Influence of metal particle size in the hydrogenation of citral over Ru/C

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Selective hydrogenation of citral has been studied under mild conditions over Ru catalysts supported on activated carbon. Geraniol, nerol, citronellal and isopulegol were the main reaction products. Isopulegol is obtained by isomerization of citronellal. Small amounts of citronellol are formed through the hydrogenation of citronellal. The specific catalytic activity per Ru surface atom as well as the products distribution remains constant with changing metal particle size. A comparison with results obtained on the hydrogenation of cinnamaldehyde on the same Ru/C catalysts is reported.

Keywords: Citral hydrogenation; ruthenium; particle size effect

1. Introduction

Hydrogenation of α, β-unsaturated aldehydes to saturated aldehydes is readily achieved over most platinum metal catalysts under mild conditions. The selective synthesis of unsaturated alcohols is, however, much more difficult to achieve and several attempts have been made to develop a suitable catalytic system [1–11].

Many factors have been reported to influence the selectivity of the reaction, among them the nature and particle size of the metal catalyst [1–3], the presence of promoters [4–8], the catalyst support [9–11].

Most of the work on the selective hydrogenation of unsaturated aldehydes has been carried out on cinnamaldehyde and crotonaldehyde and few other studies are available on aliphatic aldehydes which can be of potential industrial interest. Within the family of α, β-unsaturated aldehydes, hydrogenation of citral is important for its interest in the perfumery industry. Citral is also interesting from a scientific point of view, since it offers the possibility of hydrogenation of three different double bonds: an aldehyde group, a conjugated C=C double bond and an isolated C=C double bond.

Hydrogenation of citral has been reported to mainly produce citronellal and citronellol [12–14], which are formed by the hydrogenation of the conjugated double bond and the carbonyl group. The selective hydrogenation of the C=O group with formation of the di-unsaturated alcohol has been recently reported over rhodium modified with tin [15].

In this paper we report a study carried out over a series of Ru/C catalysts with the aim of studying the reaction pathway of citral hydrogenation and to verify the influence of Ru particle size on the products distribution.

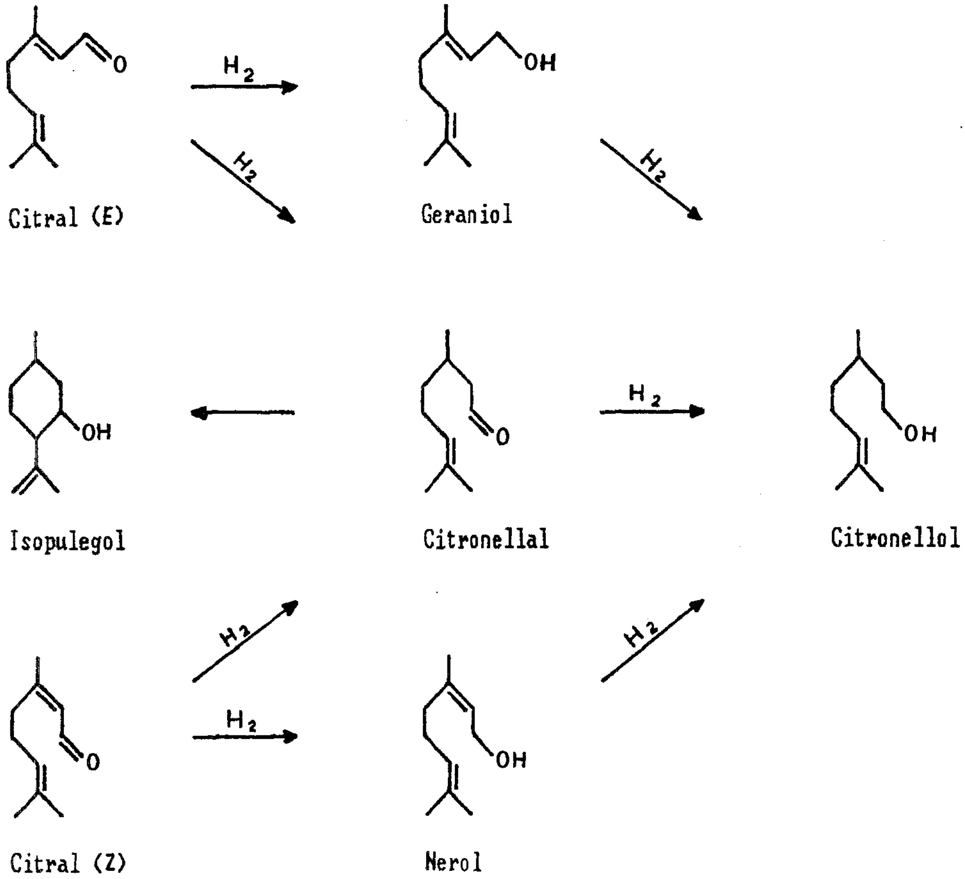
2. Experimental

Ru/C samples were prepared by impregnation of activated carbon (Chemviron SC XII 80–100 mesh, surface area 900–1100 m^2/g) with aqueous solutions of $RuCl_3$. The amount of solution used was slightly higher than the pore volume. After impregnation, the catalysts were dried at 393 K and then reduced at 573 K for 1 h. Catalyst samples were characterized by CO and O_2 chemisorption and by TEM. Details on the characterization results are reported elsewhere [2]. Citral used (Fluka, purity >97%) was a mixture 35/65 of the forms Z and E. The reduction of citral 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

