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Gold nanoparticles supported on nanoscale amine-functionalized MIL-101(Cr) as a highly active catalyst for epoxidation of styrene

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Abstract

In this study, well dispersed gold nanoparticles (Au Nps) were embedded on an aminefunctionalized nanoscale metal-organic framework MIL-101(Cr) *via* a simple solution approach. The resulting Au/NH₂-MIL-101(Cr) exhibited high isoelctric point (IEP) value with brønsted basic sites that played an important role in determining the size and dispersion of Au Nps onto its matrix. In addition, the uniform nanomorphology of the catalyst provides the advantage of its well dispersion in aqueous media. The synthesized Au/NH₂-MIL-101(Cr) catalyst was successfully characterized by different analytical techniques like powder X-ray diffraction, X-ray photoelectronspectroscopy, field emission scanning electron microscopy, transmission electron microscopy, Brunauer–Emmett–Teller (BET) surface area analysis, Fourier transform infrared spectroscopy (FT-IR), thermogravimetric analysis (TGA), Zeta potential analysis and atomic absorption spectroscopy (AAS). The catalytic activity of the synthesized material was explored for the epoxidation of styrene using tert-Butyl Hydroperoxide as oxidant. The catalyst could easily be recovered and recycled upto fourth catalytic cycle without any significant change of its catalytic activity.

1. Introduction

Metal Nanoparticles (Nps) catalyzed organic chemistry transformations have been found to be much attention in recent years¹. Particularly, supported gold nanoparticles (Au Nps) has been accepted to be a very active catalyst for a number of important organic transformations such as selective oxidation reactions like oxidation of alcohols to aldehydes,^{2,3} oxidation of D-glucose,⁴ low temperature oxidation of CO,⁵ oxidation of ethylene glycol,⁶ epoxidation of propene⁷⁻⁹ as well as asymmetrically terminal alkene.¹⁰⁻¹² In addition, Au Nps has been

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involved as a catalyst in a wide range of non-oxidative processes such as selective hydrogenation of N-O bonds,¹³ hydrogenation of crotonaldehyde,¹⁴ addition to multiple C-C bonds, benzannulations,¹⁵ hydrochlorination of ethyne to vinyl chloride¹⁶ etc. It is important to mention that catalytic activity of supported Au Nps is highly depends upon certain key parameters like its size, dispersion, the nature of the support and its interaction with the Nps.¹⁷ Different materials such as TiO₂,¹⁸ SiO₂,¹⁷ Al₂O₃,¹⁹ CuO,¹⁸ MgO,¹⁰ Fe₃O₄,²⁰ ZrO₂,²¹ CeO₂,²² CNT,²³ HAP,²⁴ SBA-15,²⁵ HMS,²⁶ MCM-41,²⁷ MSU,²⁸ TS-1,²⁹ TS-1/SiO₂,³⁰ Ti-SiO₂,³¹ Ti-SBA-15,³² MSN,³³ Ti-MCM-41,³⁴ TUD-1,³⁵ TSG,³⁶ Yb₂O₃,³⁷ CaO³⁷ and layered double hydroxide³⁸ have already been used as catalytic support for Au Nps to study their different catalytic activities. In this context, metal-organic frameworks (MOFs) can be used as a support for metal nanoparticles owing to its high surface area, porosity and tunable chemical properties.^{39, 40} In fact, noble metal Nps have already been synthesized on MOFs ⁴¹⁻⁴³ and the combination of the porous framework structures of MOFs with metal Nps offers more efficient catalytic activities in terms of reaction times and recyclability over other catalysts.⁴⁴⁻⁴⁷

