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Gold nanoparticles supported on dendrimer@resin for the efficient oxidation of styrene using elemental oxygen†

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Highly dispersed AuNPs of sizes 2–5 nm were deposited onto third generation PAMAM dendrimers attached to XAD-4. The nanocatalyst thus prepared was characterised by SEM, TEM, BET *etc.* The catalyst showed remarkable stability and activity towards the oxidation of styrene. Reaction parameters such as the nature of the oxidant, solvent, catalyst concentration, temperature and reaction time were investigated and the reaction conditions were optimized. Furthermore, the recyclability and stability of the AuNPs supported on dendrimers@resin was established. The results demonstrate that epoxidation can be carried out using molecular oxygen and the prepared heterogeneous gold nanocatalyst possesses potential applications for green and sustainable development of epoxides.

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Introduction

Olefin epoxidation is a vitally important reaction as epoxides are important intermediates for a large variety of fine chemicals, pharmaceuticals, polymers, co-polymers *etc.* Originally, styrene oxide was produced using one of two methods, namely dehydrochlorination of styrene chlorohydrin with a base or oxidation of styrene using organic peracids. Use of peracids is unsafe and, moreover, they are corrosive, expensive and generate voluminous amounts of waste. Both these methods use hazardous chemicals and show poor selectivity for styrene epoxide, thus leading to the generation of undesirable side products.^{1,2} Over a period of time, these processes have been replaced by catalytic oxidation using peroxides as oxidants. Different homogeneous and heterogeneous catalysts have been reported but the stability and isolation problems associated with homogeneous catalysts, and low activity and selectivity of heterogeneous catalysts are some of the issues that still need to be addressed completely. Therefore, there will definitely be more advances needed in the future with an aim to design benign selective protocols with lower production costs.^{3–8}

In the past decade, supported nanoparticles have emerged as sustainable alternatives to conventional homo and heterogeneous catalysts as they combine the ease of catalyst separation with high catalytic activity. Catalysis using gold nanoparticles is a topic of much current interest as catalytic activity of gold is directly related to the particle size in the nanometer length scale. Thus, gold catalysis is a benchmark for the size of gold

nanoparticles as these properties disappear completely when the particle size grows into the micrometric scale. The pioneering work by Haruta *et al.*⁹ in 1989, which showed the high potency AuNPs to oxidize CO into CO₂ by atmospheric air, also, demonstrated the ability of gold to chemisorb oxygen. The latter is an undisputed oxidant of choice for any chemical reaction from the viewpoint of sustainable and green chemistry. Literature survey revealed that gold nanoparticles have been successfully used for the aerobic oxidation of CO,^{10–14} alcohols,^{15,16} cyclohexene,^{17,18} aldehydes¹⁹ *etc.* As far as the epoxidation of styrene is concerned, gold nanoparticles supported on layered double hydroxide (LDH),²⁰ CaO,²¹ alkaline earth metal oxide,²² Ti-SBA-15,²³ polyoxometalates,²⁴ Al₂O₃,²⁵ titania,²⁶ carbon nanotube (CNT),²⁷ Au–silica,²⁸ U₃O₈,²⁹ Yb₂O₃,²⁹ Fe₂O₃,³⁰ Ti₂O₃,³⁰ SiO₂,³¹ hydroxyapatite (HAT),³² PMO-SBA-15,³³ 2S-1L-4.5³⁴ Fe₃O₄@SiO₂ yolk,³⁵ MS-55,³⁶ Thiol-functionalized silica³⁷ *etc.* have been reported for the liquid phase oxidation of styrene using mainly peroxides such as H₂O₂, *t*-butyl hydroperoxide (TBHP) as oxidants. Dimethyl formamide (DMF) and acetonitrile were the most common solvents reported for these catalytic processes. But there are hardly any references of gold nanoparticle catalysed epoxidation of styrene using elemental oxygen. Zhu *et al.* reported the oxidation of styrene using molecular oxygen on thiolate protected gold clusters but their main product was benzaldehyde.³⁸ Supports play an important role in the catalytic reactions. They not only provide a framework for anchoring the catalyst but can also change the microenvironment of the reactants and thereby, influencing the reaction rates. Catalysis by dendrimer supported metal nanoparticles is a recent concept that has largely been developed by Crooks *et al.* and Astruc *et al.* The dendrimers are particularly attractive hosts for catalytically active metal nanoparticles because of their well-defined nano-environment in the interior

