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Alkaline modifiers as performance boosters in citral hydrogenation over supported ionic liquid catalysts (SILCAs)

Eero Salminen[a,*], Pasi Virtanen[a], Krisztián Kordás[b], Jyri-Pekka Mikkola[a,c]

[a] *Industrial Chemistry and Reaction Engineering, Process Chemistry Centre, Åbo Akademi University, FI-20500 Åbo-Turku, Finland*
[b] *Microelectronics and Materials Physics Laboratories, EMPART Research Group of Infotech Oulu, University of Oulu, P.O. Box 4500 FI-90014 Oulu, Finland*
[c] *Technical Chemistry, Department of Chemistry, Chemical–Biological Center, Umeå University, SE-90187 Umeå, Sweden*

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ABSTRACT

Supported ionic liquid catalysts (SILCAs) consist of nano-scale catalytic species immobilized in an ionic liquid layer which, in turn, is immobilized on a solid support. In this work, novel SILCAs containing various inorganic alkaline modifiers (e.g. potassium hydroxide) were prepared and applied in citral hydrogenation reactions. The supported ionic liquid catalyst systems demonstrated enhanced reaction rates and improved selectivities toward citronellal in citral hydrogenation. With the addition of an alkaline modifier into ionic liquid layer, the catalyst selectivity increased from 16% to 74%. In fact, a highly selective reaction route toward citronellal was accomplished.

1. Introduction

Ionic liquids (ILs) may be referred as molten salts in which either the cation or the anion is of organic origin. Because of their tunable solvation properties, thermal stability and usually low vapor pressure, ionic liquids have already found a number of different application areas such as electrolytes in supercapacitors, batteries and in solar cells; solvents for lignocellulose species; synthesis media for unconventional metal alloys, just to mention a few [1,2]. Another important evolving field of ionic liquids is in heterogeneous catalysis, where those may act as catalyst but also as solvent at the same time [3,4]. The concept of catalysis in supported ionic liquids involves catalytically active species immobilized in a thin layer of ionic liquid, which in turn, is immobilized on a solid support material. The catalytically active species can be solid metal nanoparticles that are suspended or homogeneous catalyst (metal complexes) or even enzymes dissolved in ionic liquids [5–7]. One of the benefits for supported ionic liquid catalysis is the elimination of difficult and costly catalyst separation from the liquid reaction matrix [5,6].

Immobilization of ionic liquids can be achieved by different methods such as simple impregnation, grafting, sol–gel method or polymerization [8–11]. Immobilization of ionic liquids via impregnation of the support material with an ionic liquid is a simple and straightforward route toward supported catalysts. An ionic liquid and a metal compound are both dissolved in a molecular solvent (e.g. acetone) which is then poured over the solid support material. The molecular solvent is evaporated, leaving only a layer of ionic liquid on the support, into which metal compounds are dissolved. In addition, complexes, modifiers and other active species can be dissolved into the ionic liquid layer [12]. Organometallic compounds (e.g. $Pd(acac)_2$) can be reduced to solid metallic nanoparticles e.g. by means of a hydrogen treatment under elevated temperatures as proposed earlier for supported ionic liquid catalyst (SILCA) materials (Fig. 1) [8,12]. Though the concept works quite well for a number of different reactions, two limitations of supported IL catalysts must be mentioned. First, the reaction temperature is limited by the decomposition temperature of the ionic liquid and thermal stability of other species. Secondly, if the ionic liquid is not covalently bonded to the surface of support, the ionic liquid and the organic phase must form an immiscible biphasic system meaning that the ionic liquid should not be miscible with the reaction solvent [13]. Because the ionic liquid is non-covalently immobilized on the active carbon support, the leaching of the catalytic and ionic media must be investigated.

Selective hydrogenation of α,β-unsaturated aldehydes (e.g. citral) is a very important reaction in the preparation of different kinds of products and intermediates in fine chemical industry. Citral and its hydrogenation products are widely used in the fine chemical and perfumery industries [14]. The activity boost by ionic liquids has been observed in the hydrogenation of alkenes, citral and other α,β-unsaturated aldehydes [6,8]. The ionic liquids can influence the concentrations of compounds and intermediates on the surface of the solid catalyst [13]. Ionic liquids have different hydrogen

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* Corresponding author.
E-mail address: eesalmin@abo.fi (E. Salminen).

