Catalysis Letters 17 (1993) 55–61

Hydrogenation of citral over Ru–Sn/C

S. Galvagno, C. Milone
Dipartimento di Chimica Industriale, Università di Messina, Cas. Post. 29,
I-98166 Sant'Agata di Messina, Italy

A. Donato, G. Neri and R. Pietropaolo
Facoltà di Ingegneria, Università di Reggio Calabria, Via Cuzzocrea 48,
I-89100 Reggio Calabria, Italy

Received 25 September 1992; accepted 27 October 1992

Citral has been hydrogenated over Ru–Sn/C catalysts. The Ru–Sn/C system has been studied as a function of the Ru/Sn ratio. Under the conditions used the carbonyl group and the conjugated double bond are hydrogenated. No products obtained from the hydrogenation of the isolated double bond are formed. Addition of tin on the Ru/C decreases the number of Ru active sites on the surface with a corresponding increase in the specific catalytic activity. A higher selectivity (> 80%) to geraniol + nerol is observed on the samples with the highest Sn/Ru ratio. The higher selectivity and higher specific activity are attributed to an activation of the C=O bond by tin ions.

Keywords: Citral hydrogenation; Ru–Sn; geraniol formation

1. Introduction

The selective hydrogenation of the carbonyl function in compounds which contain ethylenic bonds is an important reaction in the preparation of various fine chemicals. Recently we have studied the hydrogenation of cinnamaldehyde over platinum and ruthenium supported catalysts. It has been observed that selectivity to unsaturated alcohols can be very much improved by varying the metal particle size [1] or adding promoters such as Fe, Sn or Ge [2–5]. On the monometallic Pt and Ru catalysts a preferential formation of cinnamyl alcohol on the larger metal particles has been observed [1,6].

An extension of the work over ruthenium catalysts supported on carbon to the hydrogenation of citral (3,7-dimethyl-2,6-octadienal) has shown that, in contrast to what has been observed on cinnamaldehyde, the selectivity to unsaturated alcohols remains constant (about 35%) regardless of the Ru particle size [7]. It has been suggested that the higher selectivity to cinnamyl alcohol on the larger particles should be interpreted in terms of a steric effect of the aromatic ring which facilitate the adsorption of cinnamaldehyde through the C=O group. Such a steric effect does not exist in the hydrogenation of citral where the aromatic ring is absent.

In this paper we report a study on the effect of addition of tin to Ru/C in order to verify the possibility of improving the selectivity to unsaturated alcohols by addition of promoters also in the case where a steric effect does not play a major role.

Hydrogenation of citral has been reported to mainly produce citronellal and citronellol [8–10]. The selective formation of unsaturated alcohols has been recently reported over rhodium catalysts promoted with tin [11].