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of the dendrimer and their chemical versatility.^{39,40} Hence, in the present studies, we decided to synthesis stable gold nanoparticles on a support, in which, a third generation PAMAM dendrimers have been attached to the surface of XAD-4 resin. So far, these kind of supported nanoparticles have not been studied for the epoxidation of styrene. Reaction parameters for epoxidation, such as solvent, nature of oxidant, catalyst concentration, temperature and reaction time, were investigated and reaction conditions were optimized. Other important parameters such as leaching of metal and the size of nanoparticles after the reaction were also studied in order to establish the recyclability of the catalyst.

Experimental section

Materials and reagents

All chemicals used were of the analytical grade or of the highest purity grade available. Gold chloride, styrene, ethane-1,2-diamine and methyl acrylate were purchased from Aldrich. 1,4-Dioxane, acetonitrile, hydrogen peroxide 30% in water (H₂O₂), *tert*-butyl hydroperoxide 70% in water (TBHP), dimethylformamide (DMF), dichloromethane (DCM), diethyl ether (Et₂O), and NaBH₄ were purchased from Finar chemicals. Amberlite XAD-4 (surface area 725 m² g⁻¹ mesh sizes 20–40) was purchased from Fluka. Water used in all experiments was purified by the Millipore-Q system. All glassware was thoroughly cleaned with freshly prepared 3 : 1 HCl/HNO₃ (aqua regia) prior to use.

Instrumentation

FT-IR spectra were recorded as KBr pellet on Bruker TENSOR-27 IR spectrophotometer in the range of 4000–400 cm⁻¹. GC-MS measurements were carried on Perkin Elmer USA Auto system XL. High resolution transmission electron microscopy (HR-TEM) pictures were taken using Hitachi (H-7500) and JEOL, JEM 2100 models. The swollen resin beads were milled and a drop of alcoholic suspension was placed onto a 200 mesh carbon coated copper grid. It was then dried to evaporate the solvent and used for microscopy. Scanning electron microscope (SEM) analysis was carried out by LEO 1430 VP scanning electron microscope. Inductively coupled plasma atomic emission spectroscopy (ICP-AES) measurements were carried out on a HJY Ultima-2 instrument: power 1000 W, nebulizer flow 1.29, nebulizer pressure 2.96, wave length 242.795 nm. The BET analysis was carried by Micromeritics, ASAP 2010 series high speed gas sorption analyzer.

Synthesis of support (XAD-4-G_{3,0} PAMAM dendrimers)

Macroporous polystyrene resin, Amberlite XAD-4, was first modified to chloroformyl XAD-4 by methods reported in the literature. A step wise growth of PAMAM dendrimers was carried out on this resin and the details are given in the ESI.†

Synthesis of catalyst (Au NPs@XAD-4-G_{3,0} PAMAM dendrimers)

The catalyst was impregnated with AuNPs by sorption reduction method. XAD-4-G_{3,0} PAMAM (5.0 g) beads were repeatedly

washed with water and ethanol to remove any sorbed salts or reagents. The swollen resin beads were then equilibrated with 20 mL of 1 mmol solution of gold chloride in ethanol. After 1 h, excess solution was drained off and the metal was reduced by passing cold aqueous NaBH₄ (0.1 mol dm⁻³) solution. The Au NPs@XAD-4-G_{3,0} PAMAM dendrimer were further washed with water to remove excess reagent and stored in ethanol.

