



## Towards one-pot synthesis of menthols from citral: Modifying Supported Ionic Liquid Catalysts (SILCAs) with Lewis and Brønsted acids

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### ARTICLE INFO

#### Article history:

Received 18 November 2008

Revised 9 February 2009

Accepted 9 February 2009

Available online 10 March 2009

#### Keywords:

Catalysis

Catalyst modification

Ionic liquids

Multiphase reactions

One-pot synthesis

Supported Ionic Liquid Catalyst (SILCA)

### ABSTRACT

The use of ionic liquids in catalysis is attracting ever more attention in chemical engineering. In line with this research we have studied Supported Ionic Liquid Catalysts (SILCAs) which consist of immobilized catalytic species, e.g. transition metal particles residing in an ionic liquid layer immobilized on a solid support. We found out that dissolution of Lewis or Brønsted acids into the ionic liquid layer of SILCA has major effects to the activity as well as the product distribution of the catalyst in citral transformation reactions. In fact, one-pot synthesis of menthols from citral was accomplished. The effects of different amounts of added Lewis and/or Brønsted acids to SILCA (one of them or both) were studied in this work.

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## 1. Introduction

Research in the field of ionic liquids is continuously attracting more interest in scientific world. Many new research areas and improved techniques were introduced at the 2nd International Congress on Ionic Liquids in July 2007 in Yokohama, Japan, including applications in: pharmaceuticals, biotechnology, solar-cells, cellulose processing and catalysis [1]. Indeed, catalysis is one of the areas where ionic liquids have already shown their capability in enhancing the reaction rates of many reactions [2–4]. Ionic liquids are completely ionic compounds, meaning that they are formed of ionic species only. Typically ionic liquids are formulated as a combination of a large organic cation with the possibility of charge delocalization and, consequently, a relatively large inorganic or organic anion. They have many exceptional properties compared to conventional ionic compounds. The main difference is their significantly lower melting point. For example, sodium chloride has a melting point of 801 °C, whereas many ionic liquids have a melting point below room temperature. Other special characteristic features that can be attributed to most of them are: often negligible vapor pressure ( $\sim 10^{-8}$  bar), they are liquid over wide temperature range, unique solvation properties, wide electrochemical window and good ion conductivity [5–7]. Still, one should remember that

these features are not common to every single ionic liquid, as has recently been stated by Deetlefs and Seddon [8]. Even if ionic liquids have shown their ability in various chemical applications [1], widespread use of ionic liquids in industrial applications is still hampered by the cost aspects, limited knowledge of their physical and chemical properties as well as concerns about their biodegradability. Thus, utilizing special characteristics of ionic liquids by immobilizing small amounts of them on solid surfaces is an alternative worth consideration [9]. In fact, catalysis is one of the areas where this concept has already been widely utilized [10–15].

Immobilization or supporting of ionic liquids can be achieved by several different techniques, such as simple impregnation, grafting, polymerization, sol-gel method, encapsulation or pore trapping [9–12,16,17]. A straightforward preparation method involves impregnation of the support material with an ionic liquid, diluted with a molecular solvent (e.g., acetone). The dilution followed by the evaporation of the co-solvent results in a uniform and thin ionic liquid layer on the pore structure of the support material. When SILCA catalysts prepared by this manner are applied in a liquid-phase process, a bulk solvent that is not miscible with the ionic liquid should be selected. In parallel to the ionic liquid immobilization, transition metal ions or complexes and other modifier compounds can be dissolved into the ionic liquid layer. The organometallic species can further be reduced to metallic nanoparticles. A catalyst which contains palladium nanoparticles, together with an ionic modifier (i.e. Lewis acid) in an ionic liquid

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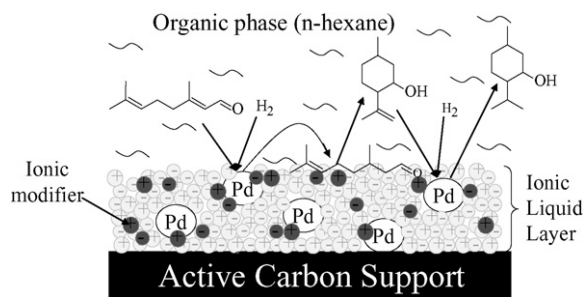


Fig. 1. A supported ionic liquid catalyst used in citral transformation.

layer which, in turn, is immobilized on an active carbon cloth (ACC), is presented in Fig. 1.

Selective hydrogenation of  $\alpha,\beta$ -unsaturated aldehydes, ketones and esters, in general, is a versatile method to obtain many interesting products that find use in the perfumery industry, hardening of fats, preparation of pharmaceuticals and synthesis of organic chemical intermediates. Citral itself and its hydrogenation products are widely used in the perfumery and fine chemical industry. Selective hydrogenations of  $\alpha,\beta$ -unsaturated aldehydes and ketones are challenging, because these species can contain three different double bonds: isolated and conjugated carbon–carbon double bonds as well as a carbonyl group. Consequently, during hydrogenation of citral, many competing and consecutive reactions can take place, including formation of ring compounds such as pulegols and menthols. Most of the menthol used worldwide is obtained by freezing peppermint and cornmint oils, but it is also produced synthetically [18]. Menthols from citral is an attractive synthetic route because citral comes from renewable feedstock and is mainly obtained by distillation of essential oils. According to previous studies, the best catalyst so far was a Ni supported on acidic zeolite H-MCM-41 [19,20]. For this reason a plausible assumption was that an acidic function incorporated into a Supported Ionic Liquid Catalyst (SILCA), previously used on citral hydrogenation [21], represented a worthwhile alternative. A lot of research in selective hydrogenation of  $\alpha,\beta$ -unsaturated aldehydes has been carried out with conventional heterogeneous and homogeneous catalysts, in conventional as well as supercritical solvents and ionic liquids [22–27]. The potential of supported ionic liquid catalysts has already been illustrated in e.g. hydrogenation of alkenes, displaying competitive performance in comparison to biphasic systems and conventional solvents [14,28,29].

## 2. Experimental

### 2.1. Catalyst preparation

Catalysts were prepared according to a similar straight-forward preparation method introduced by us previously [30]. Palladium acetylacetonate ( $\text{Pd}(\text{acac})_2$ ) (approx. 50 mg) (Aldrich 99%), a Lewis acid zinc chloride ( $\text{ZnCl}_2$ ) or ferrous chloride ( $\text{FeCl}_2$ ) and/or a Brønsted acid tetrafluoroboric acid  $\text{HBF}_4$  or acetic acid, as well as an ionic liquid *N*-butyl-4-methylpyridinium tetrafluoroborate ( $\text{NB4MPyBF}_4$ ) (approx. 150 mg) (Merck, 98%), when applicable, were dissolved in acetone (Merck, p.a.). Solution was poured over ACC Kynol® (approx. 900 mg). ACC was dried a priori at 60 °C over 12 h and cut into suitable pieces. Acetone was evaporated in rotary evaporator at 50 °C in vacuum of approx. 300 mbar and completely dried in vacuum of approx. 4 mbar. Catalysts were pre-treated in a high-pressure autoclave (Parr Inc.) at 120 °C under hydrogen flow of 10 bar. As a result, a catalyst containing palladium nanoparticles and a Lewis and/or a Brønsted acid in an ionic liquid immobilized on ACC was achieved.

