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Structured but not over-structured: Woven active carbon fibre matt catalyst

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Abstract

Catalytic hydrogenation of citral was studied on a Pt on active carbon cloth (ACC) catalyst, with a Pd in ionic liquid on ACC and a commercial Pt on active carbon powder catalysts. The metal was supported on active carbon either by direct impregnation or utilizing the ionic liquid as the intermediate phase on the carbon. The influence on selectivity and activity, of the most important variables, such as temperature and pressure, was investigated in a 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 very notable in the case of traditional impregnated catalysts, whereas the novel SSIL-TM (structured supported ionic liquid-transition metal) or Pd in ionic liquid on active carbon essentially maintained its activity in four consecutive batches. 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 fibre catalyst, 80–100% selectivity of carbonyl group hydrogenation was achieved at 15% conversion, whereas the Pd in ionic liquid on ACC catalyst displayed an impressive metal efficiency (citral-to-Pd ratio of 156, mol:mol), selectivity (45%) and activity (92% conversion at 140 min) as well as tolerance towards catalyst deactivation. Supported ionic liquids provide a new reaction environment for catalytic transformations.

Keywords: Active carbon; Fibre; Structured catalyst; Citral; Hydrogenation; Multiphase reactor; Ionic liquid

1. Introduction

One of the prominent trends in industry is certainly the quest for alternative, more structured catalytic systems instead of traditional slurry or fixed bed concepts. The driving force, naturally, is the quest for a more selective and economical process concept. A number of alternatives have been introduced, such as monoliths, Sulzer Katapak® elements, various net structures and stirrer structures containing catalytic coating/catalyst elements. A review by Matatov-Meytal and Sheintuch [1] introduces a series of different types of fibers and cloths for catalytic applications. One of the benefits common for all approaches is the elimination of often cumbersome and costly catalyst filtration step. Furthermore, more efficient usage of the catalytically active material and improved external mass transfer of reactants to the catalyst have been claimed. However, the capacity and efficiency (performance per time unit) of traditional systems is difficult to reach with any available structured alternative: the reason is that in case of, e.g. slurry systems, a huge overload of catalyst powder can be put into a reactor, whereas the structured systems (such as monoliths or coated static mixers) have macroscopic dimensions which limit the number of units that can be packed into a certain volume. Therefore, an intermediate solution – structured but not over-structured – where seemingly organized matt structure (active carbon cloth, ACC) packed relatively randomly within a reactor tube or inside a stirred tank, woven from small fibers and containing microscopic qualities (pore structure, active material) introduces a new perspective.

Traditionally, catalytically active transition metal particles have been introduced into the heterogeneous catalysts by means of various impregnation, precipitation, atomic layer epitaxy (ALE), etc., methods – or by means of direct

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mixing of the metal precursors (salts, organometallic complexes) during the synthesis of the solid material (i.e. sol–gel methods, zeolite synthesis etc.) – followed by (thermal) decomposition, restructuring and redistribution of the resulting active metal sites during calcination and reduction steps. Consequently, the catalytic properties of the resulting material are largely determined by the conditions prevailing under these post-treatment operations, such as the final temperature during calcinations and reduction, temperature gradients during these processes, reduction method (chemical or molecular hydrogen), oxygen effects, nature of the precursors etc. Moreover, the counter-deactivation characteristics – an important aspect in industrial operations – of a particular catalyst is depending not only of the process conditions applied but also on the details of the synthesis process and on the precursors used. Therefore, the development of a well-performing heterogeneous catalyst involves a tedious process upon which a huge amount of experimental work and characterization is required. We will hereby introduce a novel strategy for the preparation of structured (as well as non-structured) heterogeneous catalysts by means of an immobilized ionic liquid (IL) layer, into which the metallic transition metal species have been dissolved as illustrated by Fig. 1. The concept has been previously probed by few authors [2–7] but according to our best knowledge until now not in connection to structured heterogeneous catalysts. An ionic liquid is a ‘room temperature molten salt’ [8–9], simply a liquid composed entirely of ions. Typically, these novel materials consist of a relatively bulky organic cation (alkylimidazolium, alkylpyridinium, tetraalkylammonium, tetraalkylphosphonium, trialkylsulfonium, etc., derivatives) coupled to an inorganic anion (BF_4^-, PF_6^-, Cl^-, Br^-, $AlCl_4^-$, etc.) and have unique properties, such as a wide liquidus range (currently from −96 °C to +400 °C), unique solvation properties (at best 2:1 mol:mol solute:solvent, dissolution of materials that are difficult to dissolve, such as cellulose, high solubility of various industrially important gases like H_2, O_2, CO_2), non-flammability, extremely low vapour pressure, etc.