Catalytic oxidation of styrene with molecular oxygen

Into a 10 mL two-necked round bottom flask equipped with a reflux condenser, styrene (1 mmol), 1,4-dioxane (7 mL), and 120 mg of catalyst were placed. The flask was kept in an oil bath at 80 °C and O₂ gas at atmospheric pressure was bubbled into the reaction mixture using a balloon. After 24 h, the catalyst was filtered off and reaction mixture after appropriate dilution was analysed using a GC-MS using bromobenzene as internal standard. Thereafter, the experiments were performed for different catalyst amounts, temperatures, and solvents to obtain the optimal process conditions for the styrene oxide production.

Catalytic oxidation of styrene with peroxides

Into a 10 mL single-necked round bottom flask equipped with a reflux condenser styrene (1 mmol), 1,4-dioxane (5 mL), 120 mg of catalyst and 4 mL oxidant (H₂O₂ or TBHP) were placed. The flask was placed in an oil bath and the temperature was maintained at 80 °C. After 24 h, the catalyst was filtered off, while the reaction mixture was still hot and the filtrate after cooling was extracted with ethyl acetate. The organic solvent layer was dried over MgSO₄ and the solvent removed by rota evaporator. The liquid organic products were diluted with methanol and quantified using a GC-MS.

Results and discussion

Characterization of catalyst

Dendrimers are macromolecules with tree-like architecture having a high degree of molecular uniformity, narrow molecular weight distribution, loosely packed interior pockets and highly functionalized terminal surface. Such structural architecture has been exploited for the synthesis of nanoparticles with uniform particle sizes. Among the potential applications for dendrimers, catalysis is one of the most promising and attachment of dendrimers to resin can facilitate its separation and recyclability.^{41,42} The nanoparticles are retained within the dendrimer show primarily by steric effects and therefore, a substantial fraction is devoid of any functional group or ligand. Amberlite XAD-4 is a commercial resin which is chemically inert, thermally stable and easy to functionalize. Hence, we decided to grow third generation PAMAM dendrimers on the surface of XAD-4. The synthesized dendrimers@resin were characterized by elemental CHNS analysis, TGA FTIR spectra analysis *etc.* (see ESI† for details).

The PAMAM modified resin was impregnated with gold nanoparticles by sorption reduction method developed in our lab.⁴³ The pale yellow resin beads turned deep red on

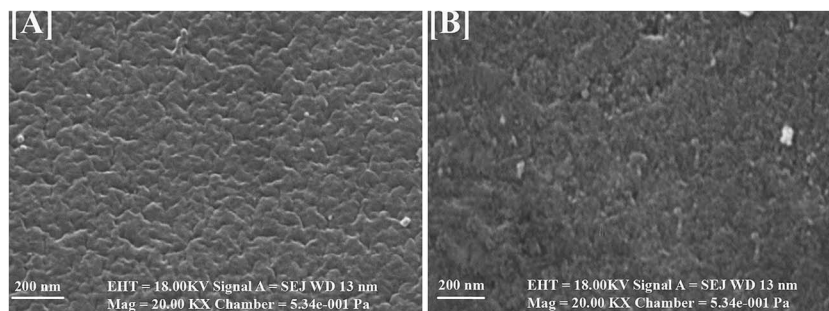


Fig. 1 SEM images (A) XAD-4 (B) Au NPs@XAD-4-G_{3.0} PAMAM dendrimer.

