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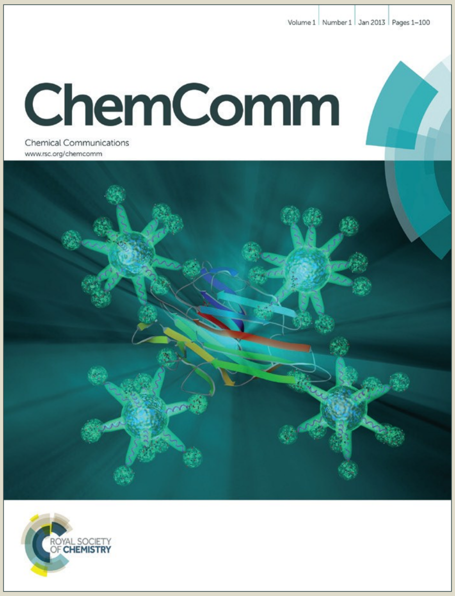

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Bentonite-Gold Nanohybrid as Heterogeneous Green Catalyst for Selective Oxidation of Silanes

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A highly efficient, environmentally benign and reusable heterogeneous bentonite-gold nanohybrid catalyst was designed and synthesized. This heterogeneous catalyst could efficaciously catalyse the oxidation of organosilanes to silanols. The reaction is 98.7% atom economic and the products were obtained in excellent yield without the formation of disiloxanes as byproduct. The catalyst was also well applicable for the gram scale preparation of silanols.

Organosilicon compounds, especially silanols, are useful synthons in various fields of organic synthesis as well as in material science.[1-6] Silanols are considered as nucleophilic partners in metal catalyzed carbon-carbon cross-coupling reactions,[7-9] hydrogen bond donors in organocatalysis,[10-12] directing groups in C-H bond activation,[13-16] and isosteres of bioactive compounds.[17,18] The classical methods for the oxidation of silanes to silanols involve the use of stoichiometric amounts of oxidants such as silver salts,[19] peracids,[20] permanganate,[21] dioxiranes,[22] osmium tetroxide,[23] oxaziridines,[24] ozone,[25] etc. But these methods are not environmentally benign because of the formation of toxic by-products and generation of disiloxanes as side product consequent from the condensation of silanols. For that reason, there is a huge demand for highly efficient catalytic systems from both environmental and synthetic perception.

Development of efficient methods which minimizes environmental problems is a great challenge for chemists in both industrial and academic research. Even though some homogeneous transition metal catalysts have emerged to overcome some of the above mentioned problems, their use is escorted with a difficulty of residual metal impurities, leading to serious problems in pharmaceutical products. In the case of silane oxidation, they have often showed inadequate practical utility.[26] Subsequently, heterogeneous catalytic systems have emerged as potential alternatives. Different nanohybrid catalyst systems were developed utilizing support materials like hydroxyapatite, carbon nanotube, amorphous carbon, etc. with anchored metal nanoparticles (Ag, Au, Pd, etc.) for the selective oxidation of silanes.[27-31] Some of these nanometal supported heterogeneous catalysts showed a major drawback of ‘leaching out’ of metal nanoparticles during the reaction leading to the formation of larger nanoparticles which in turn makes them less active. Consequently, various surface modified supports were used for the stabilization of metal nanoparticles against aggregation and to produce highly active, homogeneous size dispersed metal nanoparticles. [32,33]

In the area of heterogeneous catalysis, selection of support together with appropriate functionalization is the key factor for the effective performance of the catalyst. Bentonite is a cheap, ubiquitous and eco-friendly support material among a wide range of catalyst supports. The broken bonds on the edges of bentonite lead to the formation of free hydroxyl groups, which can be utilized for chemical modification.[34,35] When bentonite is acid activated, dealumination occurs and additional hydroxyl groups are generated in the clay skeleton, leading to the easy grafting of organic groups.[36] Among the transition metal nanoparticles, gold plays an important role in various organic transformations by making them proceed under mild conditions with high regio- and chemo-selectivities. Green and sustainable chemistry based on the catalytic activity of very small and monodispersed gold particles on a suitable support have attracted tremendous attention from the synthetic community. Owing to the structural diversity of silanols and its applications in various fields, development of reusable, easily separable and economically viable catalytic systems still remains as a great challenge.

Herein, we report a new, highly efficient, green, reusable and easily separable bentonite-gold nanohybrid as a heterogeneous catalyst for the absolute oxidation of hydrosilanes to silanols with 98.7 % atom economy and no disiloxanes as side products. By depositing gold on the acid activated bentonite functionalised with 3-mercaptopropyl) trimethoxysilane (MPTMS) and phenyltriethoxysilane (PTES),

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subsequent reduction with $NaBH_4$ led to the formation of Au nanoparticles embedded in the system. The nanoparticles then covalently form the Au-S bond with the thiol group of MPTMS leading to a stable catalyst system in total. Surface hydrophobicity of the catalyst is enhanced by introducing PTES on acidified bentonite which also favours the adsorption of substrate molecules on the catalyst surface. The thiol group in MPTMS helps in the uniform size distribution of Au nanoparticles and holds these particles strongly during the catalytic runs.

