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Well-defined dendrimer encapsulated ruthenium SCILL catalysts for partial hydrogenation of toluene in liquid-phase

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ABSTRACT

Dendrimer encapsulated ruthenium nanoparticles (RuDEN) were prepared and immobilized on silica 60 and silica 100. The size of the supported RuDENs was investigated using HRTEM and the generation six G6-RuDEN was found to be the most stable RuDEN upon immobilization. The catalysts were evaluated in the liquid-phase hydrogenation of toluene at a hydrogen pressure of 30 bar and 110 °C. Several ionic liquids were used as coatings for the G5-RuSil100 catalysts to give various Solid Catalysts with Ionic Liquid Layer (SCILL). In each case the selectivity towards methylcyclohexenes was increased compared to the uncoated catalyst, accompanied by an expected decrease in activity with the highest methylcyclohexene selectivity being observed when using [EMIM][NTf$_2$] as a coating.

1. Introduction

The catalytic hydrogenation of aromatic compounds is both an interesting topic in science and of industrial importance, an example being the hydrogenation of benzene to cyclohexene and subsequent oxidation to adipic acid and caprolactam which are important precursors in the production of nylon-6 and nylon-66 [1,2]. In addition, arene hydrogenation is applied for the removal of carcinogenic aromatic compounds from diesel fuels [3]. From an economic standpoint, simpler methods for the production of partially hydrogenated arenes are of great interest. In the 1990s, the selective hydrogenation of benzene to cyclohexene was achieved using finely divided ruthenium in an aqueous media with the incorporation of additives, known as the Asahi process [4]. In this process, high selectivity above 40% toward the partially hydrogenated cyclohexene is achieved, however, the catalyst and loading is high and product separation is tedious.

A more sophisticated method of enhancing the selectivity towards the partially hydrogenated arenes is the use of ionic liquids as additives. Known to stabilize nanoparticles, ionic liquids have also been used as solvents in the catalytic hydrogenation of arenes [5]. The utilization of ruthenium nanoparticles in ionic liquids for the hydrogenation of benzene has shown appreciable selectivity to cyclohexene [6], however, few other studies focus on the ability of an ionic liquid to enhance selectivity towards partially hydrogenated arenes. When comparing reactions conducted in bulk ionic liquid with those in the absence of ionic liquid, the latter are usually faster. This difference is fairly common for ionic liquid catalysis and can be attributed to their high viscosity and low gas solubility, limiting the overall reaction by mass-transfer [7]. There is, therefore, a need for a catalytic system that allows for high selectivity to the partially hydrogenated intermediates while maintaining a high catalytic activity.

One way to minimize the mass-transfer control is to deposit the ionic liquid over a high surface area material to form a thin film and thus minimize the diffusion barrier observed for bulk ionic liquids [8]. This concept of dispersing an ionic liquid across a large surface area support has led to the development of the supported ionic liquid phase (SILP) concept [9–12]. Given the potential to change the activity and selectivity profile of a catalyst by introducing an ionic liquid in small quantities, Kernchen et al. proceeded to develop a similar catalytic system called the solid catalyst with ionic liquid layer (SCILL) catalyst [13].

The presence of the ionic liquid can affect the activity and selectivity of the catalyst by changing the intrinsic properties of the catalyst, therefore acting as a potential chemical modifier of the catalyst itself that is encouraged by chemical interaction of the

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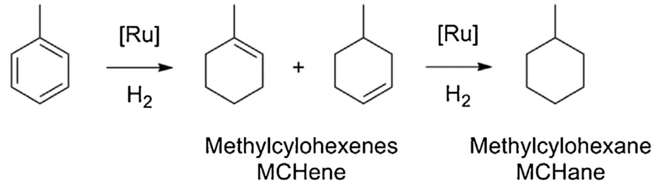
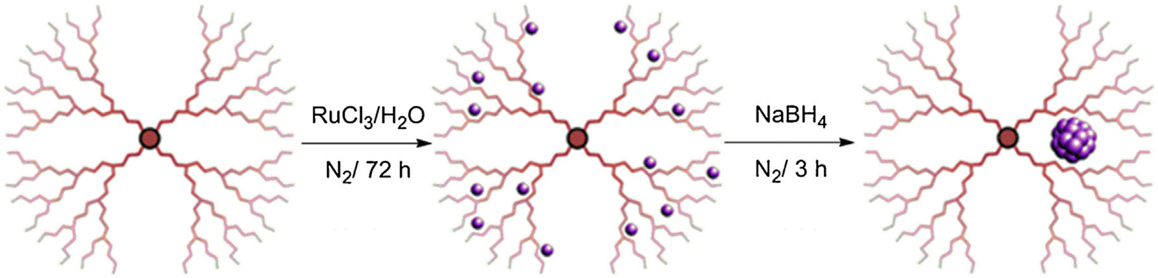