impregnation with gold nanoparticles. BET analysis is an important technique for the measurement of surface area of a catalyst. The analysis was carried out by nitrogen multilayer adsorption measured as a function of relative pressure using a fully automated BET analyser. The technique encompasses external area and pore area evaluations to determine the total specific surface area in $\text{m}^2 \text{g}^{-1}$ yielding important information in studying the effects of surface porosity and particle size in many applications. In the present case we have used a macroporous polystyrene resin as support. The reported surface area of XAD-4 is $750 \text{ m}^2 \text{g}^{-1}$. However, adsorption and desorption cumulative surface areas of the AuNPs@XAD-4-G_{3.0} PAMAM catalyst as calculated by BJH method were found to be $88.57 \text{ m}^2 \text{g}^{-1}$ and $112.47 \text{ m}^2 \text{g}^{-1}$ respectively. This large decrease in surface area was attributed to the growth of dendrimers chains inside the pores as well as on the surface of resin beads. The average diameter of pores also decreased from 20–40 nm to 12–15 nm. Though, the analysis could not convey information about the surface of catalyst, morphological changes in support were indicated. The same was corroborated by SEM studies.

Scanning emission microscopy was used to study the surface of catalyst beads. SEM images of the XAD-4 and XAD-4-G_{3.0} PAMAM dendrimer are shown in Fig. 1. Two observations were made from these studies. One, nanoparticles were present on the surface of beads and two; morphological changes with decreased pore size after the attachment of dendrimers to the surface of XAD-4 were evident.

Transmission electron microscopy was used to study the size and shape of gold nanoparticles. TEM pictures (Fig. 2) of the

catalyst showed that the encapsulated Au NPs particles are nearly monodisperse and their shape is roughly spherical. The size of the Au NPs varied between 2 to 5 nm. In our earlier studies, we have found that gold nanoparticles can be synthesized and stabilized into the pores of XAD-4 resin. So we presumed that in this case also nanoparticles are impregnating the interior as well as the exterior surface of dendrimers@resin. The amount of gold loaded onto XAD-4-G_{3.0} PAMAM dendrimer resin was determined by ICP-AES. 500 mg of the catalyst was incinerated in a crucible for 4 h at 550 °C. The residue was dissolved in 1 mL aqua regia and diluted to 10 mL with distilled water. The average concentration of gold (3 trials) as determined by ICP-AES and was found to be $0.0052 \text{ mmol g}^{-1}$ or 1.026 mg of gold per gram of catalyst.

Catalytic epoxidation of styrene

Epoxidation of styrene was carried out using different O_2 , H_2O_2 and *tert*-butyl hydroperoxide (TBHP) as oxidants and the reaction is reported in Scheme 1. The products of the epoxidation reaction were analysed by GC-MS. We found that under the analytical conditions, the retention time of styrene, styrene oxide, and benzaldehyde were 4.0, 8.0, and 5.6 min respectively. Styrene oxide was identified by its characteristic *m/z* peaks at 89, 90, 91 (base peak), 92, 105, 119. During epoxidation of styrene many side products such as benzaldehyde, acetophenone, and phenylacetaldehyde are reported in the literature. In the present case we were able to identify only benzaldehyde as the major side product (Scheme 1) and sometimes dimers of styrene were observed in GCMS studies. Other reported side products of

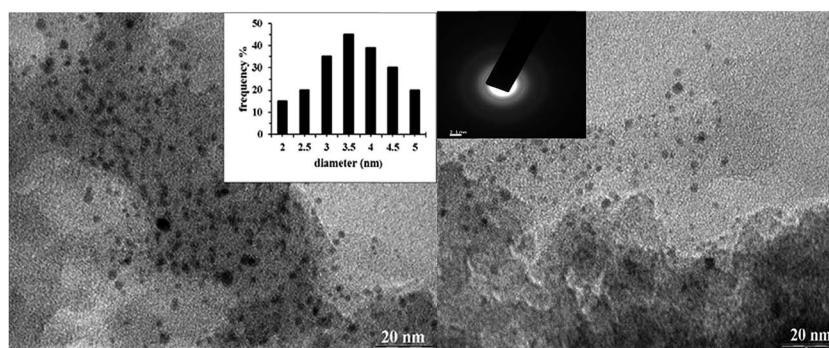
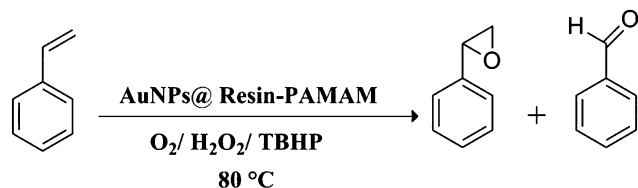


Fig. 2 TEM images of Au NPs@XAD-4-G_{3.0} PAMAM dendrimer.



