the clusters to $\gamma\text{-Al}_2\text{O}_3$ produced catalysts which were less active towards hydrogenation of 1- and 2-pentyne and more active towards hydrogenation of 1,3-*cis*- and 1,3-*trans*-pentadiene, but had no effect on product distribution.

Introduction

Anchorage of transition metal clusters has been investigated by several authors [1,2] in view of the fact that the use of the resulting systems in catalysis is not impaired by the difficulties which are often encountered in the separation and recovery of homogeneous catalysts from the reaction products. Moreover, anchored metal clusters have often shown increased stability with respect to their solutions [2–4]. In several cases, however, stabilisation of the metal cluster is accompanied by decreased catalytic activity [1,2,5].

In previous papers [6–8] we have compared the catalytic activity, in hydrogenation of organic unsaturated substrates, of $\text{Rh}_4(\text{CO})_{12}$ and $\text{Rh}_2(\text{CO})_4\text{Cl}_2$ in toluene solutions with that displayed by the catalytic systems obtained by adsorption of the same clusters on $\gamma\text{-Al}_2\text{O}_3$. In this paper we report the results of an investigation on the hydrogenation of 1- and 2-pentyne and of 1,3-*trans*- and 1,3-*cis*-pentadiene

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catalysed by toluene solutions of $\text{Ru}_3(\text{CO})_{12}$, $\text{FeRu}_2(\text{CO})_{12}$, $\text{Fe}_2\text{Ru}(\text{CO})_{12}$ and $\text{Fe}_3(\text{CO})_{12}$ and by the same clusters supported on $\gamma\text{-Al}_2\text{O}_3$.

Detailed accounts have been given of the interaction of $\text{Ru}_3(\text{CO})_{12}$ with $\gamma\text{-Al}_2\text{O}_3$, both fully hydroxylated and partially dehydroxylated by heat treatment, [9–12], and so the work described in this paper was not aimed at identifying new species formed upon interaction of the inorganic support with the metal cluster but at studying the catalytic behaviour of Ru and Ru–Fe dodecacarbonyls anchored on $\gamma\text{-Al}_2\text{O}_3$.

Ru-containing clusters are considered of particular interest in connection with their claimed activity towards hydrogenation of CO [13]. Moreover, mixed metal clusters could potentially display interesting catalytic specificities associated with their electronic properties.

Results and discussion

Attempts to anchor $\text{Ru}_3(\text{CO})_{12}$, $\text{FeRu}_2(\text{CO})_{12}$, $\text{Fe}_2\text{Ru}(\text{CO})_{12}$ and $\text{Fe}_3(\text{CO})_{12}$ to untreated $\gamma\text{-Al}_2\text{O}_3$ led to unsatisfactory results since the uptake of the cluster from the solution was very slow and required several hours for completion. These clusters were, however, readily adsorbed by partially dehydroxylated $\gamma\text{-Al}_2\text{O}_3$, and the rate of adsorption increased with increasing number of Fe atoms on the cluster. No release of the adsorbed clusters in the solution was observed when they were heated in the presence of toluene for several hours at 80 °C. Adsorbed mixed metal clusters, however, were modified within less than 1 h, as judged from the change in colour. In view of the particular objectives of this study no attempt was made to investigate the nature of the changes taking place. The absence of catalytic activity towards hydrogenation of toluene [14] rules out a complete disruption of the clusters to give metal particles.