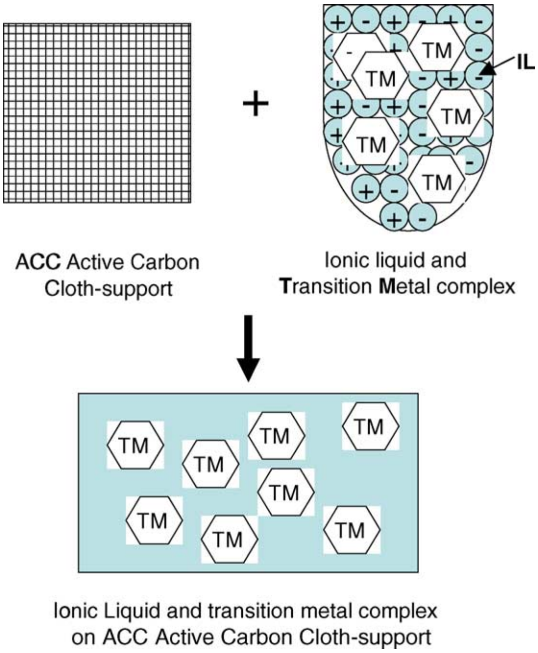

Fig. 1. The concept of ionic liquid and transition metal supported on an ACC support.

Various hydrogenation processes with molecular hydrogen are an important class of reactions that, especially in the case of fine chemical manufacturing, are often carried out by means of suspended slurry catalyst technology. Hereby, we investigated a model reaction utilizing a commercially available activated carbon matt. The carrier material was, consequently, loaded with the catalytically active transition metal catalyst. Citral, our model component, is a multi-unsaturated compound containing both an isolated and conjugated double-bond as well as a carbonyl group. Upon hydrogenation, numerous parallel and consecutive reactions typically occur simultaneously [10–13]. In previous studies from our group, Mäki-Arvela et al. [10] studied hydrogenation of citral in different alcohol solvents over Ru, Ni and Rh supported on alumina, silica and active carbon supports. Also, Raney–Nickel catalyst was studied upon use of 2-propanol solvent, in the presence and absence of acoustic irradiation in Mikkola et al. [14,15]. High selectivities for both citronellal and citronellol could be reached in alcoholic solvents, catalyst preparation procedure having a rather strong influence on the performance.

The hydrogenation products of citral are used in alimentary industry as flavoring ingredients, in pharmaceutical industries, in perfumery industry (perfumes), in household products (soaps) as well as in insect-repellent products (wristbands, towelettes, sprays and beads). The reaction scheme for citral hydrogenation is displayed in Fig. 2.

2. Experimental

2.1. Experimental setup

Hydrogenation of citral was carried out in a 600 ml (total volume) laboratory autoclave (Parr Inc., USA) equipped with a heating jacket. In the case of slurry catalyst, the reactor was equipped with a propeller mixer, coupled to a Rushton turbine for effective gas distribution, whereas in the case of active carbon matt catalysts (ACC), tailor-made internals were used: upon use of the ACC catalyst, the matt-structures were cut into suitable pieces and attached to the stirrer shaft as blades (Fig. 3). 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. In the case of impregnated catalyst, a volume of 450 ml of 0.017 M of citral (33.9/66.1 mol.% *cis*/*trans*, Lancaster 5460) was dissolved in analytical grade hexane (99%, Merck) without

