Influence of Ru precursor, support and solvent in the hydrogenation of citral over ruthenium catalysts

G. Neri[a], L. Mercadante[b], A. Donato[a], A.M. Visco[b] and S. Galvagno[b]

[a] *Università di Reggio Calabria, Facoltà di Ingegneria, Via Cuzzocrea 48, I-89100 Reggio Calabria, Italy*

[b] *Università di Messina, Dipartimento di Chimica Industriale, Cas. Post. 29, I-98166 Sant'Agata di Messina, Italy*

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A series of ruthenium supported catalysts were prepared and investigated in the liquid-phase hydrogenation of citral. The mechanism of the reaction was found to be dependent on the Ru precursor, support and solvent used. On the sample prepared from $RuCl_3$ the acetals of citronellal were formed with the subsequent hydrogenation of the isolated C=C double bond. On the samples obtained from precursors which do not contain chloride ions, citronellal was the main reaction product. Hydrogenation of the isolated C=C double bond was negligible. Using cyclohexane as solvent, a large amount of isopulegol was also obtained. The results of the hydrogenation of citral have been correlated to the presence of acid sites and incompletely reduced ruthenium which favour cyclization and acetals formation from citronellal. On the basis of the reported results, a reaction scheme for hydrogenation of citral over ruthenium catalysts is proposed.

Keywords: citral hydrogenation; ruthenium catalysis; solvent effect; support effect; Ru precursors

1. Introduction

The selective hydrogenation of unsaturated aldehydes is a reaction of great synthetic importance for the preparation of various fine chemicals. Within this class of reactions the hydrogenation of citral (3,7-dimethyl-2,6-octadienal) is of particular interest for the use of its hydrogenation products in the perfumery industry [1]. Citral is also an interesting substrate to study because it contains three functional groups: an isolated C=C double bond, a carbonyl group and a conjugated olefinic bond. Depending on the functional group which is reduced, different hydrogenation products can be obtained. Moreover, these compounds have been reported to be sensitive to the reaction conditions used, so that products of isomerization, cyclization, etc., can be also obtained [2].

Hydrogenation of citral has been found to produce mainly citronellal and citronellol [3–5]. However, the selective formation of unsaturated alcohols over Ru and Rh catalysts promoted by tin has been previously reported [6,7].

Ru catalysts are known as good systems for the liquid-phase hydrogenation of saturated aldehydes [8] and a systematic study on the hydrogenation of citral over supported Ru catalysts has been already started in our laboratory. A recent investigation carried out on Ru/C catalysts has shown that the product selectivity of citral hydrogenation is scarcely influenced by the metal particle size [9]. It is, however, well known that other factors such as the preparative conditions of the catalyst and the solvent used can modify significantly the product distribution in the hydrogenation of α,β-unsaturated aldehydes [10–12].

In this paper we report a study on the role of the Ru precursor, support and solvent in modifying the reaction pathway of citral hydrogenation.

2. Experimental

Catalysts derived from $Ru(NO)(NO_3)_3$ and $RuCl_3$ were prepared by incipient wetness impregnation of the supports with the appropriate aqueous solution. Supports used were: γ-Al_2O_3 (Rhone-Poulenc GFC, 100–200 mesh, surface area 220 $m^2 g^{-1}$), SiO_2 (Grace 923, 100–200 mesh, 320 $m^2 g^{-1}$) and activated carbon (CHEMVIRON SC XII 80–100 mesh, surface area 900–1100 $m^2 g^{-1}$). After drying for 2 h at 393 K in air, the solids were reduced in H_2 at 623 K for 3 h and cooled at room temperature in flowing H_2.

Catalyst derived from ruthenium acetylacetonate ($Ru(acac)_3$) was prepared by contacting the support with a toluene solution of the precursor for 72 h, after which time the solution was filtered and the solid was dried under vacuum at 333 K and then reduced at 623 K for 3 h in a mixture H_2/N_2 (1 : 9).

Catalysts supported on Al_2O_3 are the same as those used in ref. [13], where an extensive characterization has been reported.