Among different MOFs, MIL-101(Cr) has already been employed as catalytic support for various noble metals Nps⁴⁸ because of its hydrothermal stability, high surface area and chemical inertness. In particular, MOFs at nanoscale level having uniform and well-defined sizes and morphologies^{49, 50} show excellent catalytic activities due to their better dispersion in aqueous and other solvents.^{51, 52} These features of MIL-101(Cr) are also preserved in its amino analogue i.e. MIL-101-NH₂ in which the amino groups are introduced into the MOF lattice either via linker modification⁵³ or through post synthetic treatment.⁴⁸ Reports are available for MIL-101(Cr) supported gold nanoparticles using different synthetic protocols like deposition-precipitation method,⁵⁴ double solvent method (DSM)^{55, 56} impregnation⁵⁷ etc. Even though few reports have been available for MOF supported Au Nps,⁵⁸ yet the deposition of Au Nps on MOF catalysts in solution is considered to be a challenging task.^{59,60} Furthermore, few studies have been carried out using nanoscale MOF as catalytic support.^{61, 62} Therefore, applications of MOFs in heterogeneous catalysis have attracted extreme attention in recent times.⁶³⁻⁶⁵

Epoxidation of styrene is an important organic transformation for the synthesis of styrene oxide, an industrially important organic intermediate, widely employed for the production of valuable products such as perfumes, plasticizers, sweeteners, surfactants, paints, epoxy resins etc.⁶⁶ In conventional way, epoxidation of styrene is carried out using stoichiometric amounts of peracids⁶⁷ which acts as an oxidizing agent usually display some shortcomings like

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hazardous to handle, very expensive, non-selective toward epoxidation and lead to the formation of many undesirable products. Therefore, direct epoxidation of styrene has been found to be a promising alternative to this conventional route. Reports are available for the epoxidation of styrene by environ-friendly and safer oxidizing agents such as aqueous H_2O_2 or urea $-H_2O_2$ adduct,⁶⁶ anhydrous $H_2O_2^{68}$ or TBHP ^{69, 70} in presence of solid catalysts such as c-Al₂O₃,⁶⁸ Ti–SiO₂,⁶⁹ TS-1⁶⁷ and Ti-HMS⁷⁰ yet the catalysts show low activity and selectivity towards epoxides ⁶⁷⁻⁷⁰ or becomes deactivated in the presence of reaction water.⁶⁸

Therefore, keep all that in mind, herein we report the synthesis of Au Nps deposited on nanosized amine functionalized MIL-101(Cr) i.e. Au/NH₂-MIL-101(Cr) by employing a solution based approach and explore its catalytic activity for the epoxidation of styrene in presence of t-butyl hydroperoxide (TBHP). To the best of our knowledge there are no reports so far wherein NH₂-MIL-101(Cr) is employed as support for Au NPs in epoxidation of styrene.

2. Experimental section

2.1 Materials and methods

All the chemicals are of analytical grade and used as purchased without further purification. Cr $(NO_3)_3$.9H₂O and 2-aminoterephthalic acid, Gold (III) chloride hydrate, Sodium borohydride, are purchased from Sigma-Aldrich, USA. tri-sodium citrate dihydrate, tert-Butyl hydroperoxide (TBHP) are purchased from Spectrochem Pvt. Ltd. Styrene, C₂H₅OH, DMF are purchased from Merck, Germany.

The X-ray diffraction (XRD) patterns of the samples are performed on Rigaku, Ultima IV X-ray diffractometer using Cu-K α source ($\lambda = 1.54$ Å). Specific surface area, pore volume, average pore diameter are measured with the Autosorb-1 (Quantachrome, USA). X-ray photoelectron spectroscopy measurements are performed on an X-ray photoelectron spectrometer (SPECS Surface Nano Analysis GmbH, Germany) equipped with an X-ray source XR-50 with a twin Al/Mg anode, a hemispherical electron energy analyzer PHOIBOS-150. The size and morphology of the nanoparticles are observed by transmission electron microscopy (TEM) using JEOL (Model JEM-2011) equipment. Field-emission scanning electron microscopy (FE-SEM, SIGMA) is applied to investigate the size and morphology of the sample and EDS mapping was done in Oxford XMax 20 equipment. The basic property of the support is measured through CO₂-TPD analysis which is carried out in an AutoChem II 2920 V4.02 instrument. The Au content of the catalyst is determined through Atomic absorption spectroscopy (AAS) measurement using PerkinElmer (Model-AAnalyst-700) spectrometer. TGA analysis of the material has been carried out in a TA SDT-Q600 instrument under N₂ atmosphere. Gas- Chromatography (GC) analysis of the reaction is carried out in a gas chromatography (Thermo Scientific, TRACE 1300) equipped with a flame ionization detector (FID) and a Thermo Scientific (Polyethelene glycol, 30 m × 0.32 mm × 0.25 μ m) capillary column. Isolectric point (IEP) value of the support are analyzed by carry out zeta potential in a Zetasizer (Model No. nano ZS), MPT-2 instrument using auto titration method. FT-IR spectra (4000-400 cm⁻¹) are recorded on KBr discs in a Perkin-Elmer system 2000 FT-IR spectrophotometer.

