Digest Journal of Nanomaterials and Biostructures Vol. 12, No. 2, April - June 2017, p. 361 - 369

ASSESMENT FOR EFFICIENCY OF SILVER NANOPARTICLES AS CATALYSTS FOR OXIDANT FREE DEHYDROGENATION OF ALCOHOLS TO CARBONYL COMPOUNDS

V. K. M. SMITHA RANI[a*], B. POORNAPRAKASH[b*]
[a]*Siddartha Educational Academy Group of Institutions, Tirupati-517505, A.P. India*
[b]*Department of Electronic Engineering, Yeungnam University, Gyeongsan 38541, South Korea*

The present work demonstrates the efficacy of silver nanoparticles (AgNPs) as catalysts in dehydrogenation of alcohols to the corresponding aldehydes/ketones under oxidant-free conditions. AgNPs synthesized through green route were with sizes less than 15 nm, spherical in shape, FCC structured and highly stable with negligible agglomeration in an aqueous state. The AgNPs displayed a pronounced efficiency as catalysts in the preparation of acetaldehyde from ethyl alcohol and acetone from isopropanol in laboratory conditions. The AgNPs reduced the required temperature for the reactions, revealed the enhanced rate of reaction and % yield when compared with the results achieved in the absence of catalyst and with bulk silver. The model reactions performed using varied quantities of nanoparticles also confirmed that the quantity of silver nanocatalyst also plays an essential role in catalytic activity. Recyclable AgNPs efficiently catalysed the reaction to obtain excellent yield with short reaction times at lower temperatures in the presence of low catalyst loading.

(Received March 8, 2017; Accepted May 3, 2017)

Keywords: AgNPs, nano catalysts, Rate of reaction, Percentage yield

1. Introduction

Metal catalysts play a vital role in a broad range of chemical industries, since they render environmental friendly conversion of diverse chemicals. Nanocrystallites have garnered substantial interest due to their various applications. Several reports presented an excellent level of accomplishment of nanoparticles as catalysts in terms of selectivity, reactivity and enhanced yields of product. Previous studies reported that nanoparticles act as very efficient catalysts due to their unique electronic properties, extremely high surface-to-volume ratio providing a larger number of active sites per unit area in comparison with their bulk counter parts. Aldehydes, ketones, esters and acid products are valuable intermediates for the fine chemicals, pharmaceutical, bioactive compounds, dye chemicals and agrochemical sectors [1]. Silver catalysts have turned out to be progressively imperative in the oxidation of alcohols for the synthesis of industrially intriguing items such as ketones and aldehydes [2]. In comparison with traditional catalysts, AgNPs in particular require only mild reaction conditions to produce high yields of products in short reaction times and can also be recycled [3]. Run Xu et. al [4] demonstrated that silver nanocubes show much higher styrene oxidation activity than near-spherical or plates because of their more reactive [100] planes. Bindhu and Umadevi [5] described that spherical nanoparticles of average size of 15 nm used for the aqueous reduction of 4-NP to 4-AP with $NaBH_4$ exhibited faster reaction rate than the large particles. Amin Salehi et. al [6] studied the effect of AgNPs on its catalytic performance in the conversion of CO_2 into CO and found that the AgNPs of 5nm have 10 times higher conversion rate than bulk silver. There are other reports on silver nanoclusters supported on alumina [7, 8] and $Al_2O_3 – Ga_2O_3$ [9] affording high yields with enhanced rate of reactions. From

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*Corresponding author: mail2poorna6@gmail.com the perspective of safety, with the aim to develop more competent processes, to reduce the number of reaction steps, to minimize by-products and also in continuation of this research on the application of AgNPs, a practical method for the preparation of acetaldehyde from ethanol and acetone from isopropanol in the presence of AgNPs as potent catalysts is accounted for here.

2. Experimental

1mM aqueous $AgNO_3$ was prepared using $AgNO_3$ of analytical reagent grade in Millipore water. The reducing agent was prepared by taking 10g of fresh , well washed *Gmelina arboria* plant leaves in a conical flask containing 100 ml of Millipore water and kept in water bath at a temperature of 60°C for about 10 min.1mM aqueous $AgNO_3$ and the supernatant of the reducing agent were mixed in the ratios of 10: 0.5; 10:1; 10:1.5 and 10:2. Upon stirring, in a very short period of time the colorless solution changed to intense brown colored colloid, clearly indicating the formation of AgNPs [10]. Polyvinylpyrrolidone (PVP-8000) of 0.2 % concentration solution was added to stabilize AgNPs.

