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Hydrogenation of citral over a polymer fibre catalyst

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A polymer-supported Pd catalyst was investigated in hydrogenation of citral (3,7-dimethyl-2,6-octadienal), which is a stereoisomer with an isolated and a conjugated double bond as well as a carbonyl group. The catalyst was a fibrous polymer-supported catalyst modified with functional groups and immobilized metals. A comparison of the polymer-supported catalyst with conventional catalysts was made.

KEY WORDS: polymer-supported fibre catalyst; citral hydrogenation; Pd; Pt.

1. Introduction

Selective hydrogenation of α,β-unsaturated aldehydes has been the subject of numerous investigations [1–5]. The selectivity depends on several factors, *i.e.*, the metal and its particle size [6], the catalyst support [7–9], and the presence of promoters [9–11]. Hydrogenation of α,β-unsaturated aldehydes to saturated aldehydes can easily be achieved over most platinum metal catalysts under mild conditions [2,12]. Within the family of α,β-unsaturated aldehydes, hydrogenation of citral is important for its interest to the perfumery industry [13,14]. Citral is a very fascinating model molecule for selective hydrogenation, since it has three different double bonds, an isolated double bond, a conjugated double bond, and a carbonyl group. Furthermore, there are possibilities for *cis-trans* isomerization and for several types of side reactions (cyclization, acetalization, decarbonylation). The primary hydrogenation product is citronellal, which reacts further to citronellol and 3,7-dimethyloctanol. Additional products can be formed, namely unsaturated alcohols, nerol and geraniol, and an aldehyde 3,7-dimethyloctanal. The most important products, from an industrial viewpoint, are citronellal and citronellol. Citral is usually hydrogenated in an alcohol solvent, in the presence of a heterogeneous catalyst [13,15]. If citral reacts with an alcoholic solvent or is hydrogenated over an acidic catalyst, acetals are formed. The reactions in citral hydrogenation are shown in scheme 1 [16].

Polymer supports and functional polymers used in metal catalysis is an emerging section of the modern industrial chemical technology. The specific advantages of fiber catalysts are due to short the diffusion paths, which provide high catalyst efficiency and excellent separation abilities. Smoptech Ltd. has recently developed a new polyethylene-based fiber catalyst, and it has been shown to be effective in various industrially-relevant two- and three-phase (*e.g.*, solid–liquid and gas–liquid–solid) systems [17–19]. The catalyst can be utilized in batch and continuous processes. Grafting different functional groups, *i.e.*, pyridine, carboxylic acid and sulphonic acid, or a combination of them, can modify the polyethylene-based catalyst. This gives a possibility of replacing homogeneous catalysts. Immobilization of metals on the ion-exchange fibers and consequent reduction with hydrogen gives a possibility of preparing catalysts which are active in catalytic hydrogenation reactions. In the present study, this new pyridine-modified polymer-based fiber catalyst has been used in batchwise hydrogenation of citral in 2-propanol, Pd being the active metal. Additional experiments have also been done with Pt being the active metal. As a comparison conventional commercial catalysts have been used: Pd/C, Pt/C, and Pt/Al_2O_3.

2. Experimental

2.1. Catalyst preparation and characterization

The catalyst, available from Smoptech Ltd., is produced in several shapes. It consists of fibers, which can be knitted. The diameter of the fiber, which does not have any pores, ranges from 10 to 50 μm. The catalyst swells in solvent, which improves its diffusional properties. The catalyst structure can be investigated by scanning electron microscopy (SEM). The catalyst was prepared by electron-beam-induced pre-irradiation grafting of 4-vinylpyridine onto polyethylene fibers. The metal was immobilized on the ion-exchange fibers by using a metal salt as precursor and consecutively