### 2.2. Testing of activity and selectivity of the catalysts

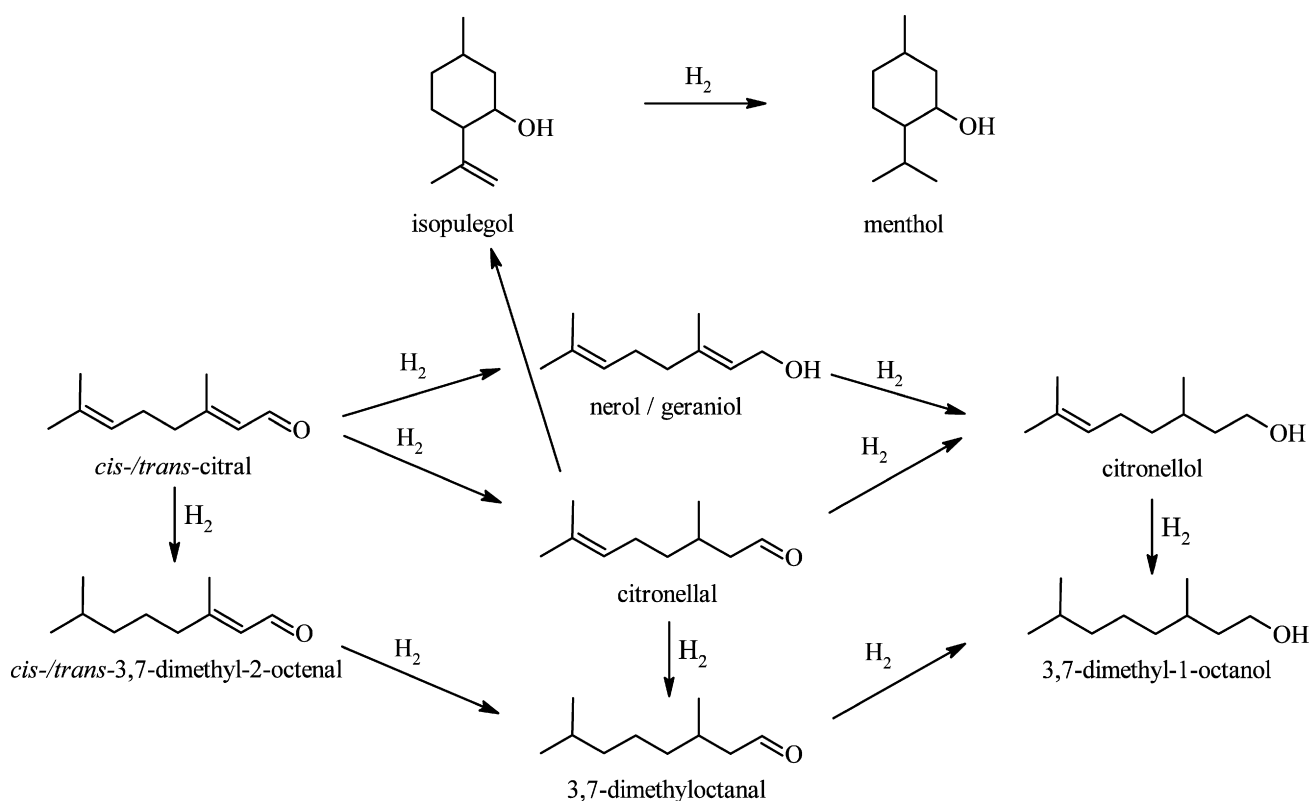
The catalysts were applied in the transformation of citral (Lancaster, 95%). Experiments were performed in a semi-batch reactor (Parr Instrument company, total volume 600 ml, liquid volume 250 ml), equipped with heating jacket and a tailor-made stirrer/catalyst holder. Suitable pieces of the catalyst carrier ACC were attached to the stirrer/catalyst holder. The temperature, pressure and stirring rate were controlled by a Parr 4843 control unit (Watlow control series 982). The stirring rate was adjusted accordingly (1400 rpm) so that external mass-transfer limitations were eliminated. That was confirmed in our previous studies [21]. All experiments were performed at a constant temperature (80–120 °C) and at a constant partial pressure of hydrogen (AGA, 99.9999%, 5–10 bar). Citral (approx. 3 g) was dissolved in 250 ml of *n*-hexane (Merck, pro analysis) and the solution was bubbled with hydrogen, in order to ensure that the solution was oxygen-free. Before each and every experiment the reactor was pre-heated to the desired temperature and hydrogen pressure was adjusted to the selected level. The citral solution was introduced to the reactor and stirring was engaged.

The progress of the reaction was monitored by withdrawing small amounts of liquid samples from the reactor analyzed by gas chromatography (Hewlett Packard 6890 GC with FI detector). Since the sampling volumes were small, compared to the overall volume of the reaction mixture, the volume changes in time were neglected. In addition, a gas chromatograph coupled to a mass spectrometer (Agilent 6890N GC with Agilent 5973 MS detector) was applied for identification of peaks. In both cases, 500  $\mu\text{l}$  of internal standard (0.02 M cyclohexanone in cyclohexane) was added into a 500  $\mu\text{l}$  of sample. The column in the system was an Agilent DB-1 with a length of 30 m, inner diameter of 0.25 mm and, the film thickness of 0.5  $\mu\text{m}$ . The samples were analyzed with the following temperature program: temperature was at first held 10 min at 100 °C, then raised 5 °C/min to 160 °C, and consequently held 10 min at 160 °C, followed by a temperature ramp 13 °C/min to 200 °C, and was held 1 min at 200 °C.

### 2.3. Catalyst characterization

The catalysts were investigated by means of X-ray photoelectron spectroscopy (XPS) in order to determine the binding energies of all compounds and oxidation states of Pd on the ACC support. A Perkin–Elmer PHI 5400 spectrometer was used for the X-ray photoelectron analysis with  $\text{MgK}\alpha$  radiation (1253.6 eV) and pass energy of 35.75 eV. Pressure during the analysis was ca.  $8 \times 10^{-9}$  mbar. Reduced samples were stored in a nitrogen atmosphere after pre-treatment process. However, during transfer to the XPS instrument the samples were in contact with ambient air and they were out-gassed overnight. Depending on the vapor pressure and the condition of the catalyst, the ionic liquid partially evaporated during out-gassing due to ultra high vacuum conditions. Hence, boron, fluorine and chlorine, which have relatively low photoionization cross-sections, were in some conditions below detection limit. The observations are largely based on residual ionic liquid in the pores of the active carbon cloth. Binding energies (BEs) were determined by line fitting procedure, where the line shape of the fitted peaks was a convolution of a Doniach–Šunjić line shape with a Gaussian line shape. A linear background was used for signal background subtraction. Accuracy of the binding energies is  $\pm 0.1$  eV. In the quantitative analysis, sensitivity factors for B 1s, Cl 2p, F 1s and Zn 2p<sub>3/2</sub> were 0.159, 0.891, 1.000 and 3.726 [31]. The catalyst reduction was carried out *ex-situ*, under a hydrogen flow at 120 °C for 60 min prior to analysis.

Leaching of ionic liquid was studied by High Performance Liquid Chromatography (Hewlett Packard 1100 series HPLC). Reversed-



**Scheme 1.** Reaction sequence for citral transformation.

phase HPLC with diode array detector (DAD) was utilized in the following conditions: sample injection volume 5  $\mu$ l, eluent: 30% acetonitrile, 70% 0.02 M phosphate buffer pH 5, flow rate 1.0 ml/min, column: Hewlett Packard, Zorbax eclipse XDB-C8: internal diameter of 4.6 mm, length 150 mm, column temperature of 40  $^{\circ}$ C, detection with DAD: qualitatively from UV spectrum and quantitatively with wavelength of 220 nm. The ionic liquid standards were prepared and analyzed with HPLC and calibration curves were drawn according to these results. Liquid phase samples were analyzed and the amount of ionic liquid was determined by using the linear part of the calibration curve.

Leaching of palladium from the catalyst was determined by means of inductive coupled plasma emission spectrometer coupled to a mass spectrometer (ICP-MS, ELAN 6000). The samples were taken at the end of the experiment. Solvent was first evaporated and the remaining solid was dissolved in Aqua Regia (1:3, concentrated nitric acid and hydrochloric acid). These samples were diluted with water prior to analysis. The amount of leached palladium from the catalyst was calculated according to these results.

The surface area and the micropore volume of the catalysts were determined by an automatic physisorption–chemisorption apparatus (Carlo-Erba Instruments, sorptometer 1900). The Dubinin method was used to calculate the surface area of the catalysts. Dollim-Heal method was used to calculate the micropore volume of the catalysts. The catalysts were analyzed as fresh and after being used in hydrogenation experiment.

Selected catalysts were also investigated by means field emission scanning electron microscopy (FESEM Jeol JSM-6300F) and energy-filtered transmission electron microscopy (EFTEM LEO 912 OMEGA), equipped with an energy dispersive X-ray detector. For the EFTEM analyses, the samples were crushed and dispersed either in *n*-hexane or in water before dispensing them on the specimen holder copper grid (formvar/carbon).