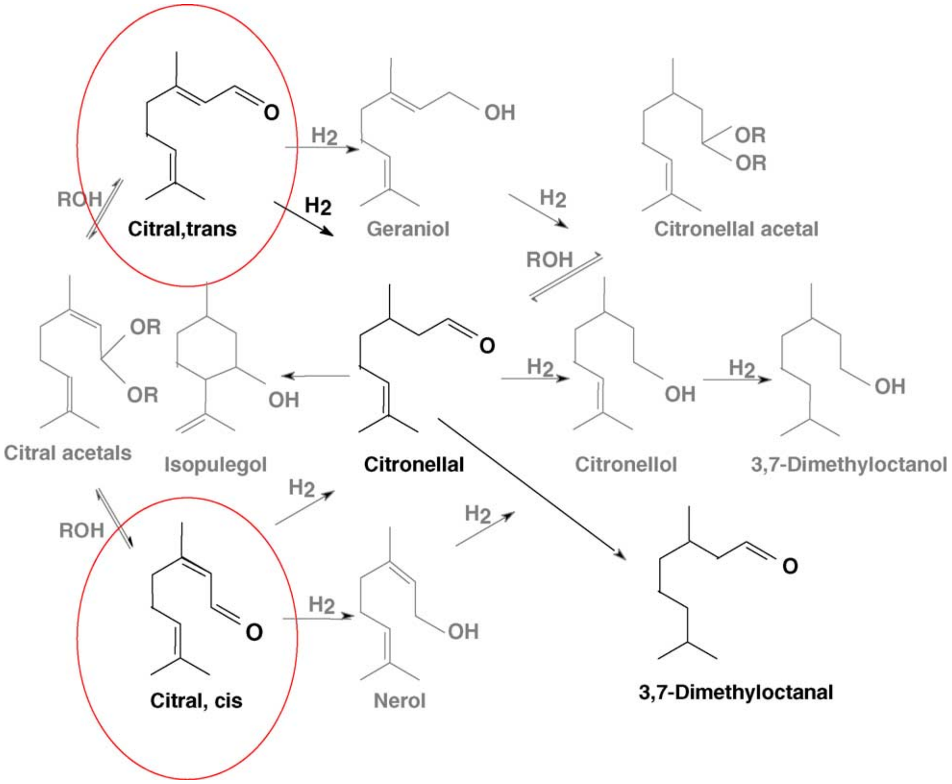

Fig. 2. The reaction scheme for citral hydrogenation. The species with dark were identified upon use of the novel SSIL-TM catalyst.

any further purification, whereas in the case of SSIL-TM (structured supported ionic liquid-transition metal) or Pd/IL/ACC (Pd in ionic liquid on active carbon cloth) catalyst, a volume of 250 ml of 0.08 M citral was hydrogenated. During the preheating of the catalyst and autoclave, the solution was saturated with hydrogen, for 10 min, in a bubbling unit. The reaction solution was injected into the reactor the pressure was adjusted to the desired level, thus commencing the reaction. The experiments were carried out at 6–51 bar of total pressure. The hydrogen partial pressure was calculated by taking into account the vapour pressure of hexane at different temperatures. Hydrogen gas used had a purity of 99.999% (AGA). Citral-to-metal ratio (mol/mol) was approximately 13 for the Pt/ACC catalyst, 156 in the case of Pd/IL/ACC catalyst and 62 for the 4.6 wt.% Pt/AC catalyst. The mass of citral in the experiments carried out with the Pt/ACC and Pt/AC catalysts was around 1.1 g, whereas in the case of Pd/IL/ACC catalyst it was around 3 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).

2.2. *Catalyst preparation and characterization*

Activated carbon cloth (woven active carbon fiber material) was utilized as a support upon preparation of catalysts. The microscopic diameter of the fibers (diameter 9.2 μm) and their high surface area facilitate rapid mass transfer. Although the specific surface area (BET) and pore volume of the material were high, 1500 m^2 and 0.63 cm^3/g (manufacturer data), respectively, the ACC (fiber carpet thickness 0.5 mm) has a very high mechanical strength (tensile strength 6 kg/50 mm). Woven active carbon cloth ACC-507-15 (Kynol^{TM}) (Fig. 4) 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). Upon preparation of the Pt/ACC catalyst, the pieces were washed with deionised water and dried overnight at 60 °C and impregnated in a aqueous solution of H_2PtCl_6 (Degussa) at pH 5, for approximately 4 h, followed by washing with deionised water. The impregnation method is commonly used for Pt catalysts [16]. After drying the catalyst cloths overnight, at 60 °C, they were attached to the stirrer and reduced in situ in flowing hydrogen, while heating 10 °C/min to 200 °C (2 h).