$\text{Ru}_3(\text{CO})_{12}$, $\text{FeRu}_2(\text{CO})_{12}$, $\text{Fe}_2\text{Ru}(\text{CO})_{12}$ and $\text{Fe}_3(\text{CO})_{12}$ all catalyse the hydrogenation of 1- and 2-pentyne and of 1,3-*cis*- and 1,3-*trans*-pentadiene under mild reaction conditions (1 atm H_2 and 80 °C) both in toluene solutions and anchored to $\gamma\text{-Al}_2\text{O}_3$. In Table 1 are shown the percentages of unreacted substrate after 16 h at 80 °C in the presence of 1 atm H_2 and of the catalytic systems studied. Under these

TABLE 1
PERCENTAGE OF VARIOUS SUBSTRATES REMAINING AFTER 16 h AT 80 °C IN THE PRESENCE OF 1 atm H_2 AND OF THE CATALYTIC SYSTEMS LISTED

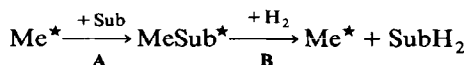
[Catalyst]/[Substrate] = 1/40

Catalyst	1-Pentyne	2-Pentyne	1,3- <i>cis</i> -Pentadiene	1,3- <i>trans</i> -Pentadiene
$\text{Ru}_3(\text{CO})_{12}$	29	–	32	35
$\text{Ru}_3(\text{CO})_{12}/\text{Al}_2\text{O}_3$	92	84	–	–
$\text{FeRu}_2(\text{CO})_{12}$	74	87	42	56
$\text{FeRu}_2(\text{CO})_{12}/\text{Al}_2\text{O}_3$	96	92	–	5
$\text{Fe}_2\text{Ru}(\text{CO})_{12}$	95	99	75	88
$\text{Fe}_2\text{Ru}(\text{CO})_{12}/\text{Al}_2\text{O}_3$	95	97	72	81
$\text{Fe}_3(\text{CO})_{12}$	99	99	98	98
$\text{Fe}_3(\text{CO})_{12}/\text{Al}_2\text{O}_3$	99	99	98	97

conditions 29% residual 1-pentyne and no 2-pentyne were found in the reaction mixture when hydrogenation was catalysed by toluene solutions of $\text{Ru}_3(\text{CO})_{12}$. The main product arising from the hydrogenation of 2-pentyne (see Table 2) was 2-*trans*-pentene, with smaller amounts of 2-*cis*-pentene, pentane and 1-pentene. Hydrogenation of 1-pentyne led to 40.0% 2-*trans*-pentene and some 2-*cis*-pentene, 1-pentene and pentane, and 28.8% of 1-pentyne remained unchanged. For both these substrates, hydrogenation is likely to take place in two steps, since only minimal amounts of pentane can be found in the mixture as long as pentyne are present, as shown in experiments in which the reaction mixture was analysed during the course of the reaction.

Substitution of Ru atoms in the cluster by Fe atoms is accompanied by a reduction of catalytic activity, as shown in the first two columns of Table 1. In the limiting case of total substitution of Ru atoms by Fe atoms to give $\text{Fe}_3(\text{CO})_{12}$, only 1% of the substrate is hydrogenated after 16 h at 80 °C in the presence of 1 atm H_2 .

Anchorage of $\text{Ru}_3(\text{CO})_{12}$ on $\gamma\text{-Al}_2\text{O}_3$ leads to a considerable reduction of catalytic activity and only some 10% of 1-pentyne and some 15% of 2-pentyne are hydrogenated after 16 h at 80 °C. By analogy with toluene solutions of the clusters, catalytic activity decreases with increasing number of Fe atoms in the dodecacarbonyl. Differences in the activities between anchored and non-anchored clusters level off for $\text{Fe}_2\text{Ru}(\text{CO})_{12}$ and $\text{Fe}_3(\text{CO})_{12}$. An explanation of the partial loss of catalytic activity following adsorption on $\gamma\text{-Al}_2\text{O}_3$ can be attempted on the basis of the mechanism of interaction of $\text{Ru}_3(\text{CO})_{12}$ on activated $\gamma\text{-Al}_2\text{O}_3$ suggested by Kuznetsov et al. [9]. According to these authors, when $\text{Ru}_3(\text{CO})_{12}$ is adsorbed on $\gamma\text{-Al}_2\text{O}_3$ activated at temperatures above 300 °C, surface adducts of the cluster with Lewis acid centres on the support are formed, a carbonyl group of the cluster acting as a Lewis base. This type of interaction involves withdrawal of electron density from Ru with consequent stabilisation of the activated complex. If we oversimplify the essential steps in the hydrogenation of the substrate in the following scheme:



(where Me^* is the activated metal species, MeSub^* the activated complex with the substrate and SubH_2 the hydrogenated substrate), withdrawal of electrons from the

TABLE 2

DISTRIBUTION OF THE PRODUCTS (%) AFTER 16 h AT 80 °C IN THE PRESENCE OF 1 atm H_2 AND OF $\text{Ru}_3(\text{CO})_{12}$ AND $\text{Ru}_3(\text{CO})_{12}/\text{Al}_2\text{O}_3$ AS CATALYSTS

[Catalyst]/[Substrate] = 1/40

Catalyst	Substrate	Pentane	1-Pentene	2- <i>trans</i> -Pentene	2- <i>cis</i> -Pentene	Substrate
$\text{Ru}_3(\text{CO})_{12}$	1-pentyne	2.2	6.5	40.1	22.4	28.8
$\text{Ru}_3(\text{CO})_{12}/\text{Al}_2\text{O}_3$	1-pentyne	0.8	6.0	0.9	0.8	91.5
$\text{Ru}_3(\text{CO})_{12}$	2-pentyne	13.4	1.7	68.5	16.4	—
$\text{Ru}_3(\text{CO})_{12}/\text{Al}_2\text{O}_3$	2-pentyne	1.4	1.3	2.9	10.6	83.8
$\text{Ru}_3(\text{CO})_{12}$	1,3- <i>cis</i> -pentadiene	0.4	7.1	48.4	11.6	32.4
$\text{Ru}_3(\text{CO})_{12}/\text{Al}_2\text{O}_3$	1,3- <i>cis</i> -pentadiene	4.3	2.7	74.3	18.7	—
$\text{Ru}_3(\text{CO})_{12}$	1,3- <i>trans</i> -pentadiene	6.8	2.4	44.1	12.1	34.6
$\text{Ru}_3(\text{CO})_{12}/\text{Al}_2\text{O}_3$	1,3- <i>trans</i> -pentadiene	6.5	2.4	73.6	17.5	—

metal atom stabilises MeSub* with consequent decrease of the rate of step **B** which could, thereby, become the rate limiting process. The decreased catalytic activity of mixed Ru-Fe clusters could also be explained on the same basis.

Hydrogenation of 1,3-*cis*- and 1,3-*trans*-pentadiene is not complete in 16 h reaction when catalysed by toluene solutions of $\text{Ru}_3(\text{CO})_{12}$, and some 30–35% of the substrate is still present at the end of the time allowed for the reaction. The main product for both substrates is 2-*trans*-pentene (see Table 2), indicating that the terminal double bond is the preferred hydrogenation site. Only small amounts of pentane are formed, showing that the hydrogenation of one of the double bonds of the diene is favoured over that of the double bond of the resulting pentene. As already noted for pentyne, the rate of hydrogenation of dienes is also a function of the number of Ru atoms in the dodecacarbonyls, and their partial or total substitution by Fe atoms leads to a progressive decrease of catalytic activity, but this decrease is less than that observed for 1- and 2-pentyne.

It is noteworthy that both $\text{Ru}_3(\text{CO})_{12}/\text{Al}_2\text{O}_3$ and $\text{FeRu}_2(\text{CO})_{12}/\text{Al}_2\text{O}_3$ display a considerably higher catalytic activity than the corresponding toluene solutions of the clusters. In fact, all the substrate undergoes hydrogenation within 16 h at 80 °C allowed for the reaction, in the presence of $\text{Ru}_3(\text{CO})_{12}/\text{Al}_2\text{O}_3$ as catalyst. Similarly, all 1,3-*cis*-pentadiene is hydrogenated and only 5% residual 1,3-*trans*-pentadiene is present after 16 h at 80 °C in the presence of $\text{FeRu}_2(\text{CO})_{12}/\text{Al}_2\text{O}_3$. The supported catalysts $\text{Fe}_2\text{Ru}(\text{CO})_{12}/\text{Al}_2\text{O}_3$ and $\text{Fe}_3(\text{CO})_{12}/\text{Al}_2\text{O}_3$ are also slightly more active towards hydrogenation of dienes than the corresponding toluene solutions.