### 3. Results and discussion

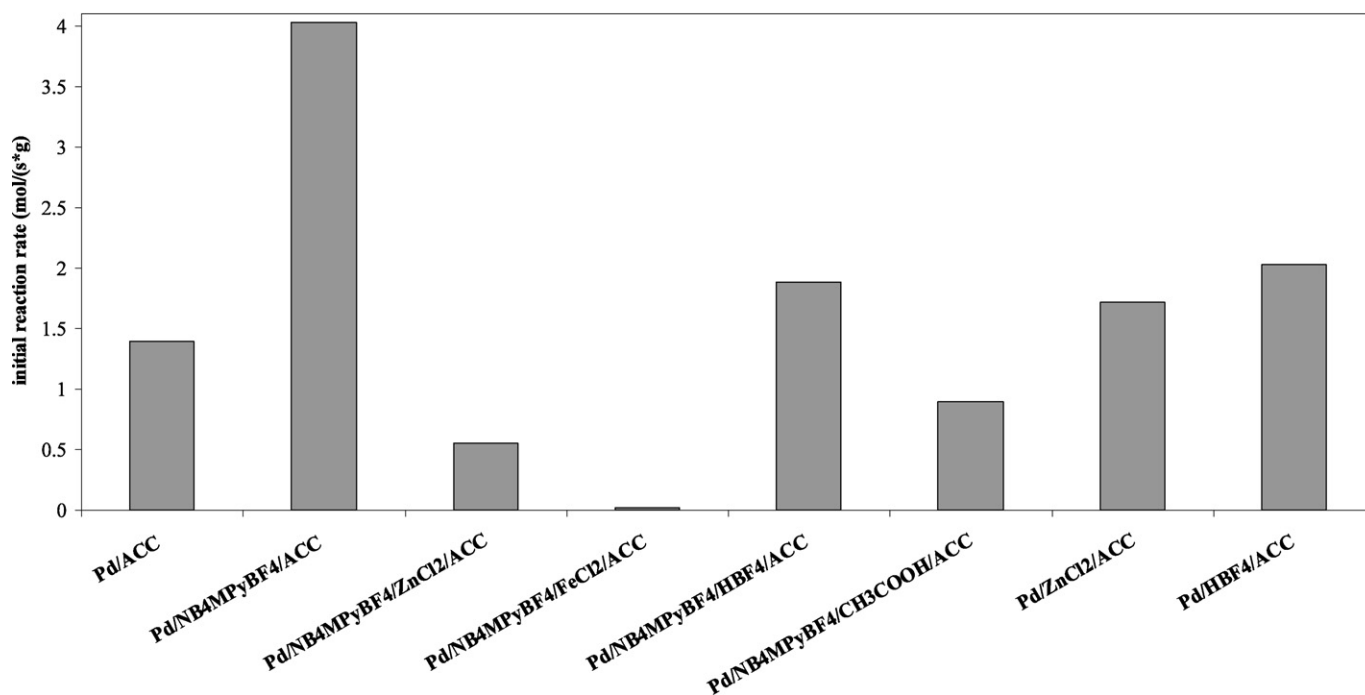
#### 3.1. Activity and selectivity of the catalysts

Citral transformation reactions were performed with thirteen different SILCA-catalysts containing approximately the same amount of palladium, ionic liquid *N*-butyl-4-methylpyridinium tetrafluoroborate and support material active carbon cloth. Only the amount of Lewis acid zinc chloride and Brønsted acid tetrafluoroboric acid were altered in catalysts which they were used. During the hydrogenation of citral in the presence of acidic modifier, a number of competing and consecutive reactions can occur. The reaction network for the main transformations is presented in Scheme 1. Other minor products formed and identified during the experiments were different alkanes and alkenes formed by dehydration and cracking.

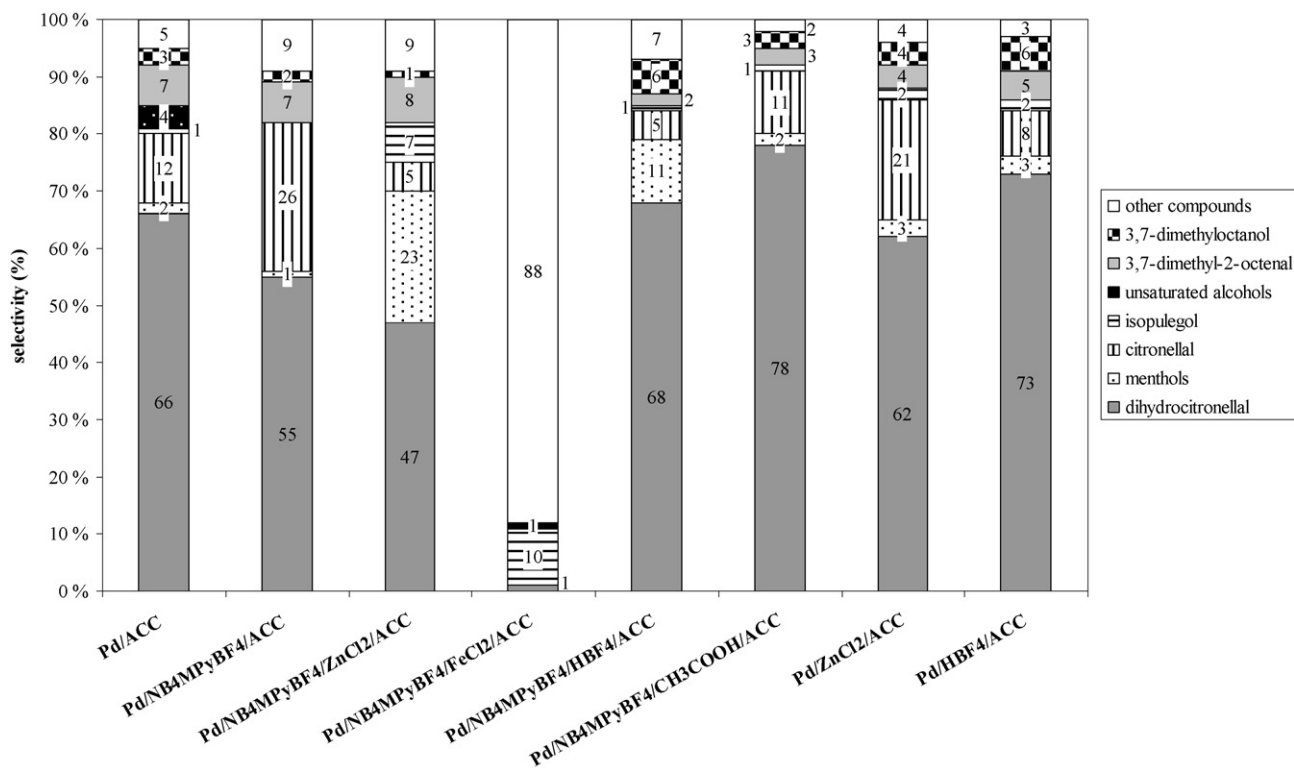
In our earlier studies we found out that the most active catalyst of SILCAs containing palladium and different ionic liquids was the one containing *N*-butyl-4-methylpyridinium tetrafluoroborate [21, 32]. Although, we tested no more than five different ionic liquids, the catalyst containing [NB4MPy][BF<sub>4</sub>] was by far the most active one and therefore was chosen for further development. We assume that the reasons for the differences in activity could be explained by differences in solubility of reactants and products between different ionic liquids and hexane. Thus, reactants are more soluble in [NB4MPy][BF<sub>4</sub>] than other ionic liquids and main product dihydrocitronellal is less soluble in [NB4MPy][BF<sub>4</sub>] than other ionic liquids.

##### 3.1.1. The effects of different acids

Since the main products for the catalysts containing both palladium and an ionic liquid only were citronellal and 3,7-dimethyloctanal, we decided to study catalyst modification by added modifier. At first we tested how the addition of different acids in SILCA and in reference catalyst without ionic liquid affects the activity



**Fig. 2.** Comparison of the initial reaction rates with catalysts containing different acid modifiers with and without ionic liquid, calculated from citral conversion at time 15 min. The reaction conditions were:  $T = 100^\circ\text{C}$ ,  $p(\text{H}_2) = 10$  bar. The initial reaction rates were calculated as follows: (moles of citral converted to products)/(time  $\times$  mass of Pd).

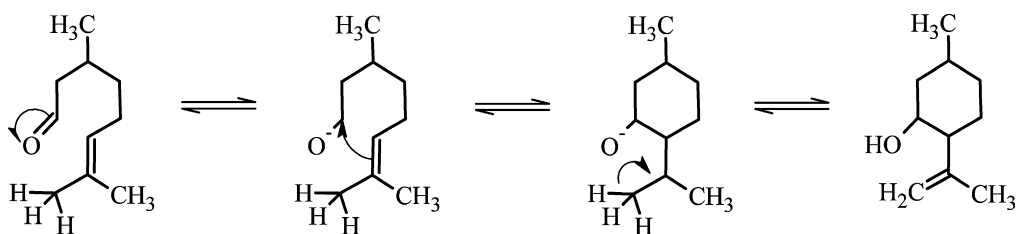


**Fig. 3.** Comparison of selectivities of products from citral reaction over catalysts containing different acid modifiers with and without ionic liquid in hydrogen atmosphere after total conversion (approximately after 6 h, 1 h, 24 h, 24 h, 6 h, 6 h, 4 h, 4 h, respectively with the catalysts from left to right). The reaction conditions were:  $T = 100^\circ\text{C}$ ,  $p(\text{H}_2) = 10$  bar. Other compounds are reaction products from dehydration and cracking of citral and its hydrogenation products.

