Hydrogenation of arenes, nitroarenes, and alkenes catalyzed by rhodium nanoparticles supported on natural nanozeolite clinoptilolite

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ABSTRACT

Nanozeolite clinoptilolite supported rhodium nanoparticles (Rh/NZ-CP) has been prepared and characterized by a variety of techniques, including XRD, BET, TEM, EDX, ICP-OES and XPS analysis. This nanomaterial contains 2 wt% Rh in the range of 5–20 nm metallic nanoparticles distributed on nanozeolite. The catalytic performance of Rh/NZ-CP was evaluated by the hydrogenation of arenes, nitroarenes, and alkenes under moderate reaction conditions. The prepared nanocatalyst can be facilely recovered and reused many times without significant decrease in activity and selectivity. The high catalytic activity, thermal stability and reusability, simple recovery and eco-friendly nature make present catalyst as a unique catalytic system, which is particularly attractive in green chemistry.

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1. Introduction

The main applications of aromatic hydrogenation are in the production of aromatic-free fuels and solvents [1]. In diesel fuel, aromatic compounds have the further effect of lowering fuel quality, they are considered as one of the largest contributors to environmental pollution caused by exhaust emissions [2]. Developing effective catalysts for hydrogenation of arenes is of vital importance because of increasing industrial demands including production of low-aromatic diesel fuels.

To date, several homogeneous catalysts have been employed for the hydrogenation of arenes and nitroarenes. However, the homogeneous catalysts are difficult and expensive to be recovered and reused and the residual metal along with the products can cause serious problems. Thus, to seek more economical heterogeneous catalysts becomes the primal concern for researchers in this field. Rhodium nanoparticles have been frequently used as heterogeneous catalyst for the hydrogenation of arenes in the laboratory [3–6]. Although the catalytic performance of this type of catalyst is excellent, their use on an industrial scale is limited due to the confined reserves and high price of rhodium. Many attempts have been made by researchers to solve these problems. Most of the published

works have focused on increasing the efficiency of the utilization of Rh that showed high activity and selectivity [7–51].

Nanozeolite clinoptilolite (NZ-CP) is attractive in material supports due their versatile structural features such as ease of availability of the natural, inexpensive, high specific surface area, large pore volumes, good thermal and chemical stability and non-toxicity. Although many kinds of Rh catalysts supported on various zeolites such as HB, A, NaY, X, Y and ZSM-5 were introduced [51], the main drawbacks of these catalysts are low selectivity, high concentration of Rh, high temperature, low TOF value, and using expensive and toxic materials for the synthesis of products on a large scale. Thus, there is a clear need, for development of a simple, eco-benign and low cost protocol using a reusable catalyst in large scale.

Continuing our study in the field of highly active and versatile solid that combine metal nanoparticles with natural functional support [52,53], here we have investigated a new material composed of Rhodium nanoparticles immobilized on nano natural zeolite as an efficient and recyclable nanocatalyst for the hydrogenation of arenes, nitroarenes, and alkenes.

2. Experimental

2.1. General

All reagents were prepared from analytical reagent grade chemicals unless specified otherwise and purchased from Merck

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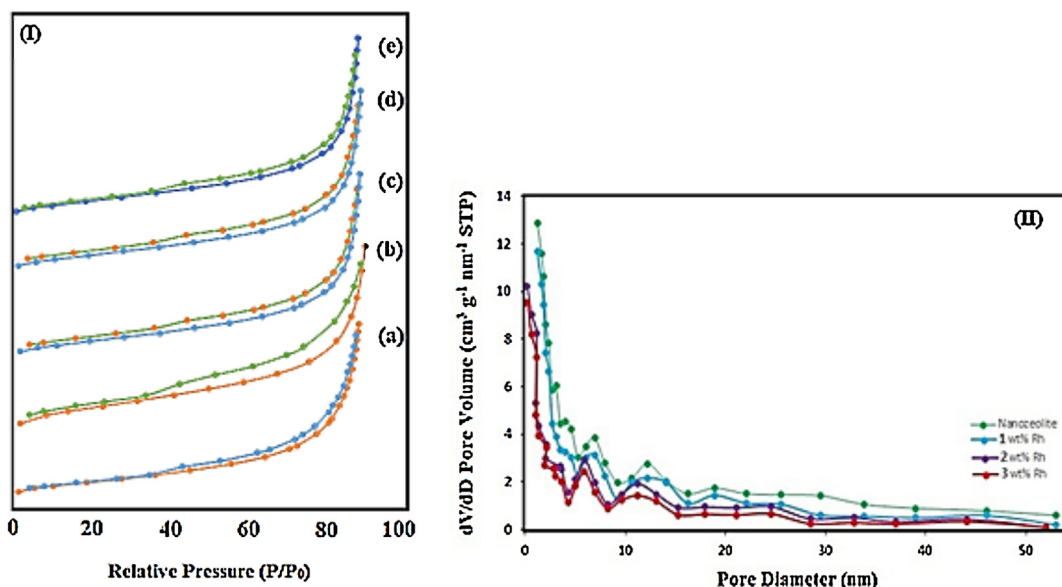E-mail address: s.m.baghbanian@iauamol.ac.ir (S.M. Baghbanian).