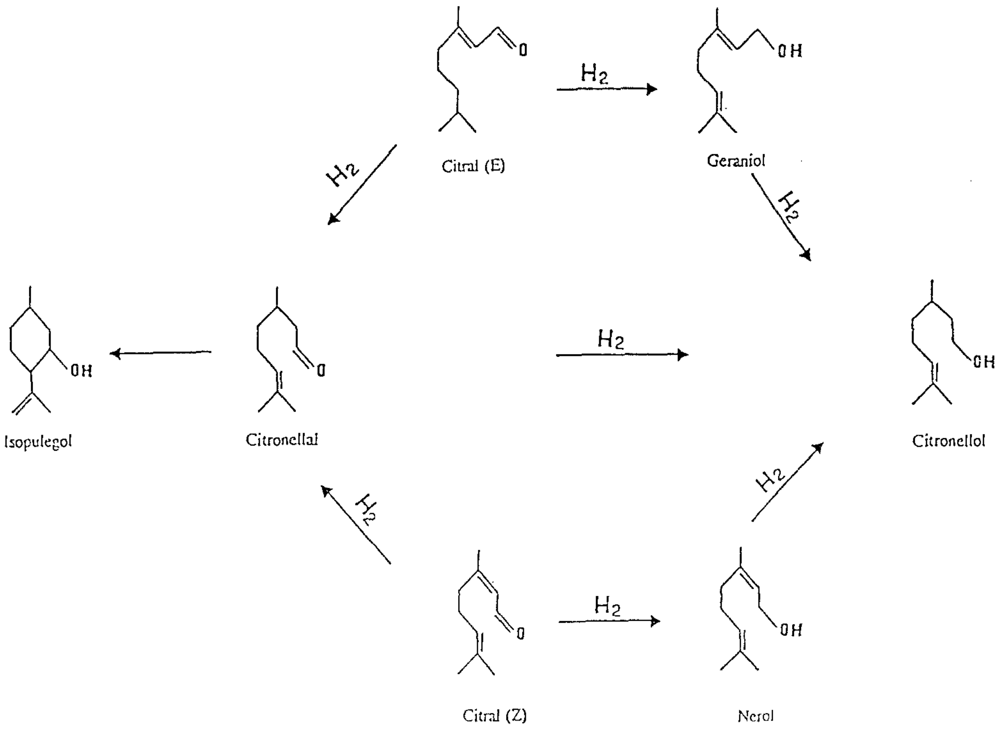
2. Experimental

Catalyst samples were prepared by incipient wetness impregnation of activated carbon (Chemviron SC XII 80–100 mesh, surface area 900–1100 m^2/g) with aqueous solutions of $RuCl_3$ and $SnCl_2$. In all catalysts the amount of Ru was kept constant at 2 wt%, whereas the Sn content was varied between 0 and 2.0 wt%. After impregnation, the catalysts were dried at 393 K and then reduced at 573 K for 1 h under flowing H_2. Catalyst samples were characterized by CO chemisorption and HREM (high resolution electron microscopy). Chemisorption of CO was measured in a conventional pulse system operating at room temperature. The Sn/C sample did not chemisorb CO. Electron microscopy studies were performed on a Jeol 2000 FX instrument operating at 200 kV and on a Jeol 4000 EX microscope operating at 400 kV. Table 1 shows the main characteristics of the Ru–Sn/C catalysts. Details of the characterization

Table 1
Characterization and catalytic activity towards citral hydrogenation of Ru–Sn/C

Catalyst code	Sn [a] (wt%)	Ru/(Ru+Sn) [b] (%)	CO/Ru	d [c] (nm)	$V_i \times 10^5$ [d]
Ru 100/C	–	100	0.261	5.9	7.34
Ru 95/C	0.12	95	0.115	3.5	5.42
Ru 80/C	0.58	80	0.096	3.4	4.84
Ru 70/C	1.01	70	0.003	[f]	0.67
Ru 60/C	1.56	60	[e]	[f]	0.16

[a] Ru = 2 wt%.
[b] Atomic ratios.
[c] by TEM.
[d] Moles g_{Ru}^{-1} s^{-1}.
[e] Not detectable.
[f] Not evaluated.



Scheme 1.

results are reported elsewhere [12,13]. The hydrogenation of citral (Fluka, purity > 97%, 35/65 mixture of the form Z and E) was 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. The catalyst was added to the required amount of solvent (25 ml of 95% ethanol) then treated at 343 K for 1 h under H_2 flow. After cooling at reaction temperature (333 K), citral (0.5 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 (HP 5890) 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.).

3. Results and discussion

Under the experimental conditions used hydrogenation of citral over Ru–Sn/C catalysts occurs through a reaction pathway which is summarized in scheme 1. Geraniol (trans-3,7-dimethyl-2,6-octadien-1-ol), and nerol (cis-3,7-dimethyl-2,6-octadien-1-ol), are formed by hydrogenation of the C=O group of

