Available online at www.sciencedirect.com

SCIENCE DIRECT®

Catalysis Today 102–103 (2005) 128–132

CATALYSIS TODAY

www.elsevier.com/locate/cattod

Novel woven active carbon fiber catalyst in the hydrogenation of citral

Jeannette Aumo, Susanna Oksanen, Jyri-Pekka Mikkola, Tapio Salmi, Dmitry Yu. Murzin *

Åbo Akademi University, Lab. Industrial Chemistry, Process Chemistry Centre, Biskopsgatan 8, FIN-20500 Åbo/Turku, Finland

---

Abstract

Catalytic hydrogenation of citral was performed in a batch reactor under elevated pressures. The reaction was studied with a Pt on active carbon fiber catalyst and a commercial Pt on active carbon powder catalyst. Platinum was supported on active carbon by impregnation. The influence on selectivity and activity, of the most important variables, such as temperature and pressure, was investigated in the batch reactor. Four consecutive experiments were carried out with each catalyst. The aim with the reuse of catalysts in the batch reactor was to elucidate eventual catalyst deactivation. The decrease in activity was fairly notable. The catalysts were characterized with scanning electron microscopy, N_2-physisorption, and inductively coupled plasma analysis combined with mass spectroscopy. With the Pt on active carbon fiber catalyst, 80–100% selectivity of carbonyl group hydrogenation was achieved at 15% conversion.

Keywords: Active carbon; Fiber; Structured catalyst; Multiphase reactor; Citral hydrogenation; Process intensification

---

1. Introduction

Process intensification and sustainable product quality by means of continuous operations can be approached by using structured catalysts. Development of new, structured catalytic materials to replace unstructured slurry or packed bed reactors, is an actively researched area nowadays. A number of new solutions are available, such as monolith structures [1], Sulzer Katapak® elements [2], micro reactors [3] and various woven fiber cloths [4–8]. In this study, we have investigated the potential of novel woven carbon textiles on which a catalytically active metal, namely Pt was supported.

Citral hydrogenation was chosen as a model reaction. Citral is a suitable model compound for selective hydrogenation, since it contains both an isolated and a conjugated double bond, as well as a carbonyl group. Furthermore, it exists as cis and trans isomers. Upon hydrogenation numerous parallel and consecutive reactions typically take place [9–12]. The reaction scheme of citral hydrogenation is displayed in Fig. 1.

2. Experimental

2.1. Catalyst preparation and characterization

Woven active carbon cloth ACC-507-15 (Kynol™) (Fig. 2) was utilized as a support upon preparation of catalysts. Four pieces of suitable dimensions of the active carbon cloth were cut according to the dimensions of the integrated gadget of a combined stirrer and catalyst holder (Fig. 3). The pieces were washed with deionised water and dried overnight at 60 °C. The fiber cloths were impregnated in a water solution of H_2PtCl_6 (Degussa) at pH 5, for approximately 4 h, and washed with deionised water. The impregnation method is commonly used for Pt catalysts [13]. After drying the catalyst cloths overnight at 60 °C they were attached to the stirrer and reduced in situ. Pt on active carbon cloth (Pt/ACC) catalyst was reduced in situ in flowing hydrogen, while heating 10 °C/min to 200 °C for 2 h, and then cooled down to ambient temperature.

The catalyst was characterized by means of nitrogen physisorption (BET) with a Sorptomatic 1900-sorptometer from Carlo Erba Instruments. Images of the catalyst was obtained with a scanning electron microscope model LEO

---

* Corresponding author.
E-mail address: dmurzin@abo.fi (D.Yu. Murzin).

