
MONOLAYER-PROTECTED PLATINUM NANOPARTICLES AS HETEROGENEOUS CATALYSTS FOR ORGANIC TRANSFORMATIONS

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Abstract

A novel heterogeneous catalyst was developed, comprising of platinum nanoparticles functionalized with sulfonic acid ligands and supported on carbon. The nanocomposite catalyst system was characterized by XRD, TEM, XPS and TG-DTA, and was further employed in the hydrogenation of D-xylose to xylitol with excellent activity and selectivity.

Keywords: platinum nanoparticles; xylose; hydrogenation; xylitol

1. Introduction

Metallic and semiconductor nanoparticles [NP] exhibit interesting size and shape-dependent physicochemical properties. Incorporation of organic and biomolecular moieties having intrinsic functionalities on the surface of NPs will result in organic-inorganic hybrid systems with novel characteristics, including (but not limited to) catalytic efficiency. In recent years, monolayer protected gold and platinum NPs have been emerging as attractive candidates for catalysis [1,2]. The primary reason is the facile separation of the NPs from the organic reaction products by simple precipitation. The chemisorbed alkanethiol monolayer can also be tailored for desired functionalities, e.g., sulfonic acid head groups which can act as acid catalysts or proton conductors.

D-Xylose is a five-carbon monosaccharide which can be metabolized into useful products, such as xylitol, using a number of microorganisms [3]. As an alternative sweetener, xylitol is recommended for diabetics and for the prevention of dental caries. Xylitol can also be produced chemically from xylose using suitable hydrogenation catalysts [4]. In this report, Pt NPs functionalized with sulfonic acid ligands and supported on carbon were employed as solid catalysts in the chemical transformation of xylose to xylitol. A range of kinetic parameters were obtained by varying the reaction temperature, reaction time, reactant ratio and catalyst weight. The reaction mixtures were analyzed by GC and HPLC. About 36% conversion and 99% selectivity towards desired product were obtained using the novel catalyst system. The activity and selectivity of the catalyst was compared with those of an industrial Raney Nickel catalyst.

2. Materials and Methods

Potassium hexachloroplatinate (K_2PtCl_6) and 3-mercaptopropanesulfonic acid sodium salt (MPSA-

Na⁺) were purchased from Sigma-Aldrich. Sodium borohydride ($NaBH_4$) and concentrated H_2SO_4 was purchased from SD Fine Chem, India. Raney Nickel (assay 50% Ni and 50% Al) was obtained from Sisco Research Lab, India. All chemicals were reagent grade and were used as received.

Sulfonic acid ligand coated Pt NPs were synthesized using K_2PtCl_6 , MPSA and $NaBH_4$ following a method reported by us elsewhere [2]. To disperse the Pt NPs on carbon support (40 wt% Pt/C), the colloidal NP solution was treated with Vulcan XC72 at 60 °C for 1 h. The terminal SO_3^- head groups were protonated by treatment with 10 mL of 1 M H_2SO_4 (per 100 mg of the solid catalyst) for 4 h at room temperature. Without this protonation step, no significant activity of the Pt NPs was observed.

Transmission electron microscopy (TEM) experiments were carried out on a JEOL 200CX instrument used at 200 kV. The core sizes of the NPs were determined using TEM images. The diameter of approximately 1000 monodispersed NPs per sample was estimated and averaged using Image J software. The size distribution was calculated using Origin Pro 8.1 software. Thermogravimetric analyses (TGA) were performed on a TGA Q50 (TA Instruments) with a Thermostat Mass Spectrometer (Pfeiffer Vacuum). The samples were equilibrated at 25 °C; then kept at 100 °C for 2 h; then ramped to 600 °C at 30°/min; and finally dwelled at 600 °C for 1 h. X-ray photoelectron spectroscopic (XPS) experiments were performed on a Kratos Axis Ultra X-ray photoelectron spectrometer employing a monochromatic Al K_α source (1486.7 eV) and an electron takeoff angle of 90° relative to the sample plane. The survey scan was conducted at 80 eV pass energy in the binding energy (BE) range of 0–1100 eV. The high-resolution scans of O 1s, C 1s, S 2p, and Pt 4f were conducted at 10 eV pass energy. The core level spectra were background-corrected using the Shirley

algorithm and the core level BE was aligned with respect to the Pt 4f BE of 71 eV.

The hydrogenation reactions were carried out in a 100 mL high pressure reactor manufactured by Amar Equipments, India. In a typical experiment, 2.5–10 g of xylose was dissolved in 50–100 mL of deionized water, and 50–800 mg of the solid catalyst was directly taken into the reaction vessel. The reaction mixture was continuously stirred during the reaction at temperatures ranging from 55–150 °C and H₂ pressure ranging from 34–65 bars, for 3–8 h. The reaction products were analyzed at room temperature by HPLC. The experiments were run on Waters HPLC equipped with a Waters pump (515), UV-Vis (2487) and RI (2414) detectors using a Aminex HPX-87H column (300 × 7.8 mm). The mobile phase used was 0.008 N H₂SO₄ with a flow rate of 0.6 mL/min. The elution was carried out with a total run time of 60 min.

3. Results and Discussion

TEM was used for high resolution imaging of the nanocomposite samples and analysis of their particle size distribution. The TEM images of all the nanocomposites reveal that the chosen synthesis procedures produce similar core sizes of the NPs (4–5 nm).

TGA was used to quantify the average amount of ligand present in the NP samples. The representative TGA scan for a Pt-MPSA/C sample revealed a two stage weight loss; the first at 200–300 °C, and the second at 300–450 °C. The approximate amount of organics was 12–15 wt% for all the samples.

XPS was used to determine the electronic structure of the surface species accurately. The representative S 2p core level spectrum shows two components at binding energies 163 and 168 eV, which can be attributed to two different oxidation states of sulfur (–2 and +5, respectively) present in the sample. The quantification of the S⁵⁺ component from the S 2p spectra was done to estimate the number of catalytically active sites. As expected, the Pt 4f spectrum has two components, namely 4f_{5/2} and 4f_{7/2} at binding energies 74 and 71 eV, respectively.

The conversion of D-xylose to xylitol is a first order reaction with respect to the concentration of substrate. In all the experiments, the selectivity towards the desired product was >99%. Some representative reaction results were shown in Table 1. The maximum conversion of xylose obtained was 36%. The same using an industrial Raney Nickel catalyst under similar condition was <10.

Table 1. Transformation of D-xylose to xylitol using Pt-MPSA nanocatalyst.

Xylose :H ₂ O	Catalyst (wt%)	Temp. (°C)	Time (h)	Conv. (%)
5	0.8	140	5	36
10	1.6	140	5	25
20	1.6	140	5	10

4. Conclusions

In conclusion, the conversion of D-xylose to xylitol has been successfully carried out with sulfonic acid functionalized Pt NPs. This work signifies the effect of morphology of the ligand shell on catalytic behavior of metallic NPs.

References

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