In order to interpret the synthesized AgNPs different instrumental techniques were applied.The UV-Visible absorption spectra of the aqueous AgNPs samples were recorded using Systronics 2202 double beam spectrophotometer (Hyderabad, India), from 400 to 600 nm, against leaf extract as blank. For XRD studies, a drop of the colloidal solution sample was deposited on a carbon-coated copper grid and dried at room temperature. The XRD analysis was conducted with a Rigaku, Ultima IV diffractometer (Tokyo, Japan) using monochromatic Cu Kα radiation (λ = 1.5406 A°) running at 40 kV and 30 mA. The intensity data for the sample was collected over 2θ range of 10–80° with a scan rate of 2° /min. Stability of synthesized AgNPs in colloidal state was analyzed by using Horiba Sz-100 Zeta potential analyzer, along with average particle size. For TEM analysis, a drop of the colloidal solution of AgNPs was placed on to a carbon coated Cu grid and dried under infrared lamp. Micrographs were obtained using a Tecnai F 12 transmission electron microscope.

Furthermore, the catalytic ability of the prepared silver nanocatalyst was tested in the synthesis of acetaldehyde from ethyl alcohol and acetone from isopropanol in the presence of air and heat by condensation method. To check the catalytic efficiency of the thus synthesized AgNPs, the reactions were experimented without catalyst, with bulk silver and with colloidal AgNPs taken in various quantities.

Reaction 1: For the synthesis of acetaldehyde, 20 ml of ethyl alcohol (99.9%) was taken in 250 ml round bottomed flask and heated in the presence of air until the condensation of reactant was completed.

Reaction 2:The production of acetone was done by taking isopropanol (20 ml, 99.9%) as reactant, in the round bottom flask subjected for condensation.

The reactions were performed without catalyst, in the presence of bulk silver (1g), with colloidal AgNPs taken by quantities of 1 ml, 5ml and 10 ml. The time required for the completion of condensation and temperature at the commencement of condensation were recorded for each experiment. Rate of reaction and percentage yield were calculated [6]. The experiments were repeated to confirm the effect of AgNPs as catalyst, as well checking the effect of various quantities of colloidal AgNPs on rate of reaction and % yield. Similar sets of experiments were performed thrice in order to check the repeatability.

Confirmation Tests: The resultant product (2 ml) was dropped into 2, 4-dinitro-phenyl hydrazine (1g) dissolved in methanol (2 ml). Then colorless solution turned in to orange solution confirming the formation of carbonyl group. Acidification of the carbonyl compound with $K_2Cr_2O_7$ (1 g) dissolved in H_2SO_4 (3 ml) resulted clear green solution confirms the aldehyde formation (**Reaction 1**)**.** In case of ketone (**Reaction 2**), upon acidification of the carbonyl compound, a green precipitate was formed [6].

3. Results and discussion

3.1. UV-Vis spectrometric studies:

For the colloidal AgNPs , thus obtained through green synthesis have appearance of single and strong absorption peak in UV-Vis spectrometric studies centered at about 425-440 nm **(**Fig 1) indicated that the nanoparticles were isotropic in shape and uniform in size. Gopinath et. al [11] stated that Surface Plasmon Resonance band intensity maximum and band width are influenced by the particle shape, dielectric constant of the medium and temperature. Saturation in the absorbance indicates the completion of bio reduction of Ag^{+1} with finest sized particles. Previous studies attributed the absorption peak around 410- 450 nm to the presence of spherical nanoparticles [12]. Among all the experimental combinations maximum absorption with sharp peak was observed for the highest concentration ratio of 10: 2, intensity of absorption increased with concentration of extract. Masumeh Noruzi et. al [13] also reported that with increased quantities of reducing agent the nanoparticles concentration increased. Therefore, the AgNPs in the aqueous suspension obtained through concentration ratio of 10: 2 only were subjected for further characterization and used in catalytic applications.

