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Short Communication

Microwave-activated dehydrogenation of perhydro-N-ethylcarbazol over bimetallic Pd-M/TiO₂ catalysts as the second stage of hydrogen storage in liquid substrates

L.M. Kustov^{a,b,*}, A.L. Tarasov^a, O.A. Kirichenko^a^a N. D. Zelinsky Institute of Organic Chemistry, 47 Leninsky prospect, Moscow 119991, Russia^b Chemistry Department, Moscow State University, Leninskie Gory 1, bldg. 3, 119992, Russia

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ABSTRACT

Reversible catalytic hydrogenation–dehydrogenation of aromatic and heterocyclic compounds is considered as a promising approach to hydrogen storage. While exploring the microwave-assisted catalytic processes, the Pd/TiO₂ catalysts were shown to be most effective. The catalytic activity of the Pd/TiO₂ system can be enhanced by introduction of a second metal after the formation of the supported Pd nanoparticles, with Pt and Ru acting as most efficient promoters. The studies of the catalytic behavior of the supported bimetallic Pd–Ru/TiO₂ and Pd–Pt/TiO₂ catalysts in perhydro-N-ethylcarbazole (H-NEC) dehydrogenation revealed that the catalytic activity under microwave activation is higher than that in a conventional thermal mode at the same reaction temperatures. Complete dehydrogenation occurred only under microwave activation, with a negligible by-product formation. This feature of the catalysts makes possible their application in the hydrogen storage systems based on the reversible hydrogenation–dehydrogenation cycles under microwave activation.

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Introduction

Hydrogen is considered as one of the most efficient energy resources for the future application in ecologically friendly (“green”) vehicles. Hydrogen can serve an alternative fuel if the hydrogen storage problem can be solved. An efficient and safe approach to hydrogen storage may be based on reversible hydrogenation–dehydrogenation of aromatic and heterocyclic

compounds (so called “liquid organic hydrogen carriers”. In general, the use of such hydrocarbons as cyclohexane, decaline, etc. via catalytic dehydrogenation for production of hydrogen was summarized [1–6].

The pair decaline–naphthalene inter-conversion looks attractive because of the liquid state of decaline at room temperature, but it has a disadvantage of continuous loss of the substrate during the dehydrogenation–hydrogenation

* Corresponding author. N. D. Zelinsky Institute of Organic Chemistry, 47 Leninsky prospect, Moscow 119991, Russia.

E-mail address: LMK@ioc.ac.ru (L.M. Kustov).

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cycles [7]. The loss of the substrate is explained not only by the high temperature and evaporation under the dehydrogenation conditions (typically above 250–300 °C), but also by the increasing possibility of the occurrence of side reactions during the repeated cycles with the substrate molecule [8]. The most important side reactions are cracking, ring opening, or hydrocracking of the aromatic/naphthenic hydrocarbons.

The storage and release of hydrogen by reversible catalytic hydrogenation of extended conjugated substrates including mostly large condensed polycyclic aromatic hydrocarbons, condensed aromatic hydrocarbons with nitrogen or oxygen heteroatoms, polycyclic aromatic hydrocarbons and other is described [9–13]. The conjugated substrates include, inter alia, pyrene, coronene, indene, carbazole, poly(methylcarbazole) and other molecules.

N-ethylcarbazole being hydrogenated to perhydro-N-ethylcarbazole looks more attractive in comparison with other substrates because of a sufficiently high hydrogen storage capacity (near 5.8 wt%) [14]. Diverse catalysts, including supported Pt and Pd catalysts on activated carbon, metal oxides such as SiO₂ and different carriers, were investigated for this substrate conversion [15–17]. A very important parameter for the chemical storage of hydrogen is the heat required for the dehydrogenation reaction. It has been indicated by Cooper et al. [18] that the heat necessary for dehydrogenation of perhydro-N-ethylcarbazole is close to 50 kJ per 1 mole of H₂, this provides milder conditions for the catalytic dehydrogenation reaction that can proceed at low temperatures, even below 200 °C.