The activation of $\text{Ru}_3(\text{CO})_{12}$ and $\text{FeRu}_2(\text{CO})_{12}$ on the support, although in apparent contradiction with the depression of catalytic activity towards hydrogenation of pentyne, can find a logical interpretation on the basis of the scheme proposed above. If we assume that formation of activated complex with the substrate is the rate-limiting step for $\text{Ru}_3(\text{CO})_{12}$ in solution when the substrate is 1,3-*cis*- or 1,3-*trans*-pentadiene, withdrawal of electron density from metal centres through interaction with $\gamma\text{-Al}_2\text{O}_3$ would increase the rate of step **A** with an overall increase of catalytic activity. This interpretation is consistent with the fact that when $\text{Ru}_3(\text{CO})_{12}$ is adsorbed on $\gamma\text{-Al}_2\text{O}_3$ which has not been activated by heat treatment and is, therefore, in its fully hydroxylated form, only some 40% of 1,3-*cis*- and 1,3-*trans*-pentadiene are hydrogenated after 16 h at 80 °C. This is in agreement with the change in the chemistry of the interaction of $\text{Ru}_3(\text{CO})_{12}$ at the surface of $\gamma\text{-Al}_2\text{O}_3$ with the degree of dehydroxylation. As suggested by Kuznetsov et al. [9], binding of $\text{Ru}_3(\text{CO})_{12}$ on hydroxylated $\gamma\text{-Al}_2\text{O}_3$ involves the formation of anionic species through the interaction of the basic hydroxyls of the support with the metal carbonyls. The remarkable difference between the catalytic activity of $\text{Ru}_3(\text{CO})_{12}$ supported on $\gamma\text{-Al}_2\text{O}_3$ with different degrees of dehydroxylation could explain the difficulties encountered in preparing reproducible catalytic systems.

Experimental

$\text{Ru}_3(\text{CO})_{12}$, $\text{FeRu}_2(\text{CO})_{12}$, $\text{Fe}_2\text{Ru}(\text{CO})_{12}$ and $\text{Fe}_3(\text{CO})_{12}$ were prepared as described in the literature [15–18].

1-Pentyne, 1,3-*cis*-pentadiene and 1,3-*trans*-pentadiene from Fluka, were checked for purity by GLC. 2-Pentyne was from Merck and was distilled before use.

Analytical grade toluene from Carlo Erba was dried over molecular sieves and

redistilled. The γ - Al_2O_3 , from Merck, had a specific area of $130 \text{ m}^2/\text{g}$ and was dehydroxylated by heating under vacuum at 300°C for 3 h.

Adsorption of the metal carbonyls on to the alumina and hydrogenation experiments were performed as previously described [6]. The molar ratio [cluster]/[substrate] was 1/40. The reaction temperature was 80°C . Samples, withdrawn after 16 h reaction, were analysed by GLC at 55°C on a 4 m column of 20% silicone oil 702 on Chromosorb P, 60–80 mesh, and at 20°C on a 2 m column of 11% AgNO_3 and 21% phenylacetonitrile on Chromosorb P, 60–80 mesh.

Blank tests, carried out, under identical experimental conditions on γ - Al_2O_3 , showed that the inorganic support has no catalytic activity in hydrogenation of the substrates employed. None of the catalytic systems used was active in hydrogenation of toluene [14], demonstrating the absence of metal particles resulting from a partial decomposition of the clusters.

Acknowledgement

This work was supported by the Italian CNR, contract 82-00716-95 Progetto finalizzato del CNR Chimica fine e secondaria).

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