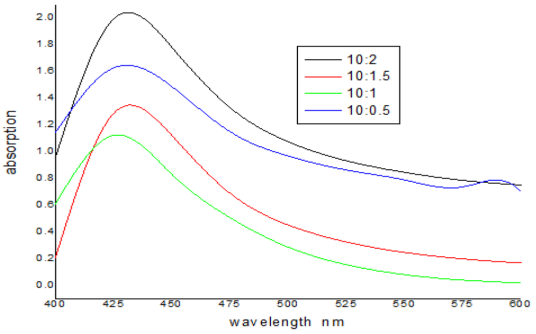


Fig.1 UV-Vis spectra of the samples

3.2. XRD studies

XRD report (Fig 2) showed well-defined characteristic diffraction peaks corresponding to (111), (200), (220) and (311) crystallographic planes. These diffraction peaks firmly represent planes of face centered cubic (FCC) crystal structure of metallic silver [14]. The broadening of peaks confirmed the formation of nanoparticles [15]. The mean size of crystallite was calculated using the Debye–Scherer’s equation by determining the width of the (111) Bragg's reflection [14]. The average size of the AgNPs evaluated through XRD was 11.78 nm (Tab.1).

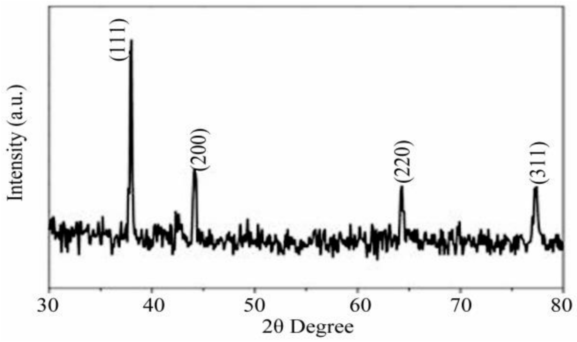


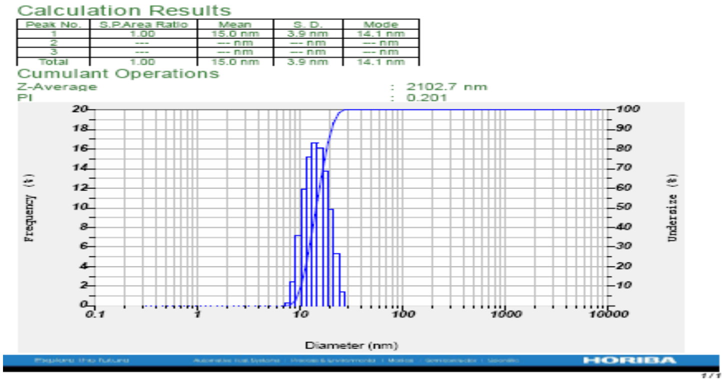
Fig 2. XRD pattern of AgNPs

Table 1. Particle size of AgNPs, evaluation through XRD

Parameters	Group I
2θ(deg)	32.59, 42.92, 61.62, 75.20
h,k,l	(111), (200),(220), (311)
Θ(deg)	16.29,21.46,30.81, 37.6
FWHM(β)radians	0.0111, 0.0112, 0.0080, 0 .0118.
Size of the particle(D)nm	11.9, 11, 14.91, 9.31.

3.3. Zeta Potential and Particle Size

Moreover, the Zeta potential of AgNPs (Fig 3) of the sample with higher negative value confirms the electrostatic repulsion among the particles and thereby increased in the stability of the formulation. This prevents the particles from agglomeration in the medium leading to long term stability [16]. The AgNPs synthesized were with Zetapotential ranging from -36 to - 48 mV indicating the particles were well dispersed and very stable. Shashi Prabha et. al [17] reported that leaf extract mediated synthesized AgNPs and AuNPs have high negative zeta potential values and thus they are stable under a wide pH range. The particle size histogram revealed that the diameter of particles was found varying from 9- 25 nm (Fig 4) and the average size was about 12 nm.

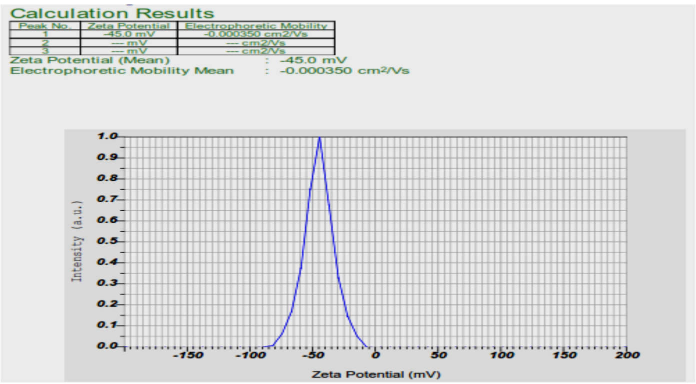


Calculation Results

Peak No.	S.P.Area Ratio	Mean	S. D.	Mode
1	1.00	15.0 nm	3.9 nm	14.1 nm
2	---	--- nm	--- nm	--- nm
3	---	--- nm	--- nm	--- nm
Total	1.00	15.0 nm	3.9 nm	14.1 nm