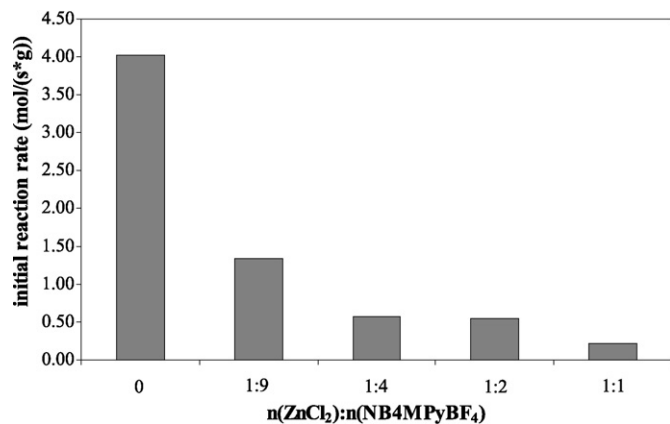
of the catalyst and the catalyst selectivity. In Fig. 2 the activity of various catalysts are compared by means of calculating the initial reaction rates.

It can be seen that the catalyst containing palladium in ionic liquid on ACC is the most active one and the catalysts containing

ionic liquid and Lewis acid are the worst when activity of the catalyst is evaluated. However, when the catalyst selectivity is compared the catalyst containing stronger Lewis acid, zinc chloride, in ionic liquid shows exceptional selectivity profile (Fig. 3). With this catalyst the selectivity of menthols was over ten times higher than



**Scheme 2.** Suggested reaction mechanism for the citronellal transformation to isopulegols in the presence of a Lewis acid.



**Fig. 4.** Comparison of the initial reaction rates with different catalysts, calculated from citral conversion at time 15 min. The reaction conditions were:  $T = 100^\circ\text{C}$ ,  $p(\text{H}_2) = 10$  bar. The initial reaction rates were calculated as follows: (moles of citral converted to products)/(time  $\times$  mass of Pd).

with the catalyst without any acid and over seven times higher than with the catalyst containing acid without ionic liquid. Also, a reasonable selectivity towards menthols was achieved with the catalyst containing strong Brønsted acid in ionic liquid.

It seems evident that reactions over the catalyst containing strong acids  $\text{ZnCl}_2$ , or  $\text{HBF}_4$  in ionic liquid produced more ring compounds, isopulegols and menthols. This is probably caused by the electron withdrawing capability of strong acids, which helps the oxygen to maintain the negative charge and thus enables the

ring formation reaction as presented in Scheme 2. It is also evident that ionic liquid must be present with acids in order to affect the selectivity. We assume that the ionic liquid also enables the formation of ring compounds by stabilizing the ionic forms in Scheme 2.

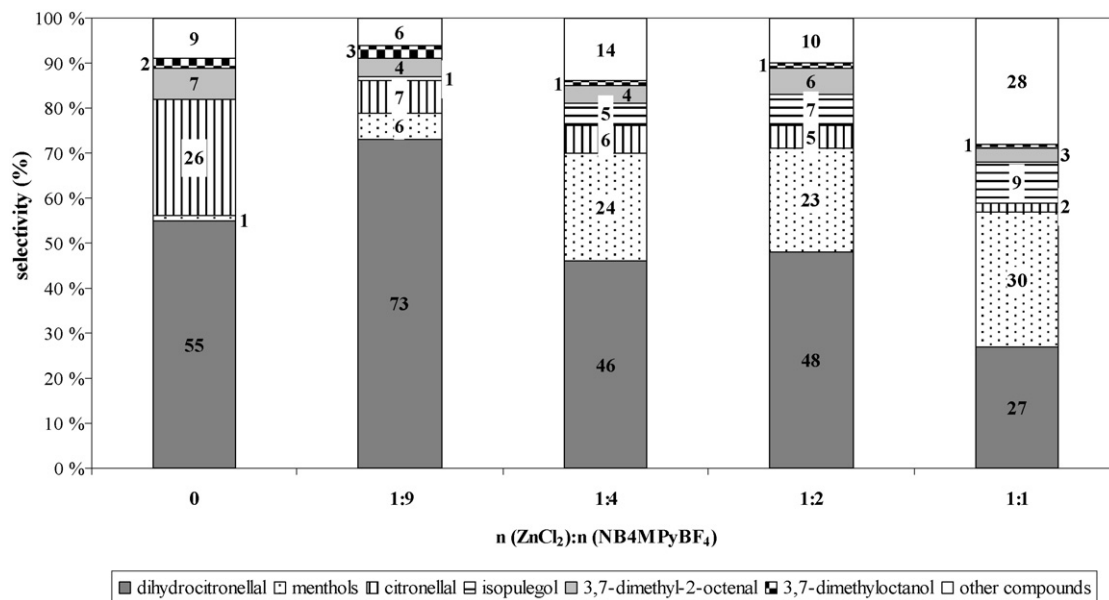
### 3.1.2. The effect of a Lewis acid

With the promising results from the experiments with catalysts containing different acids in catalysts, we decided to test how different amounts of a Lewis acid,  $\text{ZnCl}_2$  in SILCA, affects the activity and selectivity profiles in citral hydrogenation. In Fig. 4 the activity of the various catalysts are compared by means of calculating the initial reaction rates.

The catalysts in all experiments were otherwise similar, but they contained different amounts of Lewis acid  $\text{ZnCl}_2$ . When looking at Fig. 2 it can be clearly seen that the activities of the SILCAs containing  $\text{ZnCl}_2$  are much lower than the one containing Pd and ionic liquid only. However, the specific features of these catalysts become visible when selectivities of different products are compared (Fig. 5).

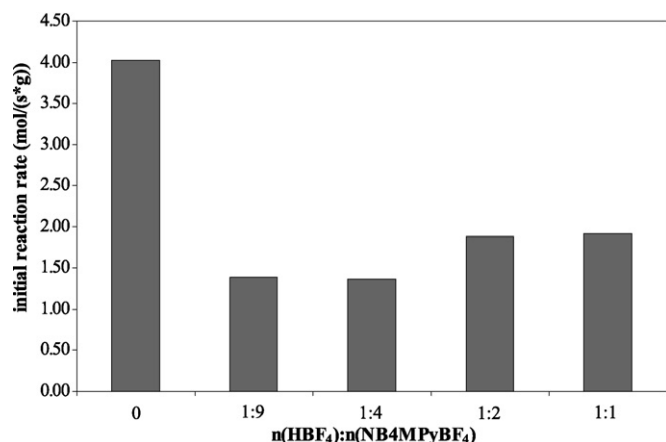
### 3.1.3. The effect of a Brønsted acid

In the next step we evaluated the effect of a Brønsted acid, tetrafluoroboric acid ( $\text{HBF}_4$ ) in SILCA.  $\text{HBF}_4$  was chosen because it has the same anion ( $\text{BF}_4^-$ ) as the ionic liquid used. The effect of  $\text{HBF}_4$  in total was not as significant as was the effect of  $\text{ZnCl}_2$ . Again, we tested the catalysts containing different amounts of  $\text{HBF}_4$ . The amount of  $\text{HBF}_4$  is not absolutely certain, since some acid evaporates during catalyst preparation procedure. The same vacuum treatment that was used in catalyst preparation was applied to the 1:1 mixture of acid in ionic liquid, in order to estimate



**Fig. 5.** Comparison of selectivities of products from citral reaction over Lewis acidic SILCAs in hydrogen atmosphere after total conversion (approximately after 24 h, with the catalyst without acid after 1 h). The reaction conditions were:  $T = 100^\circ\text{C}$ ,  $p(\text{H}_2) = 10$  bar. Other compounds are reaction products from dehydration and cracking of citral and its hydrogenation products.





**Fig. 6.** Comparison of the initial reaction rates with different catalysts, calculated from citral conversion at time 15 min. The reaction conditions were:  $T = 100^\circ\text{C}$ ,  $p(\text{H}_2) = 10$  bar. The initial reaction rates were calculated as follows: (moles of citral converted to products)/(time  $\times$  mass of Pd).

the amount of acid that evaporates. The experiment showed that over 90% of the acid remained in the ionic liquid during vacuum treatment. The amount of ionic liquid and Pd was approximately the same in all of the catalysts. In Fig. 6 the activity of the catalysts containing different amounts of HBF<sub>4</sub> are compared.

On the basis of these results, it is clear that an addition of HBF<sub>4</sub> to the SILCA lowers the activity of the catalysts, but the amount of HBF<sub>4</sub> does not seem to have any effect at all. When comparing the selectivities of different products in Fig. 7, we can clearly see that the selectivity towards menthols and dihydrocitronellal are somewhat higher with the catalysts containing larger amounts of HBF<sub>4</sub>. However, the effect of an added Brønsted acid was significantly less than the effect of an added Lewis acid.