0920-5861/$ – see front matter © 2005 Elsevier B.V. All rights reserved.
doi:10.1016/j.cattod.2005.02.017

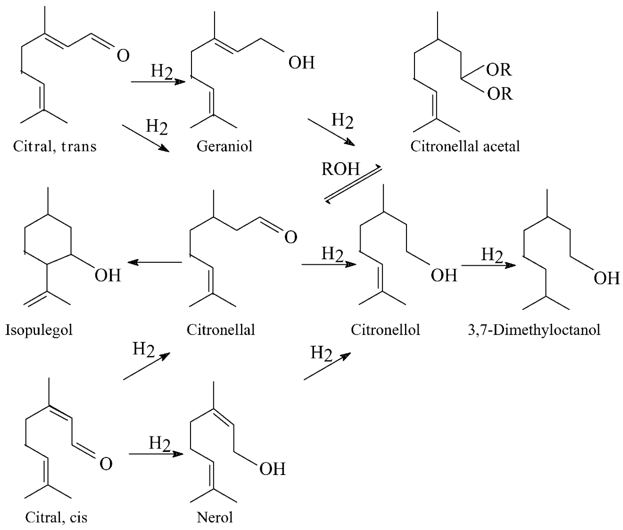

Fig. 1. Reaction scheme of citral hydrogenation.

1530 equipped with a ThermoNORAN Vantage analyzer using an acceleration voltage of 15 keV and a take off angle of 34.0411° (LEO Electron Microscopy Ltd.), and the metal contents of the catalysts were obtained by using inductively coupled plasma analyzer ELAN 6000 combined with a mass spectrometer (ICP-MS).

For comparison, a commercial Pt on active carbon (Pt/AC) powder catalyst 5R18 (Johnson Matthey) was used and characterized with BET and ICP-MS.

2.2. Experimental setup

Hydrogenation of citral was carried out in a laboratory autoclave (600 ml, Parr Inc., USA) equipped with a heating jacket. The reactor had a total volume of 600 ml and was equipped with a propeller mixer, coupled to a Rushton turbine for effective gas distribution. The temperature and stirrer controllers used were Parr 4843 (Watlow Controls Series 982). Prior to each experiment, the catalyst and reactor vessel were preheated under hydrogen atmosphere to the desired temperature. A volume of 450 ml of 0.017 M of citral (33.9/66.1 mol% *cis/trans*, Lancaster 5460) dissolved in analytical grade hexane (99%, Merck) without any further purification was saturated with hydrogen, for 10 min in a bubbling unit. The reaction solution was injected into the reactor by opening the valve to the reactor and adjusting the pressure to the desired one, and the reaction was commenced. The experiments were carried out at 6–51 bar of total pressure. The hydrogen partial pressure was calculated by taking into account the vapor pressure of hexane at different temperatures. Hydrogen gas used had a purity of 99.999% (AGA). Citral/Pt ratio was approximately 13 for the Pt/ACC catalyst. For the 4.6 wt.% Pt/AC, the ratio of citral/Pt was 121. The mass of citral in each experiment was around 1.1 g. 500 μl of internal standard (0.021 M cyclohexanone in cyclohexane) was added to the samples withdrawn from the reactor. The samples were analyzed by means of gas chromatography (GC). The column used was a DB-1 with the length 30 m, inner diameter 0.25 mm and the film thickness 0.5 μm. The following temperature program was applied: 70 °C for 1 min, 13 °C/min to 120 °C and continued with 1 °C/min to 125 °C and 0.5 °C/min to 130 °C. At the end the temperature was increased 10 °C/min to 160 °C and kept constant for 5 min. Some of the products were identified with GC-mass spectrometry (GC-MS).

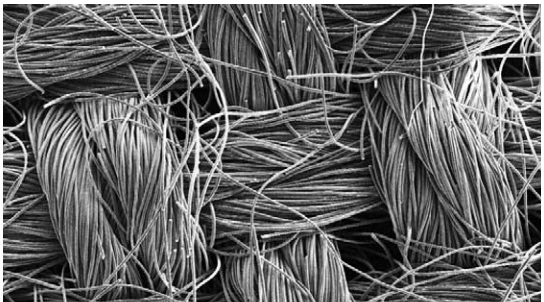

Fig. 2. SEM image of woven active carbon fiber catalyst.