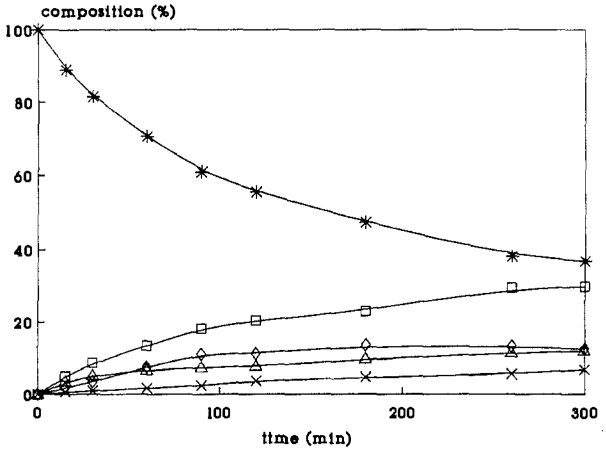


Fig. 1. Hydrogenation of citral over Ru 95/C catalyst. $T = 333$ K. (∗) Citral; (□) geraniol+nerol; (△) citronellal; (◇) isopulegol; (×) citronellol.

citral (E) and (Z), respectively. Citronellal (3,7-dimethyl-6-octenal) is obtained by hydrogenation of the conjugated C=C double bond whereas citronellol (3,7-dimethyl-6-octen-1-ol) can be formed by hydrogenation of citronellal and/or by reduction of geraniol and nerol. Isopulegol (2-isopropyl-5-methyl-cyclohexanol) is a cyclization product of citronellal. The diethylacetal of citronellal is also formed through the reaction with the solvent used. The diethylacetal was at equilibrium with citronellal, therefore in order to simplify the data they are reported together. Preliminary runs carried out with different catalyst loadings, stirring conditions and catalyst grain size showed the absence of diffusional limitations. Samples of Sn/C were found inactive for the hydrogenation of citral. The time course of the hydrogenation of citral was qualitatively similar on all catalysts investigated even though the products distribution and the catalytic activity was strongly influenced by the catalyst composition. Fig. 1 shows typical results obtained on a Ru–Sn/C catalyst. Results obtained on monometallic Ru/C samples have been previously reported [7].

Catalytic activity was found to decrease with time. The initial rates of reaction were therefore used to compare the different catalysts.

The influence of the presence of tin on the chemisorption properties and on the catalytic activity is reported in table 1. Addition of tin decreases the C=O uptakes and the catalytic activity. The rate of citral hydrogenation becomes negligible at Sn/Ru ratios higher than 2/3. Fig. 2 shows the initial turnover rates, N_i (expressed per atom of Ru on the surface). The values of N_i have been calculated from the results of CO chemisorption (table 1) assuming a stoichiometry CO/Ru = 1. Increasing the Sn/Ru ratio the turnover rate increases especially on the catalysts with the highest Sn content. The value of N_i on the sample Ru 60/C could not be evaluated since the amount of CO chemisorbed was below the detection limits of our equipment.

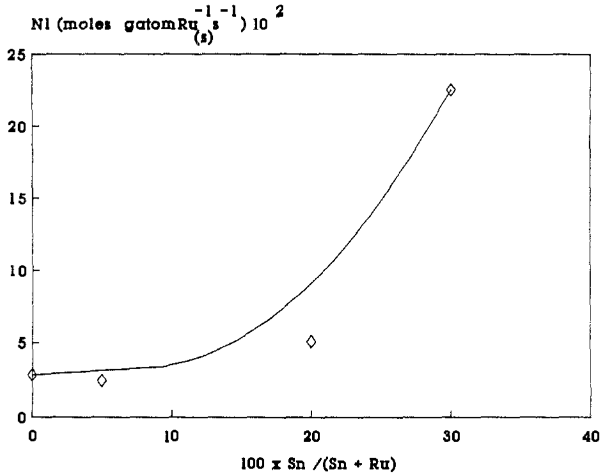


Fig. 2. Initial rate of reaction per Ru surface atom (N_i), as a function of *n* content.