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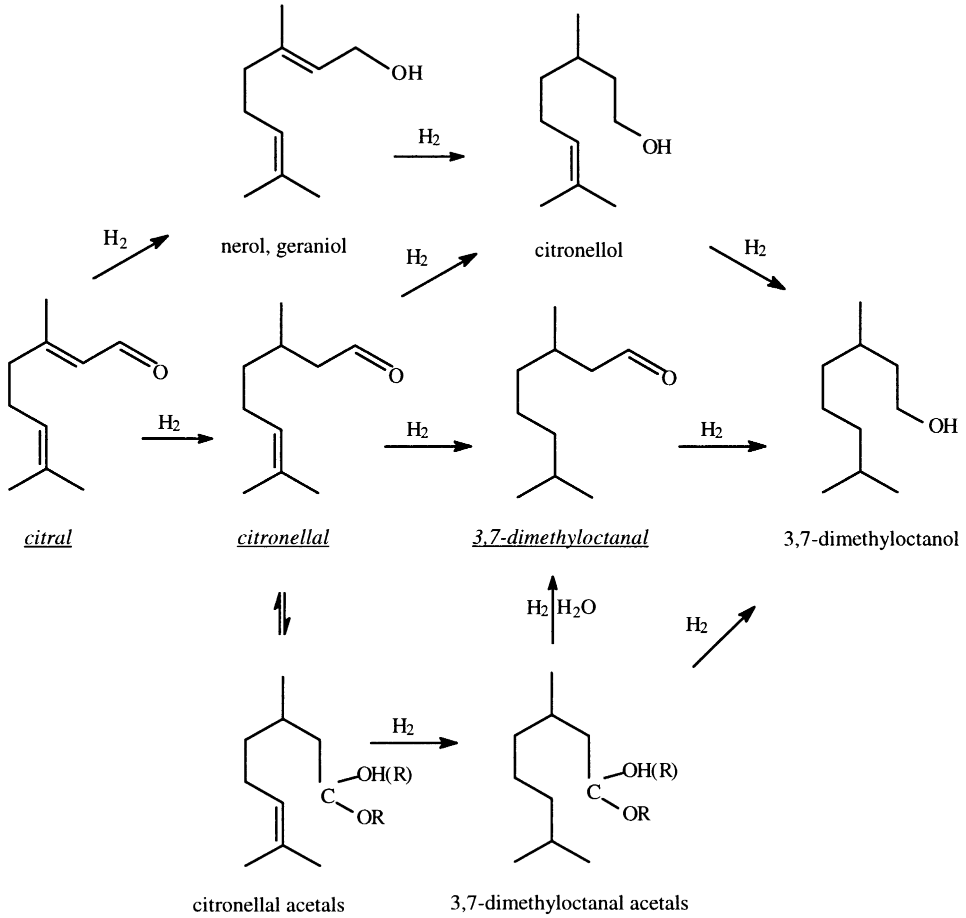

Scheme 1. Reactions in citral hydrogenation. The primary reaction route in the present study is underlined and in italics.

reduced by molecular hydrogen or sodium borohydride [20]. Afterwards, washing with either HNO_3 or NaOH modified the catalyst properties. Finally, the metal content of the catalyst was measured with atomic absorption spectroscopy (AAS). A Pd catalyst made from $Pd(NO_3)_2$ precursor on pyridine-modified polymer support, hereafter denoted as PdN, was characterized with transmission electron microscopy (TEM) at the National Centre for HREM, Delft. TEM was performed using a Philips CM30T electron microscope operated at 300 kV. X-ray diffraction measurements of a 12 wt% Pd catalyst made from $PdCl_2$ precursor on pyridine-modified polymer support, hereafter denoted as PdCl, were carried out using a Philips PW 1820 diffractometer [16]. The crystallite size analyses were performed by using the approximate and the single-line method. Additionally, XPS analyses were performed with a Perkin Elmer PHI 5400 ESCA System. An unchromatized Mg Röntgen anode (Mg K_α radiation) was used in the spectrum measurements [21]. Before the measurements, the catalyst was reduced at 75 °C in 2-propanol for 1 h. Then the deoxygenated solvent was injected into the reactor and a catalyst sample was filtered in a nitrogen atmosphere and transferred into the XPS-analysis chamber. No reliable characterization methods for the polymer-supported catalyst are available and therefore the characterization was limited.