Scheme 1. Scheme for the hydrogenation of toluene illustrating the partially hydrogenated products 1-methylcylcohexene and 4-methylcyclohexene observed during the reaction and the fully hydrogenated product methylcyclohexane.



Scheme 2. Reaction sequence for the preparation of dendrimer encapsulated Ru nanoparticles.

ionic liquid with the catalytic surface [14,15]. This behavior was observed by Schwab et al. who investigated the effect of using water-soluble ionic liquids in the aqueous, Ru catalyzed hydrogenation of benzene [16]. An increase in the selectivity towards the partially hydrogenated products was ascribed to surface modification of the Ru nanoparticles, with smaller particles of 1.4 nm resulting in higher selectivity compared to 4.1 nm ones. This facilitated dissociation of the cyclohexenes from the surface and helped prevent re-adsorption. In this case, however, unlike SCILL catalysts that comprise a physical layer of ionic liquid, the ionic liquid acts more as a ligand and not a physical coating due to its water solubility and low concentration in the ppm range.

Given the particle size dependency reported by Schwab et al. we were interested to study the use of well-defined, monodisperse Ru nanoparticles in SCILL catalyzed hydrogenation of toluene (see Scheme 1), prepared via dendrimer encapsulated synthesis shown in Scheme 2 [17]. Recently, we have explored the versatility of dendrimers as templating agents for the preparation of well-defined metal nanoparticles and their possible applications in catalytic reactions with and without ionic liquid coating [18,19].

In this work, we will present catalytic results of RuDEN materials in liquid-phase toluene hydrogenation. To the best of our knowledge this constitutes the first report on arene hydrogenation using dedicated SCILL materials where the ionic liquid constitutes a catalyst coating and not an additive to the reaction solution.

2. Experimental

2.1. Chemicals, materials and instrumentation

The hydroxyl terminated fourth- (G4-), fifth- (G5-) and sixth-generation (G6-) poly(amidoamine) (PAMAM-OH) dendrimers were purchased as methanol solutions (Sigma-Aldrich). The methanol was removed from these solutions prior to use under high vacuum at ambient temperature for 3 h. The substrate and standards, toluene, n-decane, methylcyclohexane, 1-methylcyclohexene and 4-methylcyclohexene were purchased from Sigma-Aldrich and used as received. The $RuCl_3$ hydrate (99.98%) and sodium borohydride were purchased from Sigma-Aldrich and used as received. The sodium hydroxide was purchased from Associated Chemical Enterprises (ACE) and used as is. Toluene and silica gels 60 and 100 were purchased from Sigma-Aldrich and degassed prior to use by bubbling with Ar gas for 30 min. Deionized water, from an in-house Milli-Q (18 ΩM cm) system was used in all experiments.

Transmission electron microscopy (HRTEM) images were obtained on a JEOL JEM-2100 F with an accelerating voltage of 200 kV equipped with a FEG source. HRTEM samples were prepared by a combination of drop deposition, onto a holey carbon covered TEM copper grid, and wicking utilized to remove any excess sample. The average nanoparticle size was calculated by analyzing 150 nanoparticles from the obtained HRTEM images using ImageJ software [20].

2.2. Preparation of RuSil100 catalysts

The general procedure for preparing RuDENs was adapted from a method initially described by Lafaye et al. [17], and further adapted by our group [18,19]. Ruthenium DENs were synthesized by reacting hydroxyl terminated G_i-PAMAM-OH ($i = 4–6$) with 40, 80 and 160 molar excesses of $RuCl_3$ respectively. The silica supported RuDENs were prepared using a method previously described by our group using amorphous silica gel 100, named RuSil100, or silica gel 60, named RuSil60, respectively [19]. Complete details of the catalyst preparation are listed in the Supporting Information.

