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Short Communication

Preparation of well-defined dendrimer encapsulated ruthenium nanoparticles and their application as catalyst and enhancement of activity when utilised as SCILL catalysts in the hydrogenation of citral

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ABSTRACT

Silica supported dendrimer encapsulated ruthenium nanoparticles were prepared and evaluated as catalysts in the hydrogenation of citral. The dendrimer encapsulated nanoparticles were prepared using the generation 4 (G4), generation 5 (G5) and generation 6 (G6) hydroxyl-terminated poly(amidoamine) (PAMAM-OH) dendrimers as templating agents with different Ru metal:dendrimer ratios. The effects of ionic liquids as catalyst coatings on the catalytic activity were investigated for the ionic liquids [BMIM][NTf_2], [OMIM][NTf_2], [BMIM][BF_4], [BMIM][PF_6], [EMIM][OcS] and [EMIM][EtS]. An enhancement in catalytic activity was observed when utilising [BMIM][NTf_2] as an ionic liquid coating with selectivity towards citronellal.

1. Introduction

Investigations into the chemoselective hydrogenation of α,β-unsaturated compounds date as far back as the mid-1920s. The importance of unsaturated alcohols as an intermediate in the preparation of pharmaceuticals and fine chemicals has kept the chemoselective hydrogenation of α,β-unsaturated compounds a hot topic. In practice, the chemoselective hydrogenation proves challenging as the hydrogenation of the C═C bond is thermodynamically favoured over that of C═O by approximately a 35 kJ/mol difference [1]. Additionally, for kinetic reasons, C═C bond reactivity is higher than that of the C═O bond for hydrogenation. As a result, numerous theoretical studies have been conducted and comprehensive reviews have been published in addressing this subject [2–5].

The selectivity towards hydrogenation of the C═C bond and C═O bond is usually metal specific. In the case of citral hydrogenation, when considering supported Ru catalysts, the hydrogenation reaction produces citronellal, geraniol, nerol and citronellol as shown in Scheme 1 [6–12].

Ionic liquids are low melting salts that usually remain molten at ambient temperature or temperatures below 100 °C [13]. Citral hydrogenation in the presence of an ionic liquid was realised by using supported nickel–tin [14] and palladium [14,15] catalysts. The activity of the catalyst was considerably decreased because of the low hydrogen solubility in the ionic liquid. The issue of low hydrogen solubility can be addressed by utilising the ionic liquid and the supported catalyst according to the solid catalyst with ionic liquid layer (SCILL) concept. The concept, developed by Jess et al., has been patented and entails the dispersion of an ionic liquid film across a supported catalyst [16–18]. One advantage for this system is the decrease in diffusion limitation compared to bulk ionic liquid. Claus et al. conducted one of the first studies into the evaluation of supported Ru SCILL catalysts in citral hydrogenation [19]. Similar studies revealed an increased selectivity towards the alcohols geraniol and nerol [20]. In each case, selectivity was towards the hydrogenation of the C═O bond.

This study focuses on the evaluation of Ru dendrimer encapsulated nanoparticles (DENs) supported on silica 60 as potential catalysts for the hydrogenation of citral. The dendrimer templated methodology of nanoparticle synthesis was chosen to ensure a narrow size distribution for the Ru nanoparticles. The effect of an ionic liquid layer on the activity and selectivity of the uncoated catalyst was then evaluated for the ionic liquids, 1-butyl-3-methylimidazolium tetrafluoroborate, [BMIM][BF_4], [BMIM][PF_6], [BMIM][NTf_2], 1-ethyl-3-methylimidazolium ethylsulphate, [EMIM][EtS] and 1-ethyl-3-methylimidazolium octylsulphate, [EMIM][OcS].

2. Experimental

The hydroxyl terminated fourth- (G4OH), fifth- (G5OH) and sixth-generation (G6OH) poly(amidoamine) (PAMAM) dendrimers were purchased as methanol solutions (Sigma-Aldrich). The methanol was