2.2 Synthesis of NH₂-MIL-101(Cr)

NH₂-MIL-101(Cr) was synthesized according to the reported procedure by Chen et al. ⁵³ A mixture of Cr(NO₃)₃. 9H₂O (2 mmol), 2-aminoterephthalic acid (2 mmol) and sodium hydroxide (5 mmol) were dispersed and then stirring in 15 ml of de-ionized water for 5 minutes. The resulting solution was heated in a 100 ml Teflon-lined autoclave at 150°C for 12 h. After cooling to room temperature, the green precipitate was collected by centrifugation, washed it with DMF to remove the unreacted 2-aminoterephthalic acid and then further purified by solvothermal treatment in ethanol at 100°C for 24 h. Finally, the product was dried at 80°C in air.

2.3 Synthesis of Au/NH₂-MIL-101(Cr)

The activated NH₂-MIL-101(Cr) (0.3 g)was dispersed in 50 mL of HAuCl₄ (2.5×10^{-4} M) aqueous solution at a pH ~ 3 for 10 minutes. The mixture was then stirred in a 100 ml round bottom flask for another 12 h followed by centrifugation and washed several times with deionized water. The resulting AuCl₄⁻NH₃⁺-MIL-101(Cr) was then dispersed in 20 mL of deionized water with the addition of tri-sodium citrate dihydrate (0.0036 g) and NaBH₄ (0.0056 g dissolved in 1.5 mL ice cold water) subsequently. After the addition of NaBH₄, the solution was continuously stirred at room temperature for another 6 h to yield Au/NH₂-MIL-101(Cr). It was observed that the colour of the resulting solid was changed from light green colour to dark green indicating the formation of Au Nps. The solid is then separated through centrifugation, repeatedly washed with de-ionized water and then dried under vacuum. The Au content (0.3 wt %) in the synthesized material was calculated from AAS technique.

2.4 Catalytic activity for epoxidation of styrene

A liquid reaction mixture containing styrene (1 mmol), TBHP (1.5 mmol) and toluene (5 mL) was stirred under reflux condition at 110°C for a period of 8 h in presence of Au/NH₂-MIL-101(Cr) (0.025 mol%). After the reaction, the reaction mixture was cooled to room temperature and the solid catalyst was separated through filtration. The products were analyzed by a Thermo Scientific, TRACE 1300 gas chromatograph equipped with a Thermo

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Scientific (Polyethelene glycol, 30 m \times 0.32 mm \times 0.25 µm) capillary column and a flame ionization detector (FID).