Fig. 3 shows the effect of tin on the reaction selectivity. Isopulegol is obtained by cyclization of citronellal and does not involve H_2 consumption, therefore these two products are reported together. Selectivity values shown in fig. 3 have been measured at a conversion level of 30%. Since higher conversion has not been reached on the less active catalysts, this value was chosen to compare all samples under the same conditions. It should, however, be noted that within the range of conversion measured (20–80%), selectivities were found to be scarcely influenced by the conversion levels. This indicates that consecutive reactions leading to citronellol (scheme 1) become important only when almost all citral has disappeared from the reaction vessel.

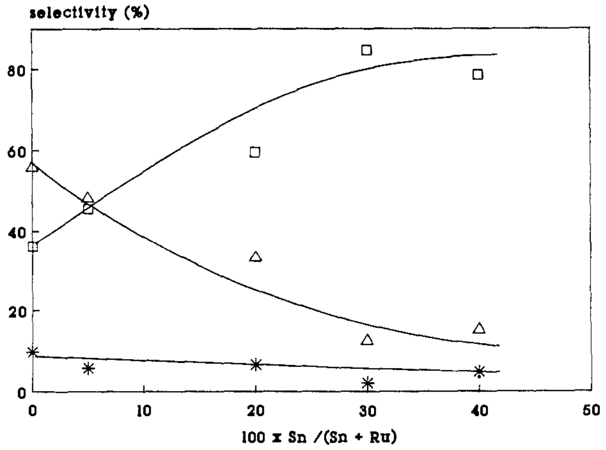


Fig. 3. Hydrogenation of citral. Influence of the Sn/Ru ratio on the products selectivity. (□) Geraniol + nerol; (△) citronellal + isopulegol; (∗) citronellol.

Addition of Sn to Ru/C increases (fig. 3) the selectivity to the di-unsaturated alcohols (geraniol + nerol) from a value of about 35 up to 80% with a corresponding decrease in the selectivity to products obtained by hydrogenation of the conjugated C=C double bond (citronellal and isopulegol). A small decrease of the selectivity to citronellol with addition of Sn was also observed. It is interesting to note that products formed by hydrogenation of the isolated C=C double bond were never detected, in agreement with previous results over ruthenium [7], rhenium [14], rhodium and platinum promoted catalysts [11,15].

In a previous study on the hydrogenation of cinnamaldehyde over the same Ru–Sn/C catalysts a similar effect of addition of tin on the overall rate of hydrogenation has been observed; namely the rate, per gram of total ruthenium on the catalyst, was found to decrease on addition of tin, whereas the specific activity (per atom of Ru on the surface) increased. Also the selectivity to cinnamyl alcohol showed a dependence on the Sn/Ru ratio similar to that observed in fig. 3, with the highest selectivity observed on the samples with the highest Sn content.

It is interesting to note that a detailed characterization of the Ru–Sn/C catalysts, used in this work, carried out by HREM (high resolution electron microscopy) has shown [13] that at low Sn/Ru ratios (table 1), addition of tin to Ru/C decreases the average metal particle size from about 60 Å on the monometallic Ru 100/C sample up to 35 Å on the Ru 80/C (20 at% Sn) sample, whereas at higher Sn/Ru ratios in addition to small particles, a massive agglomeration is observed. These agglomerates are composed by many small crystallites clustered together to form larger aggregates distributed randomly on the carbon surface. For these catalysts (Ru 70/C and Ru 60/C) it was not possible to derive a reliable particle size distribution. The presence of a very small amount of RuSn alloy was also found in the sample with the highest tin loading. No evidence for reduction of tin to metallic form was observed. Details of the HREM characterization of the Ru–Sn/C catalysts are reported elsewhere [13].

It is well known that a change in the particle size can drastically modify the catalytic behaviour of a metal catalyst. However, in our reaction, this parameter does not play an important role. An investigation on the effect of Ru particle size on citral hydrogenation has shown that the specific catalytic activity as well as the products distribution are not influenced by a change of Ru particle size between 30 and 170 Å [7].

