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Dehydrogenation kinetics and catalysis of organic heteroaromatics for hydrogen storage

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ABSTRACT

The complete recovery of the H₂ stored on dodecahydro-N-ethylcarbazole was achieved at 443 K and 101 kPa using Pd catalysts prepared by incipient wetness impregnation and calcination in He rather than air. Over a 4 wt% Pd/SiO₂ catalyst, the reaction proceeded to complete conversion within 22 min and complete H₂ recovery (5.8 wt%) within 1.6 h. The dehydrogenation rate of dodecahydro-N-ethylcarbazole and selectivity to the completely dehydrogenated product, N-ethylcarbazole, were dependent upon the Pd particle size. The dehydrogenation rate of dodecahydro-N-ethylcarbazole was compared to that of dodecahydrocarbazole and dodecahydrofluorene. The lower turn-over frequency (TOF) for dodecahydrocarbazole was attributed to a strong adsorption of the dehydrogenated products to Pd through the N atom, whereas the ethyl group in dodecahydro-N-ethylcarbazole prevented a strong N interaction with the surface. Density functional theory (DFT) results showed that dodecahydrocarbazole and dodecahydrofluorene were more strongly adsorbed on Pd than dodecahydro-N-ethylcarbazole leading to a significant decrease in their TOFs for H₂ recovery.

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1. Introduction

The use of hydrogen as an alternative, benign energy carrier is limited by the technology gap that exists for H₂ storage. Compressed or liquefied hydrogen is costly and the gravimetric storage capacity is low. A more practical option is off-board regenerable materials such as organic heteroaromatics [1], metal hydrides [2,3] and metal-organic frameworks [4,5] on which hydrogen is stored by chemical reaction or adsorption [1]. Compounds such as carbazole and N-ethylcarbazole, with gravimetric storage capacities >5.5 wt% are potential candidates. Their hydrogenated forms can release hydrogen at low temperatures (<473 K) [6–9] and can be used for on-board hydrogen recovery applications. However, dehydrogenation reactions of the aromatic compounds have been

reported to be very slow. In previous work [8,9], 100% conversion of dodecahydro-N-ethylcarbazole (with no selectivity to the completely dehydrogenated product N-ethylcarbazole) and 53% conversion of dodecahydrocarbazole was obtained after 17 h at 443 K and 101 kPa over a 5 wt% Pd/SiO₂ catalyst that had an average Pd particle size of 24 nm. In work reported by Wang et al. [10], Ir complexes were shown to be active catalysts for the dehydrogenation of dodecahydro-N-ethylcarbazole at 473 K. However, dehydrogenation to the fully unsaturated N-ethylcarbazole did not occur in most cases and octahydro-N-ethylcarbazole and tetrahydro-N-ethylcarbazole were the only products. Dehydrogenation of tetrahydrocarbazole at 413 K was reported to proceed to 81% conversion over a 5 wt% Pd/Al₂O₃ catalyst in 27 h [11,12]. Despite 100% selectivity to carbazole, product inhibition

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decreased the dehydrogenation rate significantly. Dehydrogenation of decalin, another H₂ storage candidate, using a Pt/C catalyst and a batch-type membrane reactor at high temperatures (533–593 K) resulted in conversions below 85% after 2.2 h [13] and 95% conversion within 1.5 h at 553 K [14]. However, the reported temperatures were too high and impractical for hydrogen recovery for transport applications.

Despite the available literature data, there are limited studies on the effect of catalyst particle size on the hydrogenation/dehydrogenation of aromatic compounds. In one study, the hydrogenation of 2,4-dinitrotoluene over Pd/SiO₂ was favored by increasing the Pd particle size [15]. However, in another study, the hydrogenation of 2,4-dinitrotoluene over Pd/C catalysts was found to be structure insensitive [16] where the increase in the specific activity on larger metal particles was attributed to diffusion limitations within the pores of the microporous carbon support.

Crawford et al. [11] investigated the mechanism of tetrahydrocarbazole dehydrogenation over a Pd catalyst, and showed by experiment and density functional theory (DFT) calculations, that the reaction proceeded through a flat tetrahydrocarbazole adsorption geometry involving several Pd surface sites, indicative of a structure sensitive reaction. In the present work the dehydrogenation of dodecahydro-N-ethylcarbazole, using a series of Pd catalysts with different Pd particle sizes was studied and compared with the dehydrogenation reactions of dodecahydrocarbazole and dodecahydrofluorene. DFT calculations were used to optimize and compare the adsorption geometry of each molecule on the Pd surface in order to explain the differences in the observed reaction rates.