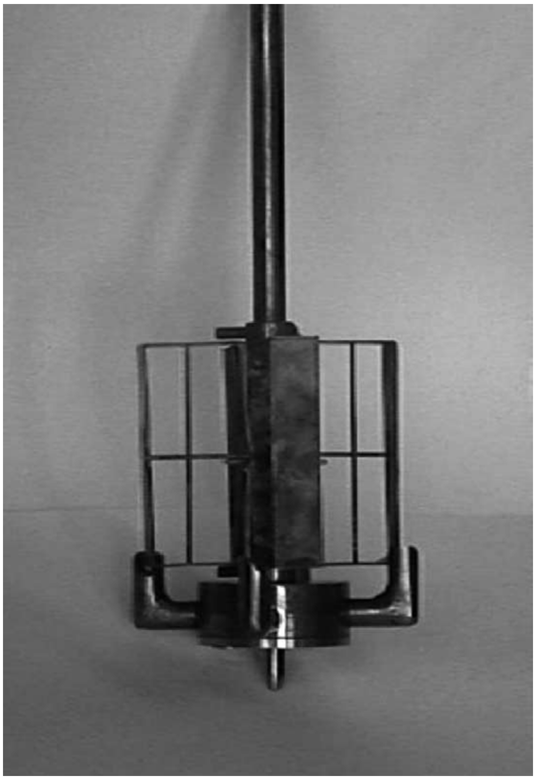

Fig. 3. Integrated gadget of a combined stirrer and catalyst holder.

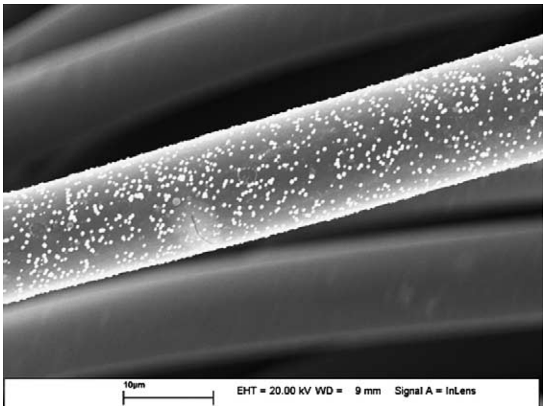

Fig. 4. SEM image of 5.9 wt.% Pt/ACC fiber catalyst.

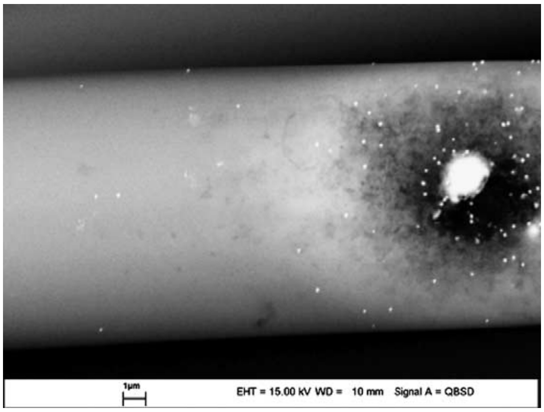

Fig. 5. SEM image of Pt/ACC fiber catalyst showing a defected site with Pt agglomerates.