In our previous works [19,20] it was shown that microwave (MW) irradiation can be used to provide energy for heating of substrates and catalysts in the hydrogen storage systems. While exploring MW-assisted catalytic processes of hydrogenation–dehydrogenation of various substrates (decaline, tercyclohexane) and catalysts, it was concluded that the dehydrogenation temperature can be substantially decreased from 280–320 °C to 150–250 °C by performing the catalytic process under the MW activation. The treatment of catalysts by MW radiation was found to be the most effective technique affecting the activity and other properties of Pd-catalysts on the carriers that can absorb MW radiation, for example, titania and carbon supports [21,22].

Obviously, the use of more complicated nano-engineered catalysts, like bimetallic and core-shell compositions [23–25] can further enhance the efficiency of the catalytic dehydrogenation of the liquid substrates like H-NEC. Most studies of reversible hydrogen storage in hydrogenation–dehydrogenation cycles with liquid organic hydrogen carriers were performed with Pt-containing catalysts [18–21]. Palladium is much cheaper than platinum and is prompt to form alloys with different metals. Therefore, we have chosen Pd and tried to improve its performance by adding a second metal, chosen among Ru, Pt, Cr, Ni, Ge, W. Whereas Ru, Pt, Cr, Ni are known to form alloys and intermetallides with Pd, the two latter (Ge, W) were chosen to check whether these metals, different from typical metals active in hydrogenation–dehydrogenation processes, can affect the reaction pattern, either by modifying the palladium nanoparticle or the titania support.

The aim of this work was to compare the performance of different bimetallic Pd-containing catalysts supported on TiO₂

in the reaction of perhydro-N-ethylcarbazol dehydrogenation under traditional thermal heating and MW activation. It is well known that TiO₂ is a good semiconductor that can absorb MW energy and thus can be heated quite efficiently with MW energy. Moreover, the highly dispersed supported metal (Pd or other) also can absorb MW energy and thereby enhance the heating efficiency.

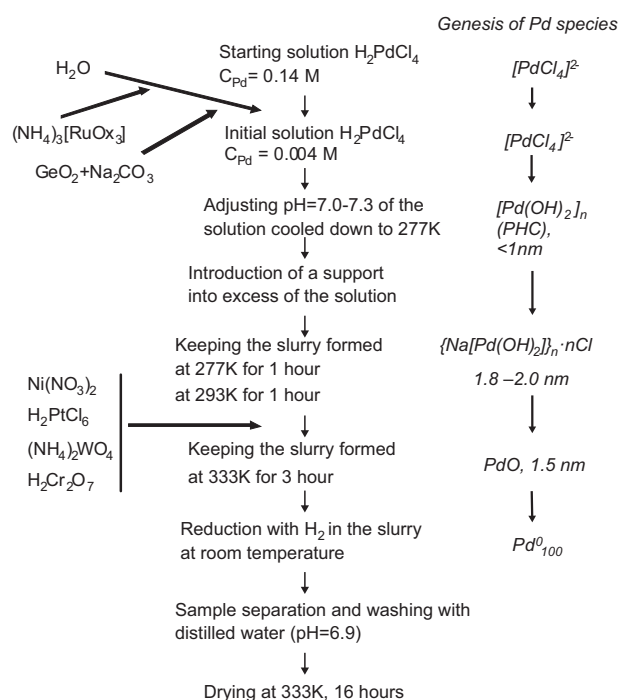
Materials and methods

Catalyst preparation

Fine powdered TiO₂ (Degussa P-25, anatase – 70%, rutile – 30%) was used as a support (apparent density – 3.8–4.0 g cm⁻³). The specific surface area of 45 m²/g and the absence of micropores allow one to distribute the precious metal nanoparticles in a highly dispersed state on the support surface and to avoid an internal diffusion problem during preparation and further catalytic processes.

The catalysts were prepared by a deposition-precipitation (DP) procedure similar to that described in Ref. [26]. The procedure consists in thermally induced deposition-precipitation of the Pd polyhydroxo complexes (PHC) on the support surface followed by their enhanced hydrolysis and reduction with hydrogen in the slurry containing a second metal precursor. A second metal compound was introduced at different steps of preparation depending on the metal nature (Scheme 1).

Preliminary reduction of a metal precursor was performed in a liquid phase with hydrogen preadsorbed on Pd to achieve more complete deposition of the second metal on the Pd nanoparticle surface. The conditions of reduction depend on the nature of the metal and on the chemical composition of its



Scheme 1 – Preparation of 1%Pd-M/TiO₂ catalysts by the DP method.

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