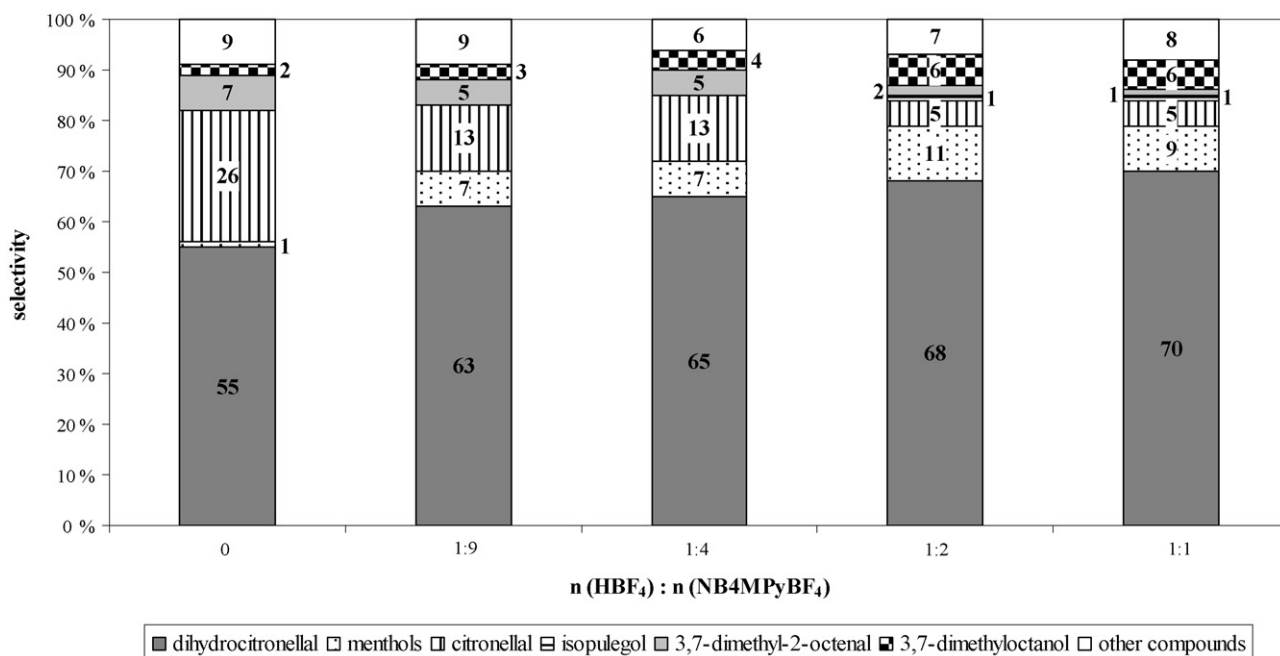
### 3.1.4. Combined Brønsted and Lewis acids

In the following phase we decided to study the effect of addition of both a Brønsted and a Lewis acid. Two different catalysts

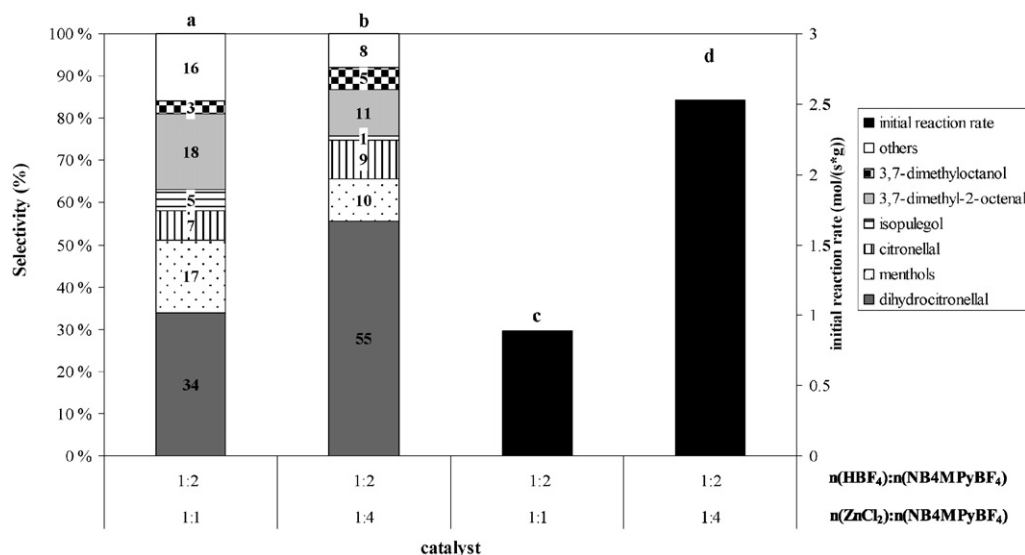
were tested. Both catalysts contained the same amount of HBF<sub>4</sub> (1:2 molar amounts compared to ionic liquid) and 1:1 as well as 1:4 molar amounts of ZnCl<sub>2</sub> in relation to the ionic liquid amount. The results were similar as with the catalyst containing a Brønsted acid only (Fig. 8). However, the activity of the catalyst containing 1:2 molar amount of HBF<sub>4</sub> and 1:4 molar amount of ZnCl<sub>2</sub> was much higher than that of the catalysts containing the same amount of only one of the acids. With the other catalyst containing the same amount of HBF<sub>4</sub> and 1:1 molar amount of ZnCl<sub>2</sub>, the activity was approximately the same as the catalyst containing HBF<sub>4</sub> only, but about twice as high than that of the catalyst containing ZnCl<sub>2</sub> alone. The selectivities of these two catalysts were in the same level as the catalysts containing HBF<sub>4</sub> only. Therefore, we decided not to continue any further investigations in this line of research.

### 3.1.5. The effects of temperature and hydrogen pressure

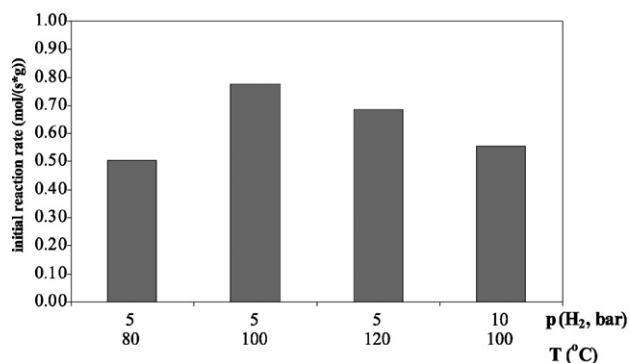
As the next step, we decided to study a catalyst that contained 1:2 molar ratio of ZnCl<sub>2</sub> and an ionic liquid NB<sub>4</sub>MPyBF<sub>4</sub> together with Pd on ACC more thoroughly, since both the activity and selectivity towards menthols were at a reasonable level with that catalyst. The catalyst was investigated at two different temperatures and two different partial pressures of hydrogen. Fig. 9 clearly illustrates that reasonable variations in temperature and pressure do not have a large effect to the activity of the catalyst. However, the selectivities towards different products were more significantly affected as illustrated in Fig. 10. When the pressure of hydrogen was lowered to 5 bar, more ring compounds were obtained. The results were understandable, since lowering the pressure of H<sub>2</sub> obviously lowers the production rate of further hydrogenated products, dihydrocitronellal and 3,7-dimethyloctanol, thus giving possibility to form ring compounds from citronellal. Also, a notable result is that with lower pressure of H<sub>2</sub> we did not produce almost any 3,7-dimethyl-2-octenal which again means that we should get more citronellal and ring compounds in accordance with Scheme 1. We previously obtained similar results with catalysts in the absence of acidic compounds, meaning that the formation of citronellal was favored by lower hydrogen pressure. Obviously, we were not



**Fig. 7.** Comparison of selectivities of products from citral reaction over Brønsted acidic SILCAs in hydrogen atmosphere after total conversion (approximately after 6 h, except with the catalyst without acid after 1 h). The reaction conditions were:  $T = 100^\circ\text{C}$ ,  $p(\text{H}_2) = 10$  bar. Other compounds are reaction products from dehydration and cracking of citral and its hydrogenation products.



**Fig. 8.** Comparison of: selectivities of products from citral reaction over SILCA containing both a Brønsted and a Lewis acids in hydrogen atmosphere after total conversion (a and b) (approximately after 6 h) and the initial reaction rates over same catalysts, calculated from citral conversion at time 15 min (c and d). The reaction conditions were:  $T = 100\text{ }^{\circ}\text{C}$ ,  $p(\text{H}_2) = 10\text{ bar}$ . The initial reaction rates were calculated as follows: (moles of citral converted to products)/(time  $\times$  mass of Pd). Other compounds are reaction products from dehydration and cracking of citral and its hydrogenation products.