2. Experimental

2.1. Catalyst preparation

Silica supported Pd catalysts with Pd loading of 0.5 wt% to 10 wt%, were prepared by the incipient wetness impregnation of silica gel (Sigma–Aldrich, BET surface area 400 m²/g, pore volume 1.15 cm³/g). The required amount of an aqueous solution of HCl and PdCl₂ (Sigma–Aldrich, 99.9+%) precursor were added dropwise to the silica gel and left to age for 48 h. The samples were dried at 393 K for 8 h and calcined at 773 K for 6 h in a 30 cm³ (STP)/min flow of He. The catalysts were then reduced in 30 cm³ (STP)/min of H₂ by heating at 10 K/min to 673 K and holding the final temperature for 1 h before cooling to room temperature in a 30 cm³ (STP)/min flow of He.

The Pd catalysts were compared to a previously reported 5 wt% Pd/SiO₂ catalyst that was prepared by wet impregnation but dried at 393 K for 24 h and calcined at 748 K for 3 h in air rather than inert He [8].

A commercial 5 wt% Pd on activated carbon catalyst (Aldrich, 5 wt% Pd, reduced) was used for comparative dehydrogenation reactions of dodecahydrocarbazole and dodecahydrofluorene.

2.2. Catalyst characterization

Temperature-programmed desorption (TPD) of CO was performed using a Micromeritics Autochem II 2920 analyzer.

About 0.2 g of the dried catalyst was calcined at 773 K for 6 h in a flow of Ar at 30 cm³ (STP)/min and reduced at 673 K in a 30 cm³ (STP)/min flow of 10% H₂ in Ar for 1 h. After flushing the catalyst in 30 cm³ (STP)/min flow of Ar for 1 h, it was exposed to 50 cm³ (STP)/min flow of 10% CO in He at 313 K for 1 h and flushed with 50 cm³ (STP)/min He for 2 h. The TPD was then started by heating the sample to 773 K at a rate of 10 K/min and holding the final temperature for 1 h.

Assuming complete reduction of the Pd particles, the CO uptake obtained from the TPD experiments was used to calculate the Pd metal dispersion according to equation (1),

$$D(\%) = \frac{M_{\text{CO}}}{M_{\text{Pd}}} \times 100 \quad (1)$$

where M_{CO} is the amount of CO desorbed in the TPD experiments in moles, and M_{Pd} the number of Pd moles available in the sample. From the Pd metal dispersion, the Pd particle size was approximated according to equation (2),

$$d_p(\text{nm}) = \frac{1}{D} \times 100 \quad (2)$$

The catalysts were also characterized by scanning electron microscopy (SEM) and energy dispersive X-ray analysis (EDX). SEM, EDX and EDX-mapping were done using a variable pressure 120 keV Hitachi S-3000N equipped with a light element EDX detector. A FEI Tecnai G2 200 kV with a LaB₆ filament capable of 1.4 Å point-to-point resolution was used for high-resolution transmission electron microscopy (HRTEM). Pd/SiO₂ samples with variable Pd loadings were ground to a fine powder using an agate mortar and pestle and dispersed in ethanol ultrasonically. A droplet of the suspension was then placed on a 200 mesh copper grid coated with formvar carbon and was left to dry before analysis.

2.3. Catalyst activity

The dehydrogenation reactions were carried out at 443 K and 101 kPa in a 50 cm³ glass flask reactor using the reduced Pd/SiO₂ catalysts and the product obtained from N-ethylcarbazole

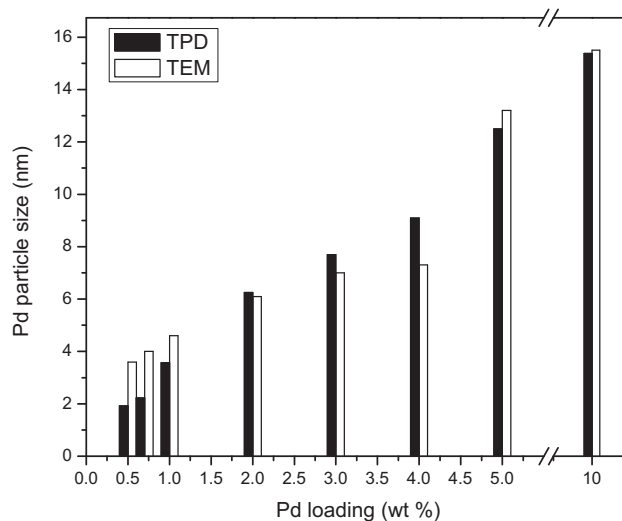


Fig. 1 – Estimated Pd particle size of reduced Pd/SiO₂ catalysts with Pd loading of 0.5–10 wt% obtained by CO TPD and HRTEM. All catalyst precursors were calcined in He.

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