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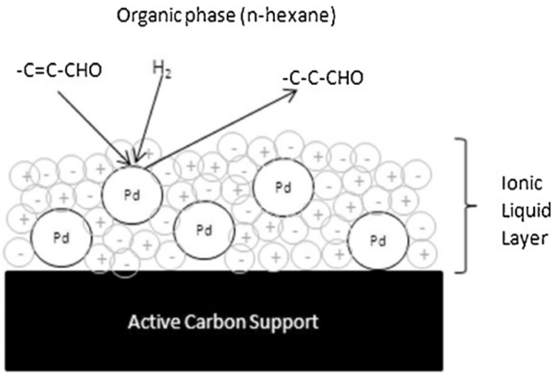


Fig. 1. The principle illustration of supported ionic liquid catalyst used in hydrogenation of citral. Palladium nanoparticles residing in an ionic liquid layer immobilized on an active carbon cloth (ACC).

solubilities and reactant solubilities. This might be one explanation for the selectivity and activity differences observed for systems comprising of various ionic liquids [6,8]. The reason for improved activity could also be that the ionic liquids are non-coordinating solvents and that is why the reactants have a better access to the catalytically active metal particles [6]. It has to be noted that the choice of ionic liquid anion can determine the coordinative or non-coordinative character of the ionic liquid. Preparation of metal nanoparticles in ionic liquids is preferred because the ionic liquid acts as a stabilizer. Also, stabilization of metal nanoparticles with ionic liquids to suppress aggregation can be an important factor contributing to the catalytic activity [15]. Supported ionic liquid catalysts are based on the stabilizing effect of ionic liquids.

2. Experimental

2.1. Catalyst preparation

A simple straightforward catalyst preparation method was applied [5]. Approximately 150 mg of ionic liquid and 50 mg of palladium acetylacetonate (Pd(acac)$_2$) (Aldrich, 99%) were both dissolved into acetone (Merck, p.a.). With alkaline-modified catalysts, an alkaline modifier (e.g. KOH or Na_2CO_3) was dissolved into methyl alcohol (Merck, p.a.). The mole fraction of KOH and ionic liquid was 4:1 whereas the mole fraction of Na_2CO_3 and ionic liquid was 2:1. The solutions were mixed together and then poured over a pre-dried active carbon cloth (ACC) Kynol® (approximately. 1.2 g). The wetted catalysts were kept in an oven, at 80 °C, for 2 h so that all solvents (acetone and methyl alcohol) evaporated. As the next step the SILCAs were pre-reduced prior to the hydrogenation experiments in a high-pressure semi-batch reactor (Parr Inc.). Pretreating was performed at 120 °C under hydrogen flow of 10 bar. Consequently, the catalyst containing palladium nanoparticles in an ionic liquid immobilized on ACC was obtained. The ionic liquids used in the preparation of SILCAs were N-butyl-4-methylpyridinium tetrafluoroborate ([C_4C_1Py][BF_4], Merck, 98%) and N-(3-hydroxypropyl)pyridinium bis(trifluoromethylsulfonyl)imide ([(C_3OH)Py][N(CF_3SO_2)$_2$], Merck, 98%), stored under inert atmosphere and used without further purification.

2.2. Hydrogenation experiments

The supported ionic liquid catalysts were used in the hydrogenation of citral (Aldrich, 95%). Hydrogenation experiments were performed in a semi-batch reactor (Parr Instrument Company). The total volume of the reactor was 600 ml whereas the effective liquid volume was 250 ml. The temperature and stirring rate were controlled by a Parr 4843 control unit (Watlow control series 982). All experiments were performed at a constant pressure and temperature. Approximately 3 g of citral (0.02 mol) was dissolved in 250 ml of n-hexane (Merck, >99%). In the beginning of each experiment, the reactor was heated to a desired temperature and, at the same time, the hydrogen pressure was also adjusted to desired level. After the citral solution was injected to the reactor, the stirring was commenced and this was considered as the starting point for the reaction.