All catalysts were characterized by H_2 chemisorption at 373 K. Details on the procedure used are reported elsewhere [13]. Catalyst code, chemical composition, precursor and H/Ru ratio (calculated from the total H_2 uptake) are reported in table 1.

Table 1
Chemical composition and H/Ru ratio of ruthenium supported catalysts

Catalyst code	Support	Precursor	Ru (wt%)	H/Ru
RuECl	Al_2O_3	$Ru(acac)_3$	0.97	0.88
RuNI1	Al_2O_3	$Ru(NO)(NO_3)_3$	0.92	0.23
RuC1	Al_2O_3	$RuCl_3$	0.78	0.22
RuC2/C	carbon	$RuCl_3$	2 [a]	0.26
RuNI2/C	carbon	$Ru(NO)(NO_3)_3$	2 [a]	0.55
RuC2/S	SiO_2	$RuCl_3$	2 [a]	0.28
RuNI2/S	SiO_2	$RuNO(NO_3)_3$	2 [a]	0.70

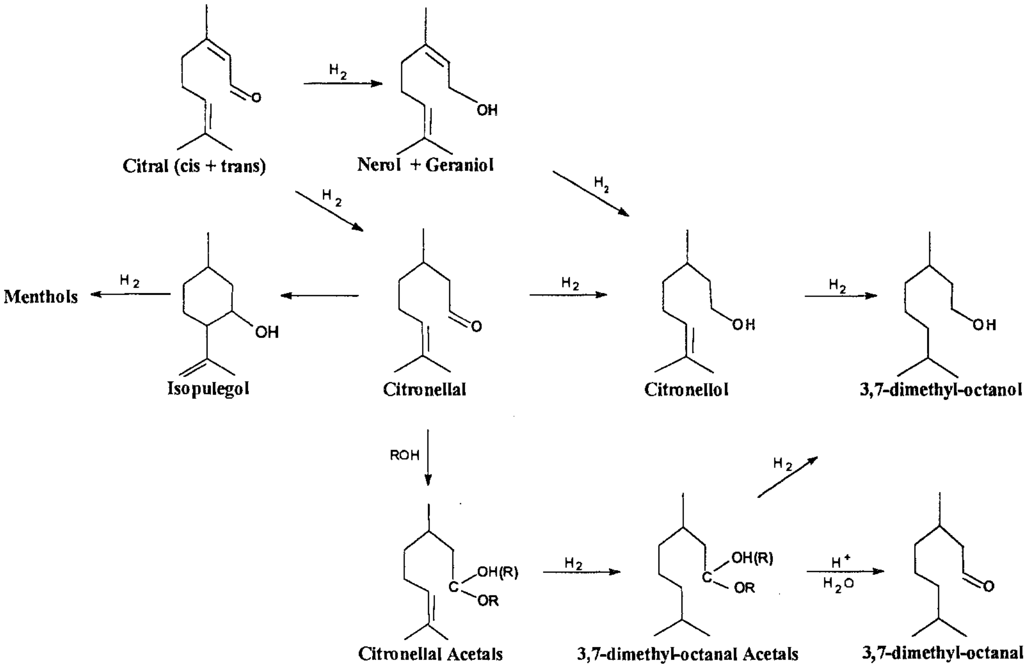
[a] Nominal content.

Catalytic hydrogenations were carried out at atmospheric pressure under H_2 flow in a 100 ml four-necked flask fitted with a reflux condenser, dropping funnel, thermocouple and a stirrer head. Substrates and solvents were commercial analytical grade products and were used without further purification. Before catalytic activity measurements the catalysts were reduced for 2 h at 623 K and then transferred into the reactor. The catalyst was added to 25 ml of solvent and then treated at 343 K for 1 h under H_2 flow. After cooling at reaction temperature, the substrate (0.1 ml) was injected through one arm of the flask. The reaction mixture was stirred at 500 rpm. The progress of the reaction was followed by sampling a sufficient number of microsamples. Chemical analysis was performed with a gas chromatograph equipped with a flame ionization detector. The gas chromatograph column used was a Supelcowax wide-bore capillary column (30 m, 0.53 mm i.d.)

Preliminary runs carried out at different stirring conditions, loading and catalyst grain size have demonstrated the absence of external and internal diffusional limitations.

