Gas-phase hydrogenation of 4-*tert*-butylphenol over Pt/SiO_2 - Kinetics and stereoselectivity

A. Kalantar Neyestanaki, J. R. Hernández Carucci, P. Mäki-Arvela, T. Salmi and D. Murzin
Laboratory of Industrial Chemistry, Process Chemistry Group, Åbo Akademi,
Biskopsgatan 8, FIN-20500 Turku/Åbo, Finland

Introduction

Stereoselective hydrogenation of aromatics is of importance in production of fine chemicals. *4-tert*-butylphenol (4-*t*-BPH) hydrogenation is usually carried out in three-phase reactor systems over supported group VIII metals. The products are valuable intermediates for the fragrance industry. In the liquid-phase hydrogenation of 4-*t*-BPH, it has been reported that hydrogenation in acid solutions leads mainly to the formation of the *cis* 4-*tert*-butylcyclohexanol, whereas, in basic solutions the formation of *trans* 4-*tert*-butylcyclohexanol isomer is favoured [1, 2]. However, there are no previous reports on gas-phase hydrogenation of 4-*t*-BPH and systematic kinetic studies on the influence of support acidity on the activity and the product distribution.

Results and Discussion

Kinetics and stereoselectivity of the gas-phase hydrogenation of 4-*t*-BPH were investigated over a 1 wt% Pt/SiO_2 catalyst in the temperature range of 410 – 490 K and hydrogen and 4-*t*-BPH partial pressures of 0.052-0.013 and 0.009-0.0153 bar, respectively. 4-*t*-BPH was brought to gas-phase by passing Ar through a saturator kept at 403 K. The total flow was kept constant using Ar as a make-up gas. 4-*tert*-butylcyclohexanol (*cis*- and *trans*-isomers) and 4-*tert*-butylcyclohexanone were the main reaction products. At temperatures exceeding 470 K, *t*-butylbenzene and *t*-butylcyclohexane were also formed. Similarly to alkylbenzene hydrogenation reactions [3-5], the rates of 4-*tert*-butylcyclohexanol and 4-*t*-butylcyclohexanone formation passed through a reversible maximum at 460 K. The catalyst exhibited higher selectivity to the formation of intermediate product 4-*t*-butylcylohexanone (ca. 55% selectivity). The *cis-to-trans* ratios of the alcohols were close to unity at temperatures studied. At temperatures exceeding 170 °C, hydrogenolysis products become of importance (Fig 1).

In order to establish the reaction mechanism, the stereoselectivity of the desired alcohols, hydrogenation of the intermediate product, *4-tert*-butylcyclohexanone, and its stereoselectivity orientation was studied. The dehydrogenation and epimerization of the products were also investigated and discussed. A reaction mechanism is proposed. In order to study the nature of the carrier on the activity and specific stereoselectivity orientation, additives altering the acidic/basic properties of the carrier (such as Ca and $ZnBr_2$) were applied to the catalyst formulation. The stereoselectivity toward the formation of *cis* and *trans* 4-*tert*-butylcyclohexanol is strongly affected by the support acidity/basicity. The factors directing to different stereoselectivities are discussed. The catalysts were characterized by N_2-adsorption, H_2-adsorption, H_2-TPD, SEM/EDXA and XPS.

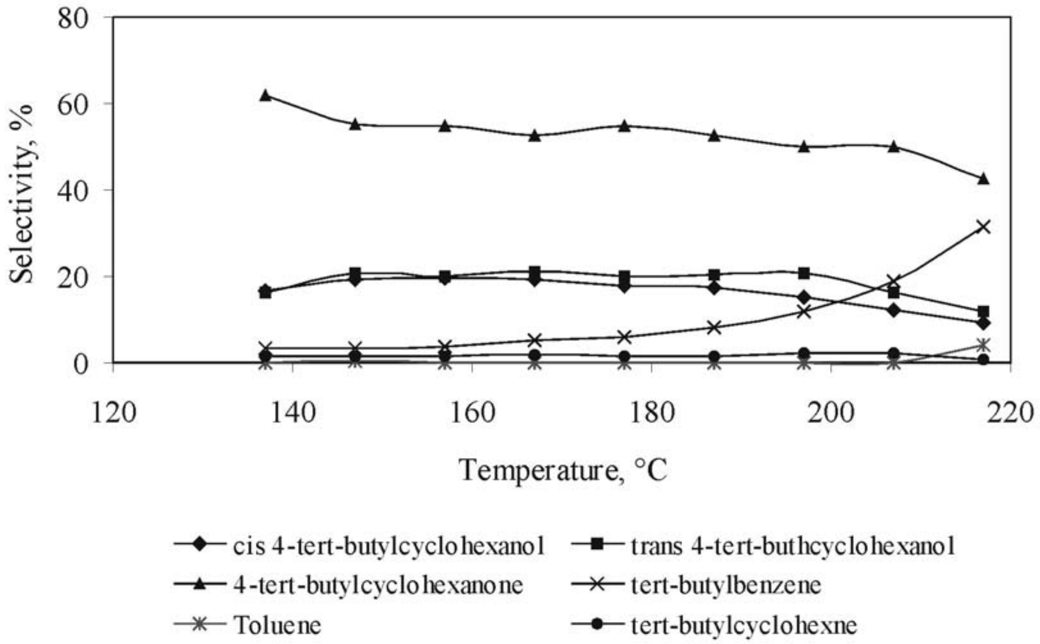

Figure 1: The product distribution in hydrogenation of 4-*tert*-butylphenol over 1wt % Pt/SiO_2 catalyst. $p_{H2} = 0.13$ bar, $p_{tbPH} = 8.8$ mbar.

Acknowledgements

This work is a part of the activities at the Åbo Akademi Process Chemistry Group within the Finnish Center of Excellence Program (2000-2005) by the Academy of Finland.

References

1. Murzin, D. Yu, Allachverdiev, A. I., Kul’kova, N. V.,“Kinetics of the liquid-phase stereoselective hydrogenation of 4-tert-butyl-phenol over rhodium catalyst”, *Stud. Surf. Science Catal.*, **78**, 243, 1993.
2. S. R. Konuspaev, K. N. Zhanbekov, N. V. Kul’kova and Dmitry Murzin, “Kinetics of 4-tert-butylphenol Hydrogenation over Rhodium”, *Chem. Eng. Technol.* **20** (1997) 144.
3. Kalantar Neyestanaki, A. Mäki-Arvela, P., Backman, H, Karhu', H., Salmi, T., Väyrynen, J., Murzin, D. Yu. ”Kinetics and stereoselectivity of o-xylene hydrogenation over Pd/Al_2O_3”, *Journal of Molecular Catalysis A:Chemical*, in Press, 2002.
4. Kalantar Neyestanaki, A., Backman, H., Mäki-Arvela, P., Wärnå, J., Salmi, T., Murzin, D. Yu. “Kinetics and modelling of o-xylene hydrogenation over Pt/alumina catalyst”, *Chemical Engineering Journal*, In Press, 2002.
5. Kalantar Neyestanaki, A. Mäki-Arvela, P., Backman, H, Karhu', H., Salmi, T., Väyrynen, J., Murzin, D. Yu. “Gas-phase hydrogenation of o-xylene over Pt/alumina catalyst, activity and stereoselectivity”, *Submitted for publication to Journal of Catalysis*, 2002.