

Improved Understanding and Rates in the Dehydrogenation of Tetrahydrocarbazole to Carbazole

R. Burch¹, P. Crawford¹, C. Hardacre^{1*}, K. T. Hindle¹, P. Hu¹, D. R. Rooney¹, B. Kalari²
¹*CenTACat, School of Chemistry and Chemical Engineering, Queen's University Belfast, Belfast, BT9 5AJ, (Northern Ireland, UK)*
²*Robinson Brothers Ltd., Phoenix Street, West Bromwich, B70 0AH, (England, UK)*
*c.hardacre@qub.ac.uk

Introduction

Carbazole (CZ) and substituted CZs are important intermediates in the synthesis of pharmaceuticals, agrochemicals, dyes, pigments and other organic compounds. CZ or dibenzopyrrole, was first isolated from coal tar in 19th century, and today thousands of tons of CZ are produced commercially from this substance and crude oil each year. As CZ and its derivatives are valuable intermediates, synthetic routes to CZ are required. CZ can be formed through the liquid phase dehydrogenation of 1,2,3,4-tetrahydrocarbazole (THCZ) via the Borsche process (figure 1) first reported in the early 20th century using lead oxide [1]. Since then many reducing agents have been employed [2]. The most appropriate method for modern chemical industries is to carrying out this reaction in a solvent using a solid catalyst such as Raney Ni or Pd supported on carbon [3]. Although more environmentally friendly than the lead based process, this method requires high temperatures and a relatively high mass of catalyst. This study explored the THCZ dehydrogenation to CZ (Figure 1) over Pd catalysts by investigating the reaction mechanism through experiment and DFT. This understanding was then utilised to increase the catalyst activity, enabling lower reaction temperatures or a lower catalyst mass to be employed.

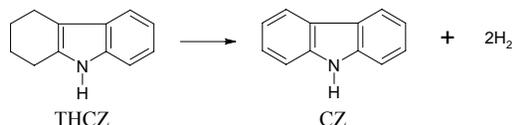


Figure 1. Reaction scheme for THCZ dehydrogenation to CZ

Materials and Methods

The catalysts used were Pd catalysts supported on either carbon or Al₂O₃ which were supplied by Johnson Matthey. Semi-batch reactions were undertaken in a glass three necked round bottomed flask under constant N₂ purge, connected to a cooling condenser while batch reactions were performed in a Premex 380 cm³ stainless steel autoclave. Typically reactions were performed with a THCZ concentration of 0.29 mol L⁻¹, with mesitylene as the solvent and a THCZ mass to catalyst mass ratio of 10:1. The density functional theory calculations were performed using the SIESTA program. The exchange-correlation energy was determined using the generalised gradient approximation (GGA) functional proposed by Perdew, Burke and Ernzerhof (PBE) [5]. A p(5x5) unit cell was used in all of the calculations.

Results and Discussion

DFT demonstrated that the THCZ adsorption geometry was such that the molecule adsorbed flat on a Pd(111) surface and presented three H atoms for the first abstraction. The

first hydrogen atom abstraction was found to be the rate limiting step as it had an activation barrier > 0.3 eV more than the subsequent three hydrogen abstractions. To find which of these three H atoms were removed in the first stage dehydrogenation, isotopic studies were undertaken. Reactions in a D₂ purge revealed, through the reversible deuteration of the first dehydrogenation intermediate, the H atoms at the 1- and 4- carbon positions were dominant. In addition, the KIE was studied using deuterated THCZ and, although these results were complicated by H/D scrambling, these experiments agreed with the D₂ purge result. Hydrogen in the system was found to be a key factor in perturbing the reaction rate as a semi-batch reaction under H₂ purge displayed no activity. Moreover, tests investigating the catalyst particle size revealed that larger catalyst particles gave slower reaction rates. All reactions were calculated to be 100 % effective with respect to THCZ internal diffusion, therefore, the rate perturbation effect was attributed to slower hydrogen diffusion out of the catalyst. As hydrogen removal was concluded as a key goal to increasing the reaction rate, reactions were performed under propene. An increase of around 5 times resulted when the reaction was undertaken under a propene partial pressure of 5 barg (Figure 2). Using the apparent activation energy calculated from the semi-batch experiments this increase corresponded to raising the temperature by 35 K. Samples of the gas phase during the reaction revealed propane was formed and propene consumed during the reaction, while DFT showed that the hydrogenation of an adsorbed propene had an energy barrier in the same region as the back hydrogenation of the first dehydrogenation intermediate. In conclusion the hydrogen accepting role of propene undoubtedly caused a decrease in the back hydrogenation of the partially dehydrogenated THCZ shifting the equilibrium to the CZ product.

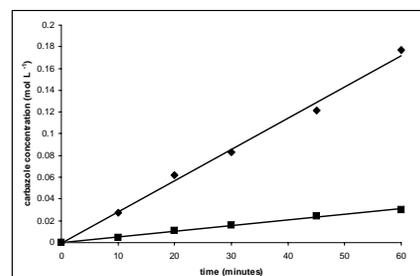


Figure 2. CZ concentration with respect to reaction time for THCZ reaction undertaken in (■) semi-batch mode with N₂ purge (◆) batch mode under initial pressure of 5 barg propene

Significance

By combining experiment and theory the mechanism of liquid phase dehydrogenation to form aromatics of commercial interest has been developed. This understanding has lead improvement in the process using a gas phase hydrogen acceptor which has increased the reaction rate significantly. This enhancement was not achievable using liquid phase hydrogen acceptors and is a step out change in process design.

References

1. W. Borsche, A. Witte, W. Bothe, *Ann.* 359, 49 (1908).
2. R. Robinson, *Chem. Rev.* 63, 373 (1963).
3. Y. Majin, C. Zhongjun, L. Dadong, *Dying Industry* 36, 21 (1998).
4. J.P. Perdew, K. Burke, M. Ernzerhof, *Phys. Rev. Lett.*, 77, 3865 (1996).