Cumulant Operations
Z-Average : 2102.7 nm
PI : 0.201

Fig 3. Zeta potential of AgNPs



Calculation Results

Peak No.	Zeta Potential	Electrophoretic Mobility
1	-45.0 mV	-0.000350 cm2/Vs
2	--- mV	--- cm2/Vs
3	--- mV	--- cm2/Vs

Zeta Potential (Mean) : -45.0 mV
Electrophoretic Mobility Mean : -0.000350 cm^2/Vs

Fig 4. Particle size distribution of AgNPs

3.4. TEM studies

The morphology studied from the TEM images (Fig 5) of samples depicted uniform distribution of spherical nanoparticles ranging from 5 to 25 nm with an average size of 12 nm. All images confirm very narrow size distributions, well separated from each other which were in good agreement with the zetapotential and particle size studies.

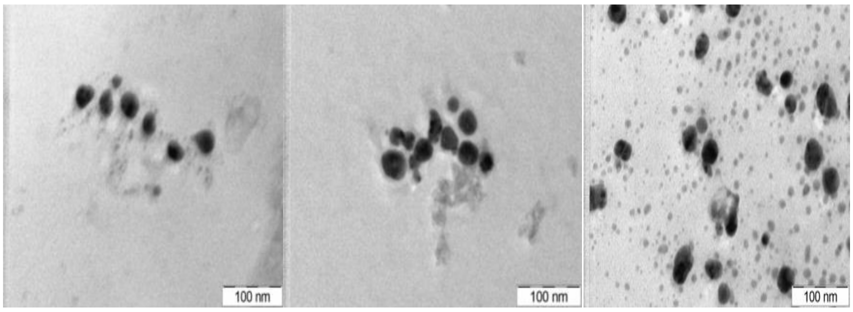


Fig. 5. TEM Micrographs of AgNPs with scale bar corresponds to 100 nm

3.5. Production of acetaldehyde and acetone

For production of acetaldehyde and acetone by condensation method, the obtained AgNPs in the aqueous satate were used as catalysts for the dehydrogenation of alcohols to carbonyl compounds and the reaction results were demonstrated in Tab 2.

Reaction 1: In the production of acetaldehyde when 1ml of the aqueous AgNPs was used as catalyse, the required temperature for the commencement of reaction was reduced by 50^{0}C , rate of reaction was enhanced by 3 times and % yield was enhanced by 4.5 times compared to that with production carriedout in the absence of catalyst. Upon the use of 1ml of the aqueous AgNP catalyst the required temperature for the commencement of reaction was reduced by 24^{0}C, enhanced rate of reaction was 2.5 times and % yield was enhanced by 3 times compared to that of final product resulted in the presence of bulk silver as catalyst (Fig.6, 7a, & 8a).

The conversion of ethyl alcohol to acetaldehyde in the presence of aqueous AgNPs taken by a quantity of 10 ml as catalyst was more beneficial compared to all other alternative combinations, demonstrated in Tab 3. The temperature required for the commencement of condensation was diminished by 68, 42, 18 and 7 ^{0}C when 10 ml of aqueous AgNPs were used as catalyst instead of carrying the production without catalyst, with bulk silver and with 1 and 5 ml of aqueous AgNPs respectively. By using 10 ml of aqueous AgNPs as catalyst, the rate of reaction was magnified by 13.01 x 10^{-4},10.9 x 10^{-4},4.48 x 10^{-4} and 2.8 x 10^{-4} (moles/sec) compared to the rate of reactions when synthesis were done without catalyst, with bulk silver and with 1 and 5 ml of aqueous AgNPs respectively. Due to usage of 10 ml aqueous AgNPs in the production of acetaldehyde, the % yield was enhanced by 31,21,07 and 3.5 compared to that resulted without catalyst, with bulk silver and with 1 and 5 ml of aqueous AgNPs respectively

