

Citral hydrogenation on supported platinum catalysts

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Abstract

Supported platinum systems have been used as catalysts for selective hydrogenation of citral to the unsaturated alcohol. The C=O bond is hydrogenated rather than the thermodynamically favorable C=C bond on supported platinum systems. This is due to the influence of the SMSI (strong metal–support interaction) state in these supported platinum catalysts. In all the supported catalyst systems the formation of geraniol (E isomer) has been observed as the sole product of the hydrogenation of citral. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Hydrogenation; Citral; Metal–support interaction; Platinum; Geraniol

1. Introduction

Supported metals have been used extensively in heterogeneous catalysis. The selective hydrogenation of unsaturated aldehydes is one of the most important reactions in the industry. The selective hydrogenation of α,β -unsaturated aldehydes has been the subject of numerous investigations [1–5]. The development and characterization of catalysts for the selective hydrogenation of α,β -unsaturated aldehydes has been reviewed by Gallezot et al. [6]. Promoted and unpromoted metals [7–13], metal oxides [14,15], carbon based support [16] and microporous support [5] have been used as catalysts. Within the class of aliphatic unsaturated aldehydes, hydrogenation of citral, apart from cinnamaldehyde and crotonaldehyde, is important for its utility in the perfume industry.

Citral (3,7-dimethyl-2,6-octadienal) has three sites of hydrogenation; the conjugate double bond, the carbonyl group and the isolated double bond. The hydrogenation of the conjugate double bond gives 3,7-dimethyl-6-octenal (citronellal) and the hydrogenation of the carbonyl group produces two isomers (*cis* and *trans*) of unsaturated alcohols, 3,7-dimethyl-6-octen-1-ol, (nerol and geraniol, respectively) [10]. Citronellal on further hydrogenation gives 3,7-dimethyl-6-octen-1-ol (citronellol) and the completely hydrogenated product formed is 3,7-dimethyl octan-1-ol. In the present investigation, hydrogenation of citral has been carried out over supported platinum catalysts in the liquid phase at 318 K.

There are very few reports, to the best of our knowledge, on the hydrogenation of citral on supported platinum systems [17]. This led to the current investigation of selective hydrogenation of citral on supported platinum catalysts. The behavior of the supported platinum catalysts has been investigated in the hydrogenation of citral in terms of its conversion and selectivity of the products of the reaction.

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2. Experimental

2.1. Chemicals

Citral (E-Merck, 99%) and ethanol (Fluka, 95%) were used without further purification. The citral used for the experiment was a mixture of both E and Z forms (1:1). The catalysts were prepared using titania, ceria and mixed oxide supports. Commercial titania (Baker, UK, $50 \text{ m}^2 \text{ g}^{-1}$) and ceria (CDH, India, $35 \text{ m}^2 \text{ g}^{-1}$) were used as the supports. Apart from these, the mixed oxide (titania–alumina prepared from the co-hydrolysis of titanium isopropoxide (E-Merck, 99%) and aluminum isopropoxide (Fluka, 99%) dissolved in isopropanol) and titania gel (prepared by the hydrolysis of titanium tetrachloride (Aldrich, 99%)) were also used as supports. The platinum source used was hydrochloroplatinic acid (HPL, India).

2.2. Catalyst preparation and characterization

The samples were prepared by the wet impregnation method and characterized by various techniques like XPS, STPR, XRD and hydrogen chemisorption measurements. The detailed procedure for preparation and characterization have been reported elsewhere [18–20]. The mixed oxide support was estimated gravimetrically by the oxine method after extracting the support from the catalyst [21]. The percentage of titania and alumina were found to be 22 and 78%, respectively. The platinum loading was estimated gravimetrically to be 5%. The titania (commercial and gel), the mixed oxide (titania–alumina) and ceria (commercial) supported platinum catalysts were prepared and reduced at 573 (low temperature of reduction, LTR) and 773 K (high temperature of reduction, HTR) prior to the commencement of the reaction. The catalysts have been designated as $\text{TiO}_2(\text{C})$ and $\text{TiO}_2(\text{G})$, for commercial and gel, respectively, T–A, for the mixed oxide and CeO_2 , for ceria.

2.3. Activity test

The liquid phase hydrogenation reaction was carried out in a 100 ml static reactor consisting of a three-necked flask fitted with a reflux condenser, septum and a thermometer. Preliminary experiments carried out with different amounts of catalyst and stir-

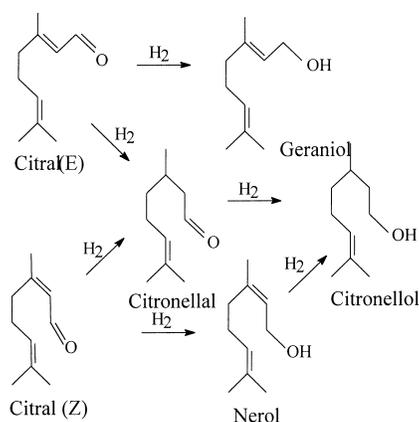
ring rate showed the absence of diffusional limitations. The freshly reduced catalysts (0.5 g) were dispersed in 15 ml of solvent (95% ethanol). The catalysts were then treated at 323 K for 1 h under hydrogen flow. After cooling the contents at the reaction temperature of 318 K, citral (1 ml) was injected through the septum fitted in one arm of the flask. The temperature of the reaction was maintained constant at 318 K using an autotransformer. Reaction samples were withdrawn at time intervals of 60 min through the septum fitted to the reactor for further analysis. The reaction was monitored as a function of time for 5 h.

