Synthesis and Characterization of Ag/Ru Bimetallic Nanoparticle Catalysts for the Reduction of *o*-Nitrobenzoic acid to Anthranilic acid

K.Sivaranjan and J.Santhanalakshmi*
Department of Physical Chemistry,
University of Madras, Guindy Campus, Chennai – 600 025
Tamilnadu, India
Email: kksivaranjan@gmail.com and jslakshmi@yahoo.co.in

Abstract—**In this work, we explore the Polyvinyl alcohol stabilized Ag-Ru, bimetallic nanoparticle as reduction catalysts in organic reactions. Such nanoparticles are prepared by successive sequential metal reduction method at 110°C. The resulting bimetallic Ag/Ru nanoparticles are size characterized with scanning electron microscopy (SEM), transmission electron microscopy (TEM) and EDAX analyses. Further the catalytic activity of Ag-Ru bimetallic nanoparticles on the reduction of *o*-nitrobenzoic acid to Anthranilic acid was studied and found to be more effective than catalysis by the respective mono metal nanoparticles.**

Key words: bimetallic nanoparticles catalysts, *o*-NBA, reduction, Anthranilic acid

I. INTRODUCTION

Metal nanoparticles are very attractive materials because of the high values of the surface-to-volume ratio and high surface energy. This makes the surface atoms more active than the bulk ones. Also these particles show unique optical, electronic, and catalytic properties [1a,b]. Therefore novel applications in sensors, catalysts, and biochemical tagging reagents etc [2a,b] become possible. Bimetallic nanoparticles are attractive because of their improvement in the catalytic properties and the changes in the surface plasma band energy relative to the separate metal nanoparticles. Many methods have been reported on the preparation of bimetallic nanoparticles including alcohol reduction [3a,b], polyol process [4], solvent extraction reduction, sonochemical method, photolytic reduction [5], decomposition of organometallic precursors, and electrolysis of bulk metals [6a,b]. Their sizes are usually controlled by the composition of protective agents such as soluble polymers, surfactants, and organic ligands. Metal nanoparticles stabilized by polymers have attracted current research because of the widened applications possible by these hybrid materials [7-8]. It is well established that polymers like polyvinyl alcohol (PVA) encapsulated metal nanoparticles can act as both the reducing and coupling reaction catalysts providing a greener process [9]. Anthranilic acid (AA) is a commercially important organic substrate and an intermediate for the synthesis of different dyes, perfumes and anticancer agents etc [10]. Until now several research groups have devoted their efforts to synthesize (AA). Herein we report the synthesis of PVA stabilized Ag-Ru bimetallic nanoparticles and their use in the catalysis of reduction of o-nitrobenzenoic acid (O-NBA) which is the precursor for (AA) preparation at 25^0C. The resulting bimetallic nanoparticles Ag-Ru NPs, catalysts are size characterized with scanning electron microscopy (SEM), transmission electron microscopy (TEM) and EDAX measurements. Further the catalytic activity of Ag-Ru bimetallic nanoparticle catalysts are compared with the catalysis of the mono metal nanoparticles of Ag and Ru. The reduction reaction was followed by adopting the pseudo first order experimental conditions and the absorbance versus time measurements. The kinetic parameters are evaluated and discussed.

II. EXPERIMENTAL SECTION

A. Reagents and Instruments

Ethylene glycol (SRL), Polyvinyl alcohol (sigma-Aldrich), Silver nitrate (SRL), Ruthenium chloride (III) hydrate (SRL), *o*-Nitrobenzoic acid (SRL), Methanol (SRL), Sodium borohydride (SRL) were procured and used as such. Double distilled water was used in all solution preparations.

UV-visible absorption spectra were recorded using a Perkin Elmer Lambda 35 instrument and 1-cm quartz cuvette. SEM analysis was performed using JEOL JSM-6360 instrument and the EDX by Horiba EMAX attached to the instrument and used to obtain the particle morphology. Transmission electron micrographs were obtained with Hitachi H-7650 instrument using an accelerating voltage 80 KV.

