

Hydrogen Storage and Release from Organic Heteroaromatic Compounds: A Kinetic Study

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Introduction

One approach to hydrogen storage for fuel-cell vehicles is to store the hydrogen in high capacity organic compounds. According to Department of Energy (DOE) criteria, the candidate compounds must have high hydrogen release rates, 5.5 wt % H₂ storage capacity, melting point <-40 °C and boiling point >200 °C [1]. Organic heteroaromatic compounds have attracted attention because they meet the storage capacity and the melting and boiling point criteria. Although some studies have been reported for H₂ storage on these materials [2], limited data are available on the kinetics of the hydrogenation and dehydrogenation reactions relevant to this approach to H₂ storage and release [3, 4].

In the present work, hydrogenation of n-ethylcarbazole (a candidate for H₂ storage with 5.7 wt % storage capacity) to dodecahydro-n-ethylcarbazole was studied over Ru/alumina catalyst at 150 °C and 7000 kPa. The hydrogenated product was then dehydrogenated over Pd/silica catalyst at 150-170 °C and 101 kPa, to determine the kinetics of the H₂ release.

Materials and Methods

The 5 wt % Pd/silica dehydrogenation catalyst was prepared by wet impregnation of 9.5 g silica gel (Sigma-Aldrich, BET area: 300 m²/g, pore volume: 1.15 mL/g) with 20 mL of a 0.2 M aqueous solution of PdCl₂ (Sigma-Aldrich, 99.9+ %). The sample was dried at 120 °C for 24 h, calcined at 475 °C for 3 h and reduced in 30 mL (STP)/min H₂ at 450 °C for 6 h and cooled to room temperature in He at 30 mL (STP)/min. A commercial 5 wt % Ru/alumina (Aldrich, 5 wt % Ru, reduced) was used for hydrogenation and was re-reduced prior to use. BET surface area and pore size of catalysts was determined using a Micromeritics ASAP 2020 analyzer. A Micromeritics Autochem II 2920 was used for Temperature Programmed Reduction (TPR) and for the determination of metal dispersion through CO pulse chemisorption.

Hydrogenation of n-ethylcarbazole was carried out at 150 °C and 7000 kPa, in an autoclave batch reactor, using a 6 wt % solution of n-ethylcarbazole (Aldrich, 97 %) in decalin (Sigma-Aldrich, 98 %) and 1 g of the 5 wt % reduced Ru/alumina (particle size < 150 µm). Small volumes (<0.5 mL) of liquid sample were removed for analysis by gas chromatography. Following hydrogenation, the recovered product was dehydrogenated in a 50 mL reactor at 150-170 °C and 101 kPa using 0.3 g of 5 wt % Pd/silica. Helium was used as a carrier gas for continuous removal of the produced H₂ and the exit gas composition was monitored using a quadrupole mass spectrometer. Liquid samples were analyzed by a 14-A Shimadzu gas chromatograph with a flame ionization detector and ATTM-5 25M x 0.53mm capillary column. Product identities were confirmed by a Shimadzu QP-2010S GC/MS using a RTX5 30M x 0.25mm capillary column.

Results and Discussion

Table 1 summarizes the catalyst characterization data. N-ethylcarbazole hydrogenation over Ru/silica at 150 °C, proceeded to 98 % conversion after 1 h, following 1st-order kinetics with > 95 % selectivity to the desired dodecahydro-n-ethylcarbazole (Fig. 1). The hydrogenated product was then dehydrogenated at 150-170 °C and 101 kPa. The reactions proceeded to 100 % conversion following 1st-order kinetics, with an apparent activation energy for dodecahydro-n-ethylcarbazole consumption of 127 kJ/mol. A 64 % recovery of the stored H₂ was obtained after 17 h dehydrogenation at 170 °C, due to the production of tetrahydro-n-ethylcarbazole and octahydro-n-ethylcarbazole and minimal n-ethylcarbazole.

Table 1. Catalyst properties

Catalyst	BET, m ² /g	Average pore size, nm	Degree of reduction, %	Metal dispersion, %
Pd/silica (calcined)	311.5	9.6	---	---
Pd/silica (reduced)	325.6	9.5	78	10.1
Ru/alumina (reduced)	76.5	8.4	3.3 ^a	6.2

^a - the commercial catalyst was supplied in a pre-reduced state

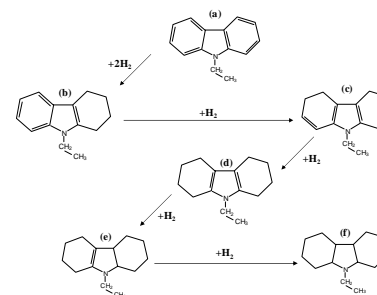


Figure 1. N-ethylcarbazole hydrogenation pathway: (a) n-ethylcarbazole, (b) tetrahydro-n-ethylcarbazole, (c) hexahydro-n-ethylcarbazole, (d) octahydro-n-ethylcarbazole, (e) decahydro-n-ethylcarbazole, (f) dodecahydro-n-ethylcarbazole.

Significance

A H₂ storage capacity of 5.1 wt % on n-ethylcarbazole was achieved at 150 °C in 1 h. However, only 64% of the H₂ was released from dodecahydro-n-ethylcarbazole because of low activity for complete dehydrogenation to n-ethylcarbazole.

References

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