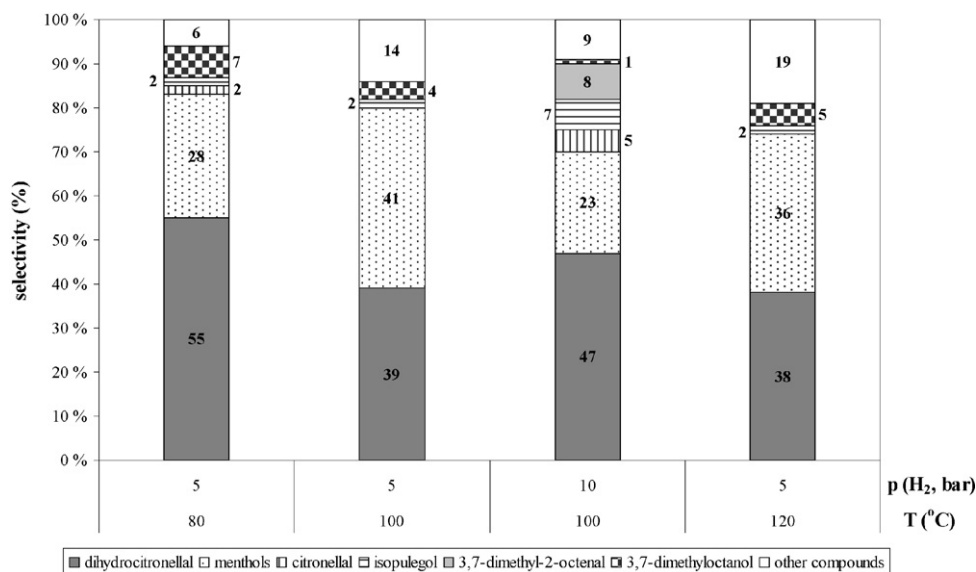


**Fig. 9.** Comparison of the initial reaction rates over catalyst Pd in  $\text{ZnCl}_2/\text{NB}_4\text{MPyBF}_4$  (1:2) on ACC, calculated from citral conversion at time 15 min. The reaction conditions are displayed in the figure. The initial reaction rates were calculated as follows: (moles of citral converted to products)/(time  $\times$  mass of Pd).

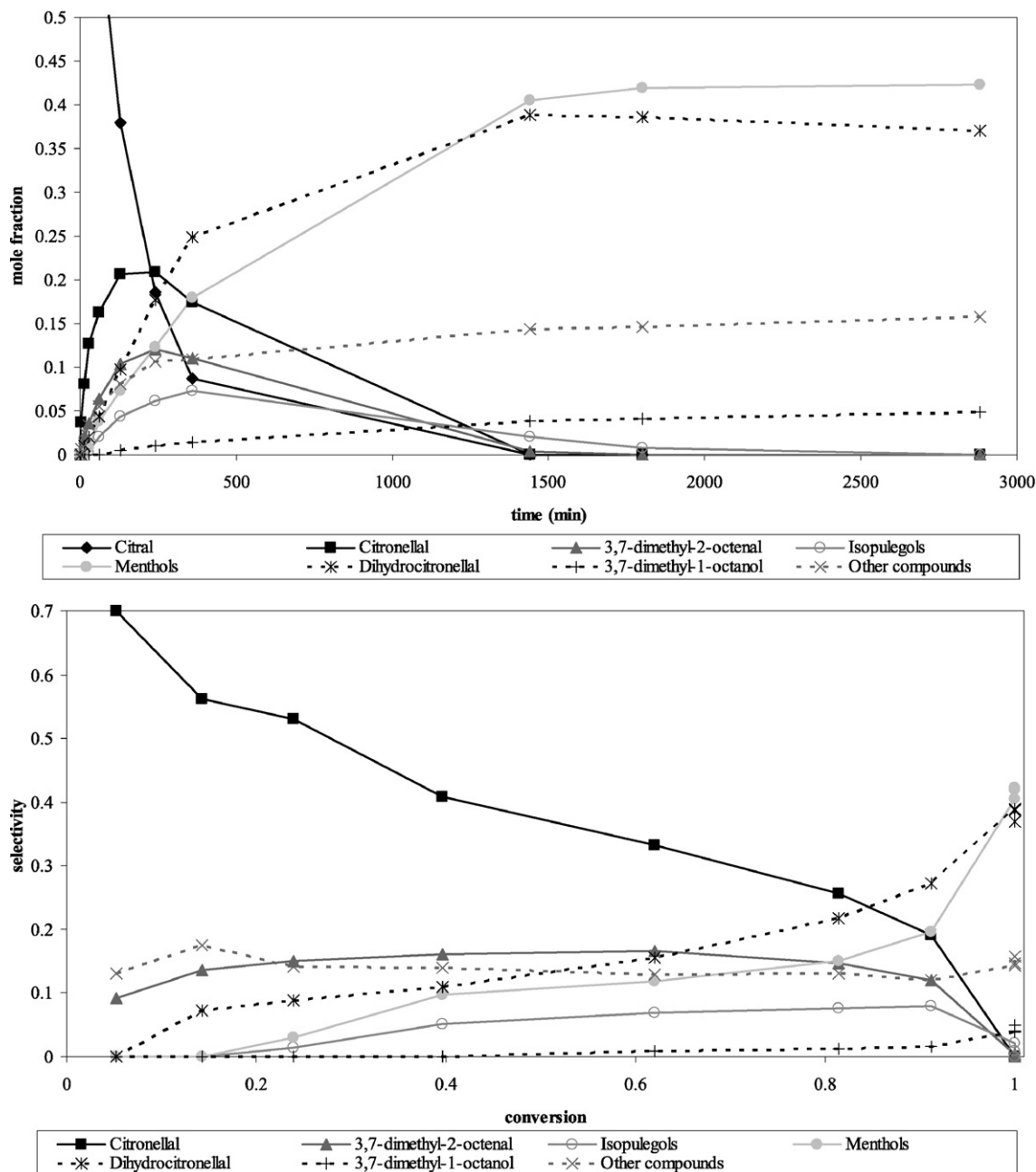
able to produce more ring compounds, since the acidic function was missing in those catalysts [21,29,30]. In Fig. 11 the mole fractions of citral and its reaction products are presented as a function of time as well as selectivities of reaction products as a function of conversion from the experiment at hydrogen pressure of 5 bar and at temperature of  $100\text{ }^{\circ}\text{C}$ . This experiment was run over 48 h in order to estimate the whether the product distribution changes with time. After total conversion was achieved, at 24 h the product distribution changes only slightly. Some isopulegols which are still present react to menthols and dihydrocitronellal reacts slowly to 3,7-dimethyl-1-octanol and decomposition products.

### 3.1.6. Catalyst deactivation

The same catalyst system (1:2 molar amounts of  $\text{ZnCl}_2$  and ionic liquid  $\text{NB}_4\text{MPyBF}_4$  together with Pd on ACC), that was used when temperature and pressure effects was demonstrated was



**Fig. 10.** Comparison of selectivities of products from citral reaction over catalysts Pd in  $\text{ZnCl}_2/\text{NB}_4\text{MPyBF}_4$  (1:2) on ACC in hydrogen atmosphere after total conversion (approximately after 24 h). The reaction conditions are displayed in the figure. Other compounds are reaction products from dehydration and cracking of citral and its hydrogenation products.



**Fig. 11.** Mole fractions of citral and its reaction products as a function of time (upper graph) and selectivities of reaction products as a function of conversion (lower graph) during a batch run. The catalyst applied consisted of Pd in a mixture of 1:2 molar amounts of  $\text{ZnCl}_2$  and ionic liquid NB4MPyBF<sub>4</sub> on ACC. The reaction conditions were:  $T = 100^\circ\text{C}$ ,  $p(\text{H}_2) = 5$  bar. Other compounds are different reaction products of dehydration and cracking.

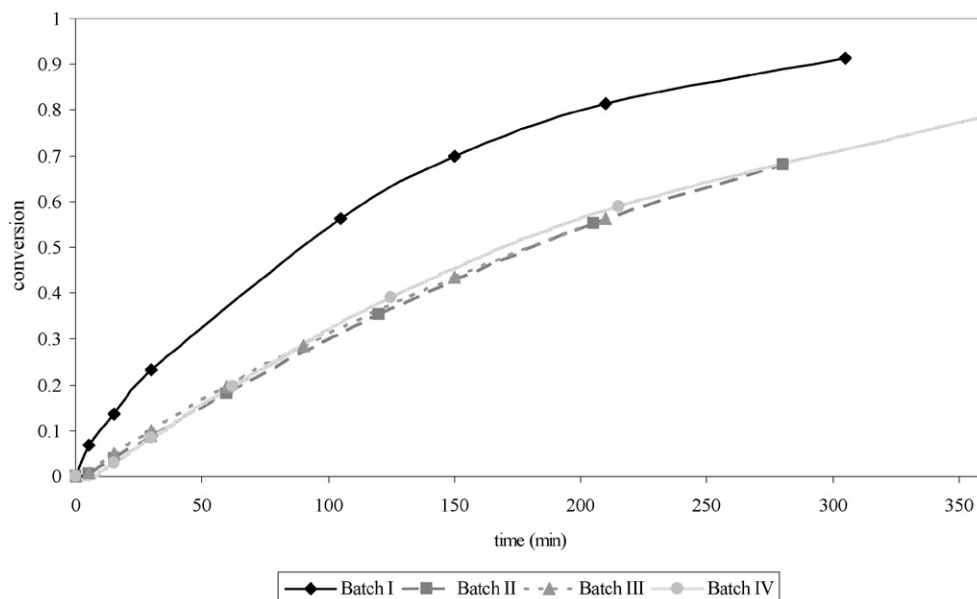
chosen for catalyst deactivation testing as well. The catalyst was re-used in four consecutive batches for transformation of citral. The temperature and hydrogen partial pressure was kept in all batches at  $100^\circ\text{C}$  and 5 bar, respectively. Between the experiments the catalyst was stored in the reactor in hydrogen atmosphere. Citral conversion as a function of time in these four consecutive batches is presented in Fig. 12. It can be seen that the catalyst is deactivated during the first experiment. However, during consecutive batches the deactivation is very minimal. The cause for deactivation is probably similar as has been reported previously in the case of hydroformylation and citral hydrogenation with similar types of catalysts [21,33].