Citral hydrogenation products were identified by means of gas chromatography (Hewlett Packard 6890 GC with FI detector). In addition, a gas chromatograph coupled to a mass-spectrometer (Agilent 6980N GC with Agilent 5973 MS detector) was used to identify the peaks of citral hydrogenation products. The peaks in the chromatogram were identified with the following reference substances: (±)-citronellal (Fluka, 80–90%), nerol (Fluka, >90%), geraniol (Alfa Aesar, 97%), (+)-neomenthol (Fluka, 98.5%), (−)-isopulegol (Aldrich, 99%), tetrahydrogeraniol (Aldrich, 99%), menthol (Aldrich, 99%), (+)-isomenthol (Fluka, >99%), and (±)-β-citronellol (90–95%, Fluka). The progress of citral hydrogenation reaction was monitored by taking samples from the reactor and analyzing them by means of gas chromatography. In the case of standard samples and samples taken from reactor, 500 μl of internal standard (0.02 M cyclohexanone in cyclohexane) was added into a 500 μl of sample. The GC column used was an Agilent DB-5 with a length of 60 m, inner diameter of 0.32 mm and a film thickness of 1 μm. The following temperature program was applied: 10 min at 100 °C, then raised 5 °C/min to 160 °C. Temperature was then held 10 min at 160 °C. At the end the temperature was increased 13 °C/min to 200 °C and kept constant for 1 min.

2.3. Catalyst characterization

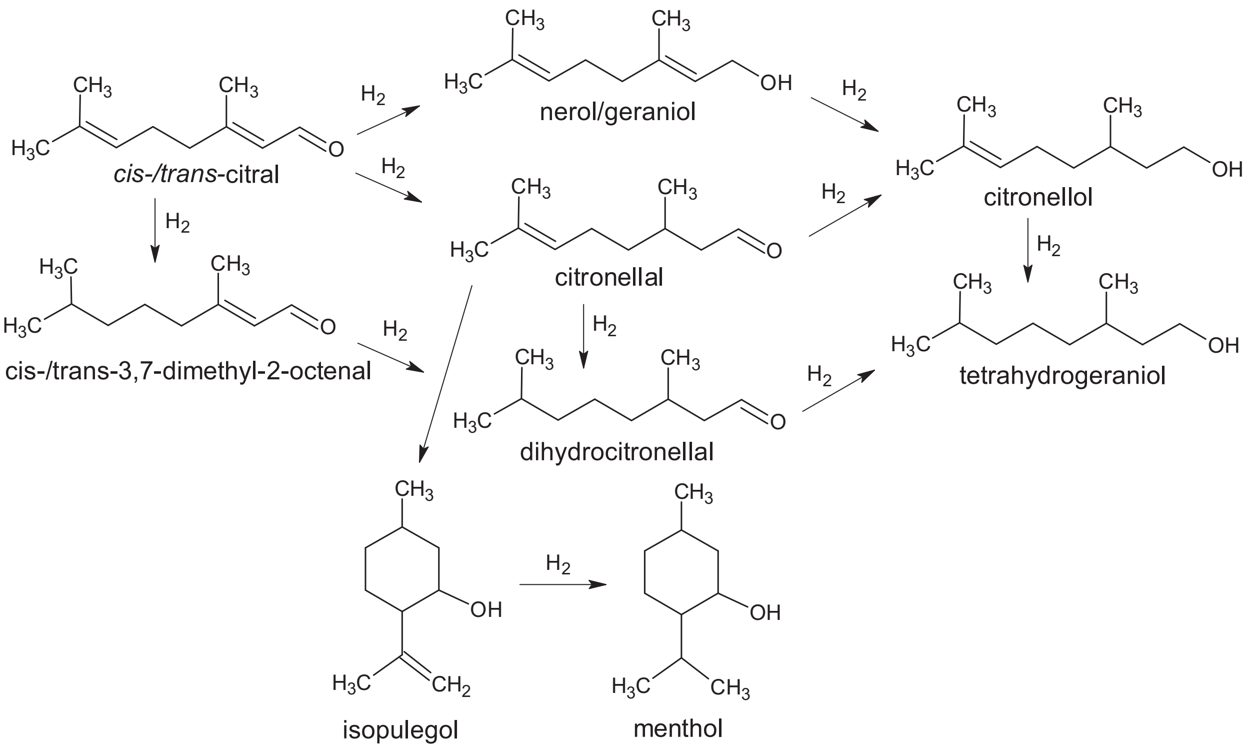
Both fresh and spent catalysts were analyzed by means of energy-filtered transmission electron spectroscopy (EFTEM Leo912 OMEGA, 120 kV, LaB_6 filament). Prior to the characterization, the samples were crushed, dispersed in n-hexane or in water and then drop cast on copper grids (coated with formvar). The leaching behavior of ionic liquids has been already determined in our earlier studies [8]. Accumulation of different hydrogenation decomposition products on the catalyst surface was studied by extracting spent catalyst with 2-propanol and analyzing this solution by means of gas chromatography, as shown in the case of the citral hydrogenation samples.