In the hydrogenation of cinnamaldehyde, a higher selectivity to cinnamyl alcohol has been instead observed on the larger Ru particles. This has been attributed to a steric effect of the aromatic ring which facilitates the adsorption of cinnamaldehyde through the C=O group on the larger metal particles [6,7]. In the hydrogenation of citral, where the aromatic ring is absent, such a steric effect does not occur. Variations observed in the reaction selectivity are therefore to be related to the presence of tin which increases the relative rate of hydrogenation of the C=O group with respect to the conjugated C=C double bond.

Under the conditions used for the preparation of the catalysts it is likely, in agreement with the HREM results [13], that tin is not reduced to the zero valent state. The hypothesis that tin ions are responsible for the enhancement of the reactivity of the C=O group was confirmed by experiments carried out on a Ru/C catalyst adding $SnCl_2$ directly into the reaction mixture.

In agreement with previous results obtained over the same Ru–Sn/C in the hydrogenation of cinnamaldehyde [4], hydrocinnamaldehyde [12] and β-methylstyrene [12] and on the basis of the characterization results [13] it can therefore be suggested that the presence of tin has two effects. One effect is to poison the Ru surface sites causing a decrease of the overall rate of reaction. The other effect is to activate the C=O group facilitating the hydrogen transfer from adjacent Ru sites. The activating effect can be ascribed to the presence of Sn ions which polarize the carbonyl group.

Acknowledgement

This work has been carried out with the financial support of CNR (Progetto Finalizzato Chimica Fine e Secondaria II).

References

[1] S. Galvagno, G. Capannelli, G. Neri, A. Donato and R. Pietropaolo, J. Mol. Catal. 64 (1991) 237.
[2] Z. Poltarzewski, S. Galvagno, R. Pietropaolo and P. Staiti, J. Catal. 102 (1986) 190.
[3] S. Galvagno, Z. Poltarzewski, A. Donato, G. Neri and R. Pietropaolo, J. Chem. Soc. Chem. Commun. (1986) 1729.
[4] S. Galvagno, A. Donato, G. Neri and R. Pietropaolo, J. Mol. Catal., in press.
[5] S. Galvagno, A. Donato, G. Neri, R. Pietropaolo and D. Pietropaolo, J. Mol. Catal. 49 (1989) 223.
[6] D. Richard, P. Fouilloux and P. Gallezot, in: *Proc. 9th Int. Cong. Catalysis*, Calgary 1988, eds. M.J. Phillips and M. Ternan (Chem. Institute of Canada, Ottawa, 1988) p. 1074.
[7] S. Galvagno, C. Milone, A. Donato, G. Neri and R. Pietropaolo, J. Mol. Catal., submitted.
[8] J. Court, F. Janati-Idrissi, S. Vidal and P. Wierzchowski, J. Chim. Phys. 87 (1990) 379.
[9] A.M. Pak, S.R. Konuspaev, D.V. Sokol'skii and L.D. Rozmanova, React. Kinet. Catal. Lett. 18 (1981) 311.
[10] D.V. Sokol'skii, A.M. Pak, M.A. Ginzburg and V.A. Zavorin, Kinet. Catal. 20 (1979) 645.
[11] B. Didillon, A. El Mansour, J.P. Candy, J.P. Bournoville and J.M. Basset, in: *Heterogeneous Catalysis and Fine Chemicals* II, eds. M. Guisnet, J. Barrault, C. Bouchoule, D. Duprez, G. Pérot, R. Maurel and C. Montassier (Elsevier, Amsterdam, 1991) p. 137.
[12] S. Galvagno, A. Donato, G. Neri and R. Pietropaolo, Catal. Lett. 8 (1991) 9.
[13] G. Neri, R. Pietropaolo, S. Galvagno and J. Schwank, J. Catal., submitted.
[14] W.E. Poscoe and J.F. Stenberg, in: *Catalysis in Organic Syntheses*, ed. W.H. Jones (Academic Press, New York, 1980) p. 1.
[15] R. Adams, B.S. Garvey, J. Am. Chem. Soc. 48 (1926) 477.