The product distribution changed little in consecutive batches. Selectivities of dihydrocitronellal and citronellal increased as selectivities of all other products decreased.

### 3.2. Catalyst characterization

The results from the XPS measurements for selected catalysts are listed in Table 1. Palladium  $3d_{5/2}$  binding energy (BE) in the studied samples was ca. 335.5 eV, which is assigned to Pd in Pd(0) state. It is chemically feasible to expect that zinc chloride is present in ionized form in the ionic liquid. The presence of Zn(0) should also be considered, since the catalyst samples were reduced under flowing hydrogen prior to analysis and/or used in reductive operating conditions, possibly resulting in the reduction of zinc. This is observed in the Zn/Cl ratios that varied from 0.39 to 4.0. In the latter case, it is evident that most of the zinc is not associated with chlorine. Metallic zinc has a binding energy of 1021.8 eV, which was not observed in the measured ionic liquid catalysts. Since the samples were in contact with air, zinc has





**Fig. 12.** Deactivation of a catalyst containing 1:2 molar amounts of  $\text{ZnCl}_2$  and ionic liquid NB4MPyBF<sub>4</sub> together with Pd on ACC during four consecutive batches. The reaction conditions were:  $T = 100^\circ\text{C}$ ,  $p(\text{H}_2) = 5$  bar.

**Table 1**  
Binding energies of atoms on selected SILCAs measured with XPS.

Catalyst	$n(\text{ZnCl}_2):$ $n(\text{IL})$	$n(\text{HBF}_4):$ $n(\text{IL})$	C 1s (eV)	O 1s (eV)	F 1s (eV)	Cl 2p <sub>1/2</sub> (eV)	Zn 2p <sub>3/2</sub> (eV)	Pd 3d <sub>5/2</sub> (eV)	B 1s (eV)	Zn/Cl (eV)	B/F (eV)
Pd/ZnCl <sub>2</sub> /NB4MPyBF <sub>4</sub> /ACC (fresh)	1:9	0	284.5	532.1	685.4	197.8	1022.1 (53%) 1023.5 (47%)	335.5	BDL <sup>a</sup>	1.1	BDL
	1:1	0	284.6	532.5	685.4	198.0	1022.7	335.4 (92%) 337.1 (8%)	BDL	1.5	BDL
Pd/ZnCl <sub>2</sub> /NB4MPyBF <sub>4</sub> /ACC (spent)	1:9	0	284.7	532.5	685.8	198.0	1022.7	335.3	193.7	0.39	0.24
	1:1	0	284.4	532.0	685.1	198.0	1022.5	335.4	BDL	0.77	BDL
Pd/HBF <sub>4</sub> /NB4MPyBF <sub>4</sub> /ACC (fresh)	0	1:9	284.5	532.3	685.5	N/A <sup>b</sup>	N/A	335.4	BDL	N/A	BDL
	0	1:1	284.6	532.8	685.8	N/A	N/A	335.6	193.7	N/A	0.26
Pd/HBF <sub>4</sub> /NB4MPyBF <sub>4</sub> /ACC (spent)	0	1:1	284.6	532.6	685.8	N/A	N/A	335.7	193.7	N/A	0.31
Pd/ZnCl <sub>2</sub> /HBF <sub>4</sub> /NB4MPyBF <sub>4</sub> /ACC (fresh)	1:4	1:2	284.6	532.1	685.2	197.9	1022.6 (78%) 1021.0 (22%)	335.4	BDL	2.0	BDL
	1:1	1:2	284.5	532.1	685.2	197.8	1022.1 (53%) 1023.5 (47%)	335.5	BDL	1.1	BDL
			284.6	532.3	BDL	BDL	1022.3	335.4	BDL	BDL	BDL

<sup>a</sup> BDL: below detection limit.

<sup>b</sup> N/A: not applicable.

formed hydrates and oxides prior to XPS analysis. In literature, binding energy values in the range of 1023.1 eV–1023.3 eV have been reported for Zn 2p<sub>3/2</sub> in ZnCl<sub>2</sub> [34–36].

In the studied catalyst samples, Zn 2p<sub>3/2</sub> was observed in vacuum conditions at a wide binding energy range, ranging from 1021.0 eV to 1022.7 eV. This is explained by the formation of hydroxides and oxides. Chlorine 2p<sub>3/2</sub> was observed at ca. 197.9 eV, which is also lower than the value of Cl in ZnCl<sub>2</sub>, 199.1 eV [37]. Binding energies that were observed for boron 1s (193.7 eV) are lower than the binding energies previously observed for tetrafluoroboron containing compounds (ca. 195 eV) [31]. Instead, the binding energies of F<sub>3</sub> containing compounds correspond well with the observed binding energy for B 1s. A feasible explanation is that BF<sub>3</sub> ligands have bonded with zinc chloride, explaining the lowest observations of binding energy values (1021.0 eV) in zinc.

Results from the ionic liquid leaching studies with HPLC indicated that, practically no leaching occurred during experiments. The results from the palladium leaching measurements with ICP–MS are listed in Table 2. The amount of leached palladium in the bulk phase from each experiment was in the range of 1 ppm, this

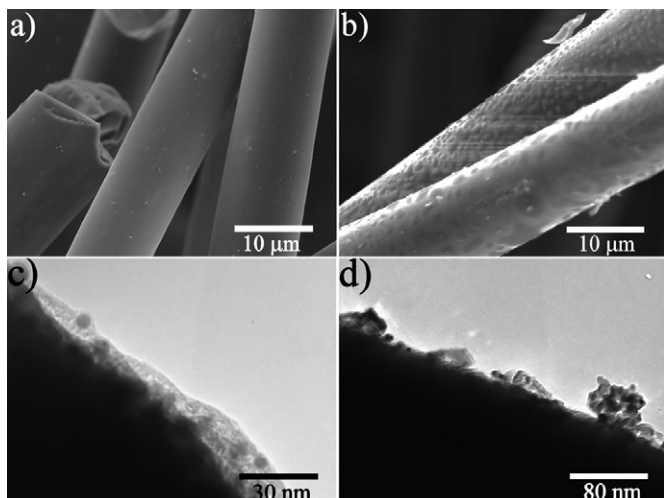
**Table 2**  
Results from Pd leaching measurements.

Catalyst	$n(\text{ZnCl}_2):n(\text{IL})$	$n(\text{HBF}_4):n(\text{IL})$	c, Pd (ppm) <sup>a</sup>
Pd/ZnCl <sub>2</sub> /NB4MPyBF <sub>4</sub> /ACC	1:9	0	0.89
	1:4	0	1.3
	1:2	0	1.5
	1:1	0	0.94
Pd/HBF <sub>4</sub> /NB4MPyBF <sub>4</sub> /ACC	0	1:9	0.98
	0	1:4	1.0
	0	1:2	0.93
	0	1:1	1.3
Pd/ZnCl <sub>2</sub> /HBF <sub>4</sub> /NB4MPyBF <sub>4</sub> /ACC	1:4	1:2	1.3
	1:1	1:2	1.3

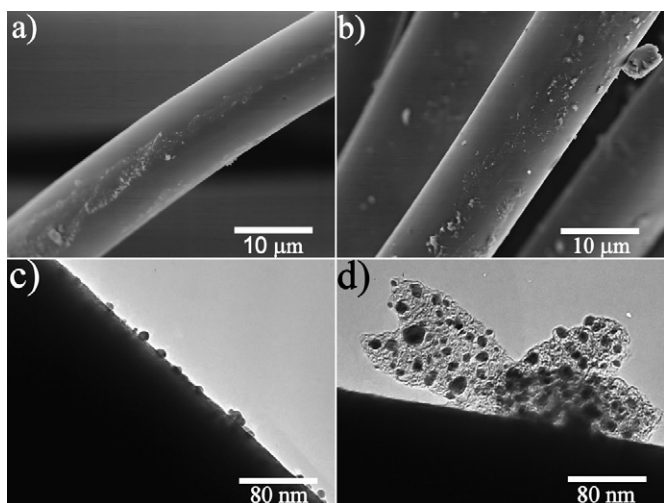
<sup>a</sup> (c, Pd) measured from the bulk phase after the experiment.

being a small amount. However, it was significantly higher than in the case of the catalysts in our previous studies, that did not contain any Lewis or Brønsted acids, varying from 25 to 48 ppb [21].