2.3. General preparation for RuSCILL catalysts

The RuSCILL catalysts were prepared by e.g. coating the RuSil100 catalyst with the appropriate amount of ionic liquid up to a pore filling of 10 vol%. To prepare a batch of RuSCILL, RuSil100 (0.4 g) was added to a methanol (5 mL) solution of the appropriate ionic liquid with a mass of e.g. either 0.0453 g, 0.0397 g or 0.0472 g for the ionic liquids [BMIM][BF_4], [BMIM][PF_6] or [BMIM][NTf_2] respectively. The solvent was then removed under vacuum at 50 °C on a rotary evaporator for 2 h. The trace amounts of solvent were then further removed under high vacuum at ambient temperature for 1 h.

2.4. Liquid-phase hydrogenation of toluene in a 100 cm^3 autoclave

Toluene hydrogenation experiments were performed in a Parr stainless steel autoclave with a volume of 100 mL fitted with a

Table 1
The average Ru NP size for each of the RuDENs, RuDENs supported on silica 60 and silica 100 and the percentage change in size upon immobilization.

Support	Generation	Catalyst name	Ru particle diameter[a] nm	Change in diameter[b] %
None (dendrimer)	G4	G4-RuDEN	1.2 ± 0.1	–
	G5	G5-RuDEN	1.4 ± 0.1	–
	G6	G6-RuDEN	2.2 ± 0.3	–
Silica 60	G4	G4-RuSil60	2.4 ± 0.3	+100
	G5	G5-RuSil60	2.1 ± 0.3	+50
	G6	G6-RuSil60	2.1 ± 0.3	0
Silica 100	G4	G4-RuSil100	1.4 ± 0.2	+17
	G5	G5-RuSil100	1.5 ± 0.2	+7
	G6	G6-RuSil100	2.2 ± 0.2	0

[a] Data derived from TEM studies.
[b] Increase in particle size compared to pure RuDEN in absence of support.

Teflon liner, operated in batch mode and stirred at 1200 rpm. Depending on the reaction, the conditions were set at 75 °C, 90 °C and 110 °C and a H_2 pressure of 10 bar. The catalyst (0.08–0.1 wt% Ru, 0.2–0.3 g, 1.84 μmol Ru) was transferred to the autoclave. The autoclave was charged with cyclohexane (30 mL) and toluene (0.34 mL, 0.2947 g, 3198.9 μmol) with n-decane as the internal standard (0.34 mL). The reactor was purged thrice at ambient temperature with H_2 gas, depressurized and heated to 90 °C and allowed to stir at this temperature for 1 h to allow catalyst activation. The desired temperature, either 75, 90 or 110 °C, was set and the reactor pressurized to a H_2 pressure of 10 bar to commence reaction. Samples of the reaction mixture were periodically taken and analyzed by gas chromatography on a Shimadzu GC-2010 equipped with a 30 m Restek Rtx®-5 capillary column.

3. Results and discussion

The nanoparticles prepared from the G_i-PAMAM-OH dendrimer are referred to as G_i-RuDEN respectively with i = 4, 5, 6. HRTEM analysis of the RuDENs prior to immobilization was conducted and the results have been previously published [21]. An average particle size of 1.2 ± 0.1 nm, 1.4 ± 0.1 nm and 2.2 ± 0.3 nm was observed for the G4-RuDEN, G5-RuDEN and G6-RuDEN catalysts respectively. A series of immobilized RuDEN catalysts were prepared using silica 60 or silica 100 as catalyst support and are referred to as G_i-RuSil60 and G_i-RuSil100 respectively. The average sizes of the nanoparticles are summarized in Table 1 (images and histograms of which can be found in the Supporting Information).

A 100% and 50% Ru NP size increase was observed for the G4-RuDEN and the G5-RuDEN respectively upon immobilization on silica 60. The increased dendrimer generation is therefore beneficial for the stabilization of the Ru NP during the immobilization on silica. The narrow Ru NP size distribution is maintained and, more interestingly, the sintering of the G4- and G5-RuDENs is minimized upon immobilization on the silica 100 support when compared to results obtained for silica 60. The immobilization of G6-RuDEN on silica 100 has no significant effect on the Ru NP diameter, which maintained an average diameter of 2.2 nm. The physical properties of the support material are therefore of great importance, especially with regards to the pore size. Most likely, the larger average pore size of silica 100 facilitates the penetration of the RuDENs into the support and therefore allows for better RuDEN dispersion.

