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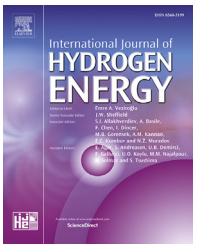

Application of microwave synthesized Ag-Rh nanoparticles in cyclohexane dehydrogenation for enhanced H_2 delivery

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ABSTRACT

The catalytic dehydrogenation of liquid organic hydrides (LOH) is a promising route to deliver H_2 for various mobile and stationary applications. However, an efficient and low-cost dehydrogenation catalyst, as an alternative to Pt, is a key for the success of LOH-based H_2 supply. In a quest for such catalysts, we synthesized stable Ag-Rh bimetallic nanoparticles (BNP) supported on activated carbon cloth (ACC) and Y_2O_3 using the microwave-assisted polyol technique. The performance of these catalysts during dehydrogenation of LOH viz., cyclohexane, was evaluated at 300 °C using an advanced spray-pulse reactor system. The Ag:Rh ratio was optimized to maximize the cyclohexane conversion and H_2 evolution. The effect of Ag:Rh ratio, catalyst support, and synthesis method was investigated, too. The most stable H_2 evolution performance was exhibited by microwave-synthesized 1:4 Ag-Rh/Y_2O_3 catalyst with the cyclohexane conversion, dehydrogenation rate and H_2 evolution rate of 35.8%, 17.2 mmol/g_{Met}/min and 400 mmol/g_{Met}/min, respectively. Finally, the performance of catalysts used in this study was compared with the Pt-based catalysts.

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Introduction

Hydrogen (H_2), by virtue of its clean nature, ample occurrence and high energy density (142 MJ/kg), is an environmentally attractive primary energy vector [1]. Besides, as a synthetic fuel, H_2 can be employed to power both mobile (e.g., automobiles) and stationary (e.g., portable electronics) applications within the existing infrastructures [2]. It is thus considered as a key contributor to achieve the goal of a sustainable energy society [3]. Nevertheless, a safe and efficient route to store, transport and distribute H_2 is an essential prerequisite to reach this goal. The storage of H_2 in either adsorbed or stabilized form with several chemicals and its utilization for onsite applications has thus gained significant attention considering its safety and relatively mild reaction conditions. A few examples of such H_2 storage methodologies include the hydrolysis reaction of hydrides (e.g., $NaBH_4$, MgH_2, NH_3BH_3 [4a], hydrogenated $CaMg_2$ [4b], Mg-oxide composites [4c]) and dehydrogenation of liquid organic hydrides (LOH) [2]. Interestingly, liquid organic hydrides (LOH) are candidate H_2 carriers that are highly efficient to store H_2 (~6–8% on a weight basis), transport it over a long-distance (~300 km) and

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successively deliver it for various applications (e.g., fuel cells) [5–8]. The reversible hydrogenation-dehydrogenation reaction pair of corresponding aromatics and naphthenes is the general configuration of an LOH-based H_2 supply system.

All along, cycloalkanes (such as cyclohexane, methylcyclohexane, and decalin) are most popular LOH's whereas the dehydrogenation activity is ruled by Pt [9]. Moreover, owing to high costs and limited reserves of Pt, various non-precious metals such as Ni, Fe, Mo, Cu, Zn were attempted for LOH dehydrogenation, too [10–12]. Alloying of the aforesaid metals with the second active analogue (e.g., Ru, Rh, Re, Pd, Ir, W, etc. [13,14]) and/or promoter (e.g., Ca [15,16]) to promote C-H cleavage, improve product desorption and thus, synergize dehydrogenation, is also being practised over several years. Withal, the majority of these catalysts, due to their poor physico-chemical and structural characteristics (e.g., morphology, texture, surface chemistry) and metal-support interactions, underperform during dehydrogenation [17,18]. The catalysts with defined structures, excellent morphological features, and novel metal combinations are thus highly desirable for LOH dehydrogenation. The bimetallic nanoparticles (BNP's), with their unique and exquisite electronic [19], magnetic [20], optical [21], physico-chemical and catalytic properties [22], finely controlled surface structures; quantum size-confinement effects, and tunable surface binding energies, therefore bring in a fascinating avenue for application in LOH dehydrogenation [23].

Presently, BNP's are being widely utilized in several large-scale industrial processes related to fuel cell fabrication [24], organic synthesis [25] and environmental remediation [25–27]. However, their application in LOH dehydrogenation is seldom discussed, e.g., Al-ShaikhAli et al. [11,28] used Ni-M (where, M = Ag, Sn, Zn, In) nanoparticles synthesized by homogeneous deposition precipitation method to catalyse dehydrogenation of methylcyclohexane. To the extent of our knowledge, this is the only information available on the use of BNP's in LOH dehydrogenation.

