



Structure-reactivity relationship in catalytic hydrogenation of heterocyclic compounds over ruthenium black; Part B: Effect of carbon substitution by heteroatom



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ABSTRACT

The effect of the type of heteroatom in the structure on the recyclability of possible candidate compounds for application as LOC (liquid organic carriers) was studied by comparing the rate and selectivity obtained in hydrogenation of carbazole, dibenzothiophene, dibenzofuran and fluorene. The effect of a partial saturation of the compound on its hydrogenation yield and reaction pathway was also considered by studying hydrogenation of 1,2,3,4-tetrahydrocarbazole. Using Ru black catalyst, the rate of hydrogenation was found to decrease in order; dibenzofuran > 1,2,3,4-tetrahydrocarbazole > carbazole > fluorene. No reaction was observed in the hydrogenation of dibenzothiophene under the conditions studied which was attributed to the immediate poisoning of ruthenium metal by sulphur compounds. The rate of hydrogenation of fluorene was around 3 times lower as compared to carbazole and over 8 times lower as compared to that of dibenzofuran under the same reaction conditions. With the exception of S containing dibenzothiophene, the presence of the heteroatom in the structure was found to be beneficial in terms of increasing the rate of hydrogen loading step. Additionally, a higher reaction rate was obtained in the hydrogenation of the partially saturated 1,2,3,4-tetrahydrocarbazole as compared to the substrate carbazole. The structure and stability of intermediates was found to be significantly influenced by the type and presence of a heteroatom in the structure. A stable octahydro-intermediate was observed only with N-heterocycles, whereas a stable hexahydro-intermediate was produced in the polyaromatic hydrocarbon-fluorene. Additionally, the theoretically obtained lowest total enthalpies using DFT calculations agreed well with the stable intermediates observed experimentally in the hydrogenation of fluorene. Theoretical DFT differences in enthalpies also indicated the products of hydrogenolysis of perhydro-dibenzofuran to be the most favourable products of its hydrogenation, which agreed well with the experimental observations. Overall, taking into account the recyclability of LOC, substitution of carbon with a N heteroatom was demonstrated to be one of the promising approaches to improve the kinetics of the hydrogen loading step.

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1. Introduction

Hydrogen is considered a vector of a clean and sustainable future energy, addressing the need for independence and security around the globe. With this regard, it represents a promising alternative to the ever-increasing use of fossil fuels [1,2]. With the so-called “Hydrogen Economy” put in place, there is a constant need for development of a feasible, cost-effective and safe hydrogen storage and distribution media [3,4]. Commodity chemicals, potential

liquid organic carriers (LOC) such as cyclohexane [5], methylcyclohexane [6–8], decalin [9], carbazole and 9-ethylcarbazole [10–12] or boron–nitrogen heterocycles like borazine [13] have been long investigated for application as hydrogen storage media [14,15].

The influence of the structural features of the LOC material on the dehydrogenation step has been extensively studied [13,16–18]. For example, it has been found that the substitution of C by a heteroatom, mainly N or O, in the LOC ring structure drastically decreases the temperature of dehydrogenation of the corresponding aromatic compound by diminishing the strength of neighbouring α -CH bonds in the ring [17]. The introduction of a heteroatom was further reported to diminish the absolute value of the standard enthalpy of hydrogenation, thus resulting

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in lower barriers for dehydrogenation [19]. In addition, a significant electronic effect caused by electron donating substituents on the ring was identified to substantially increase the rate of dehydrogenation [16]. Additionally, the dehydrogenation reaction of the LOC candidate materials studied in the present work has also been reported. For example, perhydro-carbazole (fully loaded carbazole) was dehydrogenated over 5% Rh/C catalyst at 125 °C and 1 bar hydrogen. Under these relatively mild conditions, a high conversion of 84% was obtained with 50% selectivity to tetrahydro-carbazole (removed 8 hydrogen atoms from perhydro-carbazole) and 12% to carbazole (fully dehydrogenated carrier) among other products [19]. Furthermore, a slow rate of perhydro-dibenzofuran dehydrogenation was reported by Wang [20] using homogenous iridium pincer complexes. In this work, a complete conversion of the substrate was achieved in the presence of a hydrogen acceptor (tert-butylethylene) at 200 °C during 24 h but with poor selectivity of 60% to octahydro-dibenzofuran. Substituted thiophenes were also proposed for hydrogen storage materials [21]. Sotoodeh [22] attempted dehydrogenation of cyclic carbohydrate perhydro-fluorene (6.74% of theoretical hydrogen uptake) over a 5 wt% Pd on activated carbon catalyst at 170 °C under continuous flow of He.