The changes in the physical characteristics such as surface area, pore volume and pore diameter were investigated upon coating with the ionic liquid. The uncoated catalyst was prepared with a metal loading of 0.08–0.15 wt% Ru as confirmed by ICP-OES. BET analysis of the G6-RuSil60 uncoated catalyst indicates a surface area (A_{BET}) of 462.1 $m^2\,g^{-1}$, an average pore volume (V_{pore}) of 0.82 $cm^3\,g^{-1}$ and an average pore diameter (d_{pore}) of 5.6 nm. Changes were observed for the surface area when comparing the 10% G6-RuSCILL catalysts to the 20% G6-RuSCILL catalysts. This change in the physical characteristics upon coating with an ionic liquid is consistent with literature and confirms the presence of the ionic liquid on the solid catalyst surface for the G6-RuSCILL catalysts [13]. The physical characteristics of the coated and uncoated catalysts prior to use in the reaction are listed in Table 2. Additionally, BET data obtained for the G6-RuSCILL catalysts with an ionic liquid loading, $\alpha = 0.2$, prior to and upon completion of the reaction are listed to account for possible ionic liquid leaching under reaction conditions.

Comparison of the BET results for the pre- and post-run G6-RuSCILL catalyst indicates that there was no significant change in the average pore volume values. Since the used SCILL catalysts have been carefully dried in vacuum to remove any accumulated compounds, except the ionic liquid, it can be assumed that the chosen ionic liquids are suitable for use in the preparation of the Ru-SCILL catalysts for the hydrogenation of toluene given the applied reaction conditions.

For the liquid-phase hydrogenation of toluene, commercially available Ru/Al_2O_3 was used as benchmark catalyst. As depicted in Fig. 1, the selectivity toward the intermediate methylcyclohexene (MCHe) was low at all conversion levels and declined with increasing conversion, following the generally known trends from literature [21]. The yield for MCHe reached 2.6% at maximum (see Table S1 in supporting information). Due to the high loading of 5 wt% Ru in this catalyst, the consecutive reaction of MCHe to MCHa is facilitated and lower metal loading would be beneficial. A 0.15 wt% Ru/Al_2O_3 catalyst was prepared by incipient wetness impregnation and evaluated under identical conditions. As expected, the maximum yield improved by a factor of two to 5.5% MCHe.

Deposition of the dendrimer particles on Al_2O_3 proved more difficult than on silica since it required a proper adjustment of the isoelectric point of Al_2O_3. As a result, it was more convenient to deposit the dendrimer derived metal nanoparticles (MNPs) onto

Table 2
Surface area, average pore volume and average pore diameter for the uncoated and coated G6-RuSil60 catalysts prior to and after reaction.

Ionic liquid	Loading α vol%	Surface area A_{BET} $m^2\,g^{-1}$	Pore volume V_{pore} $mL\,g^{-1}$	Pore diameter d_{pore} nm
–	–[a]	462.1	0.82	5.6
[BMIM][BF_4]	10	286.5	0.64	6.4
	20	258.0	0.56	6.2
	20[b]	275.5	0.58	6.0
[BMIM][PF_6]	10	314.5	0.64	5.9
	20	232.7	0.54	6.8
	20[b]	203.4	0.56	7.9
[BMIM][NTf_2]	10	308.3	0.57	5.4
	20	259.2	0.51	5.6
	20[b]	267.5	0.56	5.9

[a] Native, uncoated G6-RuSil60.
[b] Post-catalytic run, reaction conditions: p (H_2) = 10 bar, G6-RuSil60, 3.19 mmol of toluene, 0.00184 mmol Ru and 30 mL of cyclohexane.

Table 3
Comparison between MNPs derived from different dendrimer generations in the selective hydrogenation of toluene.

Catalyst	Conversion%	Selectivity%	Yield%	Av. Particle size nm	Ratemol$_{TOL}$ mol$_{Ru}$$^{-1}$ m^{-3} h^{-1}
0.15 wt% G4-RuSil100	13.1	25.9	3.4	1.4 ± 0.2	8.0E + 08
	37.5	16.0	6.3		
	73.5	8.8	6.5		
0.15 wt% G5-RuSil100	11.0	21.9	4.6	1.5 ± 0.2	4.7E + 08
	32.8	12.0	6.5		
	52.6	7.6	5.6		
0.15 wt% G6-RuSil100	9.2	35.3	3.2	2.2 ± 0.2	4.2E + 08
	25.3	19.3	4.9		
	51.9	10.7	5.6		

Reaction conditions: 15 ml toluene in 135 ml cyclohexane, 110 °C, 30 bar H_2, stirring at 800 rpm.