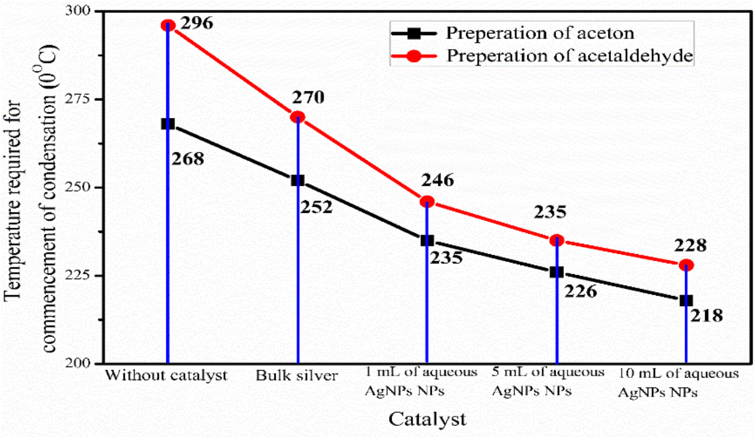


Fig. 6. Temperature required over the catalyst in synthesis of acetaldehyde and acetone

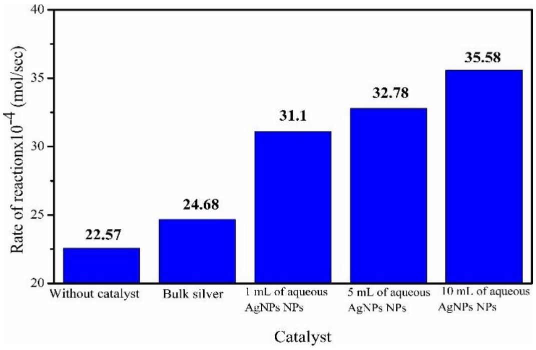


Fig. 7a. Rate of Reaction over the function of Catalyst in Production of Acetaldehyde

Reaction 2: In the synthesis of acetone with 1ml of the aqueous nanosilver catalyst, the required temperature for the commencement of reaction was dropped by 33^{0}C , rate of reaction was enhanced by 2 times and % yield was enhanced by 2.5 times over that of production done in the absence of catalyst. Utilization of 1ml of the aqueous AgNPs as catalyst the required temperature for the commencement of reaction was reduced by 17 ^{0}C , rate of reaction was enhanced by 1.5 times and % yield was enhanced by 3 times compared to those resulted with production carriedout in the presence of bulk silver as catalyst (Fig.6, 7b, & 8b).Likewise, by using 10 ml of aqueous AgNPs the reduction in required temperatures were 50, 34 ,17 and 8^{0}C; enhancement in rate of reactions were 14.17 x 10^{-4},11.56 x 10^{-4},6.8 x 10^{-4} and 3.01 x 10^{-4} (moles/sec); enhanced %yield were 26.5,19,10.5 and 4 when synthesis was carried out without catalyst, with bulk silver and with 1 and 5 ml of aqueous AgNPs respectively, results shown in Tab. 3.

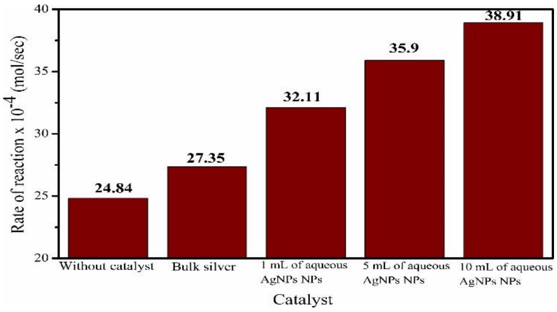


Fig. 7b. Rate of Reaction over the function of Catalyst in Production of Acetone

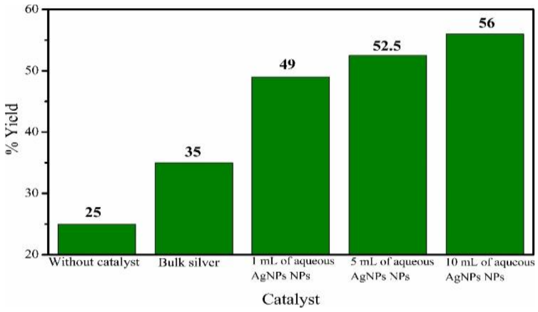


Fig. 8a. % Yield of Acetaldehyde over the function of Catalyst

Table 2. Catalytic activity of AgNPs in the preparation of aldehydes & Ketone

Reactant	Product	Catalyst	Time taken for total condensation Reaction (sec)	Temperature Required For commencement of condensation (^{0}C)	Rate of reaction X 10^{-4} (Mole/sec)	Percentage of yield %
Ethyl alcohol	Acetaldehyde	Without catalyst	350	296	22.57	25
		Bulk silver	320	270	24.68	35
		1ml of aqueous AgNps	254	246	31.10	49
		5 ml of aqueous AgNps	241	235	32.78	52.5
		10 ml of aqueous AgNps	222	228	35.58	56
Isopropanol	Acetone	Without catalyst	318	268	24.84	30
		Bulk silver	289	252	27.35	37.5
		1ml of aqueous AgNps	246	235	32.11	46
		5 ml of aqueous AgNps	220	226	35.90	52.5
		10 ml of aqueous AgNps	203	218	38.91	56.5

