Supported Ionic Liquid Phases

Selective Hydrogenation and Hydrodeoxygenation of Aromatic Ketones to Cyclohexane Derivatives Using a Rh@SILP Catalyst

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Abstract: Rhodium nanoparticles immobilized on an acid-free triphenylphosphonium-based supported ionic liquid phase (Rh@SILP(Ph3-P-NTf2)) enabled the selective hydrogenation and hydrodeoxygenation of aromatic ketones. The flexible molecular approach used to assemble the individual catalyst components (SiO2, ionic liquid, nanoparticles) led to outstanding catalytic properties. In particular, intimate contact between the nanoparticles and the phosphonium ionic liquid is required for the deoxygenation reactivity. The Rh@SILP(Ph3-P-NTf2) catalyst was active for the hydrodeoxygenation of benzylic ketones under mild conditions, and the product distribution for non-benzylic ketones was controlled with high selectivity between the hydrogenated (alcohol) and hydrodeoxygenated (alkane) products by adjusting the reaction temperature. The versatile Rh@SILP(Ph3-P-NTf2) catalyst opens the way to the production of a wide range of high-value cyclohexane derivatives by the hydrogenation and/or hydrodeoxygenation of Friedel–Crafts acylation products and lignin-derived aromatic ketones.

Introduction

The synthesis of alkyl cyclohexane derivatives has attracted considerable attention in the past decade owing to the importance of these compounds in the transportation sector[1] (kerosene-type fuels) and as building blocks for the production of coating agents[2] liquid crystals[3] and pharmaceuticals.[4] The traditional method for the synthesis of alkyl cyclohexanes consists of the hydrogenation of alkyl aromatic compounds[5] commonly produced through Friedel–Crafts alkylation reactions. However, this pathway suffers from the limited substrate scope and often low selectivity of Friedel–Crafts alkylation (overalkylation, carbocation rearrangements).[6] In this context, the hydro(deoxy)genation of aromatic ketones obtained, for example, through Friedel–Crafts acylation[7] or the oxidative depolymerization of lignin[8] appears an attractive alternative. Furthermore, the use of aromatic ketones as substrates gives the opportunity to access two classes of compounds (alkyl cyclohexanes and hydroxy-containing cyclohexane derivatives) and thus broadens significantly the range of possible products and potential applications (Figure 1). Despite recent efforts,[9] the development of versatile catalytic systems able to effectively hydrogenate and/or hydrodeoxygenate a large range of aromatic ketones remains a major challenge and constitutes the focus of this study.

Whereas in heterogeneous catalysis, hydrogenation reactions are mainly performed in the presence of transition-metal nanoparticles (Ni,[10] Ru,[11] Rh,[12] Pt,[13] etc.), the subsequent hydrodeoxygenation typically requires the presence of both a metal and a strong Brønsted or Lewis acidic catalyst.[14] Metal nanoparticles immobilized on supported ionic liquid phases (SILPs) were demonstrated to open a molecular approach to multifunctional catalytic systems with tailor-made reactivity.[15,16] SILPs are suitable matrices for nanoparticle synthesis and stabilization. The ionic liquid

Figure 1. A) Pathways for the synthesis of cyclohexane derivatives through the temperature-controlled hydrogenation or hydrodeoxygenation of aromatic ketones. B) Examples of applications of cyclohexane derivatives.
structure can be readily functionalized to bring different types of active sites in intimate contact with the active metal. Recent studies demonstrated the synthesis of monometallic[16a–c] and bimetallic[15f,16d] nanoparticles on imidazolium-based SILPs to produce catalytic systems with excellent catalytic properties for hydrogenation and hydrodeoxygenation reactions. In particular, the choice of the acid, and close proximity between the metal and acid sites were shown to be key factors in the development of effective hydrodeoxygenation catalysts.[16b–d]

Results and Discussion

We report herein the synthesis of Rh nanoparticles immobilized on a triphenyl phosphonium-based SILP. Using the resulting Rh@SILP(Ph₃-P-NTf₂) catalyst (NTf₂ = bis(triﬂuoromethane)sulfonimide), aromatic ketones were effectively hydrogenated and hydrodeoxygenated without the need for an additional acid functionality. Whereas benzylic ketones were readily hydrodeoxygenated under mild conditions, non-benzylic ketones could be selectively hydrogenated or hydrodeoxygenated depending on the temperature applied, thus providing flexible access to a wide range of substituted cyclohexanes.