3. Results and discussion

3.1. Catalyst characterization

SEM images revealed the morphology of the active carbon cloth catalyst. Fig. 4 illustrates the distribution of Pt particles observed on the surface of the carbon fibers. Furthermore, some structure defects on the fiber were noticed, where big agglomerates of Pt particles were trapped. Although the specific reason for the formation of the agglomerates is not known, the plausible explanation could be that these structure defects possess a small surface area. This is more clearly illustrated in Fig. 5. The Pt content was 5.9 wt.% on the fiber cloth catalyst and 4.6 wt.% on the powder catalyst as verified by ICP-MS. Nitrogen physisorption was measured on the fresh woven active carbon support material, used Pt/ACC catalyst and fresh Pt/AC powder catalyst. The specific surface areas and pore volumes are illustrated in Table 1. As the ACC is a microporous (72%) support the specific surface areas and pore volumes have been calculated by using the method of Dubinin, but as BET values are commonly reported in the literature they are included as a reference. Impregnation of the active carbon cloth catalysts results in a minor decrease of Dubinin specific surface area, for instance even with a higher Pt loading (10.9 wt.%) this area was 1228 m^2/g [14].

3.2. Catalytic data

The microscopic diameter of the fibers (Ø = 9.2 μm) and their high surface area facilitate rapid mass transfer. Furthermore, the effectiveness factor, $\eta_{\mathrm{eff}} \rightarrow 1$, calculated based on the procedure reported by Santen et al. and Hájek et al. assured that hydrogenation reactions over Pt/ACC catalyst were conducted in kinetic regime [15,16]. A series of four consecutive experiments were performed at different experimental conditions: 80 °C and 5 bar, 80 °C and 10 bar, 100 °C and 5 bar, and 80 °C and 5 bar. The catalyst was left in the reactor under hydrogen pressure in order to avoid the oxidation of the catalyst before the next experiment. The Pt fiber catalyst favored the production of geraniol, nerol, and citronellal. The ratio geraniol/nerol was 2.3 and it was not affected by the deactivation of the catalyst or by the conversion. At 80 °C and 10 bar, highest selectivity to geraniol 70% was achieved at 10% conversion. At 80 °C and 5 bar, as well as at 100 °C and 5 bar, at 15% conversion, the selectivity to geraniol decreased from the initial level of 70–50% due to citronellal formation. The overall selectivity of C═O group reduction (e.g. nerol and geraniol formation) was 80–100% at 15% conversion. In the first experiment the conversion after 7 h was 23%, thereafter it decreased with each consecutive experiment being 13, 11 and 3%, respectively, as illustrated in Fig. 6. Deactivation could be due to carbonaceous deposits on the surface of the support [17]. In citral hydrogenation over supported Pt catalysts, alcohol and CO depositions on the catalyst surface was found to block the active sites leading to a loss of activity [18].

With the 4.6 wt.% Pt/AC powder catalyst (mean particle size 16 μm), the following consecutive experiments were performed: 80 °C and 5 bar, 100 °C and 5 bar, 100 °C and 10 bar, and 80 °C and 5 bar. The catalyst was left in the

Table 1
Specific surface areas and pore volumes for the catalysts used

Catalyst		BET		Dubinin	
		Specific surface area (m^2/g)	Specific pore volume (cm^3/g)	Specific surface area (m^2/g)	Micro pore volume (cm^3/g)
Kynol™ active carbon fiber support		954	0.63	1348	0.48
5.9 wt.% Pt/ACC fiber	Spent	630	0.35	865	0.31
4.6 wt.% Pt/AC powder (Johnson Matthey)	Fresh	797	0.76	999	0.36

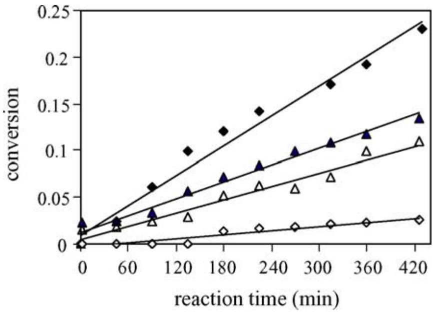

Fig. 6. The conversion as a function of reaction time in the hydrogenation of citral over a 5.9 wt.% Pt/ACC fiber catalyst at 80 °C and 5 bar (◆), 80 °C and 10 bar (▲), 100 °C and 5 bar (△) and 80 °C and 5 bar (◇). (Consecutive experiments were performed in that order).