The surface area and micropore volume of the catalysts were characterized by means of automatic physisorption–chemisorption apparatus (Carlo-Erba Instruments, Sorptometer 1900). Dollim.–Heal method was used to calculate the micropore volume of the catalysts whereas the Dubinin method was used to calculate the surface area of the catalysts.

3. Results and discussion

3.1. Catalyst activity and selectivity

Citral hydrogenation experiments were carried out in a semi-batch reactor. The stirring rate was adjusted to 1200 rpm in order that the external mass-transfer limitations from the bulk liquid to the catalyst surface were suppressed, as confirmed by our earlier studies [8]. The hydrogenation of citral was studied over unmodified and alkali-modified supported ionic liquid catalysts. In all experiments, total conversion of citral was obtained. The plausible citral hydrogenation reaction scheme is presented in Scheme 1.



Scheme 1. Citral hydrogenation reaction sequence.

3.1.1. *The effects of alkaline modifiers*

Alkaline-modified supported ionic liquid catalysts demonstrated enhanced selectivities toward citronellal. In the case of the catalyst containing the ionic liquid [C_4C_1Py][BF_4] and Na_2CO_3 as the alkali modifier, the main product was the intermediate reaction product citronellal. The addition of an alkaline modifier increased the selectivity of citronellal from 17% to 48%. For the case when the catalyst contained the ionic liquid [(C_3OH)Py][N(CF_3SO_2)$_2$], the addition of an alkaline modifier increased the selectivity of citronellal from 10% to 43% (Fig. 2). Further, for KOH-modified catalyst, at lower hydrogen pressure, the selectivity of citronellal increased from 16% to 74% (Fig. 3). Similar results were obtained when using sodium hydroxide as an alkaline modifier. As the pressure was lowered to 5 bar, more citronellal was obtained than at higher pressure (10 bar). This is predictable, since lowering the hydrogen pressure increases the yield of less hydrogenated products (e.g. citronellal). However, the selectivity improvement was much higher than what has been noted with unmodified SILCA. In the case of the catalyst containing Pd in ionic liquid [(C_3OH)Py][N(CF_3SO_2)$_2$] on ACC, the selectivity of citronellal was improved from 10% to 16% when H_2-pressure was lowered from 10 bar to 5 bar.

Sodium carbonate modified supported ionic liquid catalyst Pd in N-butyl-4-methylpyridinium tetrafluoroborate ([C_4C_1Py][BF_4]/Na_2CO_3) on ACC was the most active catalysts studied in terms of initial reaction rate (Fig. 4). For the Na_2CO_3-modified SILCA, the total conversion of citral was almost nine times faster than in the case of the unmodified SILCA (Fig. 5). Also, the conversion of citral was over four times faster with KOH-modified SILCA (Pd in N-(3-hydroxypropyl)pyridiniumbis (trifluoromethylsulfonyl)imide [(C_3OH)Py][N(CF_3SO_2)$_2$]/KOH)

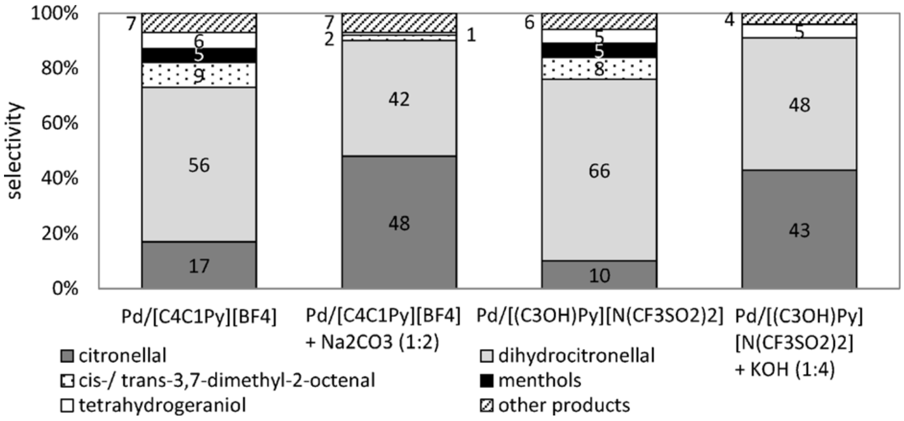


Fig. 2. Products in the hydrogenation over alkaline-modified supported ionic liquid catalysts after total conversion. The alkaline-modified SILCAs were compared to unmodified ones. The alkaline modifiers were Na_2CO_3 and KOH, respectively. The reaction conditions were $T = 100\,^{\circ}C$, $p(H_2) = 10$ bar. Other products are compounds from cracking and dehydration of citral and its hydrogenation products.