Scheme 1 Reaction scheme for the oxidation of styrene over AuNPs@resin-PAMAM dendrimer.

epoxidation such as acetophenone and phenylacetaldehyde were not observed. The performance of three oxidants towards styrene epoxidation is tabulated in Table 1. Oxygen is regarded as the most ideal oxidant since it is non-toxic and eco-friendly. According to Staykov and coworkers⁴⁴ oxygen can be activated by the partially negatively charged surface of gold atoms leading to its stable chemisorption. Haruta and coworkers⁴⁵ have shown that this ability of gold nanoparticles to act as oxidation catalysts is highly size dependent and is mainly observed with small nanoparticles of size less than 5 nm. In the present case we were able to control the size of nanoparticles below 5 nm using dendrimers and our catalyst was able to dissociate molecular oxygen and facilitate the epoxidation of styrene without using initiator. Whether, this facile dissociation is solely due to small size of nanoparticles or support has played some special role is difficult to conclude here and it will require further detailed studies using support without dendrimers and with different types of dendrimers. Another highlight of the present work was better conversion and selectivity for epoxide with oxygen as oxidant in comparison to H₂O₂ and TBHP. Though, most of the styrene epoxidation reactions in literature have been reported using these two oxidants. This was probably due to the fact that we were using aqueous solutions of these oxidants and it was observed that the activity and selectivity for epoxidation of our catalyst was low in polar solvents. The conversion of styrene and selectivity for styrene oxide with various oxidants is reported in Table 1.

The effect that a solvent exerts on the rate of a heterogeneously catalyzed reaction depends on the reaction substrates and the catalyst support. Solvents do not merely acts as diluent in which the reactants are dissolved; they can also interact with the catalyst surface and modify the extent to which different

types of substrates are absorbed. The solvents used in the experiments were ethanol (dielectric constant 24.5), 1,4-dioxane (dielectric constant 2.25), acetonitrile (dielectric constant 37.5) and dimethyl formamide (dielectric constant 109.5). 95% conversions of styrene with 50% selectivity for styrene epoxide were observed in dioxane, a nonpolar solvent. This is attributed to the fact that swelling volume of polystyrene resins is more in nonpolar solvents like dioxane as compared to polar solvents. The increased swelling can make the nanoparticles embedded deep in the matrix accessible to reactants and hence increase their conversion. In other solvents such as DMF and CH₃CN the conversion was also good but the selectivity for styrene epoxide was poor. It was, therefore, concluded that polar solvents favour benzaldehyde production rather than styrene epoxide. In all, the best conversion for styrene and best selectivity for styrene oxide was achieved in 1,4-dioxane (Table 1).

The effect of temperature on the epoxidation of styrene was investigated by changing the reaction temperature from 60 °C to 100 °C. From the experimental data we observed that conversion of styrene was 80% at 60 °C and increased with rise in temperature from 60 °C to 100 °C (99% conversion at 90 °C). Though, overall conversion increased with temperature, the concentration of styrene in the product mixture was highest at 80 °C (50% selectivity for styrene oxide) and thereafter, the concentration decreased with corresponding increase in benzaldehyde concentration. There is also a steady decrease in other side products with increase in temperature. As best selectivity for styrene oxide was obtained at 80 °C, this temperature was chosen as optimum temperature and effect of other parameters were studied at this temperature (Fig. 3).

The change in conversion of styrene and production of styrene epoxide with respect to time were monitored carefully and plotted. The results obtained over a period of 28 h at 80 °C are shown in Fig. 4. It was observed that conversion of styrene increased with time and maximum conversion of 95% was obtained in 24 h. The concentration of styrene epoxide also increased steadily to 50% upto 24 h and decreasing afterward with increase in benzaldehyde.