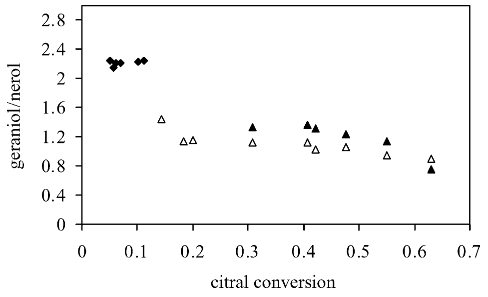

Fig. 8. Geraniol/nerol ratio as a function of citral conversion in the hydrogenation of citral at 100 °C over a 5.9 wt.% Pt/ACC fiber catalyst at 5 bar (◆), and over 4.6 wt.% Pt/AC powder catalyst at 5 bar (▲), and 10 bar (△). (Consecutive experiments were performed in that order).

reactor under hydrogen pressure in order to avoid the oxidation of the catalyst before the next experiment. The conversion values in each experiment after 6.5 h were 49, 49, 62 and 13%, respectively. As expected, increasing both temperature and pressure improved the conversion. Clearly catalyst deactivation was observed, when comparing the first and fourth run performed under the same experimental conditions. The Pt/AC powder catalyst favored the production of citronellal with a selectivity of 35–40% in each experiment independent of pressure and temperature. 3,7-Dimethyl-2,7-octadien-1-ol (trans) was produced with a 12% selectivity. Other products were 5-methyl-2-(methylethyl)-cyclohexanol, 3,7-dimethyloctanol and citronellol with selectivities in the range of 5–8%. In the fourth experiment, at 80 °C and 5 bar, the highest overall selectivity to geraniol and nerol (44%) was achieved at 8% conversion. In the other experiments the overall selectivity to geraniol and nerol was approximately 14%. The ratio geraniol/nerol was on average 1.15. At 100 °C, the ratio decreased from 1.4 to 0.9 with increasing conversion. The dependence of the geraniol/nerol ratio on conversion for both fiber and powder catalyst is illustrated in Fig. 7 at 80 °C and Fig. 8 at 100 °C. The product distribution was wider for the powder catalyst compared to the fiber catalyst. The wide product distribution could possibly be influenced by functional groups, e.g. carboxylic, on the surface of the catalyst support, as was observed in hydrogenation of cinnamaldehyde over carbon nanofiber-supported Pt catalysts [19]. Additionally, the measured pH of the ACC support was 7.6, whereas the pH was 6.7 for Pt/AC powder.

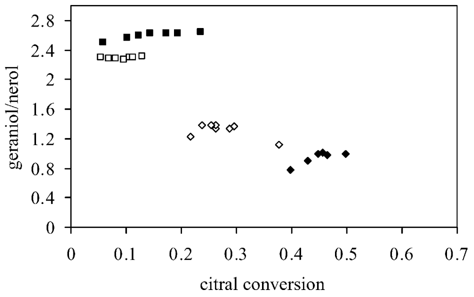

Fig. 7. Geraniol/nerol ratio as a function of citral conversion in the hydrogenation of citral at 80 °C over a 5.9 wt.% Pt/ACC fiber catalyst at 5 bar (■), and 10 bar (□), and over 4.6 wt.% Pt/AC powder catalyst at 5 bar (◆), and 5 bar (◇). (Consecutive experiments were performed in that order).

3.3. Conclusions

The results of the kinetic experiments demonstrated the feasibility of utilizing woven active carbon fibers as supports in three-phase metal catalyzed hydrogenation of α,β-unsaturated aldehyde, citral. The woven fiber catalyst favored hydrogenation of the C=O group, e.g. the formation of geraniol and nerol, whereas the commercial powder catalyst led to citronellal and various other products of its hydrogenation. The ratio of geraniol/nerol was also different, being on average 2.3 and 1.15 for the woven fiber catalyst and the powder catalyst respectively. Possible limitations for application of Pt/fiber catalyst are associated with deteriorating activity as a pronounced deactivation was observed for the fiber catalyst.