Table 4
Coating of G5-Ru MNP supported on silica 100 with different ionic liquids for selective hydrogenation of toluene in liquid-phase.

Ionic Liquid	Max. Yield$_{MCHe}$%	Ratemol$_{TOL}$ mol$_{Ru}$$^{-1}$ m^{-3} h^{-1}	Viscosity[a]mPa s	S$_{TOL}$[b]mmol L^{-1}	S$_{TOL}$/S$_{MCHe}$[c]
–	5.7[d]	8.3E + 08	–	–	–
–	4.0	5.1E + 08	–	–	–
[EMIM][NTf$_2$]	6.8	1.0E + 08	7.3	2.8	27
[BMIM][NTf$_2$]	6.5	1.0E + 08	8.6	4.1	19
[HMIM][NTf$_2$]	6.5	1.4E + 08	10.1	n.d.	n.d.
[OMIM][NTf$_2$]	6.2	2.0E + 08	11.8	7.1	14
[BMIM][PF$_6$]	4.9	0.5E + 08	24.0	1.5	71
[BMIM][BF$_4$]	3.2	0.6E + 08	14.4	1.0	11
[BMIM][OcSO$_4$]	4.3	0.6E + 08	49.5	n.d.	n.d.

[a] Literature data at 85 °C taken from Ref. [22].
[b] Solubility of toluene.
[c] Solubility ratio between toluene and methylcyclohexene.
[d] Different batch of G5-RuSil100. Reaction conditions: 15 ml toluene in 135 ml cyclohexane, 110 °C, 30 bar H_2, stirring at 800 rpm.

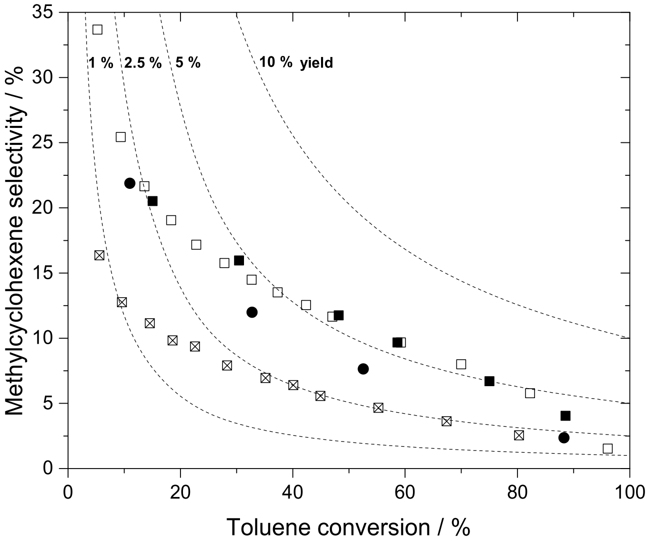


Fig. 1. Selectivity vs conversion plots for different catalyst utilized in the liquid-phase hydrogenation of toluene. Commercial 5 wt% Ru/Al_2O_3 (square, crossed), in-house synthesized 0.15 wt% Ru/Al_2O_3 (square, filled), 0.15 wt% G5-Ru/Al_2O_3 (), 0.15 wt% G5-Ru/SiO_2 (circle, filled), dashed lines indicate possible yields. Reaction conditions: 15 ml toluene in 135 ml cyclohexane, 110 °C, 30 bar H_2, stirring at 800 rpm.

SiO_2. Comparing the dendrimer particles performance on silica and Al_2O_3 revealed that the maximum obtained yield is slightly lower in the case of SiO_2 (compare 8.5% to 5.7% in Table S1). However, the activity significantly increased for the silica supported catalyst by a factor of approximately two. Due to this improved activity and taking the problems in synthesis and TEM analysis for the alumina support into account, further screening was performed with silica supported materials.