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 1530 equipped with a ThermoNORAN Vantage analyzer

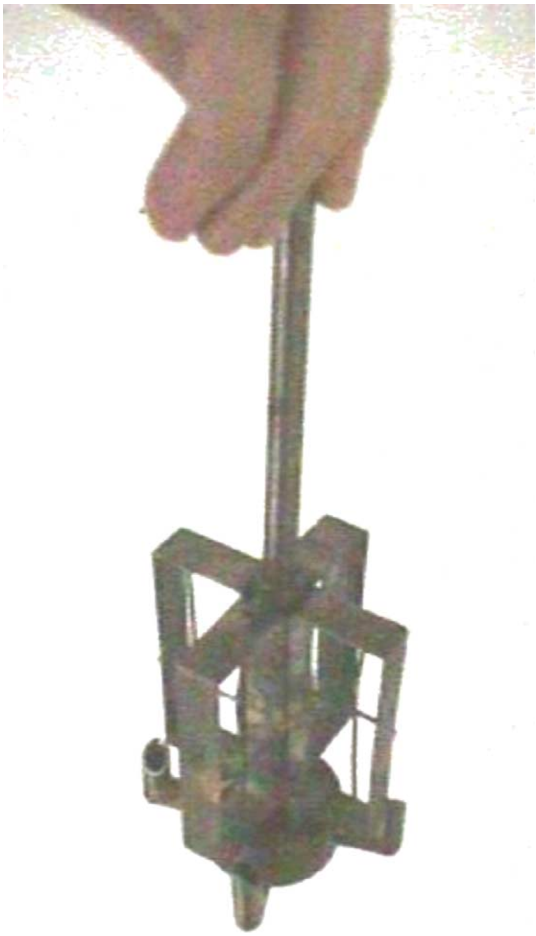

Fig. 3. Integrated gadget of a combined stirrer and catalyst holder.

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).

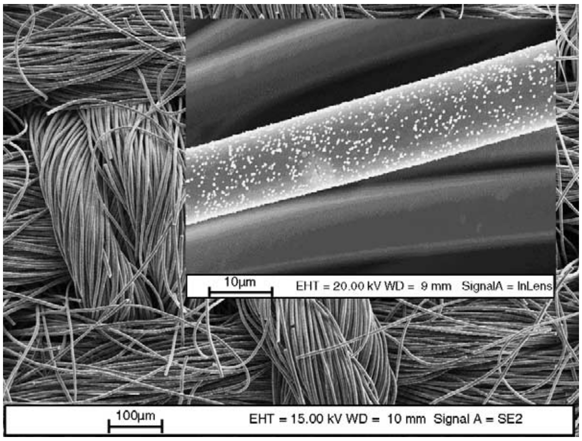

Fig. 4. SEM-images of a metal/C-fibre catalysts. The scale bars illustrate a distance of 100 and 10 μm in the large and small image, respectively.