B. Preparation of PVA Stabilized Ag/Ru bimetallic nanoparticles

Ag/Ru bimetallic nanoparticles were prepared by successive sequential reduction method. 1:1 mole ratio, salt precursor solutions of Ag and Ru are taken in a 100 ml round-bottomed flask, and 0.12 g of PVA and 20 mg of $AgNO_3$ dissolved in 30 ml of ethylene glycol solution was added with stirring. The solution was gradually heated to 110°C under N_2 atmosphere for 1 hour. A clear yellow colored solution of colloidal PVA-Ag nanoparticles resulted. 20 mg of $RuCl_3.H_2O$, 0.12 g of PVA are dissolved in 30 ml of ethylene glycol, and the resulting solution was added drop wise to the Ag nanoparticle solution at 110°C for 2 hours under N_2 atm with continues stirring. The obtained brown coloured Ag/Ru nanoparticles are washed, centrifuged and dried under N_2 atmosphere.

III. RESULT AND DISSCUSSION

A. SEM and TEM analyses

In Fig. 1 TEM image of the Ag/Ru bimetallic nanoparticles are given. The surface morphology of these Ag/Ru NPs are investigated by SEM – EDAX analyses from Fig. 2. Figs. 1 and 2 reveal that irrespective of the bimetallic nature of the particles there is an evenly distributed white dots that appeared on the surface of particles. Also EDAX results indicate high purity of the bimetallic nanoparticles. The recorded TEM image of Ag/Ru NPs shown in Fig.1 reveal spherical particles with a mean size of 25 nm ± 1 nm. In the EDAX spectrum peaks for Ag and Ru are observed at 1.0 eV, 1.4 eV, 4.1 eV, 5.8 eV and 6.4 eV respectively and the atomic percentages of Ag and Ru are found to be 5.98% and 3.29% respectively.