The effect of catalyst concentration was examined by changing the amount of catalyst while keeping the other parameters constant. In the absence of catalyst only slight oxidation of styrene was observed. This indicated that catalyst

Table 1 Optimization of reaction conditions^a

Solvent	Au NPs@resin-PAMAM dendrimer											
	Molecular O ₂				H ₂ O ₂				TBHP			
	Con. (%)	Selectivity (%)			Con. (%)	Selectivity (%)			Con. (%)	Selectivity (%)		
	SO	BZ	Others		SO	BZ	Others		SO	BZ	Others	
Dioxane*	10	00	80	20	5	—	100	—	—	—	—	—
Dioxane	95	48	33	19	92	18	80	02	95	22	75	03
CH ₃ CN	80	35	48	17	96	12	80	08	80	14	84	02
DMF	75	30	45	25	82	16	78	06	85	24	73	03
Ethanol	80	35	58	07	85	10	87	03	90	14	86	00

^a Reaction condition: 120 mg of catalyst; 1 mmol of styrene; 7.0 mL solvent; 24 hour; 80 °C. * = without catalyst, Con. = conversion of styrene, SO = styrene oxide, BZ = benzaldehyde. Conversion and selectivity determined by GC-MS analysis.

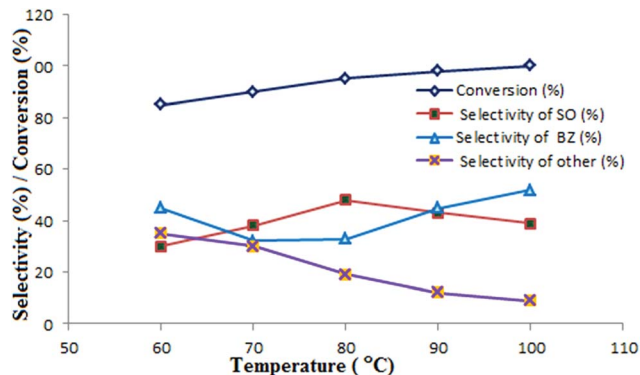


Fig. 3 Effect on styrene conversion and selectivity of products at different temperatures.

was essential for the reaction to take place at a reasonable rate. The results are shown in Fig. 5. We found that the maximum conversion was obtained with 120 mg of catalyst (0.1% of Au) further increase has no effect conversion. According to this study a TON number of 1522 was calculated for this conversion.

Recyclability of the catalyst

Ease of separation and recyclability are the fundamental requirements of a good catalytic reaction. The recycling of the heterogeneous catalysts is an important feature that makes them economical and preferable over homogeneous catalysts. The attachment of dendrimers to resin beads facilitated their separation. The Au NPs@XAD-4-G_{3,0} PAMAM were separated from the reaction mixture by simple filtration. The beads, after separation, were extracted with hot ethanol to remove any sorbed products and were reused. The results are shown in Fig. 6.

Study of catalytic leaching is another important parameter to ascertain the recyclability of catalyst. Leaching depends upon a number of factors including the type of solvent and stabilizing agents used in the reaction. The nature of leached out species is also important for investigating the mechanism of a reaction. To estimate the leaching of gold from the catalyst the filtrate after the removal of catalyst from the reaction mixture was digested with sulphuric acid and after dilution the

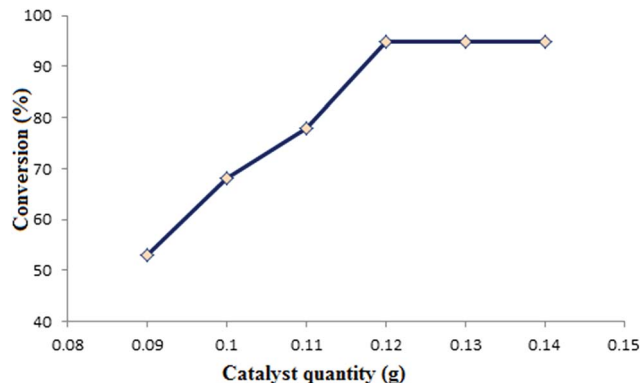


Fig. 5 Effect of catalyst concentration on styrene conversion in dioxane at 80 °C.