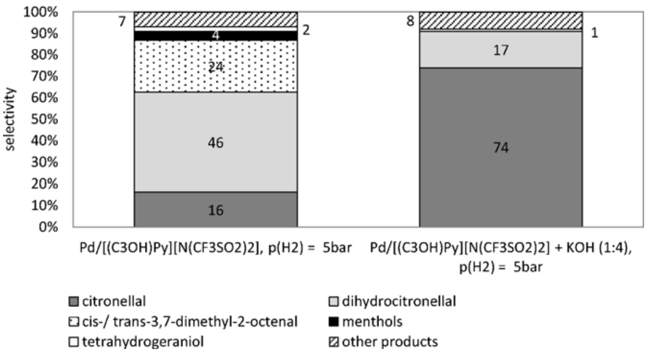


Fig. 3. Product distribution in the hydrogenation of citral after total conversion (approximately after 5 h). The catalysts used in the hydrogenation of citral were Pd in $[(C_3OH)Py][N(CF_3SO_2)_2]$ on ACC and Pd in $[(C_3OH)Py][N(CF_3SO_2)_2]$/KOH (1:4) on ACC. The reaction conditions were $T = 100\,^{\circ}C$, $p(H_2) = 5$ bar. Other products are compounds from cracking and dehydration of citral and its hydrogenation products.

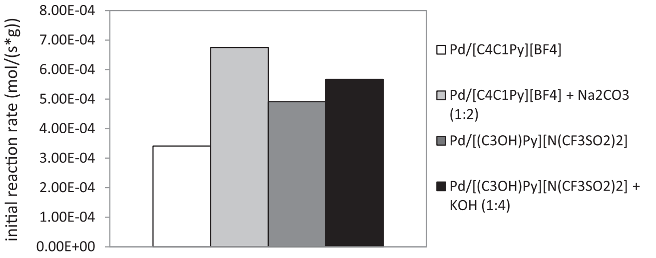


Fig. 4. Comparison of the initial reaction rates for the different alkaline-modified supported ionic liquid catalysts. The initial reaction rates were calculated at 5 min from commencing the reaction. All reactions presented here were carried out at $T = 100\,^{\circ}C$ and $p(H_2) = 10$ bar. The catalysts were Pd in an ionic liquid on ACC. The alkaline modifiers applied were Na_2CO_3 and KOH. The ionic liquids used in SILCAs were N-butyl-4-methylpyridinium tetrafluoroborate ($[C_4C_1Py][BF_4]$), and N-(3-hydroxypropyl)pyridinium bis(trifluoromethylsulfonyl)imide ($[(C_3OH)Py][N(CF_3SO_2)_2]$).

than with the unmodified SILCA (Fig. 6). In contrast to selectivity boost, no activity boost by alkaline modifiers was obtained when the hydrogen pressure was lowered from 10 bar to 5 bar.

It has been reported earlier that the heterogeneous Pd/C or Pd/SiO_2 catalysts coated with the dicyanamide based ionic liquid ($[C_4C_1IM][N(CN)_2]$) are highly selective toward citronellal (selectivities close to 100%) [16,17]. Claus et al. have proposed that the dicyanamide based ionic liquid ($[C_4C_1IM][N(CN)_2]$) takes the role of a basic promoter [16]. The selectivity of dicyanamide based ionic liquid catalyst was better than with alkaline-modified catalysts whereas the total conversion time of citral was faster with alkaline-modified SILCAs than with dicyanamide based ionic liquid catalyst.