The preparation of Pd/IL/ACC catalyst was a very straight-forward one: at first, the activated carbon cloth was dried for 1 h at 105 °C (1.11 g dry). In the meantime, 0.05 g of Pd acetylacetonate salt (Aldrich, 99%) as well as 0.1512 g of the ionic liquid (Merck, 98%) were dissolved in a small amounts (5 + 5 ml) of extra dry acetone (Acros, less than 0.005 ppm water). Thereafter, the acetone solutions were mixed and poured on the hot ACC. The amount of acetone was adjusted to 10 ml in order to obtain an 'incipient-wetness' resembling procedure. Consequently, the wetted ACC was placed into the 105 °C oven for 10 min to obtain a seemingly dry cloth, upon which excess acetone evaporated, leaving behind the non-volatile ionic liquid with dissolved Pd salt. After this the catalyst cloths were installed onto the stirrer into the autoclave. Upon exposure to molecular hydrogen, it is likely that metallic, ionic liquid stabilized nano-particles are formed during the mild reduction period [2–7]. More details and characterization of the novel types of Pd/IL/ACC or SSIL-TM (structured supported ionic liquid-transition metal) catalysts will be introduced elsewhere and only the main lines of the catalyst performance are described here [17]. After incorporation of the active ionic liquid/metal precursor solution into the active carbon cloth (1.3 wt.% Pd (metallic) on IL/ACC, 11.6 wt.% IL/ACC), the catalyst was attached to the stirrer and reduced at 100 °C in flowing hydrogen for 1 h. The immobilization is facilitated simply by the fact that the ionic liquid is non-soluble in hexane (the bulk solvent) and, therefore, remains attached inside the pore structure of the ACC. Naturally, this restricts the choice of solvents and other immobilization methods (such as covalent bounding of either the anion or cation) need to be used in case the ionic liquid dissolved into the bulk solvent.

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

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 fibres. The Pt content was 5.9 wt.% and that of Pd 1.3 wt.% on the fibre cloth catalyst. A Pt loading of 4.6 wt.% on the commercial powder catalyst was verified by ICP-MS. Nitrogen physisorption was performed and the fresh ACC, fresh Pt/ACC and spent Pt/ACC specific Dubinin and BET surface areas as well as specific Dubinin micro-pore volumes and BET pore volumes can be found in our earlier publication [18]. 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.%) the value was almost identical [19].

3.2. Kinetic experiments

Because of the high surface area and small fibre diameter (Ø = 9.2 μm) of the ACC catalyst, rapid mass transfer is facilitated. Furthermore, the effectiveness factor, $\eta_{\mathrm{eff}} \rightarrow 1$, calculated and based on the procedure reported by Santen et al. and Hájek and coworkers [20–21] assured that hydrogenation reactions over ACC catalysts were conducted in kinetic regime. In the case of Pt/ACC catalyst, a series of four consecutive experiments were performed at different experimental conditions (T/°C/P/bar): 80/5, 80/10, 100/5 and 80/5. Upon the use of Pd/IL/ACC catalyst, the experiments were performed at the following conditions (T/°C/P/bar): 100/10, 100/2, 120/10 and 100/5. In between the batches, 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/ACC fibre catalyst favored the production of geraniol, nerol, and citronellal, at a constant geraniol/nerol ratio of 2.3 and neither affected by the deactivation of the catalyst nor by the conversion. 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. 5. Deactivation could be due to carbonaceous deposits on the surface of the support [22]. 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 [23].

The Pd/IL/ACC catalyst performed well already in the first kinetic experiment, as demonstrated by Fig. 6. The highest selectivity to citronellal, 45%, was achieved at approximately 140 min, corresponding to a citral conversion of 92%. Therefore, approximately half of the starting material was converted into the valuable intermediate hydrogenation product, citronellal (see the scheme, Fig. 2). The following series of five consecutive experiments were performed at different experimental conditions (T/°C/P/bar): 100/10, 100/2, 120/10, 100/5 and, finally, again 100/10. Lower hydrogen pressures and temperatures had a dramatic effect on the reaction rate but, surprisingly, little effect on the selectivity which remained very similar regardless of the temperature and pressure. It became evident that even higher temperatures and pressures should be tried.

It is noteworthy that the Pd metal content of the catalyst (0.017 g or 1.3 wt.%), as well as that of the ionic liquid (0.15 g or 11.6 wt.%) which plays an essential role in the catalyst performance, were very low. Moreover, taking into account that the citral-to-Pd – ratio was 156 (mol:mol), especially compared to the citral-to-Pt – ratio of 62 in the commercial catalyst, this novel type of catalyst performed remarkably well – even more so, when comparing the maximum conversion level of 49% for the industrial catalyst, which was achieved after 6.5 h only. If looking at the deactivation behavior of the Pd/IL/ACC catalyst, slow deactivation was observed, since the fifth consecutive batch still displayed fair