Table 3. Beneficial effects of 10 ml of aqueous AgNPs as catalyst compared to other combinations

Reactant	Product	Catalyst	Reduction in Time taken for total condensation Reaction (sec)	Reduction in Temperature Required For commencement of condensation (^{0}C)	Enhanced Rate of reaction X 10^{-4} (Mole/sec)	Enhanced Percentage of yield
Ethyl alcohol	Acetaldehyde	Without catalyst	128	68	13.01	31
		Bulk silver	98	42	10.9	21
		1ml of aqueous AgNPs	32	18	4.48	07
		5 ml of aqueous AgNPs	19	07	2.8	3.5
Isopropanol	acetone	Without catalyst	115	50	14.17	26.5
		Bulk silver	86	34	11.56	29
		1 ml of AgNPs	43	17	6.8	10.5
		5 ml of AgNPs	17	08	3.01	04

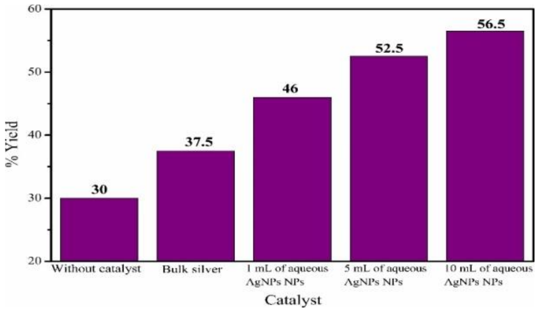


Fig. 8b. % Yield of Acetone over the function of Catalyst

The probable reason for the resulted acceleration would be ascribed to presence of more number of nanoparticles and larger area of the catalysts. Bindhu and Umadevi also [5] attributed this to small size of particles with large surface to volume ratio and more atoms on the surface as potential catalytic sites for the enhanced catalytic activities of silver nanoparticles for the aqueous reduction of 4-NP to 4-AP with $NaBH_4$.

To circumvent the drawbacks in carrying out the synthesis without catalyst and by using the bulk silver in the production, application of AgNPs is far advantageous. As well, increasing quantity of nanocatalyst improve final product yields.

Recycling and reusing of the catalyst

In an attempt to reuse, the AgNPs used were recycled by treating them with chloroform for 10 minutes at 6000 rpm and recovered. The catalyst proved active in at least three runs and catalytic performance remained unchanged with same yields showing the stability of nanoparticles in our reaction conditions. Similar enhanced catalytic efficiencies of AgNPs were reported earlier [3, 8].

4. Conclusions

The reported green synthesis of AgNPs was performed under normal laboratory conditions. The simple and economically biosynthesized, nearly spherical AgNPs of 12 nm size used in the present work strongly suggest that AgNPs are versatile over bulk material as they displayed a pronounced catalytic activity which activates the alcohol dehydrogenation to the corresponding aldehyde / ketone. The versatility of the nanocatalysts are low catalyst loading ,their recovery from the reaction medium and reuse. Through the present work, it can be emphasized that the AgNPs utilized by a very minute quantity equal to 0.216 mg instead of bulk silver processed enhanced catalytic activity which reduced required temperatures (~ 40^0C), improved rate of reactions (~10 $x10^{-4}$mole/sec) and increased % yields (~25%) in the conversion of alcohols (20 ml) to desired product. Upon second and third use, the catalytic performance remained unchanged showing the stability of the AgNPs. This protocol represents a simple and efficient method in obtaining the products in excellent yields. Hence, the utilization of AgNPs for commercial viability for industrial application may be evaluated.

Acknowledgements

The author thank DST-New Delhi for financial support to carry out this project under ‘Women Scientists Scheme’, grant No.SR/WOS-A/LS-543/2012.The author wish to acknowledge Prof.Sashidhar Rao, Prof.Sreedhar, Dr. Chandrakala and The management of Siddartha Educational Academy group of Institutions, Tirupati, A.P for their stanch support and encouragement.

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