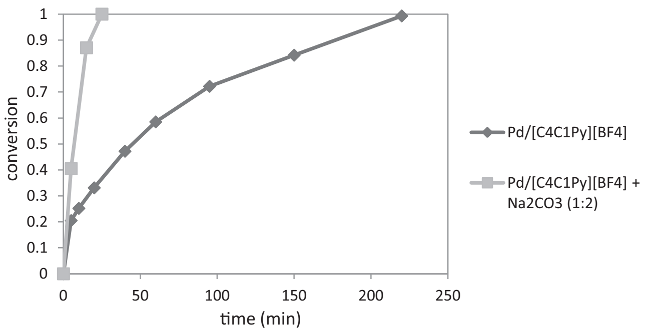


Fig. 5. Citral conversion to products as a function of time. The catalysts were Pd in $[C_4C_1Py][BF_4]$ on ACC and Pd in $[C_4C_1Py][BF_4]/Na_2CO_3$ (1:2) on ACC. The reaction conditions were $T = 100\,^{\circ}C$, $p(H_2) = 10$ bar.

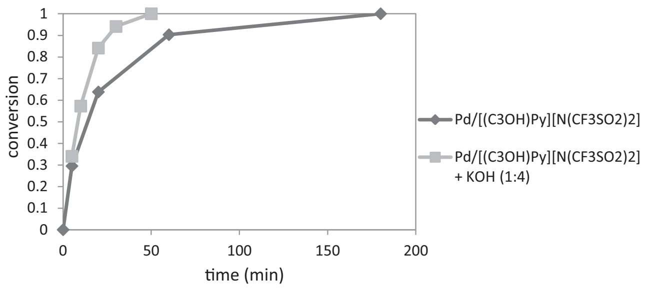


Fig. 6. Citral conversion to products as a function of time. The catalysts were Pd in N-(3-hydroxypropyl)pyridiniumbis (trifluoromethylsulfonyl)imide ($[(C_3OH)Py][N(CF_3SO_2)_2]$) on ACC and Pd in N-(3-hydroxypropyl)pyridiniumbis (trifluoromethylsulfonyl)imide/KOH (1:4) on ACC. The reaction conditions were $T = 100\,^{\circ}C$, $p(H_2) = 10$ bar.

We also tested how alkaline modifiers themselves affect the catalyst activity and selectivity without any ionic liquid present. We found out that alkaline-modified heterogeneous catalysts demonstrated similar behavior as alkaline-modified supported ionic liquid catalysts in terms of selectivity. In the case of the alkaline-modified heterogeneous catalysts, the selectivity toward citronellal was enhanced even though the selectivity was much lower than in the case of SILCAs (Fig. 7). However, the activity boost observed in the case of the alkaline-modified supported ionic liquid catalysts was surprising since the addition of KOH did not enhance the activity or citral conversion when using a heterogeneous catalysts Pd on ACC. It seems that the solid KOH does not affect the activity of classical heterogeneous catalysts in our model system. In SILCA, KOH is dissolved in the ionic liquid resulting in alkaline ionic liquid/base mixture thus having a significant influence on the catalyst activity. The presence of alkaline ionic liquid/base mixture can be observed from the decomposition temperatures of SILCAs. With KOH-modified SILCA, the decomposition temperature of IL/base mixture is approximately 140 °C whereas the IL ($[(C_3OH)Py][N(CF_3SO_2)_2]$) of unmodified SILCA decomposes approximately at 380 °C.

It has been observed earlier in citral hydrogenation that a catalyst consisting of palladium on carbon modified with an aqueous alkaline solution (KOH) leads to enhanced selectivities toward citronellal without improving the reaction rate [18]. It was previously suggested that high solubility of hydrogen in ionic liquids could increase the reaction rates in e.g. hydrogenation reactions. This is not the case since the hydrogen solubility in ionic liquids is lower than in many molecular solvents [19].

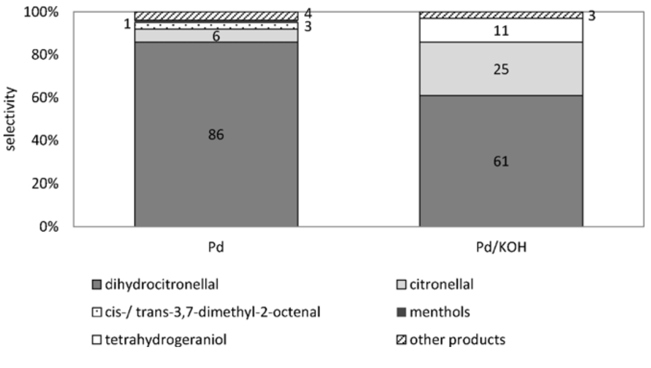


Fig. 7. Product distribution in citral hydrogenation after total conversion (approximately after 4 h). The selectivities of alkaline-modified heterogeneous catalyst and unmodified heterogeneous catalyst were compared. The 'classical' heterogeneous catalyst used was palladium on ACC. The reaction conditions were $T = 100\,^{\circ}C$, $p(H_2) = 10$ bar. Other products are compounds from cracking and dehydration of citral and its hydrogenation products.