3. Results and discussion

The synthesis of Au Nps on the amine functionalized MIL-101(Cr) was carried out using $HAuCl_4$ as the gold precursor in presence of NaBH₄ that acts as a reducing agent. Trisodium citrate was used as a stabilizer which provides the optimum citrate concentration necessary for the stabilization of the Nps. In addition, the MOF matrix, acting as a support plays its role by enhancing the distribution of HAuCl₄ over its surfaces. The amine functionality of NH₂-MIL-101(Cr) facilitate the absorption of $[AuCl_4]^-$ ions from the solution phase to the support through an electrostatic interaction between NH_3^+ and $[AuCl_4]^-$ that can be well demonstrated with UV-vis spectroscopy (Fig S1, ESI). The peak of [AuCl₄]⁻ ions at around 307 nm was completely disappeared as well as its yellow (Fig S2, ESI) colour after the addition of the support (Fig S1, ESI), conforming the absorption of [AuCl₄]⁻ on to the support. In addition, we have calculated the isoelectric point (IEP) value of the sample by determining zeta potential as a function of pH using autotitration method (Fig S3, ESI). The IEP value of the support was found to be 8.43, that confirms the positive surface charge of NH_2 -MIL-101(Cr) which facilitate the attraction of negatively charged species of $[Au(OH)_nCl_{4-n}]^-$ (n=1-4) from solution. Furthermore, the Brønsted basic sites of the support are advantageous for the formation and stabilization of small gold particles.⁷¹ We have measured the basic properties of NH₂-MIL-101(Cr) by employing CO₂-TPD analysis (Fig S4, ESI). From the analysis the desorption amount of CO_2 is found to be 0.1324 mmol g⁻¹. Therefore both the IEP value of the support as well as the brønsted basic sites plays a major role in the distribution of gold nanoparticles on NH₂-MIL-101(Cr). The successful incorporation of Au Nps after the reduction of [AuCl₄]⁻ to Au(0) on to the framework of NH₂-MIL-101(Cr) was verified by employing different characterization techniques such as PXRD, N₂-physisorption, FE-SEM, HRTEM, XPS, TGA, FT-IR analysis.

The PXRD pattern of the synthesized Au/NH₂-MIL-101(Cr) (Fig 1.(red)) remained nearly unchanged in comparison to the parent NH₂-MIL-101(Cr) (Fig 1.(blue)).The expected (111), (200), (220), (311) and (222) reflexes of face centred cubic (fcc) structure (JCPDS card no. 04-0784) of metallic⁷² Au were found in the diffractogram (red colour) in addition to the other characteristic peaks of the parent MOF. The broad Bragg reflection⁷³ clearly indicate the typical nanoscale Au/NH₂-MIL-101(Cr), confirming by the FE-SEM analysis (Fig S5, ESI) where it was observed that the morphology of the support remain unaltered after loading of the Au Nps on to its matrix. FT-IR spectra (Fig S6, ESI) display double peaks at 3463 and

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3397 cm⁻¹ which could be attributed to the asymmetrical and symmetrical stretching of the amine moieties.^{74, 75} Two other characteristics bands of amino group were observed at 1624 cm⁻¹ and 1338 cm⁻¹ that could be ascribed as the N-H bending (scissoring) vibration and C-N stretching absorption respectively. It was observed that after incorporation of the Au nanoparticles (Fig S6 (red), ESI), the chemical functionality of parent MOF remains unchanged that clearly confirmed the robustness of the support. The EDS (Fig 2 (a)) and mapping analysis (Fig 2 (b)) showed the distribution of Au Nps along with the different elements present in the material which was further confirmed by the XPS analysis (Fig S7, ESI) showing peaks of binding energies at 83.8 eV and 87.4 eV assigned to $4f_{7/2}$ and $4f_{5/2}$ of Au (0). The specific surface area and pore volumes of synthesized materials were evaluated by the N₂ physisorption analysis at 77 K (Fig 3) The BET surface area of NH₂-MIL-101(Cr) and Au/NH2-MIL-101(Cr) were determined to be 1502 m²g⁻¹ and 1055 m²g⁻¹ with pore volumes 1.674 cm³g⁻¹ and 0.594 cm³g⁻¹ respectively. The BJH plot (Fig S8, ESI) further confirms the uniform pore distribution of the support after incorporation of Au Nps on it. The considerable decrease in the surface area and pore volume of Au/NH₂-MIL-101(Cr) clearly indicates that the cavities of NH₂-MIL-101(Cr) were occupied either by the highly dispersed Au Nps or potential blockage of the pores by the Nps.

