The effect of the N atom on the dehydrogenation of heterocycles used for hydrogen storage

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A R T I C L E   I N F O

Article history:
Received 13 July 2011
Received in revised form 6 January 2012
Accepted 10 January 2012
Available online 17 January 2012

Keywords:
Dehydrogenation
Kinetics
Catalyst
Dodecahydro-N-ethylcarbazole
Hydrogen storage

A B S T R A C T

The effect of the N atom on the hydrogen release rate from heterocyclic compounds was studied by comparing the dehydrogenation rate of dodecahydro-N-ethylcarbazole, dodecahydrocarbazole and dodecahydrofluorene. Over a 5 wt% Pd/C catalyst, hydrogen recovery was fastest (TOF ~60 min−1 at 443 K and 101 kPa) from dodecahydro-N-ethylcarbazole and ~3 times faster than that of dodecahydrocarbazole. Dodecahydrofluorene dehydrogenation was the slowest among the compounds examined, with less than 1 wt% H2 recovered after more than 20 h at 443 K, although selectivity to the completely dehydrogenated product was 95%. Despite catalyst poisoning by the N in dodecahydrocarbazole and its dehydrogenated product, the presence of the N in the heterocycle increased the dehydrogenation reaction rate compared to dodecahydrofluorene, demonstrating that heterocycles are better candidates for H2 storage than polycycles.

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1. Introduction

Hydrogen is an alternative energy carrier which is non-toxic and environmentally benign because H2 is the only product when H2 is converted into thermal energy (by combustion) or electrical energy (using fuel cells). However, the very low density of hydrogen at ambient conditions makes it difficult to store and transport. Despite available methods to physically increase the density of hydrogen, such as compression or liquefaction for onboard H2 storage [1], the bulky and heavy storage equipment required for compression, as well as the low gravimetric storage capacity, remain problematic. On the other hand, off-board, chemically regenerable materials have the potential to meet the storage density demands of automotive applications [2]. These materials, including organic (hetero)polycyclic compounds, require a chemical reaction (hydrogenation) to be regenerated, and often have high gravimetric storage capacity (>5.5 wt%). Another advantage of using these storage materials is that their hydrogenated forms have been shown to release hydrogen at low temperatures (<473 K) and within the temperature limits determined by the US Department of Energy (D.O.E.) for transportation applications [3–8].

On-board hydrogen recovery from liquid carriers must occur within a reasonable time and temperature limit and therefore, the dehydrogenation reactions must be selective and have a low enthalpy so that the reaction is thermodynamically favored at low temperatures [9]. However, dehydrogenation reactions of cyclic organic compounds have been reported to be very slow. For example, the high enthalpy of dehydrogenation of 205.5 kJ/mol for cyclohexane, with a hydrogen capacity of 7.1 wt% and 202.5 kJ/mol for methylcyclohexane, with a hydrogen capacity 6.1 wt%, requires dehydrogenation temperatures above 573 K [7,10,11]. Pez et al. [6] reported that incorporation of a heteroatom in the ring can lower the dehydrogenation enthalpy of the compound, making heterocyclics better candidates for hydrogen storage. For example, dodecahydro-N-ethylcarbazole (with a theoretical H2 storage capacity of 5.8 wt%) was completely converted within 17 h at 443 K and 101 kPa over a Pd/SiO2 catalyst with Pd particle diameter of ~24 nm. However, the dehydrogenation was not selective to the completely dehydrogenated product, N-ethylcarbazole [3]. Hence only 4.0 wt% H2 was recovered from the dodecahydro-N-ethylcarbazole, rather than the theoretical 5.8 wt%. In another study, dehydrogenation of dodecahydro-N-ethylcarbazole over a homogeneous Ir-complex catalyst had no selectivity towards N-ethylcarbazole at 473 K, with octahydro-N-ethylcarbazole and tetrahydro-N-ethylcarbazole being the only products [12]. Dodecahydrocarbazole with 6.7 wt% hydrogen storage capacity showed a much slower dehydrogenation reaction rate than dodecahydro-N-ethylcarbazole, likely due to product inhibition by carbazole, with only 53% conversion achieved after 17 h at 443 K and 101 kPa over a Pd/SiO2 catalyst with