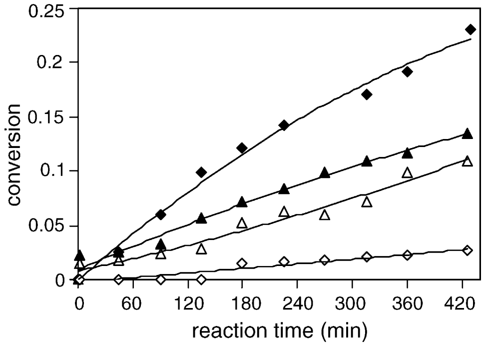

Fig. 5. The conversion as a function of reaction time in the hydrogenation of citral over a 5.9 wt.% Pt/ACC fibre catalyst at 80 °C and 5 bar (◆), 80 °C and 10 bar (▲), 100 °C and 5 bar (△) and 80 °C and 5 bar (◇). Consecutive experiments were performed in that order.

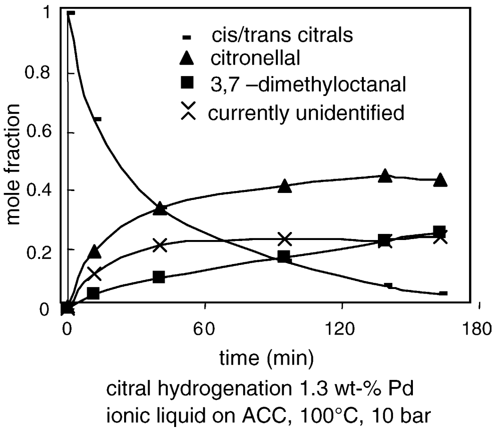

Fig. 6. The mole fractions of the components as a function of time upon hydrogenation of citral with Pd/IL/ACC catalyst at 100 °C and 10 bar.

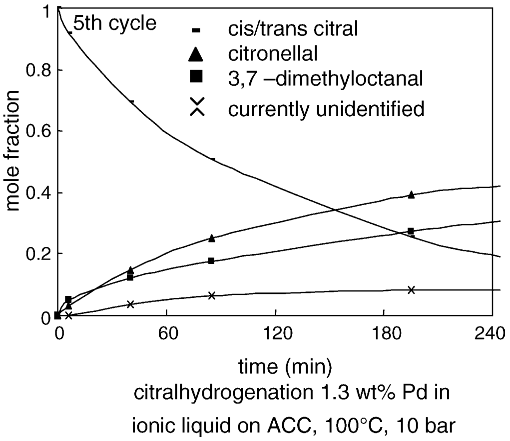

Fig. 7. The mole fractions of the components as a function of time upon hydrogenation of citral with Pd/IL/ACC catalyst at 100 °C and 10 bar, 5th cycle.

performance: 39% selectivity for citronellal and 75% conversion at 195 min. (Fig. 7). Moreover, a new activation procedure (elevated temperature and hydrogen flow) very well could rejuvenate the catalyst, since accumulated impurities probably affect the catalytic performance. Therefore, a more thorough study of this type of catalyst systems will be presented in a future publication. Also, further challenges reside in the identification of the insofar unknown hydrogenation products.

With the commercial 4.6 wt.% Pt/AC powder catalyst (mean particle size 16 μm), the following consecutive experiments were performed (T/°C/P/bar): 80/5, 100/5, 100/10 and 80/5. The catalyst was left in the reactor under hydrogen pressure in order to avoid the oxidation of the catalyst before the next experiment. The conversion values reached after 6.5 h decreased from 49% (1st batch) to13% (4th batch), respectively, illustrating remarkable catalyst deactivation. The Pt/AC powder catalyst facilitated a wider product distribution, compared to the fibre catalysts and favored the production of citronellal with a selectivity of 35–40% in each experiment, independent of pressure and temperature. In the fourth experiment, at 80 °C and 5 bar, the highest overall selectivity to geraniol and nerol (44%) was achieved at 8% conversion of citral.