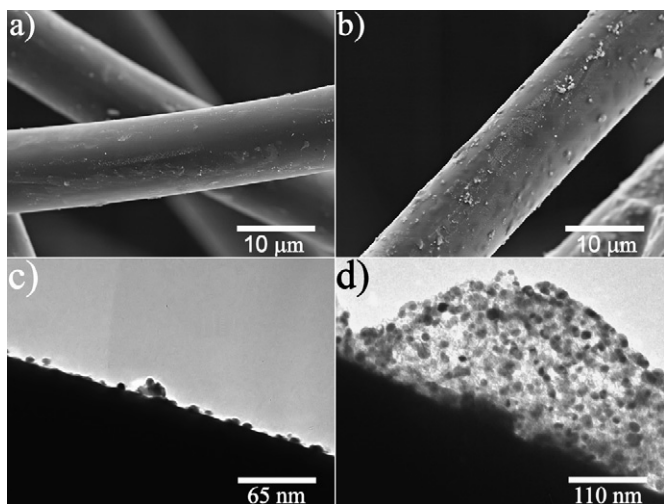
On the basis of nitrogen physisorption measurements, it was possible to calculate the specific surface area and micropore volume of the catalysts. The catalysts were analyzed as fresh and



**Fig. 13.** FESEM (a, b) and EFTEM (c, d) pictures of catalyst containing Pd in mixture of 1:1 ZnCl<sub>2</sub> and NB4MPyBF<sub>4</sub> on ACC as fresh (a, c) and after being applied in citral transformation.



**Fig. 14.** FESEM (a, b) and EFTEM (c, d) pictures of catalyst containing Pd in mixture of 1:1 HBF<sub>4</sub> and NB4MPyBF<sub>4</sub> on ACC as fresh (a, c) and after being applied in citral transformation.



**Fig. 15.** FESEM (a, b) and EFTEM (c, d) pictures of catalyst containing Pd in mixture of 1:1 ZnCl<sub>2</sub> and NB4MPyBF<sub>4</sub> as well as 1:3 HBF<sub>4</sub> and NB4MPyBF<sub>4</sub> on ACC as fresh (a, c) and after being exposed to the reaction conditions.

**Table 3**

Results from the nitrogen physisorption measurements.

Catalyst	$n(\text{ZnCl}_2):n(\text{IL})$	$n(\text{HBF}_4):n(\text{IL})$	$A_s$ (m <sup>2</sup> /g) <sup>a</sup>	mpV (cm <sup>3</sup> /g) <sup>b</sup>
Pd/ZnCl <sub>2</sub> /	1:9	0	15.2	0.0054
NB4MPyBF <sub>4</sub> /	1:4	0	482	0.17
ACC (fresh)	1:2	0	20.6	0.0073
	1:1	0	687	0.24
Pd/ZnCl <sub>2</sub> /	1:9	0	6.03	0.0021
NB4MPyBF <sub>4</sub> /	1:4	0	9.97	0.0035
ACC (spent)	1:2	0	9.85	0.0035
	1:1	0	8.62	0.0031
Pd/HBF <sub>4</sub> /	0	1:9	182	0.065
NB4MPyBF <sub>4</sub> /	0	1:4	530	0.19
ACC (fresh)	0	1:2	485	0.17
	0	1:1	1240	0.44
Pd/HBF <sub>4</sub> /	0	1:9	34.2	0.012
NB4MPyBF <sub>4</sub> /	0	1:4	9.56	0.0034
ACC (spent)	0	1:2	24.3	0.0086
	0	1:1	498	0.18
Pd/ZnCl <sub>2</sub> /HBF <sub>4</sub> /	1:4	1:2	591	0.21
NB4MPyBF <sub>4</sub> /	1:1	1:2	1490	0.53
ACC (fresh)				
Pd/ZnCl <sub>2</sub> /HBF <sub>4</sub> /	1:4	1:2	168	0.060
NB4MPyBF <sub>4</sub> /	1:1	1:2	172	0.061
ACC (spent)				

<sup>a</sup>  $A_s$  = specific surface area, calculated by Dubinin method.

<sup>b</sup> mpV = micropore volume, calculated by Dollim/Heal method.

after being applied in citral transformation experiments. The results from these experiments are listed in Table 3.

Since the specific surface area of pure ACC is 1680 m<sup>2</sup>/g and micropore volume is 0.6 cm<sup>3</sup>/g [21], one can estimate that approximately 20–70 vol% of the pores were filled with immobilized species. The accumulation of reaction products is probably the reason for the very low surface area and pore volume for spent catalysts. This kind of accumulation has previously been reported in hydroformylation and citral hydrogenation reactions with similar catalysts [21,31].

The catalysts which contained highest concentrations of modifiers were selected to be analyzed with FESEM and EFTEM. The results proved that palladium nanoparticles were formed on catalyst during pre-treatment process (Figs. 13–15). These figures illustrate FESEM and EFTEM pictures of the catalysts containing palladium in a mixture of 1:1 ZnCl<sub>2</sub> and NB4MPyBF<sub>4</sub> on ACC, palladium in a mixture of 1:1 HBF<sub>4</sub> and NB4MPyBF<sub>4</sub> on ACC and palladium in a mixture of 1:1 ZnCl<sub>2</sub> and NB4MPyBF<sub>4</sub> as well as 1:3 HBF<sub>4</sub> and NB4MPyBF<sub>4</sub> on ACC. The catalysts were analyzed as fresh and as spent ones.

FESEM images (a) and (b) reveal the fiber structures of the catalyst support and also some palladium particles are visible. In Fig. 13b one can observe that citral transformation products accumulate on the catalyst surface as were indicated by the results from nitrogen physisorption measurements where spent catalysts had lower specific surface areas than fresh catalysts. This is also a plausible explanation for the catalyst deactivation process. EFTEM pictures (c, d) show that the catalysts really contain palladium nanoparticles in ionic liquid immobilized on ACC. Also, some agglomeration of palladium particles can be observed when comparing fresh and spent catalysts. This might also contribute to the deactivation of the catalyst.

#### 4. Conclusions

During this study we successfully managed to demonstrate that it is possible to modify Supported Ionic Liquid Catalysts by co-immobilization of acidic modifiers during catalyst preparation. These modified catalysts demonstrated exceptional selectivities on

citral transformations when compared to unmodified ones. Selectivity towards menthols was raised from ~1%, gained over SILCA without acidic modifier, up to ~41%, gained over Lewis acid modified SILCA, thus being the main product in the reaction. The characterization of the catalysts verified that metallic palladium nanoparticles were formed on the catalysts during pre-treatment process and leaching of both ionic liquid and palladium were minimal. As demonstrated by this study, the supported ionic liquid catalysts are very interesting class of catalysts, since they can be easily tuned by different modifiers in order to change the selectivity profile of the reaction. Although, we only presented the acid modified catalysts we anticipate that this concept can be applied also in various other reaction. For example, it is plausible that the catalyst could be modified with chiral modifiers for production of asymmetric chemicals.

### Acknowledgments

The financial support from the Academy of Finland is gratefully acknowledged (Decisions nos. 124640, 209391 and 211463). This work is a part of the activities at the Åbo Akademi Process Chemistry Centre (PCC) within the Finnish Centre of Excellence Programs (2000–2005 and 2006–2011) by the Academy of Finland.

### Appendix A. Abbreviations

SILCA	Supported Ionic Liquid Catalyst
ACC	Active Carbon Support
Pd(acac) <sub>2</sub>	palladium acetylacetonate
ZnCl <sub>2</sub>	zinc chloride
HBF <sub>4</sub>	tetrafluoroboric acid
NB4MPyBF <sub>4</sub>	<i>N</i> -butyl-4-methylpyridinium tetrafluoroborate
GC–MS	gas chromatograph–mass spectrometer
XPS	X-ray photoelectron spectroscopy
HPLC	high performance liquid chromatograph
ICP–MS	ion coupled plasma emission spectrometer–mass spectrometer
FESEM	field emission scanning electron microscopy
EFTEM	energy-filtered transmission electron microscopy
BE	binding energy
A <sub>s</sub>	specific surface area
mpV	micropore volume

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