solution was analyzed for the presence of gold ions by ICP-AES. No trace of gold was observed above the detectable limit. This indicates that there are no stable catalytic species in the reaction mixture.

Post reaction TEM analysis of the catalyst is another important technique to ascertain leaching as it generally leads to decrease in particle size. On the contrary, TEM pictures of the catalyst taken after fifth cycle (Fig. 7) showed an increase in the size of the particles. TEM pictures show that majority of the particles were still in the size range of 2 to 6 nm. But some big particles in the size range of 10 to 20 nm were also observed. Another important observation made was that the particles on the surface were much bigger than those embedded deep in the polymer matrix. The implication is that growth occurs by particle migration and coalescence which is more feasible at the exposed surface of beads rather than inside the resin matrix. Had it been due to atom migration increase in particle size would have been uniform. This also points towards the heterogeneous nature of catalysis.

Comparison with other reported methods

We compared the catalytic activity of AuNPs@XAD-4-G_{3,0} PAMAM dendrimers for the styrene epoxidation and selectivity for styrene epoxide with that of the earlier reported gold-based

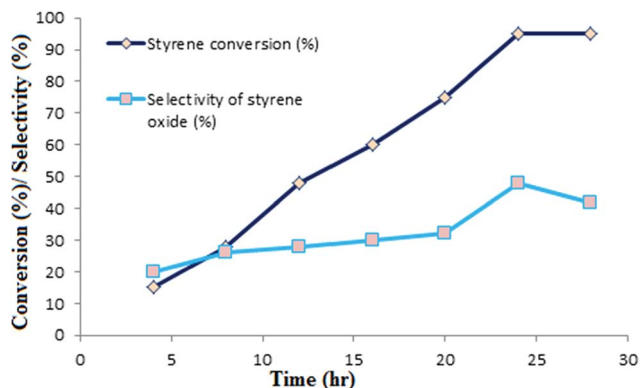


Fig. 4 Effect of styrene conversion and selectivity of styrene oxide in dioxane with time at 80 °C.

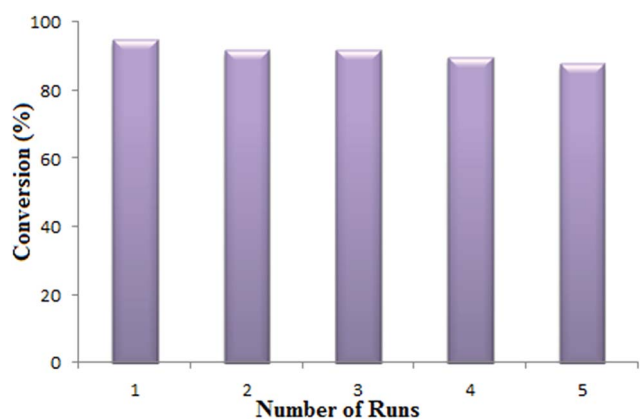


Fig. 6 Recycling of the catalysts.

