



# 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<sub>2</sub>] as a coating.

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## 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

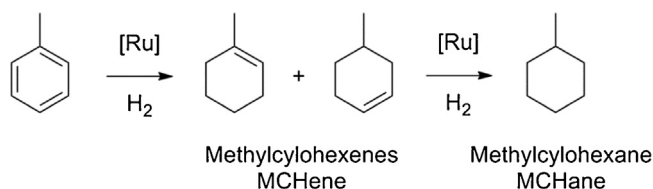
[5]. The utilization of ruthenium nanoparticles in ionic liquids for the hydrogenation of benzene has shown appreciable selectivity to cyclohexene [6], however, few other studies focus on the ability of an ionic liquid to enhance selectivity towards partially hydrogenated arenes. When comparing reactions 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].

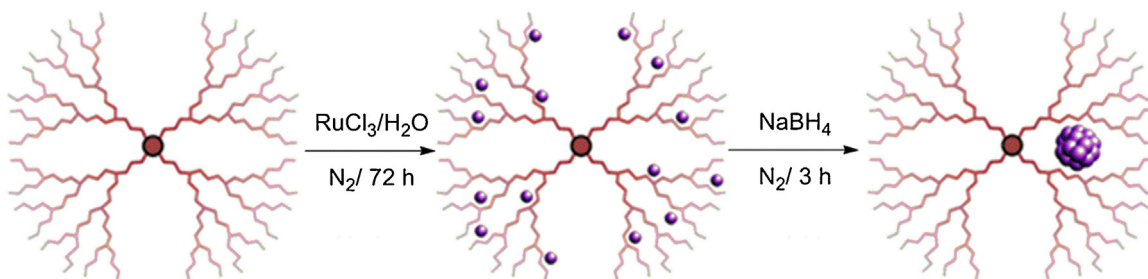
The presence of the ionic liquid can affect the activity and selectivity of the catalyst by changing the intrinsic properties of the catalyst, therefore acting as a potential chemical modifier of the catalyst itself that is encouraged by chemical interaction of the

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**Scheme 1.** Scheme for the hydrogenation of toluene illustrating the partially hydrogenated products 1-methylcyclohexene 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 catalytic 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  $\text{RuCl}_3$  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  $\Omega\text{M cm}$ ) system was used in all experiments.

Transmission electron microscopy (HRTEM) images were obtained on a JEOL JEM-2100F 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  $\text{RuCl}_3$  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<sub>4</sub>], [BMIM][PF<sub>6</sub>] or [BMIM][NTf<sub>2</sub>] 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<sup>3</sup> autoclave

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

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