For the conventional Pt catalysts, hydrogen chemisorption measurements were performed by using an automatic chemisorption apparatus (Sorptomatic 1900, Carlo Erba Instruments). Adsorption isotherms were recorded at 25 °C and within the pressure range of 1.3–130 mbar. The catalyst was first reduced at 400 °C for 2 h with flowing hydrogen. After the reduction, the catalyst was evacuated at 10^{-4} bar for 1 h at 400 °C. The specific surface area of the catalyst (BET) was measured with an automatic physisorption–chemisorption apparatus (Sorptomatic 1900, Carlo Erba Instruments). The catalyst was degassed at 300 °C *in vacuo* prior to the surface area measurements by nitrogen adsorption. The mean particle sizes of the Pt catalysts were measured with a Malvern Zetasizer IIc apparatus.

2.2. Experimental setup

The hydrogenation experiments were carried out at 5 bar hydrogen (AGA 99.999%) pressure in a semi-batch reactor (Parr, 300 ml), equipped with a Rushton turbine stirrer, an electrical heating jacket with a temperature controller and thermocouples. The temperature was 70 °C, the citral-to-Pd mass ratio was varied from 25 to 75 and the initial citral concentration was 0.1 M. The catalyst was activated at 75 °C at 5 bar for 1 h in 75 ml 2-propanol. The citral solution was saturated with hydrogen before injecting it into the reactor and the reaction was commenced. The total volume of the solution was 150 ml. Samples were periodically withdrawn for analysis. Approximately 50 μg was injected into another flask, which contained 1 ml of a solution of 1.5–2 mg cyclohexanone (>99%, Merck, 822269) in methylcyclohexane (>98%, Merck 806145). These samples were analyzed with a gas chromatograph (Hewlett-Packard 6890) equipped with a DB-wax capillary column (with length = 30 m, i.d. = 0.32 mm, and a film thickness of 0.25 μm) and a flame ionization detector (FID). The following temperature program was used: 100 °C (for 26 min) then at 5 °C/min up to 160 °C. The injector and detector temperatures were 250 and 275 °C, respectively. The peak identification was based on the retention times obtained from a reference solution containing commercial citral hydrogenation products. The identification was confirmed by GC-MS. Citronellal ethyl- and 2-propylacetals were identified by GC-MS.

3. Results and discussion

3.1. Catalyst characterization

The PdN catalyst characterized with TEM had a narrow palladium particle-size distribution. Most metal particles were present as single particles, 5–10 nm in diameter. Sometimes the metal particles were present with 3 or 4 close to each other. XRD measurements on PdCl indicated a mean crystallite size of approximately 10 nm. The metal distribution in the catalyst fiber is uniform, as confirmed by scanning electron microscopy–electron probe X-ray microanalysis (SEM-EPMA). The catalyst structure was investigated with SEM (figure 1). Due to limited characterization methods, the state of palladium in the reduced catalyst could not be confirmed.

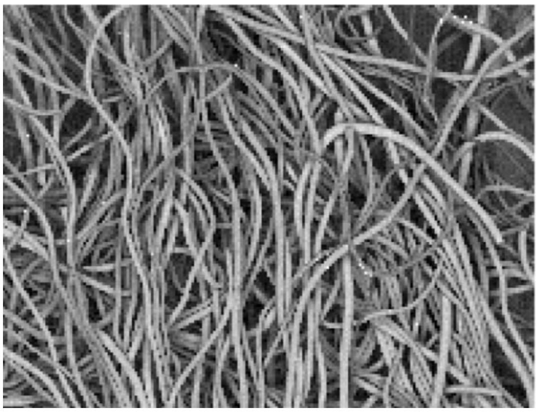

Figure 1. SEM micrograph of the catalyst fibers, $\varnothing = 30\,\mu$m.

The results of the characterization of Pt catalysts are: Pt/C (Alfa 5R18), metal content 5 wt%, BET specific surface area 988 m^2/g, mean metal particle size 1.5 nm (XRD), mean catalyst particle size 15.1 μm (Malvern), and for Pt/Al$_2$O$_3$ (Strem Chemicals, 78-1660), metal content 5 wt%, BET specific surface area 95 m^2/g, mean metal particle size 8.3 nm (XRD), dispersion 40% (hydrogen chemisorption), mean catalyst particle size 18.2 μm (Malvern).