The reaction of citral (3,7-dimethyl-2,6-octadienal) with hydrogen can give a large variety of products which are formed by addition of H_2 to the isolated and conjugated C=C double bonds and to the C=O group. Moreover, cyclization products can be also obtained. Under the experimental conditions used and up to a citral conversion of about 90% the main reaction products on our Ru/C catalysts are: geraniol (trans-3,7-dimethyl-2,6-octadien-1-ol), nerol (cis-3,7-dimethyl-2,6-octadien-1-ol), citronellal (3,7-dimethyl-6-octenal), citronellol (3,7-dimethyl-6-octen-1-ol), and isopulegol (2-isopropyl-5-methyl-cyclohexanol). As shown in scheme 1, geraniol and nerol are formed by hydrogenation of the C=O group of citral (E) and (Z), respectively. Citronellal is formed by hydrogenation of the conjugated C=C double bond whereas citronellol can be obtained by hydrogenation of citronellal and/or by reduction of the unsaturated alcohols (geraniol and nerol). Isopulegol is a product of isomerization of citronellal. The diethylacetal of citronellal is also formed through the reaction with the solvent used. In order to simplify the data the diethylacetal and citronellal are reported together. Fig. 1 shows a typical time course of the hydrogenation of citral over Ru/C which has been recorded up to a citral conversion of about 90%.

It is interesting to note that under the conditions used the isolated C=C bond is not reduced. The higher reactivity of the α, β-unsaturation with respect to the isolated unsaturation has been previously reported over rhenium [16] and over rhodium and platinum promoted catalysts [15,17]. A higher reactivity of the C=O group has been also found in the hydrogenation of citronellal on Ru supported catalysts [18].



Scheme 1.

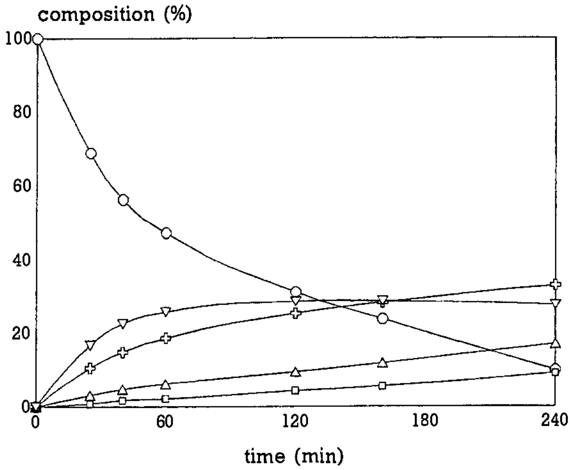


Fig. 1. Hydrogenation of citral over 2% Ru/C catalyst. $T = 333$ K; (○) citral; (✚) geraniol + nerol; (▽) citronellal; (□) isopulegol; (△) citronellol

Formation of isopulegol has been reported in the hydrogenation of citronellal over Ru/TiO_2 and Ru/SiO_2 and attributed to the presence of chlorine, which in turn is responsible for the presence of incompletely reduced Ru [18].

Experiments carried out with different amounts of catalysts (0.1–0.5 g of 2% Ru/C) showed a linear increase of the rate of reaction with the amount of catalysts used. These results, together with runs carried out under different stirring conditions (200–800 rpm) and catalyst grain size (90–150 μm), indicate that the reaction is performed in the absence of diffusional limitations.

Fig. 2 shows typical results of the change in the selectivities towards the main

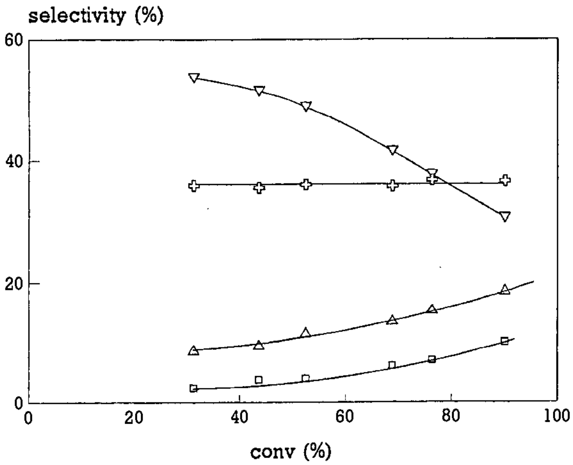


Fig. 2. Influence of citral conversion on the products selectivity. Catalyst 2% Ru/C; (✚) geraniol + nerol; (□) isopulegol; (▽) citronellal; (△) citronellol.

reaction products as a function of the level of citral conversion. It can be noted that the selectivity to α, β-unsaturated alcohols (geraniol + nerol) is nearly constant in all ranges of conversion investigated. The increase observed in the selectivity to citronellol and isopulegol is accompanied by a decrease in the selectivity to citronellal. Hydrogenation of geraniol and nerol has been observed only after citral has almost disappeared from the reaction vessel. This indicates that hydrogenation of the C=C double bond of the unsaturated alcohols is inhibited by the strong adsorption on the catalyst surface of the molecules containing a carbonyl group. The strong adsorption of the carbonyl group can also well explain the inactivity of the isolated C=C double bond.