3. Results and discussion

The reduction of citral in the presence of solvents such as ethanol can lead to a large variety of products obtained by addition of hydrogen, by cyclization and by reaction with the solvent. An overall reaction pathway, showing the main products, is reported in scheme 1.



Scheme 1.

Under our experimental conditions the products of hydrogenation of citral over Ru catalysts were found to be dependent on the support, solvent and precursor used. A previous investigation on the hydrogenation of citral over Ru/C has shown that the metal particle size does not significantly modify the product selectivity [9].

Fig. 1 shows a composition–time plot for the reduction of citral, in ethanol, over sample RuEC1 prepared from Ru(acac)$_3$. In the first step of the reaction the main product was citronellal. Small amounts of unsaturated alcohols (geraniol and nerol) and citronellol were also obtained. No products formed by the hydrogenation of the isolated C=C double bond were detected. At higher reaction time, when almost all citral has disappeared from the reaction vessel, a further hydrogenation is also observed with the formation in two consecutive steps of citronellol and 3,7-dimethyloctanol.

The results obtained on the Ru catalysts prepared by different precursors and on different supports are summarized in table 2, which shows the maximum yield to the reaction products calculated from plots similar to fig. 1. As shown in table 2, sample RuNI1 supported on Al_2O_3 and prepared by using $Ru(NO)(NO_3)_3$ as precursor shows a behaviour similar to that found on catalyst RuEC1.

On sample RuC1 (Ru/Al_2O_3 ex-$RuCl_3$), a different route in the hydrogenation of citral has been found. Fig. 2 shows the composition of the reaction mixture as a function of time. In the first step of the reaction the acetals of citronellal were formed in large amounts reaching yields higher than 60%. No attempt was made to discriminate between mono- and diacetal and, later on, they will be indicated as "acetals". Citronellal was obtained in a very low amount indicating that it is easily transformed to the corresponding acetals.

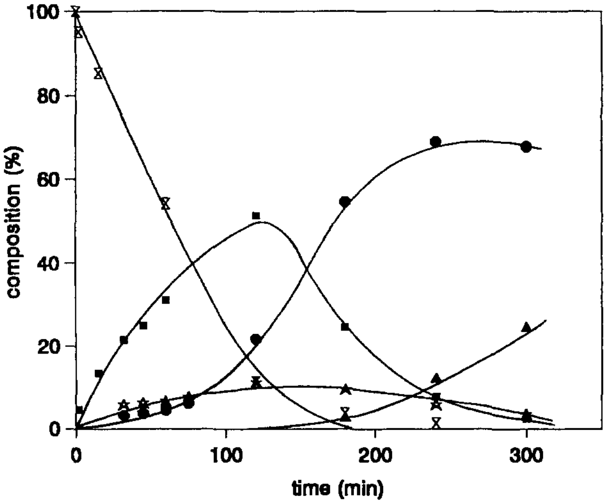


Fig. 1. Hydrogenation of citral over RuEC1 catalyst. $T = 333$ K. (⧗) Citral; (☆) geraniol + nerol; (■) citronellal; (●) citronellol; (▲) 3,7- dimethyloctanol.

Table 2
Hydrogenation of citral in ethanol solution over Ru supported catalysts

Run	Catalyst code	Maximum yield				
		citronellal	unsat. alcohols [a]	acetals	isopulegol	citronellol
1	RuEC1	52	11	<1	<1	70
2	RuNI1	50	10	<1	<1	68
3	RuC1	<3	8	70	<1	5
4	RuC2/C	9	30	16	9	40
5	RuNI2/C	37	25	–	–	67
6	RuC2/S	<3	12	50	<1	15
7	RuNI2/S	58	4	<1	<1	55

[a] Geraniol + nerol.

When citral has almost disappeared, a further addition of hydrogen gives the acetals of 3,7-dimethyloctanal through the hydrogenation of the isolated C=C double bond. It should be noted that on ruthenium catalysts the hydrogenation of the isolated C=C double bond is difficult [6,9]. Formation of 3,7-dimethyloctanal has been reported over other group VIII metal catalysts by using more severe reaction conditions [4].