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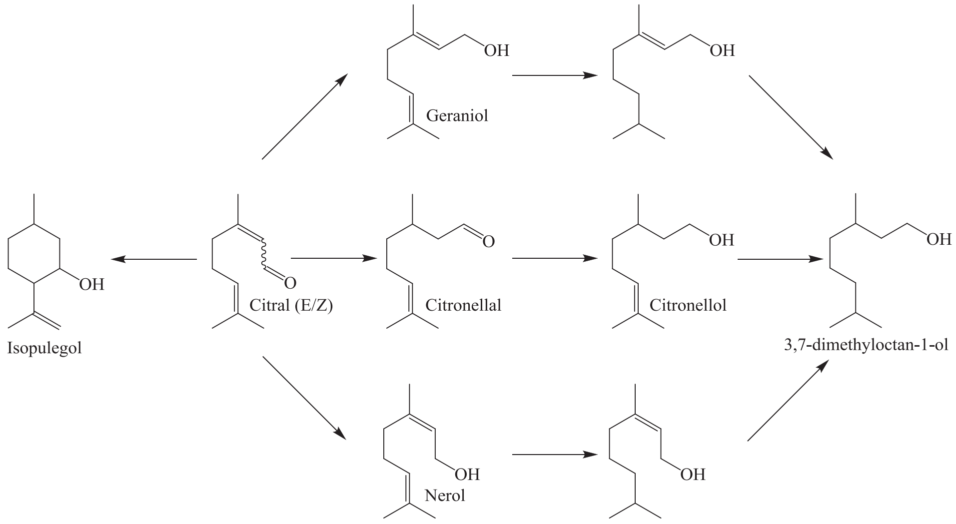

Scheme 1. Scheme for the hydrogenation of citral.

removed from these solutions prior to use under high vacuum at ambient temperature for 3 h. The $RuCl_3$ hydrate (99.98%) and sodium borohydride were purchased from Sigma-Aldrich and used as received. Milli-Q (18 MΩ·cm) deionised water was used in all experiments and degassed for 30 min prior to use. The amorphous silica 60 was purchased from Merck and used as received. The ionic liquids [BMIM][NTf_2], [BMIM][BF_4] and [BMIM][PF_6] were purchased from Sigma-Aldrich and used as received. The ionic liquids [EMIM][OcS] and [EMIM][EtS] were purchased from Solvent Innovation and used as received. The substrates, standards and internal standard, citral, citronellal, citronellol, geraniol, nerol, and n-decane were purchased from Sigma-Aldrich and used as received.

2.1. Preparation of silica supported RuDEN catalysts, RuSil

The RuDENs were prepared from aqueous solutions of G4-PAMAM-OH, G5-PAMAM-OH, G6-PAMAM-OH and $RuCl_3$ in a dendrimer:Ru ratio of 1:40, 1:80 and 1:160 respectively. The RuDENs were deposited on amorphous silica 60 by agitation of a mixture of the RuDENs and amorphous silica on a reciprocating shaker. Complete details of the catalyst preparation are listed in the Supporting Information.

2.2. General preparation of RuSCILL catalysts

The RuSCILL catalysts were prepared from G5-RuSil60. The required amount of ionic liquid was weighed into a round bottom flask (50 cm^3). A methanolic solution of the ionic liquid was prepared by transferring methanol (10 cm^3) to the ionic liquid. The RuSil catalyst was transferred to the methanolic solution of the ionic liquid and allowed to agitate on a rotary evaporator without vacuum for 15 min and at ambient temperature. The solvent was then removed at 60 °C on the rotary evaporator to yield a free-flowing grey powder. The catalyst was further dried under high vacuum for 6 h at ambient temperature. Full experimental details are listed in the Supporting Information.

2.3. Hydrogenation of citral

The hydrogenation of citral was performed in a Parr stainless steel autoclave with a volume of 100 cm^3 fitted with a teflon cup, operated in batch mode and stirred at 1200 rpm. Depending on the reaction, the reaction conditions were set at 90 °C, 110 °C and 130 °C and a H_2 pressure of 10 bar and 30 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 cm^3) and citral (0.156 cm^3, 0.1393 g, 921.6 μmol) with n-decane as the internal standard (0.156 cm^3). The reactor was purged thrice at ambient temperature with H_2 gas, depressurised and heated to 90 °C and allowed to stir at this temperature for 1 h to allow for catalyst activation. The desired temperature, either 90, 110 or 130 °C, was set and the reactor was pressurised to a H_2 pressure of 10 bar or 30 bar to commence reaction. Samples of the reaction mixture were taken every 30 min over a 240 min period and analysed by gas chromatography on a Shimadzu GC-2010 Plus equipped with a 30 m Restek Rtx-5 capillary column.