3.2. Hydrogenation of citral over Pt catalysts

Prior to the catalytical hydrogenation experiments the activity of the support was investigated. One hydrogenation experiment using only the pyridine-modified polymer support, excluding an active metal, was done and no reaction occurred. In citral hydrogenation catalytic reactions from the pyridine-modified polymer support could be excluded.

When comparing Pt/C and Pt/Al$_2$O$_3$ with pyridine-modified polymer-supported H$_2$PtCl$_6$, hereafter denoted as Pt–Cl (figure 2), it was apparently clear that, although

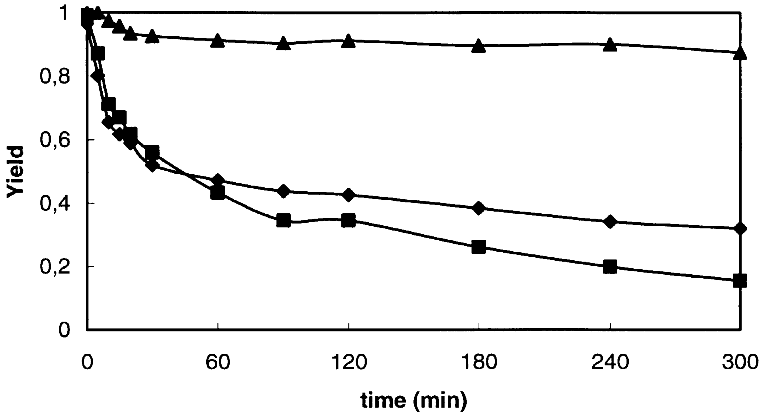

Figure 2. Batchwise hydrogenation of citral on Pt/C (◆), Pt/Al$_2$O$_3$ (■) and Pt–Cl (▲) at 70 °C, 4.5 bar, with a 0.1 M initial concentration of citral and a stirring rate of 750 rpm. Citral-to-Pt ratio = 25.

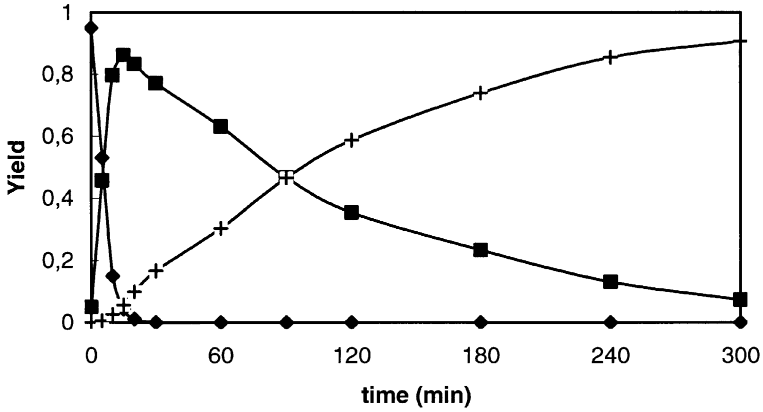

Figure 3. Batchwise hydrogenation of citral on PdN 2.3 wt% Pd. Citral (◆), citronellal (■), 3,7-dimethyloctanal (+), at 70 °C, 4.5 bar, with 0.1 M initial concentration of citral and the stirring rate 750 rpm. Citral-to-Pd ratio = 25.