The morphological evaluation of Au Nps in the Au/NH₂-MIL-101(Cr) was investigated through TEM analysis (Fig 4). From the images it was observed that the synthesized Au NPs were highly dispersed on the MOF matrix with a narrow size distribution between 2–10 nm (Fig 4(e)) which may be attributed to the presence of amine functionality attached to the framework structure that stabilizes the ion pair (NH₃)⁺AuCl₄ as well as the effect of trisodium citrate, acting as stabilizer for the Nps formed upon treatment of NaBH₄. HR-TEM image of a single Au Np (Fig 4 (d)) shows lattice fringes with fringe spacing about 0.23 nm further confirms the fcc (111) structure of Au (0) crystals. Thermal stability of the synthesized Au/NH₂-MIL-101(Cr) material (Fig S9, ESI) was examined through thermogravimetric analysis (TGA). Two major weight loss step has been obtained, the first step in the range 30-100° C (calculated loss 8%) is due to the loss of adsorbed water molecules and the second weight loss step in the range 300-600° C (Calculated loss 34%) may ascribed to the framework decomposition as shown by the corresponding derivative curve.

The catalytic activity of Au/NH₂-MIL-101(Cr) was tested for the epoxidation of styrene in presence of TBHP (Scheme-1). The effect of various key parameters like catalyst dosage, temperature, solvent was also examined in order to get the optimized reaction condition. The effect of different mol% of the catalyst was summarized in Table 1. With neat NH₂-MIL-

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101(Cr), the reaction was not proceeded, ensuring the catalytic role of Au Nps on the MOF support to carry out the chemical transformation. With increase in the mol% of the catalyst, both the conversion of the reaction and selectivity to styrene oxide was increased and attained maximum conversion (88.2%) and selectivity (74.7%) (Table 1, entry 3) with 0.025 mol% of the catalyst which could be attributed to the increase in the number of catalytically active centres with increase in catalyst dosage. However, beyond 0.025 mol%, conversion of the reaction decreased abruptly (44.1%) with slightly increase in the selectivity (78.2%) (Table 1, entry 4). Hence, 0.025 mol% was taken as the optimized catalyst dosage for this epoxidation reaction and all further studies were performed using this amount of catalyst.

The effect of different solvent system in the styrene epoxidation was examined by employing solvents having different polarities (Table 2). The highest conversion was obtained in DMF (96.7%) (Table 2, entry 2) with a very low styrene oxide selectivity (5.6%) (Table 2, entry 2). In case of acetone, although a highest selectivity towards styrene oxide was obtained (85.3%) (Table 2, entry 3), yet the conversion of the reaction was found to be low (7.6%) (Table 2, entry 3). A moderate reaction conversion and styrene oxide selectivity was observed in ethanol, acetonitrile and THF solvent system (Table 2, entry 5, 1, 7) while DCM displayed lowest reaction conversion (5.1%) (Table 2, entry 4) with medium styrene oxide selectivity (58.3%) (Table 2, entry 4). In comparison to other solvents, toluene showed better reaction conversion (88.2%) (Table 2, entry 6) as well as selectivity for styrene oxide (74.7%) (Table 2, entry 6). Under solvent free condition (Table 2, entry 8) no formation of styrene oxide was obtained although the conversion of the reaction was around 97.8% with 95.5 % selectivity towards the side products. Hence, toluene was found to be the most suitable solvent for this reaction and all further studies were performed in toluene.

The effect of different oxidizing agents like H_2O_2 , air and TBHP was also explored for the epoxidation of styrene using our catalytic system (Table 2). With H_2O_2 the reaction was not proceeded while with air the reaction conversion was found to be 7.2% with 100% styrene oxide selectivity. Using TBHP as oxidizing agent, maximum conversion of 88.2% was observed with 74.7% selectivity towards styrene oxide and therefore, TBHP was found to be an appropriate oxidizing agent for the mentioned chemical reaction.

The reaction temperature had a pronounced effect on styrene epoxidation as listed in Table 3. At room temperature the reaction was not proceeded as indicated by reaction conversion <1% (Table 3, entry 1). Increase in reaction temperature resulted in the increase in conversion (Table 3, entry 2, 3, 4, 5) and slightly increased in selectivity at high temperature (Table 3, entry 3, 4, 5). Temperature above 110°C was found to be detrimental for the reaction (Table

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3, entry 6) as the conversion of the styrene was decreased with slight increase in styrene oxide selectivity, perhaps due to the instability of the BuO/OH radical species at high temperature. At 110°C the reaction conversion and selectivity to styrene oxide were maximum (Table 3, entry 5), establishing it as the optimum reaction temperature for the chemical transformation.

