INTERNATIONAL JOURNAL OF HYDROGEN ENERGY XXX (2018) 1–9

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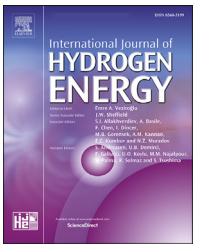

Ruthenium stabilized on transition metal-on-transition metal oxide nanoparticles for naphthalene hydrogenation

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ARTICLE INFO

Article history:
Received 11 December 2017
Received in revised form
26 May 2018
Accepted 30 May 2018
Available online xxx

Keywords:
Ruthenium
Transition metal
Transition metal oxide NPs
Hydrogenation
Synergetic effect

ABSTRACT

The multi-metallic nanocatalysts of ruthenium nanoclusters-on-transition metal/transition metal oxide nanoparticles (TM/TMO NPs) then supported on carbon (Ru/Ni/NiO/C or Ru/Co/Co_3O_4/C) were designed and synthesized. The Ni/NiO or Co/Co_3O_4 NPs strongly stabalized the ruthenium nanoclusters by the interfacial interaction among them. These catalysts exhibited high catalytic activity and 100% selectivity to decalin for naphthalene hydrogenation due to the synergy effect of multiple catalytic sites, where naphthalene was absorbed and activated at the TMO sites (NiO or Co_3O_4), H_2 was activated at the Ru sites and it produced the activated H* species, H* was transferred to the surface of NiO or Co_3O_4 by the hydrogen spillover effect of TM (Ni or Co), reacting with the activated naphthalene and forming decalin. The nanostructures and synergetic effect of the Ru/Ni/NiO/C and Ru/Co/Co_3O_4/C catalysts were revealed by a series of techniques, such as high-resolution transmission electron microscope (HRTEM), temperature-programmed reduction (TPR), scanning transmission electron microscopy-energy dispersive X-ray spectroscopy (STEM-EDS) mapping, high-sensitivity low-energy ion scattering (HS-LEIS) and X-ray absorption spectroscopy (XAS). It is promising that the hydrogen storage can proceed at room temperature via catalyzing naphthalene hydrogenation over the Ru/Ni/NiO/C or Ru/Co/Co_3O_4/C catalyst.

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https://doi.org/10.1016/j.ijhydene.2018.05.170
0360-3199/

Introduction

Noble metal (NM) catalysts have significant application prospect in the chemical production processes and environmental protection fields [1–3]. But the storage of precious metals is limited and thus their price is so high. As a consequence, the efficient use of noble metals has attracted more and more interests of chemical and material scientists, and it has become one of research focuses [4,5]. At present, the main methods to improve the utilization of precious metal atoms and keep outstanding catalytic performance, selectivity and stability of the nanocatalysts containing NM are divided into the below four means: (1) reduce the size of metal nanoparticles (MNPs) (nano-effect) [6]; (2) MNPs are loaded on the support by the strong interaction effect of metal-support [7]; (3) synthesize MNPs with particular exposing crystallographic planes (crystal facet effect) [8]; (4) synergistic effect of various metallic components (synergy effect) [9]. Take synergy effect as an important example to discuss, it plays an important role not only in heterogeneous catalytic oxidation but also in heterogeneous catalytic hydrogenation reactions [10,11]. It is well known that the combination use of noble metals (eg. Pt, Au, Rh, Ru etc.) and non-precious metals (or other components) (such as Ni, Cu, Fe, and Co) can not only largely enhance the catalytic properties, selectivity and stability, but also decrease the consumption of precious metals and thus the cost of the catalysts [12,13]. For example, the Ni-Pd alloy nanoparticles@MIL-101 (Ni-Pd@MIL-101) were prepared and applied in the reduction of phenol and cyclic and dialkyl ketones, and the Ni-Pd@MIL-101 catalyst showed more excellent catalytic performance than Pd@MIL-101, Ni-Pd@MIL-101 or the physical mixture of Pd@MIL-101 and Ni@MIL-101 due to a synergistic effect between Ni and Pd [14]. Zhang' group found that the Ni-based bimetallic catalysts (such as 1%Ir-5%Ni/MC, 1%Pt-5%Ni/MC, 1%Pd-5%Ni/MC, 1% Ru-5%Ni/MC, and 1%Rh-5%Ni/MC) exhibited higher yield to hexitols in cellulose conversion reaction than corresponding monometallic catalysts (eg. Ni/MC or Ir/MC) and the mixture of Ni/MC or Ir/MC [15]. The Pt-Ni/AC catalyst was prepared in Cheng' group, and its catalytic property for tetralin hydrogenation was largely improved by the synergistic effect of Pt and Ni [16]. Song et al. found that the cooperation of Pd/C and [bmim]Cl-$AlCl_3$ could enhance the catalytic activity of this complexing catalyst for benzene hydrogenation [17]. However, the accurate mechanism of the synergy effect has not been directly observed up to now. With the purpose of further understanding the synergy in the multi-metallic catalysts, in situ spectroscopic investigations and advanced characterization are needed [14]. In this work, the strong interaction and synergistic effect of NM (ruthenium), TM and TMO are also expected to improve the catalytic hydrogenation property and reduce the catalyst cost. And we try our best to confirm this synergy.