the polymer-supported catalyst was able to hydrogenate the C=O bond, the activity was 10 times less than those of the conventional catalysts. Pt/Al_2O_3 gave the following maximum yields: 15% citronellal, 34% citronellol, 21% geraniol, and 8% nerol at a conversion of 84%. For Pt/C, the maximum yields were 36% citronellal, 12% citronellol, 5% geraniol, and 2% nerol at a conversion of 68%. The influence of metal–support interactions on the hydrogenation of citral has been observed on Pt/SiO_2 and Pt/TiO_2, which gave the unsaturated alcohols (geraniol and nerol) as main products [22]. For Pt/SiO_2, 50% citronellal, 23% citronellol, and 15% 3,7-dimethyl-2-octenal was achieved [7]. A strong metal–support interaction was observed in citral hydrogenation over Pt/TiO_2 gel, Pt/TiO_2, Pt/TiO_2–Al_2O_3, and Pt/CeO_2 [8]. The authors stated that the migration of reduced TiO_2 species to the surface of the metal enhances the hydrogenation of the C=O bond over the more thermodynamically favorable C=C bond. Clearly there must be a strong interaction between Pt and Al_2O_3 causing the hydrogenation of the C=O bond, whereas, Pt/C and Pt–Cl gave somewhat similar results, the yield of citronellal being 7% at a conversion of 13% for the latter. A comparison of product distribution at 10% conversion of citral, with different catalysts, is presented in table 1. Obviously there is no interaction between Pt and the polymer support.

The deactivation is rapid for the Pt catalysts, but their initial selectivity coincides. Deactivation could be attributed to inhibition by adsorbed CO produced by the decomposition of either citral or unsaturated alcohol as observed on Pd, Pt, Ir, Os, Ru, Rh, and Co on SiO_2 in liquid-phase hydrogenation of citral [7].

Table 1
Selectivity in citral hydrogenation at 10% conversion over Pt catalysts.

Catalyst	Citronellal (%)	Citronellol (%)	3,7-Dimethyloctanal (%)	Geraniol (%)
Pt/C	11.0	0	1.0	0.4
Pt/Al_2O_3	5.8	1.2	0.4	2.1
Pt–Cl	8.6	0.1	0	0

3.3. Hydrogenation of citral over Pd catalysts

The influence of support on the hydrogenation of citral on Pd catalysts has not been widely studied. A preliminary testing of the polymer-supported fiber catalyst with Pd showed that it was active in hydrogenating citral to citronellal, which was further hydrogenated to 3,7-dimethyloctanal. When comparing Pd/C with PdCl and PdN it was clear that the selectivity to citronellal was better with the polymer-supported catalyst, the selectivities being 67.5, 87.5, and 82.5% respectively. When comparing PdCl to PdN at different Pd loadings (2–12 wt%) it could be observed that the initial selectivity of the primary reaction, hydrogenation of citral to citronellal, over PdN was not dependent on the Pd loading. The selectivity to citronellal was approximately 85% at 40% conversion of citral. A typical hydrogenation experiment is presented in figure 3. The independence of the Pd loading might be due to a limited amount of exposed sites on the catalyst surface, despite the difference in metal loading. The results of Yen and Chou [23] showed that the maximum palladium acetate concentration on SDB copolymer was 0.6%. Kralik *et al.* [24] noted that, in the hydrogenation of cyclohexene, when the size of the resin-supported Pd catalyst particles was relatively small, the catalyst with 2.2 and 0.22% Pd were almost equally active with respect to the amount of palladium in the reaction mixture.

3.4 Acetalization

Citronellal can interact with an alcohol solvent forming acetals [25]. Acetalization was observed over Pd/C, and the yield of acetals was very high, reaching 52%. Acetal formation can be due to the acidity of the support. Formation of acetals was observed with three Pd catalysts made from chloride precursor, and the maximum yield of acetals reached 50% (figure 4). The