To elucidate a possible size effect on the reaction, supported catalysts using MNPs derived from different dendrimer generations were prepared, which allowed tuning of the resulting particle size. Both activity and selectivity were found to depend significantly on the particle size, with smaller particles resulting in higher yields as well as higher rates (see Table 3 and Fig. S4 in the supporting information). For the selective hydrogenation of arene compounds using Ru this is the first particle size dependency study reported so far [21]. As a result, G5-RuSil100 catalysts were chosen for further studies.

The coating with selected ionic liquids was investigated next, with the goal to improve the selectivity and yield of the consecutive reaction. Ionic liquids were selected with respect to their hydrophilic and hydrophobic character as well as their nucleophilicity. It was anticipated that the ionic liquid might be able to selectively block the most active (and least selective) sites of the MNPs, thereby improving the yield [15]. In addition, the ionic liquid might help to control the local concentration of substrate and intermediate by means of solubility.

It should be noted that the batch of G5-RuSil100 used in these studies showed a lower activity and selectivity compared to the previous batch shown in Fig. 1 and Table S1. Between these two batches the maximum yield for MCHe decreased from 5.7 to 4.0% and the rate decreased from 8.3×10^8 to 5.1×10^8 mol$_{TOL}$ mol$_{Ru}$$^{-1}$ m^{-3} h^{-1}. Slight deviations during nanoparticle synthesis and immobilization might be responsible for this deviation. Since the reproducibility within one batch was high, the ionic liquid variation presented in Table 4 was carried out using the batch showing lower activity.

When the less active catalyst was coated with hydrophobic [RMIM][NTf$_2$] ionic liquids (R = Ethyl, Butyl, Hexyl, Octyl) the activity decreased significantly to low values between 1.0×10^8 mol$_{TOL}$ mol$_{Ru}$$^{-1}$ m^{-3} h^{-1} and 2.0×10^8 mol$_{TOL}$ mol$_{Ru}$$^{-1}$ m^{-3} h^{-1}. Higher activity was obtained for longer chain imidazolium cations. This trend is in contrast to the viscosity of the ionic liquids at 85 °C but correlates well with the toluene solubility. Since the ionic liquid film is only a few nm thick, the diffusion inside the film will play a minor role on the overall rate. More important seems to be the amount of substrate that can be dissolved within the film and thus access the catalyst surface. The activity toward the intermediate methylcyclohexene MCHe is following the activity trend, with more active SCILL catalysts yielding less MCHe. Within the [RMIM][NTf_2] series this trend can be partly explained by the relative solubility of toluene and MCHe as indicated in Table 4. The more selective SCILL catalyst contains the ionic liquid with the highest ratio, thereby indicating that the intermediate is not dissolving well in the ionic liquid film. Such an in-situ extraction back into the organic phase seems to help to prevent consecutive hydrogenation.

However, the solubility ratio alone is not able to explain the yields with other ionic liquids, exemplified for [BMIM][PF_6] in Table 4. Here, the highest solubility ratio of 71 was measured, while the yield remained lower than for all [RMIM][NTf_2] ionic liquids. In summary, no clear correlation between solubility and yield can be derived. This can be regarded as a hint that solubility alone is not the only reason for improved yields in SCILL catalysis. More probably it is a complicated interplay between e.g. surface interaction, solubility and viscosity.

4. Conclusion

In this work, coating of either commercial Ru/Al_2O_3 as well as dendrimer templated Ru/SiO_2 with different ionic liquids yielded solid catalysts with ionic liquid layer (SCILL). The native commercial catalyst was active in the batch-type liquid-phase hydrogenation of toluene but achieved low selectivity toward the desired intermediate methylcyclohexene MCHe. The well-defined size distribution of the dendrimer templated MNPs was beneficial in achieving a higher activity in hydrogenation of toluene compared to the commercial catalysts. In addition, a threefold higher yield toward MCHe could be obtained. At low conversions around 10% the selectivity toward MCHe was as high as 35% but dropped with increasing conversion as expected for a consecutive hydrogenation reaction.

The coating of these dendrimer derived MNPs with ionic liquids helped to improve the selectivity further, however, at the cost of activity. The influence of the ionic liquid cannot be related to modification of the local concentration at the catalyst surface alone. Selective poisoning of the most active centers is possible, but could not be validated yet. A more detailed understanding of such multiple parameters seems necessary to make these SCILL catalysts more feasible for partial hydrogenation of arene compounds in the future.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.molcata.2016.05.010.

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