The assembly of the nanohybrid catalyst commenced with the acid activation of bentonite by refluxing bentonite with 4 N HCl for 4 h. The resultant product was then stirred with MPTMS and PTES at room temperature in dried toluene for 12 h under argon atmosphere to give organofunctionalized bentonite (Ben-MP). Finally, gold-bentonite nanohybrid (Au-MPBen) was synthesized by impregnating organo-functionalized bentonite with $HAuCl_4$ followed by reduction using $NaBH_4$ (see ESI). Then it was characterized using XRD, FT-IR, ICP-MS, XPS, TEM, etc.

The XRD spectra revealed the intercalation of MPTMS and PTES into the bentonite gallery. Acid activated bentonite (Ben-4h) showed basal spacing, 'd' value of 12.12 Å. The MPTMS and PTES grafted bentonite sample exhibited a peak at 'd' value of 65.8 Å (see ESI, SFig. 1a) which is greater than the acid activated bentonite by 54 Å. This confirmed the intercalation of MPTMS and PTES into the bentonite gallery. To give more evidence for successful grafting, FT-IR analysis of Ben-4h and Ben-MP was performed (see ESI, SFig. 1b). The peak at 3646 cm^{-1} is attributed to the structural hydroxyl stretching vibrations and the peak at 3426 cm^{-1} is assigned to the OH stretching vibration of the adsorbed water. The peak around 1051 cm^{-1} is assigned to Si-O stretching vibrations. In the organofunctionalized bentonite, peaks at 2933cm^{-1} and 1428 cm^{-1} are attributed to the antisymmetric stretching and bending vibrations of CH_2 respectively. Peak at 2565 cm^{-1} is assigned to the presence of thiol group. This revealed the existence of organic moieties in the grafted bentonite.

The presence of reduced gold nanoparticles on the organofunctionalized bentonite was confirmed by TEM analysis. Figure 1 confirmed the presence of monodispersed, spherically shaped gold nanoparticles with an average size of 4 nm on the support.

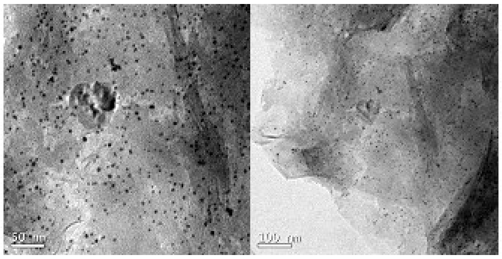


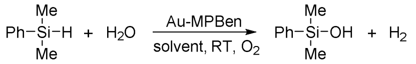
Fig. 1 TEM images of Fresh Au-MPBen (scale bar=50 nm and 100 nm).

Usually small sized nanoparticles have the tendency to aggregate, leading to the formation of inactive catalyst. But in this case, the presence of organic thiol moiety on the clay surface facilitates the monodispersion and stabilization of gold nanoparticles.

The gold concentration on the catalyst was measured by ICP-MS analysis and it was found to be 5.24×10^{-7} M in 1 mg of catalyst. The electronic state of the Au center was investigated using XPS analysis (see ESI, SFig. 2) which revealed that all the Au species in the catalyst were present in its metallic state, corresponding to the binding energies of 88.1 and 91.8 eV, which are characteristics of the 4f $^{7/2}$ and 4f $^{5/2}$ peaks of Au(0).

The catalytic performance of Au-MPBen nanohybrid was explored for the oxidation of silanes. The silane-silanol transformation conditions were optimized by selecting dimethylphenylsilane as the model substrate and the results are presented in table 1. Initially the reactions were carried out by changing the ratio of THF and H_2O and the optimized solvent condition was found to be a mixture of THF and H_2O in a ratio of 7:3. Then the reactions were performed in the presence and absence of O_2 as well as in the open air which revealed that O_2 accelerated the rate of silane oxidation (Table 1, entries 4, 5 & 7).

Table 1 Optimization of solvents in the oxidation of silanes



$$PhSi(Me)_2H + H_2O \xrightarrow[\text{solvent, RT, } O_2]{\text{Au-MPBen}} PhSi(Me)_2OH + H_2$$

Entry	Solvent	Time (h)	Yield (%)
1	THF	24	0
2	THF/H_2O (9:1)	2.5	99
3	THF/H_2O (1:1)	1	99
4	THF/H_2O (7:3)	0.5	99
5	THF/H_2O (7:3)	5	99[a]
6	H_2O	24	95
7	THF/H_2O (7:3)	3	99[b]

Reaction conditions: phenyldimethylsilane (0.37 mmol), Au-MPBen (1 mg, 52μmol%), solvent (1 mL), O_2 balloon (1 atm). [a] Without O_2, [b] With open air.