The products were analyzed by gas chromatography (NUCON GL 5700) equipped with a carbowax column.

3. Results and discussion

The scheme of citral hydrogenation has been provided in Scheme 1 [11]. As can be seen from the scheme, the major products of the hydrogenation of citral are citronellal and the unsaturated alcohols (geraniol and nerol). The results of the hydrogenation on various supported platinum catalysts are shown in Table 1.

From the table it can be observed that, in all cases in the present investigation, the reaction produces only the unsaturated alcohol, geraniol, in 100% selectivity in both LTR and HTR catalysts. In the case of the mixed oxide supported catalysts, trace amounts of citronellal were also detected. However, it is



Scheme 1. Schematic representation of citral hydrogenation.

Table 1
Percentage conversions of hydrogenation of citral (in mol%)^a

Time (min)	5% Pt/TiO ₂ (C)		5% Pt/TiO ₂ (G)		5% Pt/T-A(22-78)		5% Pt/CeO ₂	
	573 K	773 K	573 K	773 K	573 K	773 K	573 K	773 K
30	–	11	–	–	17	5	2	–
60	–	13	–	5	27	4	7	1
90	–	14	–	7	–	–	–	2
120	–	16	2	18	25	23	7	6
180	–	16	3	22	26	–	5	12
210	–	17	7	27	25	28	–	–
240	12	17	10	30	26	30	7	25
300	13	17	8	29	29	27	20	22

^a The selectivity is 100% towards geraniol in all the cases.

interesting to observe geraniol (E isomer) as the sole product in the case of all the catalysts after reduction. On supported ruthenium catalysts on the other hand, both geraniol (E isomer) and nerol (Z isomer) have been observed as products as reported by Galvagno et al. [22]. Court et al. [10] have observed that the nickel–cobalt bimetallic catalyst selectively produces citronellol. A similar result was also obtained for rhodium–tin bimetallic catalysts by Didillon et al. [23]. As shown in Table 1, it can be seen that the maximum conversion of 29% was obtained for the titania gel and mixed oxide supported catalyst. The selectivity to geraniol was found to remain constant on all samples after a certain interval of time.

The plots of percentage conversion against time are given in Figs. 1 and 2, respectively. The percentage conversion increased with increase in reduction temperature on all samples. The increase in conversion with an increase in temperature of reduction can be attributed to the presence of the reduced support on the surface of the metal particles after HTR (SMSI state). The formation of geraniol in 100% selectivity probably indicates the possible role of metal–support interaction as the cause for the formation of the unsaturated alcohol. Encapsulation of the metal crystallites by the reduced support species enhances the catalytic activity for hydrogenation of the carbonyl group as has also been observed earlier by Malathi et al. [19] and Coq et al. [14]. The study on strong metal–support interaction (SMSI) has been reported elsewhere on these catalysts [19].

The hydrogen uptake measured at room temperature after reduction of the sample in hydrogen flow at 573 and 773 K on 5% Pt/TiO₂(G) was determined to be

4.4 and 0.0 $\mu\text{mol g}^{-1}$, respectively [18]. The gel sample thus exhibits SMSI behavior and the increase in conversion of the unsaturated alcohol after HTR may probably be attributed to the role of SMSI. The mixed oxide support showed only moderate SMSI behavior. The hydrogen uptake on this catalyst measured at room temperature after reduction of the sample in hydrogen flow at 573 and 773 K was determined to be 5.3 and 3.9 $\mu\text{mol g}^{-1}$, respectively [18]. Thus, in the mixed oxide support the metal particles are not reduced completely after HTR and hence the conversion of citral to geraniol does not differ significantly after HTR. The

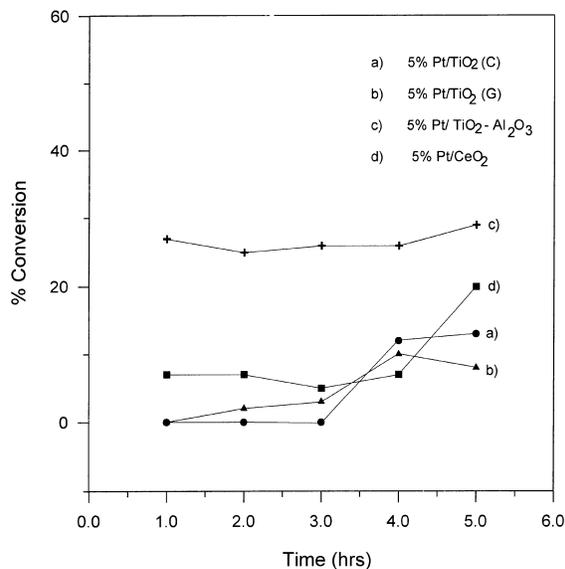


Fig. 1. Percentage conversion against time for platinum supported catalysts reduced at LTR for citral hydrogenation.