On the other hand, there is only scarce amount of works dealing with the impact of the chemical structure of the LOC material on the hydrogenation step [17,23–25]. The often neglected fuel regeneration step (hydrogen loading) is assumed to be taking place off-board of the vehicle where much harsher conditions can be used than those required for an on-board dehydrogenation step. In spite of that, the LOC recyclability should be considered in the search for an appropriate H₂ carrier material as it is unquestionably an important parameter from both economic and environmental points of view. Thus, it is important to study the parameters of the off-board hydrogen loading step to optimise cost and to avoid production of waste which would render a more competitive and feasible H₂ storage strategy. Correspondingly, in our previous works, we have focused on the influence of the catalytic system on the hydrogenation of 9-ethylcarbazole as a prototype of LOC [10,26,27]. We have found that the hydrogenation of this compound over a ruthenium black catalyst results in the production of a very stable intermediate (9-ethylcarbazole, which corresponds to the addition of 8 hydrogen atoms to the substrate, abbreviated +8 [H]). Interestingly, we observed that further hydrogenation of this compound was strongly hindered by its geometry affecting its adsorption on the catalyst surface [10]. Following these findings, it was decided to focus on the influence of the chemical structure of the LOC material on its reactivity in the hydrogenation reaction. In this regard, in Part A of the present work [28] we investigated the influence of the number of fused aromatic rings (acridine vrs carbazole) and the presence and length of a side chain (9-ethylcarbazole ethanol, 9-ethylcarbazole and carbazole) on the rate and selectivity of hydrogenation over a commercial Ru black catalyst. On the other hand, the present study is a continuation of the previous investigations that focuses on the influence of the presence and type of heteroatom in the structure as well as partial hydrogenation of LOCs on their reactivity during the hydrogen loading step using the same Ru black catalyst. Finally, a set of guidelines leading to the design of a more effective and eco-friendly hydrogen storage materials for LOC based hydrogen storage methodology will be discussed.

2. Experimental

2.1. Materials

1,2,3,4-Tetrahydrocarbazole (99% purity), Carbazole ($\geq 95\%$), Fluorene (98%), Dibenzofuran (98%), Dibenzothiophene ($\geq 98\%$), 1,4-Dioxane (99%) and Ru black commercial catalyst were

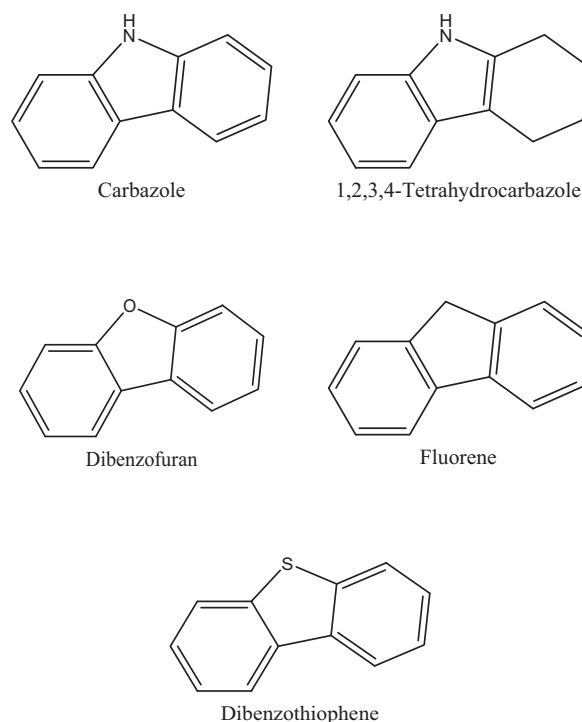


Fig. 1. Organic molecules studied in the present work for application in LOC based hydrogen storage methodology.

purchased from Sigma Aldrich and used as received. Hydrogen gas (99.9%) was supplied by Air-Products.

The structures of the LOC compounds are depicted in Fig. 1. The investigated structural factors included: type of heteroatom substituting carbon in five-membered ring and the effect of partial saturation of one of the benzenoid rings in the carbazole substrate (hydrogenation of 1,2,3,4-Tetrahydrocarbazole).

The choice of the Ru black catalyst was motivated by the geometry of its active sites, which resulted in the production of a very stable intermediate (PI 8 [H]—addition of 8 hydrogen atoms to the 9-ethylcarbazole substrate) in the hydrogenation of 9-ethylcarbazole [10]. The aim of the present work is to gain an insight into which structural features of the LOC candidate compounds directly influence the production of stable intermediates during hydrogenation over the same Ru black commercial catalyst.

2.2. Hydrogenation reactions

The hydrogenation reactions of the heterocyclic compounds shown in Fig. 1 were performed in a set of conditions optimised previously for the hydrogenation of 9-ethylcarbazole [10]. In a typical experiment, 3 grams of substrate (Fig. 1) was dissolved in 100 ml of 1,4-dioxane solvent with the aid of an ultrasonic bath where needed, followed by the addition of 0.15 g of Ru black catalyst. Subsequently, the mixture was sealed in a Parr stainless steel reactor equipped with a thermocouple and a pressure gauge. The reaction mixture was magnetically stirred and heated to 130 °C at 1 bar of H₂. When the desired temperature was reached, 70 bar of hydrogen was charged into the reactor and the reaction time was measured. In order to obtain the change of concentration of the intermediates and products in time, aliquots of reaction mixture were withdrawn from the reactor periodically for analysis of their composition by Gas Chromatograph-Mass Spectrometer (GC-MS) as described in our previous work [10]. Control experiments were carried out, in which the hydrogenation reaction of 9-ethylcarbazole over the Ru black catalyst was tested four times under same reaction

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