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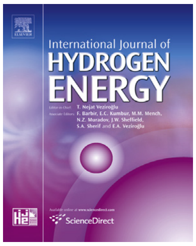

A comparative study of catalytic dehydrogenation of perhydro-N-ethylcarbazole over noble metal catalysts

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ABSTRACT

N-ethylcarbazole is one of the most promising liquid organic hydrogen carriers (LOHCs) as it can be catalytically hydrogenated and dehydrogenated at relatively moderate temperatures. In the present work, we report a systematic study on dehydrogenation of perhydro-N-ethylcarbazole over several important supported noble metal catalysts to identify the optimal catalyst for temperature-controlled dehydrogenation. The reaction takes three consecutive stages with two intermediates of octahydro-N-ethylcarbazole and tetrahydro-N-ethylcarbazole. The initial catalytic activity of the selected noble metal catalysts for the dehydrogenation process was found to follow the order of Pd > Pt > Ru > Rh. 100% selectivity toward the final product of N-ethylcarbazole and fully dehydrogenation was achieved over the supported Pt and Pd catalysts. The kinetics of the three stage dehydrogenation processes over the catalysts was studied and the rate constants were derived. The results indicate that the dehydrogenation reaction rate decreases significantly with the reaction stage for all the selected noble catalysts and the conversion from tetrahydro-N-ethylcarbazole to N-ethylcarbazole was found to be the rate-limiting step of the entire reaction process.

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Introduction

Hydrogen is one of the most efficient energy carriers for a broad range of industrial applications. Materials development for safe, high capacity and energy efficient hydrogen storage and delivery at near ambient conditions is one of the technical challenges towards large scale utilization of hydrogen energy. With the specific system targets of gravimetric density of 5.5 wt% and volumetric density of 40 g H_2/L by 2015 as suggested by the U.S. Department of Energy (DOE), development of high capacity storage materials and utilization technologies is essential for the success of the incipient hydrogen economy.

Hydrogen storage can be realized via a variety of techniques including cryogenic, compressed gas and sorption methods [1–4]. To date, high capacity hydrogen storage based

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on physisorption has only been observed at cryogenic temperatures and significant storage at room temperature for practical applications has yet to be demonstrated [5]. Extensive research on chemisorption has been carried out worldwide since hydride formation appears to be the only means to achieve a sufficiently high hydrogen capacity. Numerous hydrides of light metal alloys [6–10] and complex chemical hydrides [11–14] have been discovered over the last decade. Although many of these compounds exhibit highly desirable properties, such as high capacity [14], facile hydrogen release [13] and good reversibility [6], the majority of them are solids at near ambient conditions. Even if the storage methods meet the DOE targets, implementation of solid-based storage technologies (SBSTs) for automotive applications would require a dramatic change of the current energy infrastructure and thus incur a tremendous cost for the hydrogen economy.

Recognizing the limitation of SBSTs, a concept based on liquid organic hydrogen carriers (LOHCs) was proposed [15] Hydrogen storage and release are realized through catalytic hydrogenation and dehydrogenation. Both the organic carriers and their hydrogenated forms are supposed to be in a liquid state at room temperature. Thus, safe and high capacity hydrogen storage at near ambient conditions can be achieved. The LOHC-based technology is advantageous over other storage methods by offering important benefits for industrial scale production, such as low-cost, scalable manufacturing via conventional chemical processes and maximum compatibility with the existing chemical and energy infrastructure [16–18]. Early attempts were primarily devoted to cycloalkanes [19–23], such as cyclohexane [19,21] and naphthane [22,23]. It turns out that dehydrogenation of these compounds is both thermodynamically and kinetically difficult, requiring highly active catalysts at elevated temperatures. As a consequence, undesirable side reactions, such as C–C cleavage, may adversely occur, which would negatively influence the performance of fuel cell devices with poor hydrogen purity [24]. Clearly, the use of the selected cycloalkanes for hydrogen storage may not be suitable for onboard vehicular applications.