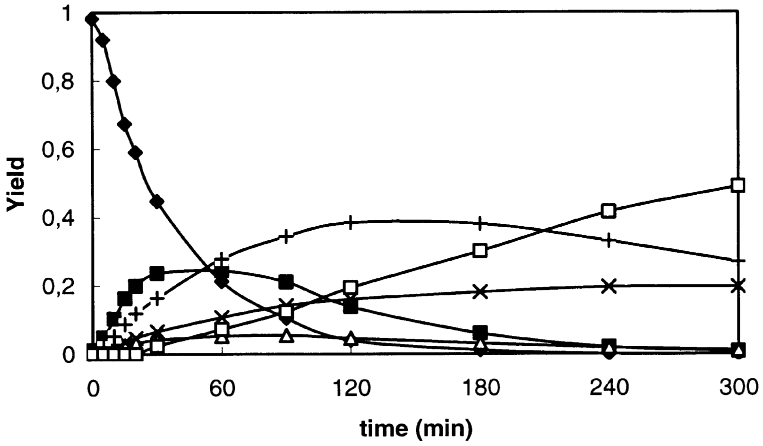

Figure 4. Batchwise hydrogenation of citral on PdCl 12.2 wt% Pd, washed with HNO_3. Citral (◆), citronellal (■), citronellol (△), 3,7-dimethyloctanal (+), 3,7-dimethyloctanol (×) and acetal (□) at 70 °C, 4.5 bar, with a 0.1 M initial concentration of citral and a stirring rate 750 rpm. Citral-to-Pd ratio = 25.

cause of acetalization can be explained by the washing procedure during catalyst preparation. The chloride precursor catalysts had been washed with HNO_3, leaving the catalyst in an acidic form. When these catalysts were washed with NaOH, acetal formation was clearly suppressed to yields of 10% (figure 5). If the catalyst support is in an acidic state, acetalization is favored [26]. In addition, a chloride precursor has been shown to favor acetalization [3]. Chloride traces of 0.2% were confirmed with XPS measurements. No acetals were observed when using Pd catalysts from nitrate precursor, which had been washed with NaOH.

4. Conclusions

Citral hydrogenation over polymer-supported Pd and Pt catalysts, and Pd/C, Pt/C, and Pt/Al_2O_3 were studied. The polymer-supported catalysts were characterized with SEM, XRD, XPS, and TEM, and the conventional catalysts with hydrogen chemisorption, BET specific surface area and XRD. Citral was hydrogenated at 5 bar pressure at 70 °C. The citral-to-Pd ratio was varied from 25 to 75 and the initial citral concentration was 0.1 M. The fibrous polymer-supported catalyst was shown to be effective in hydrogenating the conjugated and isolated C=C double bonds. However, surprisingly, the amount of Pd loading had no effect on reaction rate. The maximum yield of citronellal (86%) was reached with 2.3 wt% Pd from nitrate precursor on pyridine-modified polymer support. The conventional Pt catalysts hydrogenated mainly the C=O bond and the conjugated C=C bond. Therefore, maximum yield of citronellol was only 34% over Pt/Al_2O_3. Additional development is needed, especially in the field of characterization, for understanding the behavior of the polymer-supported metal catalysts.

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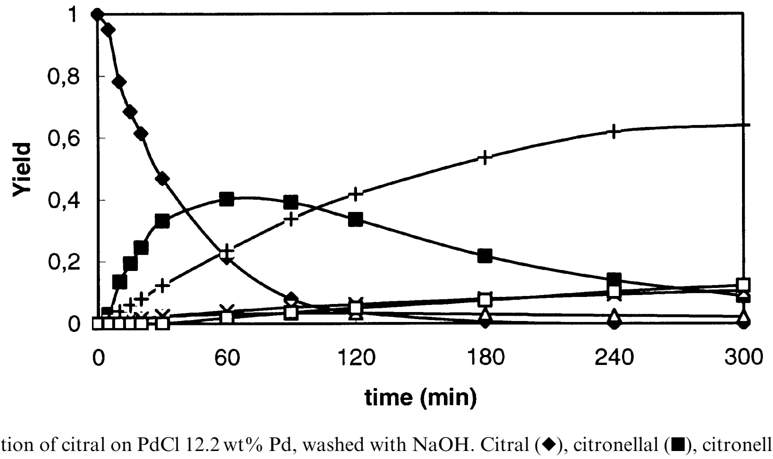

Figure 5. Batchwise hydrogenation of citral on PdCl 12.2 wt% Pd, washed with NaOH. Citral (◆), citronellal (■), citronellol (△), 3,7-dimethyloctanal (+), 3,7-dimethyloctanol (×) and acetal (□) at 70 °C, 4.5 bar, with a 0.1 M initial concentration of citral and a stirring rate 750 rpm. Citral-to-Pd ratio = 25.

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References

[1] P. Gallezot, A. Giroir-Fendler and D. Richard, Catal. Lett. 5 (1990) 169.