Herein, we selected two neighboring atoms of 4d transition metal series viz. Ag and Rh to synthesize BNP's for application in LOH dehydrogenation. The scarce and expensive Rh finds wide applications in catalytic processes; whereas abundant and cheap, pure Ag is inherently unreactive [23]. Interestingly, the ensemble effect between Rh and Ag leads to a cost-effective alloying [29]. Besides, the use of Ag-Rh complex appears promising in LOH dehydrogenation, e.g., Pande et al. [30] reported the H_2 evolution rate of 12.34 mmol/g_{Met}/min and H_2 yield of 39% over a 10:1 Ag-Rh/ACC catalyst in cyclohexane dehydrogenation at 300 °C. The H_2 evolution performance of this catalyst was comparable to 10:1 Ag-Pt/ACC (13.4 mmol/g_{Met}/min); whereas it was superior against the performances of 10% Ag/ACC (6.9 mmol/g_{Met}/min) and 1% Pt/ACC (2.5 mmol/g_{Met}/min) under identical conditions. However, the synthesis of Ag-Rh bimetallic catalysts is severely influenced by the immiscibility of Ag and Rh metals [29]. Nonetheless, this barrier can be effectively tackled in the nano regime with quantum size confinement effects and a stable mixture of Ag-Rh BNP's can be achieved [23,29].

In the present work, stable Ag-Rh compositions were prepared by using a novel microwave-assisted polyol technique and their role on H_2 evolution activity during dehydrogenation of LOH viz., cyclohexane was studied in a spray pulse reactor system. Backed by our previous studies [31,32], we anticipated ACC and metal oxide, Y_2O_3, as active and stable supports for Ag-Rh nanoparticles under strident dehydrogenation conditions (300 °C). The carbon supports are known to prevent the C-H bond cleavage and reduce carbon formation; while Y_2O_3 is earmarked to improve metal-support interaction [31,32].

Experimental

Catalyst synthesis

The monometallic Ag and Rh (with a 5% nominal metal content) and their varying bimetallic nano compositions (in the Ag-Rh ratios of 1:1, 1:4 and 4:1, respectively) used in this work were synthesized using microwave-assisted polyol technique. In a typical recipe, a colloidal solution of the metal precursors viz., $AgNO_3$ (99%) and/or $RhCl_3{\cdot}3H_2O$ (≥96%) was prepared using ethylene glycol as a reducing agent followed by the addition of a stabilizing agent, poly (N-vinylpyrrolidone) (PVP) to avoid aggregation of Ag and Rh particles. The resulting solution was then exposed to high-intensity microwave irradiation for 1 min in the domestic microwave oven. The microwave heating enables a homogeneous nucleation at shorter crystallization times and thus, narrowly distributed, highly pure and nano-sized metal particles can be realized with advanced physicochemical properties [33–35]. The Ag and Rh nanoparticles so obtained from the microwave-irradiated homogeneous mixture, were loaded onto ACC (having specific surface area 1200 m^2/g) or Y_2O_3 (with specific surface area 6.37 m^2/g) by wet-impregnation method as described in our previous article [30]. A typical composition prepared by physical mixing method was used to benchmark the performance of microwave-synthesized Ag-Rh nanoparticles.

Catalyst characterization

The characteristics of the Ag-Rh/ACC BNP's were studied using various techniques. The catalysts were first reduced in the H_2 atmosphere for this purpose. The XRD patterns and lattice constants of Ag-Rh/ACC (scanning rate of 0.01° s^{-1}, angle range: 5–80°) catalysts were obtained using a Desktop X-ray diffractometer (Miniflex II, Rigaku, Japan) with Cu-Kα radiations (λ = 1.5405). The presence and oxidation state of surface metals viz., Ag, Rh and Ag-Rh on ACC, before and after the reaction, was identified with X-ray photoelectron spectroscopy (XPS) technique. The XPS measurements were performed on a VG Microtech Photoelectron Spectrometer (ESCA 3000, Microtech) with monochromatized Mg-Kα radiations (λ = 1253.6) at a pressure of $>1 \times 10^{-9}$ Pa. The output spectra were corrected with a subtracted Shirley-type background and a C1s binding energy value of 285 eV. The high-resolution microscopy images of the Ag-Rh BNP's were captured with an HR-TEM (JEM 2100, JEOL Ltd., Japan) operated at 200 kV. The sample for the same was prepared by placing a drop of the colloidal dispersion onto a Cu grid coated with perforated carbon film, followed by evaporating the solvent at ambient temperature. The nanoparticle structures were

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