It is likely that the hydrogenation of the terminal C=C double bond of citronellal does not occur owing to the strong adsorption of the carbonyl group on the active sites of the catalyst which keeps the terminal C=C double bond oriented far away from the catalytic surface. When the carbonyl group is replaced by an acetal group, the adsorption occurs through the isolated C=C double bond, thus favouring the addition of hydrogen on the olefinic bond (scheme 2).

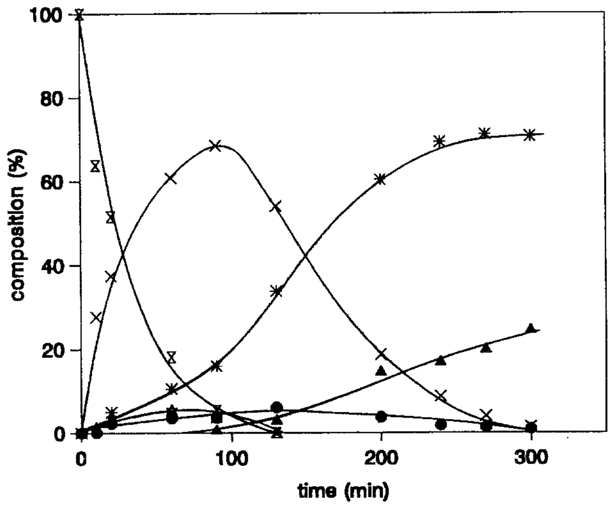
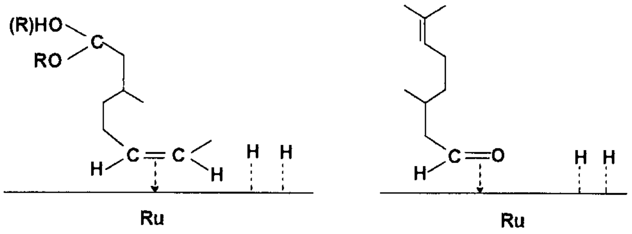


Fig. 2. Hydrogenation of citral over RuC1 catalyst. $T = 333$ K. (⧖) Citral; (☆) geraniol + nerol; (×) citronellal acetals; (∗) 3,7-dimethyloctanal acetals; (●) citronellol; (▲) 3,7-dimethyloctanol.



Scheme 2.

The acetals can be easily and successfully transformed into the corresponding aldehydes by hydrolysis in acidic medium [14]. In our case, if the reaction is stopped when the acetals of 3,7-dimethyloctanal have reached their maximum concentration, the addition of water to the reaction mixture affords the formation of 3,7-dimethyloctanal with a yield of about 60%. At our knowledge, this is the first paper which reports such a high yield of the full saturated aldehyde in the reduction of citral over Ru catalysts under mild conditions. In the presence of hydrogen the acetals of 3,7-dimethyloctanal are transformed to 3,7-dimethyloctanol (fig. 2).

To confirm the mechanism proposed for the hydrogenation of the intermediate citronellal, the reduction of this latter compound has been carried out over samples RuEC1 and RuC1. Over sample RuEC1, citronellol and 3,7-dimethyloctanol were formed by a consecutive pathway. Instead, over sample RuC1, the acetals of 3,7-dimethyloctanal are obtained, while no citronellol and only minor amounts of the full saturated alcohol were found. The concentration of this latter compound increases slowly with reaction time. These results can be explained by considering that on sample RuC1 citronellal reacts immediately with the solvent giving the corresponding acetals and, as the equilibrium is entirely shifted towards the acetals, only hydrogenation of this species can occur.

In order to obtain more information on the influence of the support on the product distribution, catalysts of Ru supported on silica and active carbon were also tested. The results obtained over Ru/SiO_2 catalysts prepared from $RuCl_3$ and $Ru(NO)(NO_3)_3$, samples RuC2/S and RuNI2/S respectively, are summarized in runs 6 and 7 of table 2. The two catalysts show a behaviour similar to that of the corresponding Ru/Al_2O_3 samples. Sample RuC2/S prepared from $RuCl_3$ produces mainly the acetals of citronellal. On sample RuNI2/S instead, citronellal is the main reaction product with citronellol being formed by a further hydrogenation of citronellal. On sample RuC2/C (Ru/C prepared from $RuCl_3$) the addition of hydrogen gives a mixture of unsaturated alcohols, citronellal, acetals of citronellal and isopulegol. Formation of isopulegol has not been detected over Al_2O_3 and SiO_2 supported samples.