The effect of reaction time in the epoxidation of styrene was also studied and the results are summarized in Table S1, ESI. After 4h of the reaction, the styrene conversion was found to be 55.9% with 84.4% selectivity to styrene oxide (Table S1, entry 1, ESI). Extension of reaction time from 4h to 8h led to a significant increase in reaction conversion with slight decrease in selectivity (Table S1, entry 2, ESI). However, further increase in reaction time from 8h to 12h (Table S1, entry 3, ESI) resulted in the increase of conversion with a very low selectivity towards styrene oxide may be attributed to the sequential oxidation of styrene oxide to benzaldehyde and/or phenyl acetaldehyde as the reaction proceeds.⁶¹

The influence of the amount of TBHP in the styrene epoxidation was observed and the results were summarized in Table 4. Without TBHP, the reaction was not move forward with a very low conversion of 1.1%. With the increase of amount of TBHP (Table 4, entry 1, 2, 3), the conversion increased continually from 50.9% (Table 4, entry 1) to 88.2 % (Table 4, entry 3) whereas the selectivity to styrene oxide decreased from 87.9% (Table 4, entry 1) to 74.7% (Table 4, entry 3). However, further increased in the TBHP amount (Table 4, entry 4) resulted low conversion and selectivity. All these observations clearly confirmed the requisite TBHP amount, i.e 1.5 mmol for carried out the epoxidation reaction.

In order to assess the efficiency of the present catalytic system, different Au based catalytic system was screened based on the reactivity and selectivity to epoxides (Table S2, ESI) under similar reaction conditions. The present Au/NH₂-MIL-101(Cr) exhibited excellent catalytic activity as compared to the previously reported catalysts available in the literature. The key advantages of our protocol are low catalyst dosage, facile recovery and reusability, High TOF etc. Furthermore, the high surface area of the parent MOF, it provides not only a better dispersion of the Au Nps but also controls its size which seemed to be a critical role in enhancing its catalytic activity.

The heterogeneous nature of catalyst was evaluated by removing the catalyst from the reaction medium after 4h of the reaction and then allowed the reaction to run for another 4h. No further increase in the styrene conversion was observed after the removal of the catalyst. The atomic absorption spectroscopic (AAS) analysis revealed the absence of the Au in the supernatant solution of the reaction mixture, confirming that the Au Nps were not leached out

from the NH₂-MIL-101(Cr) matrix during the reaction condition, establishing the true heterogeneous nature of the catalyst.

A plausible reaction mechanism has been proposed for the epoxidation reaction catalysed by Au/NH₂-MIL-101(Cr) in presence of TBHP. In fact the reaction was proceeded through the formation of a hydroperoxy species ((I) Scheme 2) which undergo dehydration and rearrangement to form peroxyformate intermediate ((II) Scheme 2). Styrene is then activated on the surface of Au Nps via its nucleophilic C=C group and further reacts with O-O group of peroxyformate intermediate through a side-by-side interaction to yield species (III) (Scheme 2). The final product of the reaction, i.e. styrene oxide is formed through a metalloepoxy intermediate by the transfer of oxygen to the olefinic bond of styrene. The formation of benzaldehyde may be attributed to the breaking of the C-C bond of the species (III) whereas phenylacetaldehyde is formed through isomerisation of styrene oxide.⁷⁶

