Short Communication

Poly (styrene-co-divinylbenzene) amine functionalized polymer supported ruthenium nanoparticles catalyst active in hydrogenation of xylose

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ABSTRACT

Poly (styrene-co-divinylbenzene) amine functionalized polymer supported ruthenium nanoparticles catalyst is evaluated first time in selective hydrogenation of xylose to xylitol. The catalyst Ru/PSN is characterized by different techniques such as X-ray powder diffraction, transmission electron microscopy and CO chemisorption. To develop our understanding for the activity of catalyst Ru/PSN, xylose hydrogenation experiments were carried out using catalyst of Ru/PSN with different ruthenium loading (from 1.0% to 3.0%), at different temperatures (from 100 to 140 °C) and hydrogen pressures (from 30 to 55 bar). For deactivation test, the catalyst of Ru/PSN recovered from the product solution was reused up to the four times.

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1. Introduction

Catalytic hydrogenation of xylose has widely been studied and used to produce xylitol, one of the top twelve platform molecules and building block molecules [1–3] that can further be transformed into a variety of chemicals [4–6]. Xylitol, a pentose sugar alcohol, is also known to be a best sweetener similar to sucrose, nearly twice that of sorbitol and approximately three times that of mannitol, occurs in a small amount in nature [7–10]. Xylitol has some other interesting properties such as anti-carcinogenic, sugar substitute and higher sweetening capacity than different alcohols. It has wide range of applications in food, pharmaceutical, cosmetic, and synthetic resin industries [11–13].

Over the last few decades, the hydrogenation of xylose was carried out in three phase slurry reactor using Raney nickel catalyst, and later using nickel metal supported catalysts [14,15]. During hydrogenation experiments of xylose, it was seen that the formation of by products and accumulation of organic impurities on the catalyst surface easily deactivated nickel catalyst due to the poisoning of the active sites and also led to metal leaching-off by the morphological changes take place on the metal surface [16–19]. To overcome these problems, research was continued in search for proper metals and support materials combination catalyst systems for the hydrogenation of xylose that can lead to high activity and selectivity towards xylitol

production, less sensitive to the deactivation and recyclable. It was found that activated carbon supported ruthenium catalyst highly active than Ni metal was capable to replace conventional nickel catalysts for the hydrogenation of xylose to xylitol [20]. Recently, our research group spotlighted on a catalyst of ruthenium and NiO-modified TiO_2 support is active and highly selective to the main product, xylitol [21].

Even though a number of catalysts based on ruthenium and inorganic metal oxide supports as such or their modified forms are used and active for catalytic hydrogenation of xylose to xylitol, there have been no reports in the literatures so far on use of polymer supported ruthenium catalyst. In this study, preparation method of hitherto unreported poly (styrene-co-divinylbenzene) amine functionalized (PSN) polymer supported ruthenium nanoparticles catalyst is described. The results obtained from xylose hydrogenation experiments using catalyst Ru/PSN are discussed.

2. Experimental section

2.1. Materials

Ruthenium trichloride ($RuCl_3.3H_2O$) was supplied by Strem Chemicals, USA. Granules of poly (styrene-co-divinylbenzene) amine functionalized (PSN) polymer, xylose and sodium borohydride ($NaBH_4$) were purchased from Sigma-Aldrich Chemicals, USA. Ethanol was purchased from Sigma-Aldrich Chemicals, USA and used as solvent.

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All the chemicals were used as such without further purification. Hydrogen gases (99.9%) used was from Deokyang Co. Ltd.

2.2. Preparation of PSN supported ruthenium nanoparticles catalyst

PSN supported Ru nanoparticles catalysts were prepared by impregnation method. Granules of poly (styrene-co-divinylbenzene) amine functionalized (PSN) polymer were crushed until the fine powders were formed. The fine powders of PSN were then impregnated into $RuCl_3.3H_2O$ solution prepared in ethanol. The mixture was stirred under N_2 atmosphere for a period of 24 h. For reduction, $NaBH_4$ solution prepared in ethanol was added drop wise to resultant mixture with constant stirring and entire reaction mass was stirred (500 rpm) at room temperature. Finally, catalyst Ru/PSN was separated by filtration, washed with ethanol and dried to give dark black. The catalysts with different ruthenium contents, 1.0Ru/PSN and 3.0Ru/PSN, were also prepared by varying the amount of $RuCl_3.3H_2O$.

2.3. Catalyst characterization

Powder X-ray diffraction patterns of all samples were obtained by a Rigaku diffractometer (D/MAX IIIB, 2 kW) using Ni-filtered Cu Kα-radiation (40 kV, 30 mA, λ = 1.5406 Å) and a graphite crystal mono-chromator. FT-IR spectra were recorded using KBr pellet on a Nicolet Magna-560 IR spectrophotometer. Surface area measurements were carried out using Micromeritics, Tristar II analyzer. The samples were activated at 250 °C for 4 h under vacuum (5×10^{-2} mmHg) prior to N_2 adsorption measurements. The specific surface areas, pore diameters, and pore volumes of the samples were calculated from nitrogen adsorption isotherms measured at 77 K as per Brunauer, Emmett, Teller (BET) method. Scanning electron microscopy (SEM) images of support and catalyst were seen on SEM, JEOL JSM-840 A. Transmission electron microscope (TEM) images were taken with a Maker FEI, Model Technai G2 microscope with acceleration voltage of 200 kV using carbon coated 200 mesh copper grids. Thermogravimetric analyses (TGA) were performed using TA instrument model, TGA Q500 V6.7 with heating rate of 10 °C/min in N_2 atmosphere. CO chemisorption was carried out by using an instrument model ASAP 2020C V1.09 G. The metal contents, ruthenium catalyst in product solution obtained after xylose hydrogenation, were determined by inductively coupled plasma mass spectrometry (ICP-MS).