To rule out the possibility that the support itself plays a role in the investigated reactions, citral and citronellal were treated with hydrogen in the presence of the pure support under the same reaction conditions used for the Ru catalysts. No formation of acetals or isopulegol was observed confirming that the support does not catalyze these reactions. Hydrogenation products were also absent. Formation of acetals has been already reported to be catalyzed by acids [15]. This has been confirmed by experiments carried out by addition of HCl to the pure support which leads to the formation of the acetals of citronellal. Isopulegol is not formed even in the presence of HCl.

The above reported results indicate that acetals are obtained on the acid sites formed by interaction of the chloride ions (derived from the Ru precursor used) with the surface of the support.

The formation of isopulegol is a more complicated question. It is interesting to note that on sample RuNI2/C (Ru/C prepared from $Ru(NO)(NO_3)_3$) isopulegol is not obtained. It can be therefore concluded that, when the reaction is carried out in ethanol, isopulegol is formed only on sample RuC2/C (see table 2).

In a previous study of Wismeijer et al. [2] on the hydrogenation of citronellal over Ru/SiO_2, carried out by using cyclohexane as solvent, isopulegol has been obtained in large amounts (about 50%) and its formation has been attributed to the presence of partially oxidized $Ru^{(\delta+)}$ sites which are more abundant on catalysts which contain residual chlorine. These results have been confirmed by experiments carried out over our Ru/SiO_2 catalysts using cyclohexane as solvent. Under these conditions, the catalyst RuC2/S (ex-$RuCl_3$) gives a yield of isopulegol of 55%, whereas on catalyst RuNI2/S the maximum yield of isopulegol is only 23% (table 3).

The results reported in table 3 confirm that using cyclohexane, isopulegol is an important product in the hydrogenation of citral and that higher isopulegol yields are obtained on the catalyst prepared from $RuCl_3$.

The explanation of the effect of the solvent on the catalytic hydrogenations has been always a contradicting issue. Even though we realize that further investigations are necessary to elucidate this point, the following explanation can be suggested to interpret the different selectivities observed on the two solvents used. On the catalyst prepared from $RuCl_3$ (RuC2/S) the absence of isopulegol when ethanol is used as solvent, in contrast to the 55% yield when the reaction is carried out in cyclohexane, could be attributed to the fast transformation of citronellal to acetals which prevents the isomerization of the aldehyde. This hypothesis does not, however, explain the results on the sample RuNI2/S which does not form acetals. It can be therefore suggested that the absence of isopulegol, in ethanol, is related to a

Table 3
Hydrogenation of citral in cyclohexane solution over Ru/SiO_2 catalysts

Run	Catalyst code	Maximum yields			
		citronellal	unsat. alcohols [a]	isopulegol	citronellol
9	RuC2/S	5	<1	55	<5
10	RuNI2/S	40	8	23	19

[a] Geraniol + nerol.

strong adsorption of the alcohol on the sites responsible for isopulegol formation ($Ru^{\delta+}$) which blocks the isomerization reaction.

On the basis of this latter hypothesis, the formation of isopulegol on sample RuC2/C even in the presence of ethanol, could be related to the hydrophobic nature of the carbon support which leads to a weaker interaction between the catalyst and the solvent thus decreasing its poisoning effect on the $Ru^{\delta+}$ responsible for the isopulegol formation. It should be, however, noted that on the samples supported on carbon (table 2) larger amounts of unsaturated alcohols are obtained. This can be attributed to the presence of iron impurities (about 1000 ppm in our carbon) which are known to improve the selective hydrogenation of unsaturated aldehydes to unsaturated alcohols. The effect of such impurities on the isopulegol formation has never been reported and therefore further investigations would be necessary to clarify this point.

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