The effect of Ru particle size on the rate of reaction and on the product distribution has been investigated on a series of Ru/C samples with different (0.5–10 wt%) metal loading.

Table 1 reports the average metal particle size of the catalysts used determined by O_2 and CO chemisorption and by TEM. Details on the physico-chemical characteristics of the catalysts are reported elsewhere [2].

Catalytic activity was found to decrease with time. The initial rates of reaction were therefore used to compare the different catalysts. Fig. 3 shows the initial rate of reaction as a function of ruthenium surface area (expressed as m^2 of Ru on the surface/gram of Ru). A linear relationship between catalytic activity and metal surface area was observed over the entire range of Ru dispersion studied. The specific rate of hydrogenation (expressed per atom of ruthenium on the surface) is therefore constant, independent of ruthenium particle size. Also the product distribution was found to be scarcely influenced by the Ru particle size. Fig. 4 shows that selectivity to geraniol + nerol is about 36% on all catalysts investigated regardless of metal particle size.

It is interesting to note that in a previous investigation on the hydrogenation of cinnamaldehyde on the same Ru/C samples [2], the specific catalytic activity was found independent of the Ru particle size as observed in the present paper. Selectivity to unsaturated alcohol (cinnamyl alcohol) was instead found to increase significantly with metal particle size. It was suggested that on the smaller Ru particles, chemisorption of the unsaturated aldehyde through the C=C double bond is favor-

Table 1
Average metal particle size (d) of Ru/C samples (from ref. [2])

Ru (wt%)	Average particle size (nm)		
	$d(O_2)$	d(CO)	d(TEM)
0.5	3.7	4.0	<3
1	3.6	3.0	6.0
2	6.4	5.2	7.4
5	9.6	7.1	10.6
10	10.3	10.4	16.8

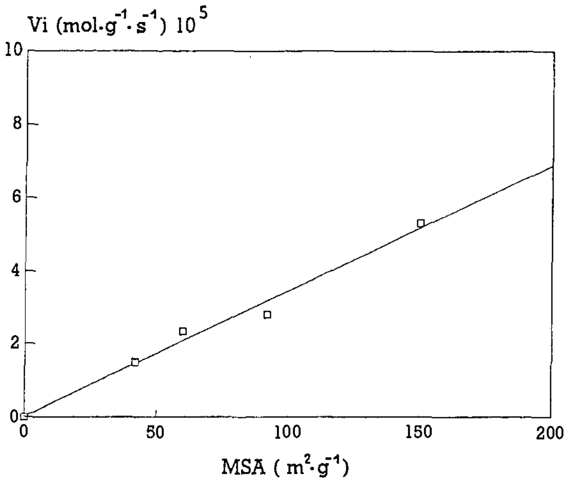


Fig. 3. Influence of Ru surface area (MSA) on the initial rate of reaction.

ite whereas on the larger metal particles the aromatic ring of cinnamaldehyde which is not bonded to the surface lies to a distance exceeding 0.3 nm [19]. Under these conditions the cinnamaldehyde is tilted and the C=O extremity will be closer to the surface facilitating on these larger particles the hydrogenation of the C=O bond.

This hypothesis is confirmed by the results reported in this paper. In fact, in the case of citral, where no aromatic ring is present, the steric effect cannot play an important role and therefore no difference in the product distribution is observed with a change of the metal particle size.

It can be therefore concluded that the hydrogenation of an unsaturated aldehyde has to be regarded as a "structure insensitive" reaction. However, the pres-

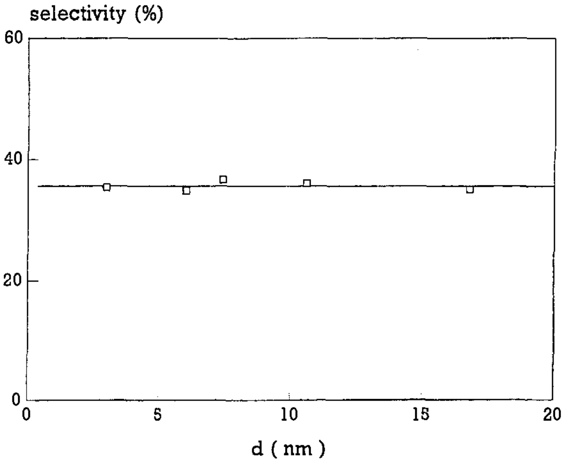


Fig. 4. Influence of Ru particle size (d) on the selectivity to geraniol + nerol.

ence of steric constraints can modify significantly the product distribution. The importance of steric contraints in the selective hydrogenation of unsaturated aldehydes has been also demonstrated by Blackmond et al. [11] in the hydrogenation of cinnamaldehyde and 3-methylcrotonaldehyde over Ru, Pt and Rh supported on zeolites.

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