The reusability of the catalyst is an important feature of heterogeneous catalyst that makes it economically preferable over homogeneous catalyst. After completion of the reaction the catalyst was separated through filtration, washed it with acetone for several times and then dried in an oven at 70°C for 5h. The catalyst was then further employed for the next catalytic runs under identical reaction condition. It was observed that the catalyst showed effective catalytic performance up to fourth catalytic cycles without any significant loss of its catalytic activity (Fig 5) which was in good agreement with the results of PXRD, FE-SEM, TEM, FT-IR analysis of the recovered catalyst. PXRD analysis (Fig 1(black)) of the recovered catalyst displayed the conservation of its crystallinity to that of the fresh one. The nanoscale morphology of the support i.e. NH_2 -MIL-101(Cr) was well maintained in the recovered catalyst as indicated by the FE-SEM analysis (Fig S5 (c), ESI). The EDS-mapping analysis of the recovered catalyst (Fig S10, ESI) further clarified the presence of Au Nps on the support after the catalytic runs. The dispersion of the Au Nps in the recovered catalyst (Fig S11, ESI) was well preserved during the chemical transformation as demonstrated by TEM analysis. The BET surface area of the recovered catalyst was found to be 947 m^2g^{-1} (Fig 3.(blue)) which was slightly lower than that of the fresh catalyst may be owing to the blockage of pores of the support by the reactant molecules. From the FT-IR analysis (Fig S6, (blue), ESI) it was observed that the chemical functionality of parent MOF remained unchanged after the catalytic cycles, confirming the robustness of the support. Finally all the results clearly signified the true heterogeneous nature of the synthesized Au/NH₂-MIL-101(Cr) material as well as the robustness of the host matrix.

4. Conclusion

The work demonstrated the Au NPs embedded on an amine-functionalized nanoscale metal-organic framework by a facile solution approach. The resultant Au/NH₂-MIL-101(Cr) exhibited excellent catalytic activity for the epoxidation of styrene in the presence of aqueous TBHP. Low catalyst dose, high turnover frequency (TOF) and reusability make this method superior to some of the reported catalytic methods available in the literature. The better catalytic activity may be owing to the high surface area of the parent MOF with high isolectric point value (IEP) and the presence of brønsted basic sites together provides a better dispersion of the catalytically active Au nanoparticles that results a better catalytic activity of the catalyst. Furthermore, the catalytic activity and selectivity. The present work also demonstrated that the chemical functionalization can significantly improves the catalytic activity of MOF materials which can be extended to other metal NPs for implementing important organic transformations.

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Captions

- 1. Fig 1.PXRD pattern of NH₂-MIL-101(Cr) (blue), Fresh Au/NH₂-MIL-101(Cr) (red) and recovered Au/NH₂-MIL-101(Cr) (black)
- 2. Fig 2. a) EDS analysis of Au/NH₂-MIL-101(Cr), b) mapping of different elements of Au/NH₂-MIL-101(Cr)
- 3. Fig 3. N₂ adsorption isotherm of NH₂-MIL-101(Cr) (red) and Au/NH₂-MIL-101(Cr) (black)
- Fig 4. (a-c) TEM images of Au/NH₂-MIL-101(Cr) (a-c), (d) HRTEM image of a Au (0) NP showing the lattice fringes and (e) size distribution of Au Nps
- 5. Fig 5. Catalyst recycling test for Au/NH₂-MIL-101(Cr)
- 6. Table 1. Effect of catalyst dosage
- 7. Table 2. Effect of solvent
- 8. Table 3. Effect of temperature
- 9. Table 4: Effect of amount of TBHP
- 10. Scheme 1. Epoxidation of styrene using Au/NH₂-MIL-101(Cr) as catalyst.
- Scheme 2. Plausible reaction mechanism for the epoxidation of styrene in the presence of Au/NH₂-MIL-101(Cr)



Fig 1 PXRD pattern of NH₂-MIL-101(Cr)(blue), Fresh Au/NH₂-MIL-101(Cr)(red) and recovered Au/NH₂-MIL-101(Cr) (black)



Fig 2 a) EDS analysis of Au/NH₂-MIL-101(Cr), b) mapping of different elements of Au/NH₂-MIL-101(Cr)



Fig 3 N₂ adsorption isotherm of NH₂-MIL-101(Cr) (red) and Au/NH₂-MIL-101(Cr) (black) and recovered Au/NH₂-MIL-101(Cr) (blue)



Fig 4 (a-c) TEM images of Au/NH₂-MIL-101(Cr) (a-c), (d) HRTEM image of a Au (0) NP showing the lattice fringes and (e) size distribution of Au Nps



Fig 5 Catalyst recycling test for Au/NH₂-MIL-101(Cr)

Table 1 Effect of	catalyst dosage ^a
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Entry	Catalyst	Conversion	Selectivity (%)			
	Dosage	(%)	Styrene oxide	Benzaldehyde	Phenylacetaldehyde	Other
	(mol%)					products
1	0.008	59.7	35.5	44.6	0.0	19.8
2	0.016	84.0	40.3	33.0	2.1	24.4
3	0.025	88.2	74.7	0.0	0.4	24.9
4	0.038	44.1	78.2	0.0	0.6	21.2
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^aReaction condition: Styrene (1 mmol), TBHP (1.5 mmol), toluene (5 mL), time (8 h), Temperature (110° C), GC conversion and selectivity.