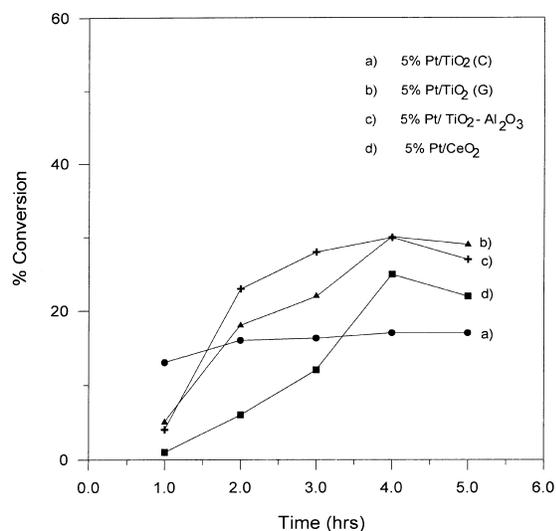


Fig. 2. Percentage conversion against time for platinum supported catalysts reduced at HTR for citral hydrogenation.

hydrogen uptake of platinum supported on ceria catalyst exhibits a similar trend as that of the mixed oxide support and the trends in the conversion are hence similar to the mixed oxide support [20]. The activity of 5% Pt/TiO₂(C) was found to be lower compared to the gel sample probably because of its lower surface area. Court et al. [10] in their work on liquid phase hydrogenation of citral using ruthenium–tin/carbon have indicated the formation of geraniol and nerol in small amounts along with the saturated aldehyde, citronellal, as the major product. The formation of geraniol in both the cases (LTR and HTR) for all the catalysts can be attributed to the homogeneous distribution and decreased dispersion of the metal on the support, thereby decreasing the effective number of the exposed surface metal atoms. The decrease in the number of active sites for the hydrogenation of the olefinic double bond enhances the selective hydrogenation of the carbonyl group thereby forming the unsaturated alcohol.

The results obtained from the hydrogenation of α,β -unsaturated aldehydes have been discussed in terms of (1) electronic or ligand effect of the support or doped metal and (2) formation of catalytic sites which are able to coordinate oxygen atom in the carbonyl group and activate it. The electronic ligand effect produced by basic supports such as magnesia supported Sn–Pt bimetallic catalysts was invoked by

Recchia et al. [17] to explain the enhanced selectivity to unsaturated alcohols. Englisch et al. [24] have invoked the ‘decoration model’ to explain the results obtained from the hydrogenation of crotonaldehyde over Pt/TiO₂ catalysts. The presence of coordinatively unsaturated Ti cations was found to enhance the selectivity to C=O bond hydrogenation.

In the present study, the selective hydrogenation of the C=O bond compared to the C=C bond can thus be attributed to the presence of the reduced support species on the surface of the metal particles (‘decoration model’). The formation of these new catalytic sites due to migration of the support to the surface enhances the specific activity for hydrogenation of the C=O group preferentially to C=C group. Further evidence is provided by the conversion being maximum for titania gel and mixed oxide sample which indicate a strong interaction between the metal and the reduced support [18]. The reason for SMSI state in the gel catalyst has been attributed to its increased reducibility than the commercial sample as observed from the characterization results reported earlier [18]. In the case of the mixed oxide, it can be attributed to a homogenous distribution of the support.

4. Conclusions

- Supported platinum systems have been investigated for the selective hydrogenation of citral. The C=O bond is hydrogenated rather than the thermodynamically favorable C=C bond on supported platinum systems. This is attributed to the influence of the SMSI (strong metal–support interaction) state in these supported platinum catalysts thus selectively producing the unsaturated alcohols rather than the saturated aldehydes.
- The titania gel and mixed oxide supported platinum catalysts indicates the maximum conversion and a higher activity. This has been attributed to the influence of the SMSI state in both the titania supported samples (gel and mixed oxide, titania–alumina). The migration of the reduced TiO₂ species to the surface of the metal has been observed to enhance the preferential hydrogenation of the C=O bond than the more thermodynamically favorable C=C bond thus resulting in the unsaturated alcohol

(geraniol) than the saturated aldehyde (citronellal) [24].

- In all the supported catalyst systems the formation of geraniol (E isomer) has been observed as the sole product of the hydrogenation of citral.
- The formation of geraniol has been attributed to the influence of SMSI state in the selective hydrogenation of C=O bond as concluded earlier. However, the isolated C=C bond is unaffected throughout the course of the reaction or was never detected even if otherwise.

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