The functionalized support material SILP(Ph₃-P-NTf₂) was synthesized through the condensation of a triethoxysilane-functionalized phosphonium ionic liquid, ([triethyl(phosphonium)propyl]phosphonium)[NTf₂], on dehydroxylated silica following a modified established procedure.[17] Analysis by DRIFT spectroscopy (see Figures S1–S3 in the Supporting Information) showed signals at 1440, 1484, 1590 cm⁻¹ and 2897, 2930, 2977, 3072 cm⁻¹ characteristic of the triphenylphosphine moiety. Si solid-state NMR spectroscopy further confirmed the presence of the desired triphenylphosphonium–NTf₂ ionic liquid. Si solid-state NMR spectroscopy further confirmed the presence of the desired triphenylphosphonium–NTf₂ ionic liquid in the SILP(Ph₃-P-NTf₂) (see Figures S5–S8A).

Rhodium nanoparticles were generated on the SILP by impregnation with a solution of [Rh(allyl)] in dichloromethane, followed by a robust and impregnated SILP under a hydrogen atmosphere (100 bar H₂, 100 °C, 2 h) to give a black powder. The Rh loading on Rh@SILP(Ph₃-P-NTf₂) was determined to be 0.1 mmol g⁻¹ by ICP-AAS, in agreement with the theoretical value. The BET surface area of the support decreased slightly from 292 to 271 m² g⁻¹ upon Rh loading (see Table S2 in the Supporting Information). Analysis of Rh@SILP(Ph₃-P-NTf₂) (illustrated schematically in Figure 2A) by transmission electron microscopy showed that the NPs were small (1.2 nm) and well-dispersed over the SILP support (Figure 2B).

The catalytic activity of Rh@SILP(Ph₃-P-NTf₂) and several reference catalysts for hydrogenation and hydrodeoxygenation was first studied using acetophenone (1) as a model substrate (Table 1). The use of SiO₂-supported Rh NPs resulted in the hydrogenation of acetophenone (1) to form the saturated alcohol 1a in 95% yield (entry 1). In contrast, Rh@SILP(Ph₃-P-NTf₂) produced the fully hydrodeoxygenated alkane 1b in quantitative yield (entry 2). Since neither Rh NPs nor phosphonium salts are known to catalyze the deoxygenation of ketones/alkohols individually, we investigated this intriguing reactivity by systematically modifying the catalyst structure.

With Rh NPs synthesized on an imidazolium-based SILP (SILP(Oct-n-P-NTf₂), see the Supporting Information for details and Figure S9 for TEM characterization), the substrate was converted into the alcohol 1a (95%) without any significant hydrodeoxygenation activity, thus suggesting that SILP(Ph₃-P-NTf₂) plays a key role in the deoxygenation step (entry 3). However, a physical mixture of Rh@SILP(Oct-n-P-NTf₂) and SILP(Ph₃-P-NTf₂) also gave 1a as the main product (97%), showing the importance of the intimate contact of metal and support (entry 4). Using Rh NPs immobilized on a different phosphonium-based SILP (Rh@SILP(Oct-P-NTf₂), see the Supporting Information for synthetic details and Figure S10 for TEM characterization) led to a mixture of products with the alcohol 1a as the main product (87%); entry 5). Use of a fluorine-free counteranion (BPh₄, entry 6) resulted in the selective conversion of the substrate into the alcohol 1a. In the case of another fluorine-containing anion (BF₄, entry 7), no significant deoxygenation activity was observed, indicating that the deoxygenation-active species was not formed. These results demonstrate the importance of
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to the release of HF when hydrogenating fluoroaromatic substrates.[21] Taking advantage of this reactivity, we performed a first reaction involving the hydrogenation of fluoroacetophenone with Rh@SiO2. This reaction gave a mixture of hydrogenated and hydrodefluorinated products, with the release of small quantities of HF (see Table S3). The catalyst was recovered, washed carefully, and characterized by 19F solid-state NMR, which showed the appearance of a signal at −122.3 ppm, similar to that previously observed for the Rh@SILP(Ph3P-NTf2) catalyst (see Figure S14). Furthermore, the application of this recycled catalyst to the conversion of acetophenone led to the formation of ethylcyclohexane, thus evidencing deoxygenation activity that the starting Rh@SiO2 did not possess (see Table S3). This result demonstrates that the deoxygenation activity is related to the formation of RhF species, which can be generated by the action of small quantities of HF on Rh nanoparticles. It supports the hypothesis that the RhF species observed on Rh@SILP(Ph3P-NTf2) are formed through the decomposition of the NTf2 anion, a process which is known to generate HF among other products.[20] The involvement of free HF in catalysis can, however, be ruled out, as a recycling experiment did not show any decrease in activity (Figure 3). Furthermore, the supernatant obtained after a catalytic reaction did not catalyze the deoxygenation of 1-phenylethanol.