4. Conclusions

The results from the kinetic experiments demonstrated the feasibility of utilizing woven active carbon fibres as supports in three-phase metal catalyzed hydrogenation of the α,β-unsaturated aldehyde, citral. The woven fibre catalyst prepared in line with traditional heterogeneous catalyst preparation procedures 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 hydrogenation products. Possible limitations for application of Pt/ACC catalyst are associated with deteriorating activity as a pronounced deactivation was observed for this type of fibre catalyst. However, the promising performance of the novel SSIL-TM (structured supported ionic liquid-transition metal) catalyst inspires us to advance further into this direction. Moreover, for this catalyst, the optimum conditions of operation need more exploration. Moreover, the remarkably easy preparation (and activation) procedure that will be introduced in a future publication brings forth entirely new prospects in the feasibility of utilizing ionic liquids in heterogeneous catalysis.

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References

[1] Y. Matatov-Meytal, M. Sheintuch, Appl. Catal. A 231 (2002) 1.
[2] M.H. Valkenberg, C. deCastro, W.F. Hölderich, Green Chem. 4 (2002) 88.
[3] B. Gadenne, P. Hesemann, J.J.E. Moreau, Chem. Commun. 15 (2004) 1768.
[4] R.T. Carlin, J. Fuller, Chem. Commun. (1997) 1345.
[5] C.P. Mehnert, Chem. Eur. J. 11 (1) (2004) 50.
[6] A. Riisager, P. Wasserscheid, R. van Hal, R. Fehrmann, J. Catal. 219 (2003) 452.
[7] J. Dupont, G.S. Fonseca, A.P. Umpierre, P.F.P. Fichtner, S.R. Teixeira, J. Am. Chem. Soc. 124 (2002) 4228.
[8] R. Sheldon, Chem. Commun. (2001) 2399.
[9] H. Olivier-Bourbigou, L. Magna, J. Mol. Catal. A: Chem. 182–183 (2002) 419.
[10] P. Mäki-Arvela, L.-P. Tiainen, N.A. Kalantar, R. Sjöholm, T.-K. Rantakylä, E. Laine, T. Salmi, D.Y. Murzin, Appl. Catal. A 237 (2002) 181.
[11] J.-P. Mikkola, T. Salmi, P. Mäki-Arvela, J. Aumo, J. Kuusisto, Catal. Org. React. 8 (2000) 91.
[12] U.K. Singh, M.A. Vannice, J. Catal. 199 (2001) 73.
[13] G. Neri, L. Mercadante, A. Donato, A. Visco, S. Galvagno, Catal. Lett. 29 (1994) 379.
[14] J.-P. Mikkola, T. Salmi, P. Mäki-Arvela, J. Aumo, J. Kuusisto, Catal. Org. React. 8 (2002) 91.
[15] J.-P. Mikkola, B. Toukoniitty, E. Toukoniitty, J. Aumo, T. Salmi, Spec. Issue Ultrason. Sonochem. 11 (2004) 233.
[16] A. Bernas, N. Kumar, P. Mäki-Arvela, N.V. Kul'kova, B. Holmbom, T. Salmi, D.Y. Murzin, Appl. Catal. A: Gen. 245 (2003) 257.
[17] J.-P. Mikkola, et al., unpublished results.
[18] J. Aumo, S. Oksanen, J.-P. Mikkola, T. Salmi, D.Yu. Murzin, Catal. Today 102–103 (2005) 128–132.
[19] J. Aumo, S. Oksanen, J.-P. Mikkola, T. Salmi, D. Yu. Murzin, Ind. Eng. Chem. Res. 44 (14) (2005) 5285–5290.
[20] R.A. Van Santen, P.W.N.M. Van Leeuwen, J.A. Moulijn, B.A. Averill (Eds.), Catalysis: an integrated approach, 2nd revised and enlarged edition, Stud. Surf. Sci. Catal. (1999) 123.
[21] J. Hájek, D.Y. Murzin, Ind. Eng. Chem. Res. 43 (2004) 2030.
[22] D.Y. Murzin, E. Toukoniitty, J. Hájek, React. Kinet. Catal. Lett. 83 (2) (2004) 205.
[23] U.K. Singh, M.A. Vannice, J. Catal. 191 (2000) 165.