3. Results and discussion

3.1. The immobilisation of RuDENs on silica 60 and preparation of RuSCILL catalysts

The G4-, G5- and G6-RuDEN catalysts were prepared using a similar method as previously published [21]. The RuDEN catalysts were immobilised on amorphous silica 60 using wetness impregnation and subsequently washed with an aqueous ammonia solution to remove any trace chloride present on the catalyst surface, the presence of which acts as a catalyst poison [22]. The silica supported RuDEN catalysts will be referred to as Gn-RuSil60 where “n” denotes the generation of dendrimer, 4, 5 or 6 respectively. The average Ru NP size upon immobilisation was 2.4 ± 0.3, 2.1 ± 0.3 and 2.1 ± 0.3 nm for G4-RuSil60, G5-RuSil60 and G6-RuSil60 respectively (HRTEM data presented in the Supporting Information). The RuSil60 catalysts were not calcined prior to evaluation and the presence of the dendrimer was confirmed by TGA data obtained (see Supporting Information). This helps maintain the stabilising effect of the dendrimer on the nanoparticle.

The changes in the physical characteristics such as surface area, pore volume and pore diameter of the RuSil60 catalysts were investigated upon coating with the ionic liquid. The surface area and pore volume of 462.1 $m^2 \cdot g^{-1}$ and 0.82 $cm^3 \cdot g^{-1}$ were observed for the uncoated G5-RuSil60 catalyst respectively. The RuSCILL catalysts presented in Table 1 represent a series of SCILL catalysts for a 10% pore volume filling with ionic liquid represented by an α-value of 0.1. An expected decrease in surface area and pore volume to 323–358 $m^2 \cdot g^{-1}$ and 0.63–0.67 $cm^3 \cdot g^{-1}$ was observed respectively when compared to the results obtained for the uncoated catalyst. The presence of the ionic liquid was further confirmed by TGA data obtained (see Supporting Information).

Table 1
Typical surface area, average pore volume and average pore diameter changes for the uncoated and coated G5-RuSil60 catalysts.

Catalyst	Surface area, S_{BET} ($m^2 \cdot g^{-1}$)[a]	Total pore volume, V_T ($cm^3 \cdot g^{-1}$)[b]	Average pore diameter, D_p (Å)[b]
Uncoated G5-RuSil60	462.1	0.82	56.2
10% [BMIM][BF_4] G5-RuSCILL	323.5	0.66	58.4
10% [BMIM][PF_6] G5-RuSCILL	344.9	0.65	55.7
10% [BMIM][NTf_2] G5-RuSCILL	357.5	0.65	53.6
10% [EMIM][EtS] G5-RuSCILL	342.1	0.63	55
10% [EMIM][OcS] G5-RuSCILL	347.8	0.67	56.7

[a] Determined by BET analysis.
[b] Determined by BJH analysis.

Post-catalytic BET N_2 physisorption analysis confirms maintained interaction of the ionic liquid with the catalyst surface.

3.2. Catalytic evaluations

3.2.1. Evaluation of RuSil60 catalysts in the hydrogenation of citral

Brief investigations into the effects of temperature and pressure on the activity of the catalyst were conducted using cyclohexane as the solvent. The conversion of citral at these conditions is illustrated in Fig. 1(a). A minimal 5–6% increase in conversion upon increasing the pressure from 10 bar to 30 bar was observed. The selectivity observed in each reaction was towards citronellal exclusively.

A high initial conversion of citral was observed with a levelling-off of the citral conversion during the course of the reaction. Inhibition of the reaction was observed after the higher initial activity. The decrease in conversion with time can be explained by an increase in the inhibitory decarbonylation reaction [12,23–25]. The carbon monoxide that forms competitively adsorbs to active sites on the nanoparticle surface. The overall kinetic behaviour resulting from the decay in catalytic activity was seen for all citral hydrogenation reactions concerning the evaluation of RuSil60. The highest conversion was observed for the G4-RuSil60 catalyst for reactions conducted at 90 °C (Fig. 1c). The lower conversion observed for the higher generations can be explained by the possible increase in steric hindrance that inhibits adsorption of citral. An increase in temperature from 90 to 130 °C caused no significant increase in conversion except for G4-RuSil60. This marked increase in conversion at 130 °C for G4-RuSil60 is however ascribed to the formation of unwanted side products.