Through extensive first-principles-based computations, a new class of heteroaromatic compounds was identified for reversible hydrogen storage at moderate conditions. Dehydrogenation can be realized at a substantially lower temperature than the dehydrogenation temperature of cycloalkanes without producing unwanted impurities [25–28]. The computational results suggest that introduction of heteroatom(s) into cyclic aromatic rings to form heteroaromatic compounds would significantly reduce the enthalpy of dehydrogenation, allowing the reaction to be carried out at a temperature substantially lower than the temperature required for dehydrogenation of the selected cycloalkanes. Furthermore, the new LOHCs allow full catalytic hydrogenation with a gravimetric density surpassing 5.0 wt%.

Among the proposed LOHC compounds, N-ethylcarbazole (NECZ) stands out to display properties well suited for hydrogen storage with a capacity of 5.79 wt% and boiling point of 348.3 °C. Intense research efforts have been focused on catalytic hydrogenation of NECZ [29–35] and dehydrogenation of perhydro-N-ethylcarbazole (12H-NECZ) in recent years [36–44]. NECZ hydrogenation kinetics and mechanisms were extensively studied over several noble metal catalysts and Raney nickel [29,31]. It was revealed that NECZ can be fully hydrogenated catalytically at 150 °C in both molten and solution forms [29,30,33], demonstrating that the hydrogenation can be carried out at moderate conditions. For onboard application of the storage technology, dehydrogenation of 12H-NECZ relies on temperature swing sorption (TSS) technology to operate. Therefore, to maintain optimal operation of proton exchange membrane fuel cell (PEMFC) devices, hydrogen release must be controllable by tuning the reaction temperature in a narrow working range. To this end, the dehydrogenation mechanisms, catalytic selectivity and reaction kinetics must be well understood. Sotoodeh et al. investigated the catalytic dehydrogenation process of 12H-NECZ over a Pd catalyst both experimentally and computationally [37–41,43]. It was found that full dehydrogenation can be achieved below 200 °C, producing high purity of hydrogen gas up to 99.99% [39,40]. The homogeneous catalysts with the PCP pincer iridium based complexes developed by Jensen and coworkers for dehydrogenation of 12H-NECZ were also found to be effective; however, full dehydrogenation could not be achieved [42].

In a previous study [44], we reported temperature-controlled three-stage catalytic dehydrogenation and cycle performance of 12H-NECZ. Our results indicate that NECZ displays excellent cycle performance with little capacity degradation after 10 cycles of catalytic hydrogenation and dehydrogenation. In this paper, we report a systematic study on dehydrogenation of 12H-NECZ over several important supported metal catalysts, i.e., palladium, platinum, ruthenium and rhodium, to identify the optimal catalyst for temperature-controlled dehydrogenation. To date, comparative studies on 12H-NECZ dehydrogenation over noble metal catalysts have been rare. We show that the supported palladium catalyst (5 wt% Pd/Al_2O_3 catalyst) is most active among all the metals for driving the dehydrogenation to completion with the highest selectivity and rhodium displays inferior catalytic activity toward full dehydrogenation. Comprehensive understanding of the catalytic behavior of the metal catalysts is imperative for design of more efficient catalysts and for control of product yields via TSS technologies.

Experimental

Materials

N-ethylcarbazole (AR, 99.5%) was purchased from Alfa-Aesar. Ultra high purity hydrogen (99.999%) and argon (99.999%) were supplied by Sichuan Ally High-Tech Company. The commercially available catalysts of 5 wt% Ru, 5 wt% Rh, 5 wt% Pd and 5 wt% Pt on alumina support were purchased from Shanxi Kaida Chemical Company.

Preparation of perhydro-9-ethylcarbazole

The 12H-NECZ reactant was prepared via hydrogenation of NECZ at 180 °C and a hydrogen pressure of 80 bars in a stainless steel autoclave batch reactor (Parr 4568). 200 g of NECZ and 10 g of the 5 wt% alumina-supported Ru catalyst

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