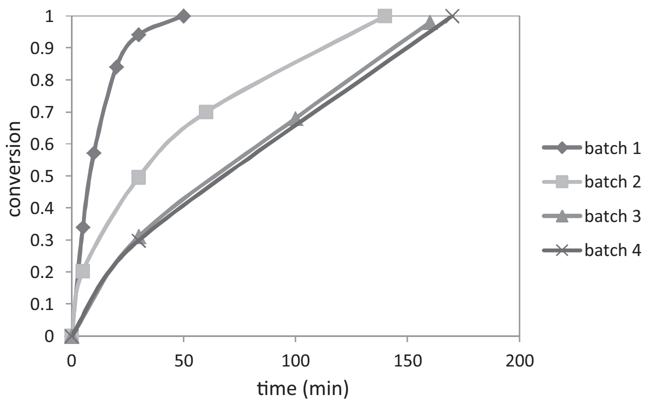


Fig. 8. Deactivation of the catalyst Pd in N-(3-hydroxypropyl)pyridiniumbis (trifluoromethylsulfonyl)imide/KOH (1:4) on ACC during four consecutive batches. Citral conversion to products is presented as a function of time. The reaction conditions were $T = 100\,^{\circ}\mathrm{C}$, $p(H_2) = 10$ bar.

Further, Pak et al. stated that an addition of an alkaline modifier (e.g. Na_2CO_3) changes the surface properties and adsorption/desorption, with respect to various unsaturated groups [20]. We assume that the reason for the improved selectivity in our case is of similar nature. In the same paper the authors reported that soda (Na_2CO_3) addition to a catalyst ($Ni–Cr_2O_3$) increases the citral concentration on the catalyst surface. Sodium adsorbs on the surface of the metallic catalyst and has an influence to the adsorption of citral and its selectivity [20]. At lower hydrogen pressures (5 bar), reactants were less soluble to ionic liquids than at higher pressures. Moreover, the hydrogen concentration in the ionic liquid layer is low. As the hydrogen pressure was lowered to 5 bar, no activity boost by alkaline-modifiers was obtained. We assume that the activity boost effect of an alkaline modifier is dependent on hydrogen pressure. The influences of a modifier on citral adsorption and hydrogen adsorption are weaker at lower pressures. Ionic liquid also influences to the adsorption of hydrogen.

3.1.2. Deactivation of the catalysts

As the sample system, Pd in $[(C_3OH)Py][N(CF_3SO_2)_2]$/KOH on ACC was also subject to a catalyst deactivation test cycle. The catalyst was reused four times in consecutive batches in the transformation of citral (Fig. 8). The temperature and pressure were $100\,^{\circ}\mathrm{C}$ and 10 bars in every batch, respectively. Even though the catalyst activity decreases, the selectivity boost of SILCA was still observed in all consecutive experiments. In the last consecutive experiment, the citronellal yield was 53 mol%. With the unmodified SILCA containing the same ionic liquid, citronellal yield was only 10 mol%. It can be noticed that the catalyst deactivation is mostly occurring during the first experiment. The plausible reasons for catalyst deactivation are the accumulation of citral hydrogenation products into the ionic liquid layer and agglomeration of palladium particles on the catalyst surface as shown in catalyst characterization section.

3.2. Catalyst characterization

Transmission electron micrographs show palladium nanoparticles in the ionic liquid layer immobilized on ACC (Figs. 9 and 10). In a fresh catalyst (sodium carbonate modified SILCA), the palladium particle size is even below 20 nm. The particle size of spent catalyst