When considering the selectivity results obtained (Fig. 2), there is a clear indication that the increased conversion of citral is a result of the increased formation of the side product isopulegol, formed by the cyclisation of citronellal [12,25]. The overall percentage of citronellal in the reaction mixture does not change significantly when utilising G5-RuSil60 and G6-RuSil60, which indicates that the formation of citronellal is rapid enough to compensate for the intrinsic rate of formation of isopulegol. Increase in temperature to 130 °C causes a dramatic increase in the selectivity towards isopulegol when evaluating G4-RuSil60. In this case, the formation of isopulegol is rapid enough to exceed formation of citronellal. The result suggests that the dendrimer stabiliser decomposes at 130 °C when the solvent and substrate are present. This results in a more exposed nanoparticle surface, allowing for an increase in the conversion of citral albeit with the formation of isopulegol. This was not observed for G5-RuSil60 and G6-RuSil60 possibly as result of a more stable dendrimer architecture. Additionally, studies into factors affecting the selectivities observed in the hydrogenation of α,β-unsaturated compounds reveal that basic promoters such as sodium hydroxide increase selectivity towards the saturated aldehyde [26]. This helps further explain why the higher generation dendrimers with increased tertiary amines, which can act as basic promoters, help promote C=C double bond hydrogenation.

3.2.2. Evaluation of RuSCILL catalysts in the hydrogenation of citral

The use of ionic liquid as a catalyst coating can influence the product selectivity observed when evaluating different catalysts however, in this study only the activity was affected since selectivity towards citronellal was maintained. RuSCILL catalysts with different ionic liquids are presented with focus on the effect of the ionic liquid on the catalyst activity. The reactions were run at 90 °C to help minimise formation of ionic liquid decomposition products which could further modify the catalyst surface [27]. When comparing the results of the RuSCILL catalysts to that of the RuSil60 catalyst (Table 2), both increases and decreases in the conversion of citral were observed upon coating with the various ionic liquids. A decrease in the conversion was observed compared to the uncoated catalyst when using the ionic liquids [EMIM][EtS], [EMIM][OcS], [BMIM][PF_6] and [BMIM][BF_4] as coatings with an α-value of 0.1 as seen for entries 4–7.

A significant increase in the conversion of citral to 50% was observed when using the ionic liquid [BMIM][NTf_2] as a catalyst coating with an α-value of 0.1. This suggests that the [BMIM][NTf_2] ionic liquid coating minimises the effect of decarbonylation. The increase in activity is most likely competitive displacement of CO by the ionic liquid. The [NTf_2] ionic liquids are known to displace CO showing strong ligand-like interactions with the surface of the nanoparticle [27]. This would suggest that the ionic liquid has a negative effect on the activity of the

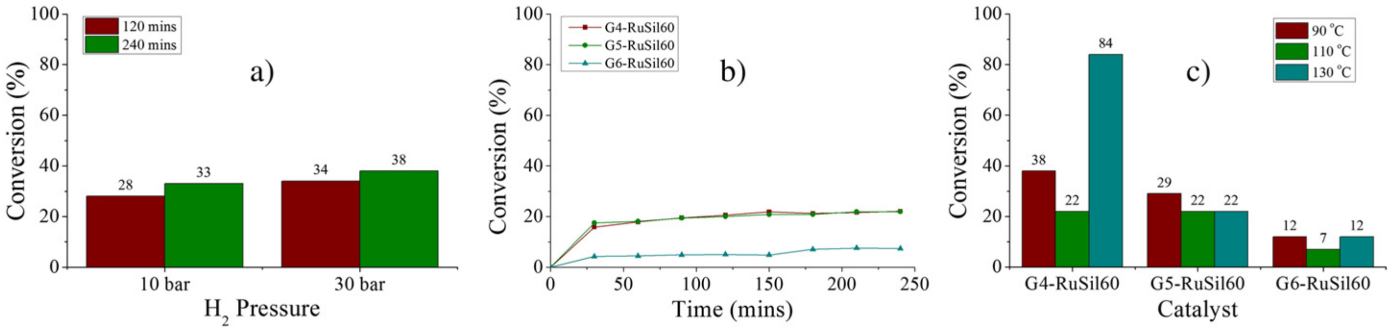

Fig. 1. Conversion of citral illustrated for a) pressure dependant conversion of citral at 120 min and 240 min for a H_2 pressure of 10 bar and 30 bar using the G4-RuSil60 catalyst, and conversion of citral using the various RuSil60 catalysts and at various temperatures illustrated by the b) time-resolved conversion of citral at 110 °C and c) end of run conversion of citral at 90 °C, 110 °C and 130 °C.