[2] M. Englisch, A. Jentys and J. A. Lercher, J. Catal. 166 (1997) 25.

[3] G. Neri, L. Mercadante, A. Donato, A. Visco and S. Galvagno, Catal. Lett. 29 (1994) 379.

[4] G.R. Cairns, R.J. Cross and D. Stirling, J. Catal. 166 (1997) 89.

[5] N. Ravasio, M. Antenori, F. Babudri and M. Gargano, in: *Studies in Surface Science and Catalysis* 108, eds. H.U. Blaser, A. Baiker and R. Prins (Elsevier Science, Amsterdam, 1997) p. 625.

[6] S. Galvagno, C. Milone, A. Donato, G. Neri and R. Pietropaolo, Catal. Lett. 18 (1993) 349.

[7] U.K. Singh and M.A. Vannice, J. Catal. 199 (2001) 73.

[8] R. Malathi and R.P. Viswanath, Appl. Catal. A: General 208 (2001) 323.

[9] M. Consonni, D. Jokic, D. Yu. Murzin and R. Touroude, J. Catal. 188 (1999) 165.

[10] Z. Poltarzewski, S. Galvagno, R. Pietropaolo and P. Staiti, J. Catal. 102 (1986) 190.

[11] M.A. Aramendia, V. Borau, C. Jiménez, J.M. Marinas, A. Porras and F.J. Urbano, J. Catal. 172 (1997) 46.

[12] U.K. Singh and M.A. Vannice, J. Catal. 199 (2001) 73.

[13] T. Salmi, P. Mäki-Arvela, E. Toukoniitty, A. Kalantar Neyestanaki, L.-P. Tiainen, L.-E. Lindfors, R. Sjöholm and E. Laine, Appl. Catal. A: General 196 (2000).

[14] R.S. De Simone and P.S. Gradeff, US Patent 4,029,709, 1977.

[15] A.M. Pak, S.R. Konuspaev, G.D. Zakumbaeva and D.V. Sokolskii, React. Kinet. Catal. Lett. 16 (1981) 339.

[16] P. Mäki-Arvela, L.-P. Tiainen, A. Kalantar Neyestanaki, R. Sjöholm, T.-K. Rantakylä, E. Laine, T. Salmi and D. Yu. Murzin, Liquid phase hydrogenation of citral: suppression of side reactions, Appl. Catal. A: General (in press).

[17] J. Lilja, J. Aumo, T. Salmi, D. Yu. Murzin, P. Mäki-Arvela, M. Sundell, K. Ekman, R. Peltonen and H. Vainio, Appl. Catal. A: General 228 (2002) 253.

[18] I. Lehtonen, Masters Thesis, Helsinki University of Technology, Helsinki, 1999.

[19] J. Aumo, J. Lilja, P. Mäki-Arvela, D. Yu. Murzin, T. Salmi, K. Ekman, R. Peltonen and M. Sundell, 3rd European Congress of Chemical Engineering, Nuremberg, CD-Rom #097, 2001.

[20] J. Näsman, M. Sundell and K. Ekman, US Patent 5,326,825, 1994.

[21] P. Mäki-Arvela, L.-P. Tiainen, M. Lindblad, K. Demirkan, N. Kumar, R. Sjöholm, T. Ollonqvist, J. Väyrynen, T. Salmi and D. Yu. Murzin, Liquid phase hydrogenation of citral for production of citronellol: catalyst selection, Appl. Catal. A: General (submitted).

[22] U.K. Singh and M.A. Vannice, J. Mol. Catal. A: Chem. 163 (2000) 233.

[23] P.-W. Yen and T.-C. Chou, Appl. Cat. A: General 182 (1999) 217.

[24] M. Kralik, M. Zecca, P. Bianchin, A.A. D'Archivio, L. Galantini and B. Corain, J. Mol. Catal. A: Chem. 130 (1998) 85.

[25] A. Wismeijer, A. Kieboom and A. Van Bekkum, Appl. Catal. 25 (1986) 181.

[26] S. Galvagno, C. Milone, A. Donato, G. Neri and R. Pietropaolo, Catal. Letters 17 (1993) 55.