Acknowledgements

The authors are grateful to colleagues from Åbo Akademi University for their analytical assistance: Clifford Ekholm, for the SEM analysis, Paul Ek and Virpi Väänänen, for the ICP-MS analysis, and Markku Reunanen, for the GC-MS analysis. The financial support from the Finnish Graduate School in Chemical Engineering (GSCE) is gratefully acknowledged. This work is part of the activities at the Åbo Akademi Process Chemistry Centre (PCC) within the Finnish Centre of Excellence Programme (2000–2005) by the Academy of Finland.

References

[1] T. Boger, A.K. Heibel, C.M. Sorensen, Ind. Eng. Chem. Res. 43 (2004) 4602.
[2] S. Steinigeweg, J. Gmehling, Ind. Eng. Chem. Res. 41 (2002) 5483.
[3] G. Kolb, V. Hessel, Chem. Eng. J. 98 (2004) 1.

[4] T. Salmi, P. Mäki-Arvela, E. Toukoniitty, A. Kalantar Neyestanaki, L.-P. Tiainen, L.-E. Lindfors, R. Sjöholm, E. Laine, Appl. Catal. A: Gen. 196 (2000) 93.
[5] Yu. Matatov-Meytal, M. Scheintuch, Appl. Catal. A: Gen. 231 (2002) 1.
[6] L. Kiwi-Minsker, I. Yuranov, V. Höller, A. Renken, Chem. Eng. Sci. 54 (1999) 4785.
[7] V. Höller, D. Wegricht, L. Kiwi-Minsker, A. Renken, Catal. Today 60 (2000) 51.
[8] E. Joannet, C. Horny, L. Kiwi-Minsker, A. Renken, Chem. Eng. Sci. 57 (2002) 3453.
[9] J. Aumo, J. Lilja, P. Mäki-Arvela, T. Salmi, M. Sundell, H. Vainio, D.Yu. Murzin, Catal. Lett. 84 (2002) 219.
[10] U.K. Singh, M.A. Vannice, J. Catal. 199 (2001) 73.
[11] P. Mäki-Arvela, L.-P. Tiainen, M. Lindblad, K. Demirkan, N. Kumar, R. Sjöholm, T. Ollonqvist, J. Väyrynen, T. Salmi, D.Yu. Murzin, Appl. Catal. A: Gen. 241 (2003) 271.
[12] G. Neri, L. Mercadante, A. Donato, A. Visco, S. Galvagno, Catal. Lett. 29 (1994) 379.
[13] A. Bernas, N. Kumar, P. Mäki-Arvela, N.V. Kul'kova, B. Holmbom, T. Salmi, D.Yu. Murzin, Appl. Catal. A: Gen. 245 (2003) 257.
[14] J. Aumo, S. Oksanen, J.-P. Mikkola, T. Salmi, D. Yu. Murzin, Ind. Eng. Chem. Res., in press.
[15] R.A. van Santen, P.W.N.M. van Leeuwen, J.A. Moulijn, B.A. Averill (Eds.), Catalysis: An Integrated Approach, Stud. Surf. Sci. Catal. 123 (1999).
[16] J. Hájek, D.Yu. Murzin, Ind. Eng. Chem. Res. 43 (2004) 2030.
[17] D.Yu. Murzin, E. Toukoniitty, J. Hajek, React. Kinet. Catal. Lett. 83 (2) (2004) 205.
[18] U.K. Singh, M.A. Vannice, J. Catal. 191 (2000) 165.
[19] M.L. Toebes, Y. Zhang, J. Hajek, T.A. Nijhuis, J.H. Bitter, A. Jos van Dillen, D.Yu. Murzin, D.C. Koningsberger, K.P. de Jong, J. Catal. 226 (2004) 215.