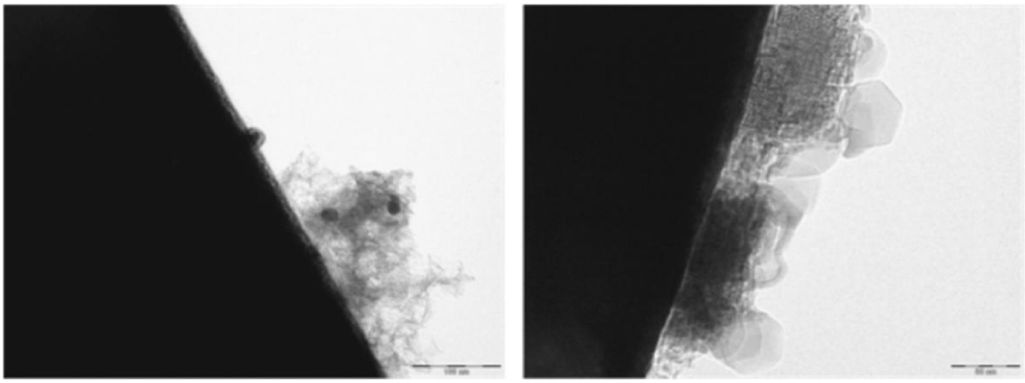


Fig. 9. EFTEM pictures of the catalyst containing palladium in a mixture of 1:2 N-butyl-4-methylpyridinium tetrafluoroborate and Na_2CO_3 on ACC as fresh (left) and after being applied in citral hydrogenation.

Fig. 10. EFTEM pictures of the catalyst containing palladium in a mixture of 1:4 ionic liquid (N-(3-hydroxypropyl)pyridiniumbis-(trifluoromethylsulfonyl)imide) and KOH on ACC as fresh (left) and after being exposed to the reaction conditions.

Table 1
Results from the nitrogen physisorption measurements.

Catalyst		Surface area (m^2/g)[a]	Micropore volume (cm^3/g)[b]
Pd/[(C_3OH)Py][N(CF_3SO_2)$_2$]/ACC	Fresh	966	0.34
	Spent	110	0.04
Pd/[(C_3OH)Py][N(CF_3SO_2)$_2$]/KOH/ACC	Fresh	616	0.22
	Spent	58	0.02
Pd/[C_4C_1Py][BF_4]/ACC	Fresh	1408	0.50
	Spent	380	0.13
Pd/[C_4C_1Py][BF_4]/Na_2CO_3/ACC	Fresh	664	0.24
	Spent	135	0.06

[a] Calculated by Dubinin method.
[b] Calculated by Dollimore/Heal method.

is approximately 40 nm. Without the presence of ionic liquid more agglomeration occurs. With the spent catalyst Pd/ACC, the particle size can be over 100 nm [8]. However, agglomeration of palladium particles can be observed when spent catalysts are studied. Consequently, this might be one important reason to the deactivation of the catalysts. In our previous work, it was shown that no leaching of ionic liquid [C_4C_1Py][BF_4] occurred during hydrogenation experiments [8]. The solubility of ionic liquid [(C_3OH)Py][N(CF_3SO_2)$_2$] to n-hexane (Merck, >99%) was evaluated and it was shown that ionic liquid was not miscible into the solvent. The GC-analysis of the extractant (2-propanol) revealed that fairly significant amounts of citral hydrogenation products were agglomerated on the catalyst surface.

Table 1 demonstrates the results of selected nitrogen physisorption measurements. The micropore volume of pure ACC is 0.6 cm^3/g whereas the specific surface area of pure ACC is 1680 m^2/g. Smaller surface areas and pore volumes of the spent catalysts with respect to the fresh catalysts indicated that some products and by-products are accumulating into the ionic liquid layer. This is one of the primary reasons for catalyst deactivation. Similar accumulation effects have been observed in the hydroformulation of propene over supported ionic liquid phase catalysts [21]. The densities of the ionic liquids, [C_4C_1Py][BF_4] and [(C_3OH)Py][N(CF_3SO_2)$_2$], were 1.18 g/cm^3 and 1.55 g/cm^3, respectively, at ambient conditions [22]. The amount of ACC was 1.2 g whereas the amount of ionic liquid was 0.150 g. Using these values it can be estimated that approximately 20% of the pore volumes were filled with an ionic liquid.

4. Conclusions

In this work, we showed that simple mixing of affordable inorganic bases and ‘standard’ ionic liquids leads a cost-effective way of introducing alkalinity into the system to enhanced reaction rates and improve selectivity toward the product (citronellal). In the first phase, the reaction proceeds toward citronellal by hydrogenating the conjugated carbon–carbon double bond. In the case of the catalyst containing ionic liquid [(C_3OH)Py][N(CF_3SO_2)$_2$], the addition of alkaline-modifier boosted the selectivity of citronellal from 16% to 74%. In fact, modified catalysts with very high activity and highly selective reaction route were accomplished.

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