

Kinetics of Selective hydrogenation of α,β -unsaturated aldehydes over Supported Ionic Liquid Catalysts (SILCA)

Pasi Virtanen¹ and Jyri-pekka Mikkola^{1,2*}

¹Process Chemistry Centre, Åbo Akademi University, Laboratory of industrial chemistry and reaction engineering

FI-20500, Turku, (Finland)

²Technical Chemistry, Department of Chemistry, Umeå University, SE-90187, Umeå, (Sweden)

*jpmikkol@abo.fi (corresponding author designated with a star)

Introduction

The research of ionic liquids and applications in catalysis is attracting more attention in chemical engineering. Ionic liquids have many special characteristic features common to most of them. Some of the most important ones are the often negligible vapor pressure ($\sim 10^{-8}$ bar), wide liquidus range, unique solvation properties, wide electrochemical window as well as good ion conductivity^{1,2}. Ionic liquids have shown a good performance for various kinds of catalytic reactions as well as in preparation of nanostructured materials and nanoparticles suitable for catalysis^{3,4}. Also, including the fact that the immobilized ionic liquid catalysts result in a very efficient use of the ionic liquid and relatively short diffusion distances compared to conventional two-phase systems.

Materials and Methods

Catalysts were prepared according to the method described previously.⁵ Palladium acetyl acetonate, and ionic liquid were dissolved in acetone. Solution was poured over an active carbon cloth (ACC), Kynol®. Acetone was evaporated in a rotary evaporator leaving Pd(acac)₃ dissolved in ionic liquid supported on ACC. The catalysts were pre-treated in a batch reactor at 120 °C under 10 bar hydrogen flow. This procedure resulted into formation of Pd nano-particles in ionic liquid immobilized on ACC (Fig. 1). The catalysts were applied in the hydrogenation of cinnamaldehyde. Cinnamaldehyde, a multi unsaturated aldehyde, is an industrially important precursor for many fine chemical products, flavoring agents, perfumes, fungicides and steel corrosion inhibitors. Experiments were conducted in the batch reactor, at constant temperature (varying between 60 and 150 °C) and constant hydrogen pressure (varying between 5 and 30 bar). The progress of the reaction was monitored by withdrawing small samples from reactor and analyzing them by gas chromatography.

Kinetic evaluation of catalysts with two different ionic liquids was performed with the results obtained from the hydrogenation experiments. Kinetic modeling was based on the reaction scheme in Fig 2. A classical Langmuir-Hinshelwood-Hougen-Watson type of kinetic model was applied in the estimation of rate and adsorption parameters. The software applied was Modest 6.1 parameter estimation software.⁶

Results and Discussion

Experiments showed that ionic liquid layer on ACC can improve the hydrogenation reaction rate and tune the selectivity for various products, depending on the ionic liquid applied. A kinetic model based on surface reactions as the rate determining steps was derived

for the hydrogenation of cinnamaldehyde. Thus following rate equations were obtained (See Fig. 2).

$$R_i = k_{rds,j} \theta_k \theta_H^2 = \frac{k_{rds,j} K_k C_k K_{H_2} P_{H_2} f_{DA}}{(1 + K_{CAL} C_{CAL} + K_{HCAL} C_{HCAL} + K_{HCOL} C_{HCOL} + \sqrt{K_{H_2} P_{H_2}})^3}$$

The model explained the differences in the catalyst activity and selectivity, in the case of different ionic liquids.

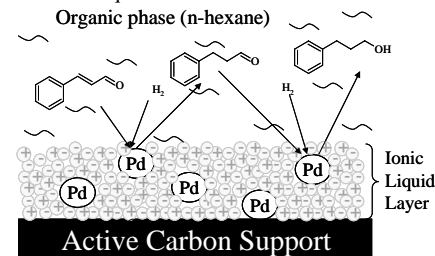


Figure 1. Picture of SILCA used in hydrogenation of cinnamaldehyde.

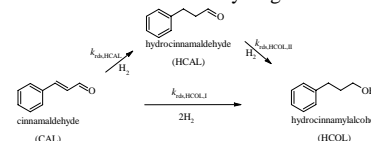


Figure 2. A reaction scheme for cinnamaldehyde hydrogenation over SILCA

Significance

As demonstrated by this sample hydrogenation process, it is obvious that an ionic liquid layer residing on a heterogeneous support can enhance the reaction rate and affect the selectivity profile of the reaction, even though small amounts of ionic liquids and active metals were used in the catalysts. Thus, enhanced catalyst performance can be reached in an economic and elegant way. We anticipate that this concept has potential in many other chemical transformations.

References

1. P. Bonhôte, A.-P. Dias, N. Papageorgiou, K. Kalyanasundaram, M. Grätzel, *Inorg. Chem.*, 35, 1168 (1996).
2. R. D. Rogers, K. R. Seddon, *Science*, 302, 792 (2003).
3. J. Dupont, G. S. Fonseca, A. P. Umpierre, P. F. F. Fichtner, S. R. Teixeira, *J. Am. Chem. Soc.*, 124, 4228 (2002).
4. R. Sheldon, *Chem. Comm.*, 2399 (2001).
5. J.-P. Mikkola, P. Virtanen, H. Karhu, T. Salmi, D. Y. Murzin, *Green Chem.*, 8, 197 (2006).
6. Haario, H. *Modest User Manual*; ProfMath Ltd.: Helsinki, Finland, 1994.