Fig. 1. (I) Nitrogen adsorption–desorption isotherms (nanozeolite (a), activated nanozeolite (b), 1 wt% Rh (c), 2 wt% Rh (d) and 3 wt% Rh (e)) and (II) pore distributions isotherms for different loadings Rh-based catalysts (1–3 wt%).

Company. The raw zeolite material was an Iranian commercial Clinoptilolite (Afrandtooska Company) obtained from deposits in the region of Semnan (ca. 1 \$ per kg).

2.2. Instrumentation

The X-ray powder diffraction (XRD) of the catalyst was carried out on a Philips PW 1830 X-ray diffractometer with Cu Kα source (λ = 1.5418 Å) in a range of Bragg's angle (10–90°) at room temperature. N_2 sorption measurement was performed using Belsorp mini II at 77 K. Prior to the measurements, all the samples were degassed at 77 K in a vacuum line overnight. The specific surface area and pore volume were calculated with the Brunauer–Emmett–Teller (BET) method, and the pore size distribution was expected with desorption branch based on the Barrett–Joyneer–Halenda (BJH) model. Transmission electron microscopy (TEM) experiments were conducted on a JEOL-2100 microscope operated at 200 KV. The TEM model Samples are sonicated by mixing with 95% ethanol for 30 min, and subsequently dropped onto copper grids coated with carbon film, and dried thoroughly in an electronic drying cabinet at a temperature of 25 °C and relative humidity 45%. X-ray photoelectron spectra (XPS) was recorded on a BESTEC GmbH-8025 spectrometer using an Mg Kα ($h\nu$ = 1253.6 eV) and Al Kα ($h\nu$ = 1486.6 eV) X-ray source. The metal content in the materials was determined using Inductively Coupled Plasma (ICP) in a Philips PU-70000 sequential spectrometer equipped. ^{1}H and ^{13}C NMR spectra were recorded on a BRUKER DRX-400 AVANCE spectrometer.

2.3. Catalyst preparation

2.3.1. Preparation of activated NZ-CP

The nanozeolite clinoptilolite was converted to the homoionic Na$^+$-exchanged form by stirring in 2 M NaCl solution for about 24 h. The Na$^+$-nanozeolite clinoptilolite was filtrated, washed with distilled water (50 mL) two times and then dried at 80 °C. Next, Sulfuric acid (100 mL, 4 M) was added into the Na$^+$-nanozeolite clinoptilolite (5 g) disperse solution and refluxed for 1 h. After cooling, the activated nanozeolite clinoptilolite was repeatedly washed with deionized water (250 mL) until the solution became neutral and dried in oven at 80 °C overnight to give the white solid product. The activated nanozeolite clinoptilolite was designated as AT-Nano CP.

2.3.2. Synthesis of the Rh/NZ-CP catalyst

2.3.2.1. Formation of borohydride exchanged activated NZ-CP. The solution of NaBH$_4$ (100 mg) in water (30 mL) was added to the activated NZ-CP (5 g) and the mixture was stirred for 4 h at room temperature. The resulting precipitate was washed with water until pH became neutral. The zeolite beads (borohydride exchanged) were dried at 80 °C for 12 h.

2.3.2.2. Procedure for Rh/NZ-CP preparation. The borohydride exchanged nano zeolite (1 g) was suspended in 5 mL ethanol solution containing an appropriate amount of RhCl$_3$·H$_2$O. Then, the mixture was stirred at room temperature to 80 °C for 30 min or till the red color of suspension was changed to blackish to color less and concurrently white solid particles were turned to dark grey. After cooling, the resulting grey residue was filtered, washed with hot water (10 mL) and dried at 80 °C to afford 1–3 wt% the rhodium nanoparticles loaded on nanozeolite (1–3 wt% Rh/NZ-CP).

2.4. Catalyst evaluation

The hydrogenation reactions were carried out in a 100 mL stainless steel high-pressure batch-type reactor. 20 mmol of the substrates and a certain amount of catalyst samples (1–3 wt% Rh/NZ-CP) were charged into the reactor and the reactor was sealed with 1.0 MPa N_2 and H_2 to remove the air and then, the reactor was then heated up to the desired temperature. After completion of the reaction, the reactor was cooled down to room temperature and then depressurized. The catalyst was easily isolated from the reaction mixture using centrifuge technique. The composition of reaction mixture was analyzed by GC using an Agilent gas chromatograph fitted with a FactorFour HP5-MS capillary column. The turnover frequency (TOF) was calculated as the number of moles of reactant consumed per mol of catalyst exposed on surface per hour.