Table 2: Hydrodeoxygenation of substituted benzylic ketones using Rh@SILP(Ph3P-NTf2).[a]

| Entry | Substrate | $T[^{\circ}C]$ | $t$ [h] | Product | Yield [%][h] |
|-------|-----------|----------------|--------|---------|-------------|
| 1     | ![image](image1) | 100 | 1 | ![image](image2) | 52[^i] |
| 2     | ![image](image3) | 100 | 18 | ![image](image4) | > 99 |
| 3     | ![image](image5) | 100 | 18 | ![image](image6) | > 99 (73)[^i] |
| 4     | ![image](image7) | 100 | 18 | ![image](image8) | > 99 |
| 5     | ![image](image9) | 100 | 18 | ![image](image10) | > 99 |
| 6     | ![image](image11) | 100 | 18 | ![image](image12) | 40 (6b)^[i], 10 (1b)^[i] |
| 7     | ![image](image13) | 100 | 18 | ![image](image14) | 62 (6b), 24[^i] (1b) |
| 8     | ![image](image15) | 100 | 18 | ![image](image16) | 25 (6b), 75 (1b) |
| 9     | ![image](image17) | 175 | 18 | ![image](image18) | 87 (1b), 13 (dimers) |
| 10    | ![image](image19) | 175 | 18 | ![image](image20) | > 99 |

[a] Reaction conditions: Rh@SILP(Ph3P-NTf2) (20 mg, metal content: 0.002 mmol Rh), substrate (0.1 mmol, 50 equiv), n-heptane (375 mg), H2 (50 bar), 18 h, 500 rpm. [b] Determined by GC-FID using tetradecane as an internal standard, conversion > 99%. [c] Remaining product: corresponding saturated alcohol. [d] The yield of the isolated product is given in brackets. [e] Total hydrodeoxygenation products: 71 %, 40 % 6b, 22 % 4-ethyl-cyclohexan-1-ol, 10 % 1b, 25 % 1-[(4-methoxy)cyclohexyl]ethan-1-ol, 3 % cyclohexylethanol. [f] Remaining: 4-ethyl-cyclohexan-1-ol (10 %), cyclohexylethanol (3 %), (1-methoxyethyl)cyclohexane (2 %).
The catalytic properties of Rh@SILP(Ph₃-P-NTf₂) were further studied for the conversion of non-benzylic ketones, which are known to be more challenging to hydrodeoxygenate than acetophenone derivatives.[23] Benzylideneacetone (11) was used as a model substrate for this class of ketones (Scheme 1).

Keeping the conditions previously used for the hydrodeoxygenation of acetophenone derivatives led to almost exclusive formation of the saturated alcohol (11a). However, the conversion of 11 into the hydrodeoxygenated product 2b occurred with excellent selectivity at higher temperatures (175°C). By adjusting the reaction temperature, both products (hydrogenated and hydrodeoxygenated) could be produced in quantitative yield. Again, the hydrodeoxygenation activity could not be switched on for Ru@SILP(Ph₃-P-NTf₂), and 11a was the only product at both 100 and 175°C (see Table S6). To see whether such a “temperature switch” between hydrogenation and hydrodeoxygenation could be more generally applied to other substrates, we tested the conversion of a selection of non-benzylic ketones at 100 and 175°C using Rh@SILP(Ph₃-P-NTf₂) as the catalyst (Table 3).

At 100°C, substrates 11–16 (entries 1–6) possessing a phenyl ring in β or γ position to the carbonyl group were converted into the saturated alcohols in high yields (81–99%). Substrate 13, however, was converted into a mixture of the saturated alcohol 13a (32%) and partially hydrodeoxygenated product 11a (50%).