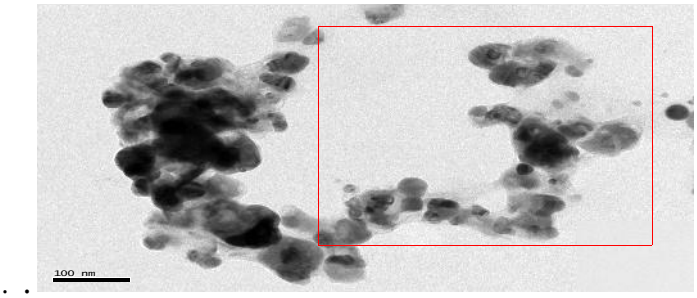

Fig. 1.TEM image of Ag/Ru bimetallic nanoparticles

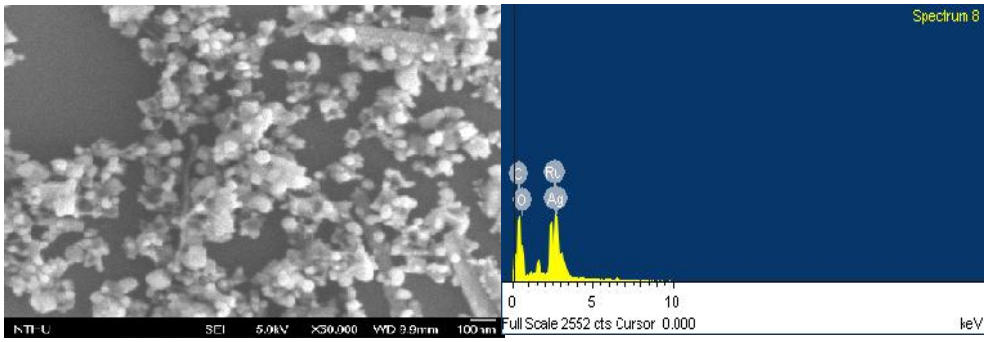

Fig. 2.SEM image with EDAX of Ag/Ru bimetallic nanoparticles

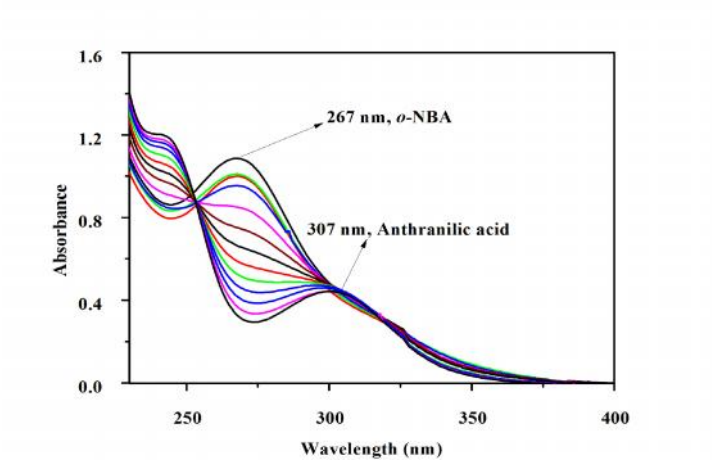

Fig. 3. UV-VIS spectra of successive reduction reaction mixtures of *o*-NBA with Ag/Ru NPs as Catalysts

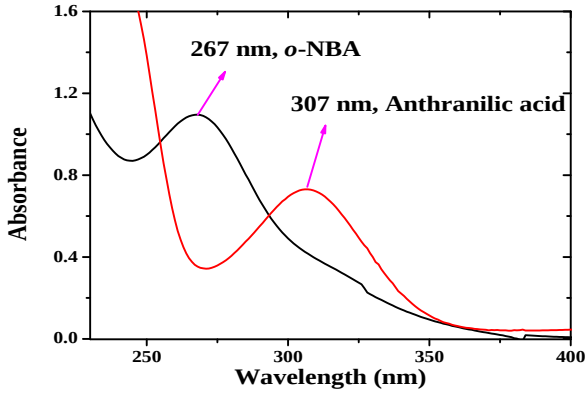

Fig. 4. UV-VIS spectra of *o*-NBA and Anthranilic acid product

IV. CATALYTIC ACTIVITY

The catalytic reduction of *o*-NBA using $NaBH_4$ aqueous solution as the reductant and Ag/Ru bimetallic nanoparticles as catalyst was studied the progress of reaction was monitored by recording UV.VIS spectra of the reaction mixture at various intervals of time as shown in Fig. 3. An aqueous solution of *o*-NBA (1.2 mM) shows peak at wavelength maximum 267 nm as shown in Fig. 4. Upon addition of a freshly prepared ice cold aqueous solution of $NaBH_4$ (0.1 M) without the catalyst there was no reduction reaction and only a slight decrease in the reduction peak even for a long time interval was observed. However the addition of 2 mg Ag/Ru NPs catalyst initiated and the reaction immediately and the absorbance of the peak at 267 nm gradually decreased red shifted to 307 nm as shown Fig. 3. This new peak at 307 nm has been attributed to the presence of Anthranilic acid which is formed as the product, (shown in Fig.3). UV-visible spectrum of *o*-NBA and the product peak of anthranilic acid are shown separately for comparative analysis in Fig.4. The characteristic peak of Anthranilic acid gradually increased. The overall pseudo first order rate constant value was determined to be $2.80 \times 10^{-3} s^{-1}$. Similarly the pseudo first order rate constant value are obtained for *o*-NBA reduction to Anthranilic acid in the presence of mono metal nanoparticles of Ag and Ru and are found to be $1.1 \times 10^{-3} s^{-1}$ and $1.5 \times 10^{-3} s^{-1}$ respectively. Therefore upon using Ag/Ru bimetallic nanoparticles the catalytic efficiency was found to be doubly enhanced in this reaction.

V. CONCLUSION

In this work successfully prepared PVA stabilized Ag/Ru bimetallic nanoparticles are prepared. The size and shape parameters are analyzed using TEM, SEM and EDAX measurement analyzed. The catalytic activity was tested using reduction of *o*-NBA to Anthranilic acid formation. Excellent catalytic performance of Ag/Ru bimetallic nanoparticles was observed and was better than the individual metal nanoparticles.

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