Selective Hydrogenation of Fluorinated Arenes using Rhodium Nanoparticles on Molecularly Modified Silica

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PURPOSE OF THE ABSTRACT

While fluorinated cycloalkane derivatives are largely explored in different fields of the chemical industry as important building blocks for the production of pharmaceuticals,[1] agrochemicals and materials like liquid crystals,[2] their production remains challenging and typically requires multistep syntheses including the use of toxic and difficult-to-handle reagents. Alternatively, the synthesis of fluorinated cyclohexanes through the hydrogenation of readily available and inexpensive fluorinated arenes appears as an attractive and benign approach. However, the competing hydrodefluorinating pathway is predominant in most of the reported attempts involving heterogeneous catalysts, significantly reducing the efficiency of this transformation.[3] Despite recent very promising advances made in the selective hydrogenation of fluorinated arenes,[4] the development of catalytic systems combining high activity and selectivity with stability and easy recyclability remains a major challenge.

In this context, we herein describe the development of catalytic systems composed of Rhodium nanoparticles (Rh NPs) immobilized on molecularly modified silica (Si-R), their characterization, and application to the hydrogenation of fluorinated arenes.[5] The influence of the catalysts' physico-chemical properties (hydrophobicity, nanoparticles size, etc.) and of the experimental conditions (temperature, H2 pressure, reaction time, concentration, solvent) on the hydrogenation/hydrodefluorination selectivity was investigated. While the importance of using apolar solvents to favor the hydrogenation pathway was previously outlined in the literature,[3] we show that generating a hydrophobic environment for the Rh NPs plays also a key role in determining the selectivity of the reaction. Regarding safety issues and catalyst stability, the effect of the traces of HF released through the competing hydrodefluorination reaction was examined. The addition of CaO as a scavenger for HF was found crucial to maintain the catalyst stability and improve its recyclability.

Using a Rh@Si-Dec catalyst (where Si-Dec stands for silica functionalized with decyl triethoxysilane, Figure 1) with heptane as solvent under optimized conditions, a scope of fluorinated cyclohexane derivatives could be produced in high selectivity and yields (70-92%) (Figure 2, First row). Meanwhile, for substrates with polar functionalities, the selective hydrogenation was found to be more challenging.

To tackle this challenge, supercritical carbon dioxide (scCO2) was explored as an alternative hydrophobic and

environmentally benign reaction media. With challenging substrates (e.g. 4-fluorophenol, 2,4-difluorophenol, methyl 2,3,4-trifluorobenzoate), significantly higher selectivity for the desired fluorinated products was obtained in scCO2 as compared to heptane (Figure 2, Second row). This significant increase in selectivity is presumably due to the extreme hydrophobicity of scCO2, as well as to the high solubility of fluorinated compounds in scCO2 and an enhanced mass transfer.[6] Based on these promising results, the implementation of this reaction system in a continuous flow reactor is under study.
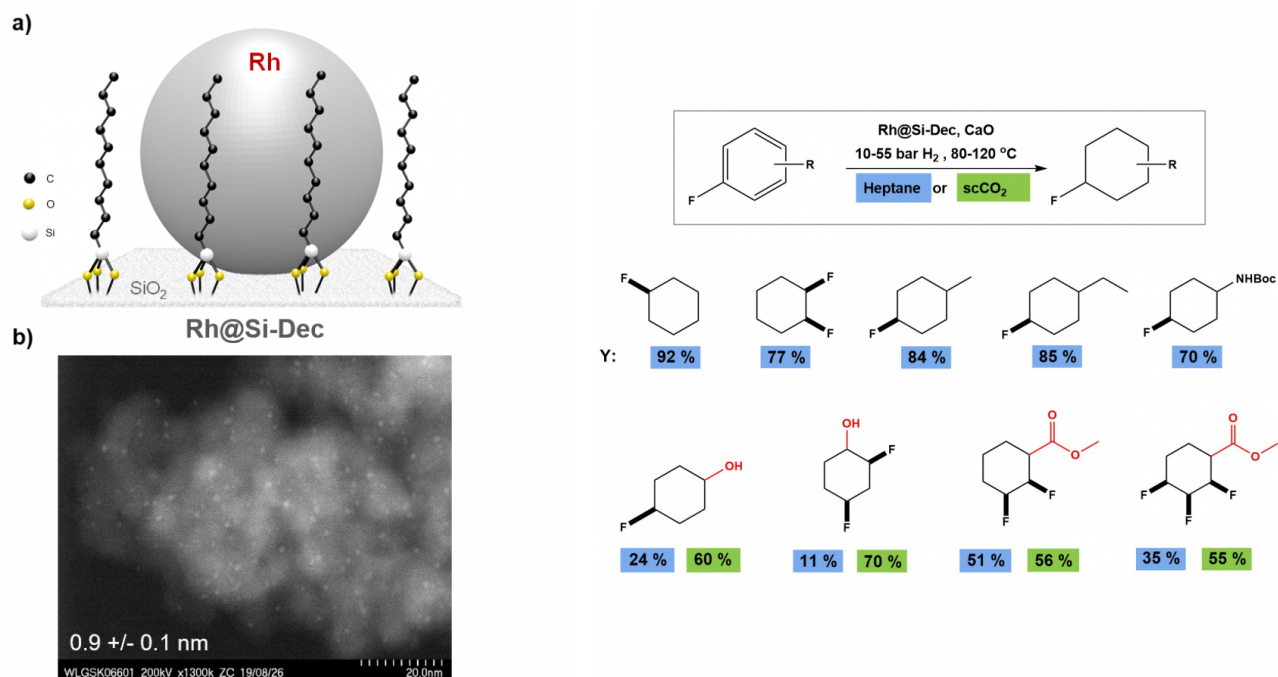
FIGURES

FIGURE 1

Rh nanoparticles immobilized on silica functionnalized with decyl triethoxysilane (Rh@Si-Dec) catalyst.

a) Schematic representation; b) Scanning Transmission Electron Microscopy with High Angle Annular Dark Field (STEM-HAADF) picture.

FIGURE 2

Catalytic results for the hydrogenation of fluorinated arenes using a Rh@Si-Dec catalyst in heptane and in scCO2.

First row: Yields (Y) for the desired fluorinated cyclohexanes in heptane (highlighted in blue).

Second row: Yields for the desired fluorinated cyclohexanes with polar functionalities in heptane and in scCO2 (highlighted in green).

KEYWORDS

Selective Hydrogenation | Fluorinated Arenes | Rh nanoparticles | Supercritical Carbon Dioxide (scCO2)

BIBLIOGRAPHY

[1] V. P. Reddy, Organofluorine Compounds in Biology and Medicine, Elsevier, 2015.

[2] M. Hird, Chem. Soc. Rev. 2007, 36, 2070-2095.

[3] K. J. Stanger, R. J. Angelici, J. Mol. Cat. A: Chem. 2004, 207, 59-68.

[4] a) M. P. Wiesenfeldt, Z. Nairoukh, W. Li, F. Glorius, Science 2017, 357, 908-912 ; b) D. Moock, M. P. Wiesenfeldt, M. Freitag, S. Muratsugu, S. Ikemoto, R. Knitsch, J. Schneidewind, W. Baumann, A. H. Schäfer, A. Timmer, M. Tada, M. R. Hansen, F. Glorius, ACS Catal. 2020, 10, 6309-6317.

[5] S. Kacem, M. Emondts, A. Bordet, W. Leitner, Catal. Sci.Technol. 2020, 10, 8120–8126.

[6] W. Leitner, Acc. Chem. Res. 2002, 35, 746-756.