As expected, the hydrodeoxygenation of the benzylic alcohol was favored over the non-benzylic alcohol, thus resulting in high amounts of 11a (50%) as compared to 1-cyclohexylbutanol (8%). In the case of substrate 17, only low mass balances were observed, indicating likely competing acid-mediated condensation reactions of the enone substrate. All the substrates were efficiently hydrodeoxygenated at

### Table 3: Temperature-controlled hydrogenation or hydrodeoxygenation of non-benzylic ketones using Rh@SILP(Ph₃-P-NTf₂).

| Entry | Substrate | Product 100°C | Yield 100°C [%] | Product 175°C | Yield 175°C [%] |
|-------|-----------|--------------|----------------|--------------|---------------|
| 1     | 11        | 11a          | >99f (87)      | 2b           | >99           |
| 2     | 12        | 11a          | >99f           | 2b           | >99           |
| 3     | 13        | 11a, 13a     | 50 (11a), 32 (13a) | 2b           | >99           |
| 4     | 14        | 14a          | 81g            | 14b          | 97            |
| 5     | 15        | 15a          | 92             | 15b          | >99           |
| 6     | 16        | 16a          | 96 (92)        | 16b          | >99 (99)      |
| 7     | 17        | –            | –              | 17b, 2b      | 20 (17b), 80 (2b) |
| 8     | 18        | –            | dimerization   | 18b, 18c     | 61 (18b), 22 (18c) |

[a] Reaction conditions: Rh@SILP(Ph₃-P-NTf₂) (20 mg, metal content: 0.002 mmol Rh), substrate (0.1 mmol, 50 equiv), n-heptane (375 mg), 100 or 175°C, H₂ (50 bar), 18 h, 500 rpm. [b] Determined by GC-FID using tetradecane as an internal standard, conversion >99%. [c] Reaction time: 1 h. [d] The yield of the isolated product is given in brackets. [e] Determined by protection of the diol with benzaldehyde (see Scheme S1 in the Supporting Information). [f] 80°C, 30 equiv. [g] Additional products: octanol (10%), octane (7%).
175°C to give the corresponding alkanes in excellent yields (97–99%). In agreement with previous observations for substrate 6, the methoxy group of substrate 17 was partially cleaved at 175°C (entry 7). With biomass-derived 4-(tetrahydrofuran-2-yl)butan-2-ol (18), obtained from the complete hydrogenation of furfuralacetone as the substrate, only various dimers were obtained when the reaction was carried out at 100°C. However, the substrate was efficiently hydrodeoxygenated at 175°C to produce a mixture of 2-butyltetrahydrofuran (18b), 2-propyltetrahydro-2H-pyran (18c), octanol, and octane (entry 8). Interestingly, these products are currently under discussion as potential alternative fuels and fuel additives.[24]

Conclusion

In conclusion, we have shown that immobilizing Rh nanoparticles on a triphenylphosphonium-based SILP produces a Rh@SILP(Ph3-P-NTf2) catalyst possessing excellent properties for the hydrogenation and hydrodeoxygenation of a wide range of aromatic ketones with various substituents. The required bifunctionality is enabled by a specific interaction between the Rh NPs and the SILP(Ph3-P-NTf2)) support, presumably leading to the formation of acidic Rh fluoride species. Using Rh@SILP(Ph3-P-NTf2), acetoephene derivatives were readily hydrodeoxygenated under mild conditions. For non-benzylic ketones, the product distribution could be switched with high selectivity between the hydrogenated and hydrodeoxygenated products simply by tuning the temperature. The flexibility and modularity of the molecular approach used to prepare NP@SILP catalysts allowed for the assembly of the exact key components required to achieve this unique reactivity. This approach opens the way to the efficient production of highly valuable cyclohexane derivatives from readily available aromatic ketones.

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Conflict of interest

The authors declare no conflict of interest.

Keywords: hydrodeoxygenation · ionic liquids · nanoparticles · rhodium · supported ionic liquid phases

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Selective Hydrogenation and Hydrodeoxygenation of Aromatic Ketones to Cyclohexane Derivatives Using a Rh@SILP Catalyst

Some like it hot: Rhodium nanoparticles immobilized on an acid-free triphenylphosphonium-based supported ionic liquid phase (Rh@SILP(Ph₃P-NTf₂)) enabled ready access to high-value cyclohexane derivatives from aromatic ketones. The product distribution could be switched with high selectivity between the completely hydrogenated (alcohol) and hydrodeoxygenated (alkane) products by changing the reaction temperature (see scheme).