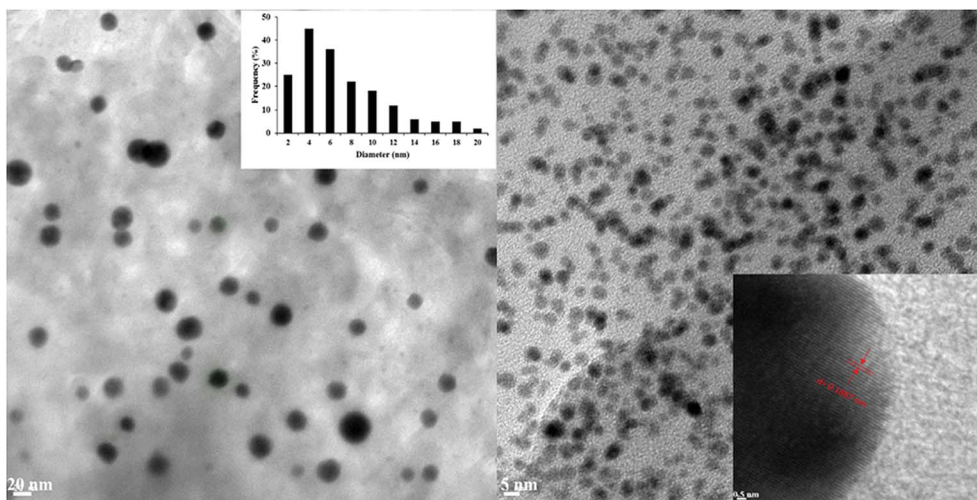


Fig. 7 TEM of the catalyst after fifth cycle.

Table 2 Comparison of catalytic activity of gold nanoparticles deposited on different supports towards styrene epoxidation^a

Catalyst system	Au loaded (%)	Oxidant	Con. (%)	Selectivity (%)				Ref.
				SO	PA	BZ	Other	
Au/LDH	5.48	TBHP	79.4	74.2	—	13	—	20
Au/CaO(HDP)	4.7	TBHP	53.6	60.2	14.4	6.3	—	21
Au/MgO(DP)	7.5	TBHP	67.0	36.1	11.7	22.8	29.4	22
Au/MgO(HDP)	4.1	TBHP	44.6	54.3	16.8	10.8	18.1	22
Au/SrO	0.6	TBHP	21.4	44.8	26.0	11.7	17.4	22
Au/BaO	5.3	TBHP	55.9	53.5	17.6	10.2	18.7	22
Au/Al ₂ O ₃	6.36	TBHP	44.0	28	13.0	24	—	25
Au/CNT	0.3	H ₂ O ₂	10.2	—	—	100	—	27
Au/CNT	0.3	O ₂ (TBHP as initiator)	2.3	74.7	15.3	10.0	—	27
Au-silica	4.0	TBHP	63.5	84.7	1.5	1.8	—	28
Au/PMO-SBA-15	2.0	TBHP	94.8	75.0	2.5	16.6	—	33
Au-2S-1L-4.5	4.5	H ₂ O ₂	60.4	92.9	4.7	1.2	—	34
Au NPs@XAD-4-G _{3,0} PAMAM dendrimer	0.10	O ₂ (no initiator)	95	48	—	33	19	This work

^a DP (deposition-precipitation), HDP (homogenous deposition precipitation). Con. = conversion of styrene, SO = styrene oxide, PA = phenyl acetaldehyde, BZ = benzaldehyde.

catalysts and results are shown in Table 2. It was observed that conversion of styrene using this catalyst was comparable to those reported earlier. The selectivity towards styrene oxide was slightly less. But significant feature of this protocol is that we were able to carry out these conversions using elemental O₂ without any initiator whereas, in most of other cases toxic organic peroxides have been used. Another important feature is the amount of catalyst. We have used only 0.1% of catalyst (120 mg of catalyst = 0.13 mg of Au) which is substantially low in comparison to other catalysts.

Conclusion

From the experimental data it was concluded that epoxidation of styrene using oxygen is possible on the surface of Au NPs@XAD-4-G_{3,0} PAMAM dendrimer. The developed catalyst for the heterogeneous epoxidation of styrene was equally recyclable

and stable as any other support. The high TON of the catalyst more than compensates for the expensive nature of gold. The developed protocol definitely opens new possibilities for the usage of gold nanoparticles as a green and economical catalyst of future in many more reactions than envisaged till now.

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