2.4. Catalytic hydrogenation of xylose to xylitol

Hydrogenation experiments of xylose (20 wt.% in 200 ml of H_2O) were carried out batch wise in 300 mL of three phase slurry reactor in the temperature range from 80 to 120 °C at hydrogen pressure (40–65 bar) at constant stirring rate (1200 rpm). In a typical hydrogenation experiment, required amount of catalyst Ru/PSN and 200 ml of xylose solution were charged into stainless steel autoclave reactor. The reactor was fitted air tight and flushed with nitrogen gas three times at room temperature. Then, reactor was brought to desired temperature and pressurized with hydrogen which was considered as the zero reaction time. Hydrogenation reaction was initiated by stirring the entire reaction mass. During hydrogenation at different time intervals, the product components were analyzed using a HPLC (Younglin Instrument, Acme 9000) equipped with refractive index (RI) detector and Sugar-Pak column [21].

3. Results and discussion

3.1. Characterization

Fig. 1 represents the XRD patterns of PSN, 1.0RuPSN, 3.0RuPSN, and 5.0RuPSN. It can be seen that the XRD pattern of PSN support looks alike to its corresponding PSN supported ruthenium catalysts,
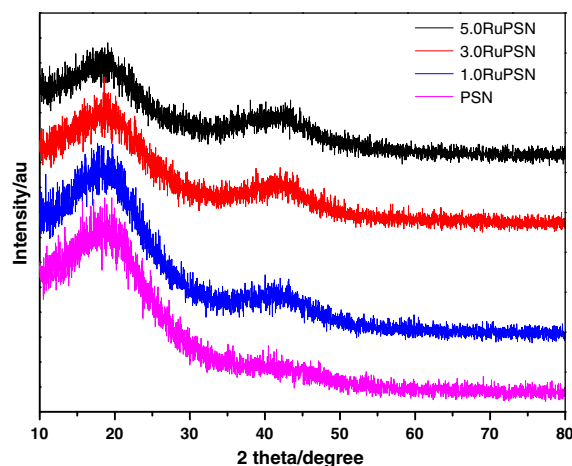

Fig. 1. XRD patterns of PSN and its corresponding catalysts.

1.0Ru/PSN, 3.0Ru/PSN and 5.0Ru/PSN. No diffraction peaks of ruthenium metal appeared in the XRD patterns of the catalysts (1.0Ru/PSN, 3.0Ru/PSN and 5.0Ru/PSN). These indicate that ruthenium nanoparticles were highly dispersed on PSN support during the catalyst preparation. However, CO chemisorption results of 5.0Ru/PSN showed that the dispersion of ruthenium nanoparticles and metallic surface area were 24 % and 87.8 m^2/g_{metal}, respectively.

TEM image of 5.0Ru/PSN is given in Fig. 2. It can be seen clearly that the ruthenium particles with average size of 2.5 nm are homogeneously distributed on the surface of PSN support which is responsible for efficient xylose hydrogenation.

FT-IR spectra (as shown in Fig. S1) of samples without reduction confirmed that ruthenium chloride was strongly sorbed on PSN support. The sorption behaviour was also confirmed from the SEM images. On comparing the images (PSN1 and PSN 2), it can be seen that morphology of PSN is different from that of catalyst, 5.0 Ru/PSN (as shown in Fig. S2). In TGA analysis (Fig. S3), the curves of PSN and its corresponding catalysts are identical. That's why the PSN could be used as support material due to its high thermal stability. As expected, the BET surface area of 5.0Ru/PSN (812.91 m^2/g) which is comparatively less than that of PSN i.e. 1165.97 m^2/g. This remarkable change in surface area value might be due to the pore blockage by ruthenium metals as strong active sites on the surface of PSN support.

Ruthenium leaching was estimated by the analysis of product solution for the catalyst of 5.0Ru/PSN and the result is summarized in Table S1. It has been found that ruthenium metal could not be detected, and there is no ruthenium leached into the product solution after filtration.
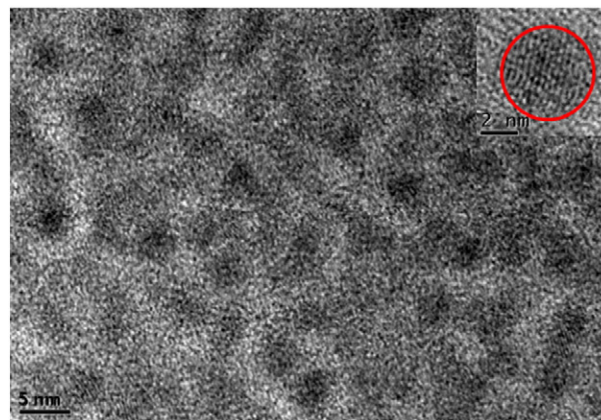

Fig. 2. TEM view of 5.0Ru/PNS.