The excessive levels of aromatics in air are harmful to human health and environment [18,19]. And aromatic compound also decreases the combustion properties of diesel fuel [20]. So the removal of arenes is of great significance. It is well known that the catalytic hydrogenation of aromatics is an effective way to remove them [21]. In addition, the products of aromatics hydrogenation are vital chemical intermediates (eg. naphthalene hydrogenation). The selective hydrogenation of naphthalene can produce tetralin, octahydronaphthalene and decalin, which can be used as important organic solvents and industrial chemicals [22].

Naphthalene catalytic hydrogenation to decalin is also an important method for hydrogen storage because decalin is a simple and suitable compound to perform catalytic tests due to its sufficient hydrogen content (7.3 wt%; 64.8 kg-H_2 m^{-3}) [23,24]. Currently, the reported catalysts applied in naphthalene hydrogenation are consisted of Ni-based [25], Pt-based [26], Rh-based [27], Pd-based [28], Ru-based [29], Pt-Pd bimetallic catalyst [30] and some metal carbide, nitride, phosphide and silicide catalysts [31]. In our previous work, the Ru/Ni/$Ni(OH)_2$/C catalyst with the nanostructure of Ru nanoclusters-on-Ni/$Ni(OH)_2$ NPs was prepared and it showed excellent catalytic performance in naphthalene hydrogenation, attributable to the nano-synergy of Ru, Ni and $Ni(OH)_2$ sites [32].

Herein, a facile strategy to prepare the Ru/Ni/NiO/C and Ru/Co/Co_3O_4/C catalysts at room temperature (RT) is reported. The Ru/Ni/NiO/C (Ru/Co/Co_3O_4/C) catalysts are composed of Ru nanoclusters-on-Ni/NiO (Co/Co_3O_4) NPs and used in naphthalene hydrogenation. 100% conversion of naphthalene and 100% selectivity to decalin can be achieved over these two catalysts at 25 °C due to the synergistic effect of the Ru, Ni (Co) and NiO (Co_3O_4) sites. This investigation provides an important example to illustrate the synergy effect of NM, TM and TMO can largely improve the catalytic hydrogenation activity. And this study also contributes an efficient method to realize hydrogen storage by catalytic naphthalene hydrogenation over the Ru/TM/TMO/C catalysts.

Experimental

Carbon black was used as catalyst support, and the method of hydrazine hydrate reduction was used to prepare the Ni/$Ni(OH)_2$/C and Co/$Co(OH)_2$/C samples at RT [33,34]. And then they were calcined in N_2 at 380 °C, producing Ni/NiO/C and Co/Co_3O_4/C, respectively. The Ru/Ni/NiO/C and Ru/Co/Co_3O_4/C catalysts were gained at ambient temperature for 6 h via the galvanic replacement reaction [35–39], the total Ni element content in Ni/NiO/C = 12.5% and that in Ru/Ni/NiO/C = 6.0%. The total Co element loading in Co/Co_3O_4/C and Ru/Co/Co_3O_4/C was 12.5% and 6.0%, respectively. The amount of Ru element in Ru/Ni/NiO/C or Ru/Co/Co_3O_4/C was 7.2%. 7.2%Ru/C was prepared by a conventional incipient wetness impregnation method. The experimental details of preparing catalysts were given in Supplementary Material.

Thermal-gravity (TG) tests for Ni/Ni/$Ni(OH)_2$/C and Co/$Co(OH)_2$/C were performed on TG 209F1 thermal gravimeter to investigate the change law of the samples during the thermal-treatment process in N_2. And the measurement temperature increased from 30 °C to 700 °C, with heating rate of 10 °C min^{-1} and the flowing rate of 20 mL min^{-1} N_2. Powder X-ray diffraction (XRD) patterns for the catalysts were obtained by using a Rigaku X-ray diffractometer equipped with

Please cite this article in press as: Deng X, et al., Ruthenium stabilized on transition metal-on-transition metal oxide nanoparticles for naphthalene hydrogenation, International Journal of Hydrogen Energy (2018), https://doi.org/10.1016/j.ijhydene.2018.05.170