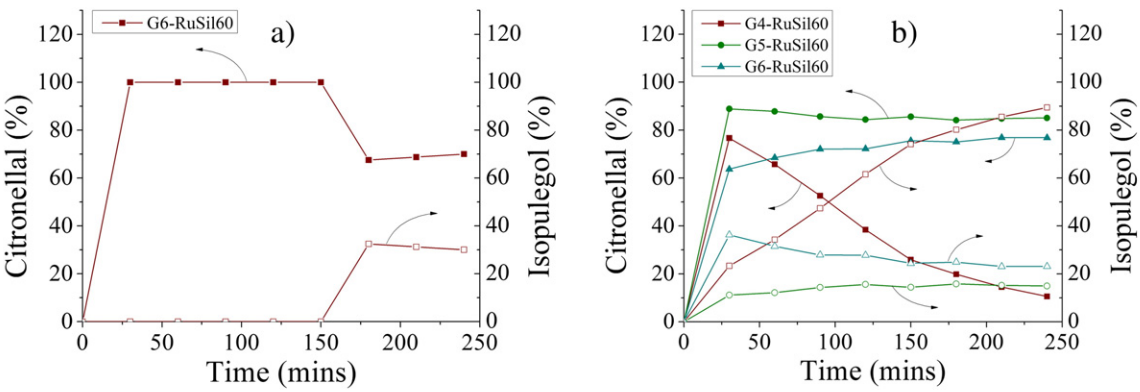

Fig. 2. Selectivity observed for the citral hydrogenation reaction using the RuSil60 catalysts at a) 110 °C while evaluating G6-RuSil60 and b) 130 °C when evaluating G4-RuSil60, G5-RuSil60 and G6-RuSil60.

nanoparticle given the strong interaction, possibly leading to an overwhelming competitive inhibition of adsorption of the substrate during reaction. This possible inhibition by a [BMIM][NTf_2] ionic liquid layer over a Pd/SiO_2 catalyst is, however, minimal in the hydrogenation of citral as observed by Claus et al. [20]. The adsorption of H_2 to the catalyst surface is dependent on the partial pressure of the gas, especially when evaluating a SCILL catalyst. Given the considerably lower partial pressure of CO when compared to H_2, diffusion of CO back to the nanoparticle surface is not favoured. In this sense, the ionic liquid has a twofold purpose, providing a diffusional barrier for the CO gas, a poison, and additionally displacing any CO gas that coordinates to the nanoparticle surface. Despite these advantages, the inhibitory effects of CO were not completely overcome. Increase in [BMIM][NTf_2] to an α-value of 0.2 caused a decrease in activity. The decrease in conversion of citral with an increase in the amount of [BMIM][NTf_2] most certainly is ascribed diffusion limitation by the ionic liquid layer for the substrate and reactants.

4. Conclusion

In the present study a series of silica supported RuDENs were synthesised and evaluated in the chemoselective hydrogenation of the α,β-unsaturated compound, citral. The effects of changes in reaction parameters were investigated and a strong dependence on temperature was observed when considering the selectivity. The use of ionic liquids as catalyst coatings had a positive effect on the catalytic activity in some instances, which is ascribed to the displacement of the adsorbed CO poison on the catalyst surface formed during decarbonylation. This increase in activity with the addition of an ionic liquid coating was not observed for all the ionic liquids and might be related to the coordination strength of the ionic liquid on the nanoparticle surface. Further studies are underway to better understand the details surrounding the effects of ionic liquids on the activity and selectivity of the catalyst.

Table 2
Citral hydrogenation results with G5-RuSil60 and RuSCILL catalysts in cyclohexane using various ionic liquids as coatings at a temperature of 90 °C and a H_2 pressure of 30 bar. Results shown are for end of run (240 min).

Entry	Ionic liquid	α	Citral conversion (%)	Citronellal (%)
1	None[a]	–	29	100
2	[BMIM][NTf_2]	0.1	50	100
3	[BMIM][NTf_2]	0.2	22	100
4	[BMIM][PF_6]	0.1	14	100
5	[BMIM][BF_4]	0.1	7	100
6	[EMIM][EtS]	0.1	21	100
7	[EMIM][OcS]	0.1	19	100

[a] Uncoated G5-RuSil60 catalyst.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at http://dx.doi.org/10.1016/j.catcom.2014.08.012.

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