Entry ^⁵	Solvents	Conversion	Selectivity (%)			
		(%)	Styrene oxide	Benzaldehyde	Phenylacetaldehyde	Other
				-		products
1	Acetonitrile	29.4	78.5	0.08	11.2	10.1
2	DMF	96.7	5.6	6.5	0.0	87.8
3	Acetone	7.6	85.3	14.6	0.0	0.0
4	DCM	5.1	58.3	0.0	41.3	0.2
5	Ethanol	47.1	42.7	0.0	3.4	53.8
6	Toluene	88.2	74.7	0.0	0.4	24.9
7	THF	14.5	70.2	5.7	0.0	24.0
8	Solvent free	97.8	0.0	4.4	0.0	95.5

Table 2 Effect of solvents^a

^aReaction condition: Styrene (1 mmol), TBHP (1.5 mmol), solvent (5 mL), time (8 h), Au/NH₂-MIL-101(Cr) (0.025 mol%), Reflux condition, GC conversion and selectivity

101(Cr) (0.025 mol%), Reflux condition, GC conversion and selectivity ^b H_2O_2 = No reaction, ^bAir = Conversion (7.2%), Selectivity (100%), ^bTBHP = Conversion (88.2%), Selectivity (74.7%)

Table 3 Effect of temperature^a

Entry	Temperature	Conversion	Selectivity (%)			
	(° C)	(%)	Styrene oxide	Benzaldehyde	Phenylacetaldehyde	Other
						products
1	RT	<1	18.3	0.0	0.0	81.6
2	50	1.3	32.4	34.5	1.2	31.6
3	70	30.9	73.8	0.0	10.0	16.1
4	90	53.3	73.6	0.0	1.2	25.0
5	110	88.2	74.7	0.0	0.4	24.9
6	120	66.5	76.6	0.0	0.0	23.3

^aReaction condition: Styrene (1 mmol), TBHP (1.5 mmol), toluene (5 mL), time (8 h), Au/NH₂-MIL-101(Cr) (0.025 mol%), GC conversion and selectivity

Table 4 Effect of amount of TBHP^a

Entry	Amount of	Conversion	Selectivity (%)			
	TBHP ^c	(%)	Styrene oxide	Benzaldehyde	Phenylacetaldehyde	Other
	(mmol)		-	-		products
1	0.5	50.9	87.9	0.0	0.97	11.06
2	1	61.2	84.0	0.0	1.3	14.5
3	1.5	88.2	74.7	0.0	0.35	24.9
4	3	48.4	18.2	49.5	10.0	22.1

^aReaction condition: Styrene (1 mmol), Au/NH₂-MIL-101(Cr) (0.025 mol%), toluene (5 mL), time (8 h), Temperature (110° C), ^bGC conversion and selectivity

^c Without TBHP, conversion= 1.1%



Scheme 1 Epoxidation of styrene using Au/NH2-MIL-101(Cr) as catalyst



Scheme 2 Plausible reaction mechanism for the epoxidation of styrene in the presence of Au/NH_2 -MIL-101(Cr)

Gold nanoparticles supported on nanoscale amine-functionalized MIL-101(Cr) as a highly active catalyst for epoxidation of styrene

Gold nanoparticles can effectively be incorporated on to the matrix of an amine-functionalized MIL-101(Cr) by a facile solution approach. The resulting nanocatalyst, Au/NH_2 -MIL-101(Cr) can act an as efficient heterogeneous catalyst for epoxidation of styrene in presence of tert-Butyl hydroperoxide.