Moreover it was observed that water played an important role in the oxidation reactions of silanes and no silanol was detected in the absence of water (Table 1, entry 1). When the reaction was carried out using water alone as solvent, silanol was obtained in 95% yield but the reaction took 24 h for completion without the formation of disiloxane (Table 1, entry 6). Finally the optimized condition for the silane oxidation with Au-MPBen catalyst was found to be a combination of 0.37 mmol of silane in a 7:3 mixture of THF:H_2O (1 mL) in presence of 1 atm of O_2. This reaction afforded dimethylphenylsilanol in 99 % yield within 30 min (Table 1, entry 4) with 98.7 % atom economy (see ESI). It's worthy to mention that disiloxane was not detected as a by-product and notably further purification was not required for this reaction.

To highlight the supremacy of Au-MPBen catalyst, the above reaction was performed using Ben-4h, Ben-MP, Au-Ben (gold nanoparticle impregnated bentonite with no additional stabilizing agents), Au-MPBen catalytic systems and $AuCl_3$ (Table 2). When the oxidation of dimethylphenylsilane was performed with Ben-4h/ Ben-MP as catalysts, silanol was not formed even after 24 h. When Au-Ben was used as the

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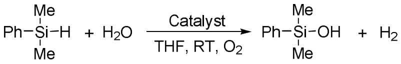
catalyst, though the conversion of silane to silanol occurred, Au nanoparticles were found to leach out from the support, decreasing its credibility as a viable catalyst. The oxidation of silane with 0.1 mol % loading of $AuCl_3$ gave less than 10% of silanol. Only the Au-MPBen gave efficient conversion of silane to silanol. The covalent linkage of Au nanoparticles to the support in Au-MPBen resulted in a stable nanohybrid assembly thereby preventing leaching of Au nanoparticles.

Table 2 Comparison of various catalysts in the oxidation of silanes



$$\mathrm{Ph{-}\overset{Me}{\underset{Me}{Si}}{-}H} + H_2O \xrightarrow[\text{THF, RT, } O_2]{\text{Catalyst}} \mathrm{Ph{-}\overset{Me}{\underset{Me}{Si}}{-}OH} + H_2$$

Entry	Catalyst	Yield (%)
1	Ben-4h	0
2	Ben-MP	0
3	Ben-Au	90
4	Au-MPBen	99
5[a]	$AuCl_3$	< 10 %

Reaction conditions: phenyldimethylsilane (0.37 mmol), catalyst (1 mg), THF:H_2O / 7:3 (1 mL), 1 h, [a] $AuCl_3$ (0.1 mol %)

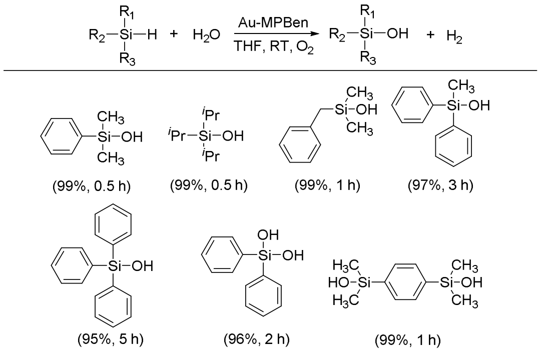
To further prove the stability of Au nanoparticles in Au-MPBen, the oxidation of dimethylphenylsilane under the optimized condition was performed. After 15 min, half of the reaction mixture was siphoned out and the catalyst was removed by centrifugation. This reaction was kept for stirring to monitor the progress of the reaction in the absence of the catalyst. The remaining half of the reaction mixture was kept stirring without disturbance. After an additional 30 min, both the reactions were analysed. The reaction was completed in the gold-nanohybrid containing sample whereas no further progress was detected without Au-nanohybrid indicating the absence of leached out gold nanoparticles in the reaction mixture. This proves the reliability of the Au-nanohybrid as a stable catalyst.

To further confirm the role of both water and oxygen in the silane oxidation reaction, two experiments were carried out. While the first reaction was performed using dried THF under oxygen atmosphere, the second reaction was run under inert atmosphere in the presence of water. It was observed that the first reaction totally failed to convert the silane to silanol. The second reaction was completed very slowly (5 h) in comparison with the optimized reaction time which was less than 30 min. But when oxygen was bubbled through the second reaction mixture and water was added to first reaction mixture, oxidation was completed within 30 min. From these observations, it is evident that water plays an important role in silane oxidation using gold-bentonite nanohybrid as catalyst and oxygen enhances the reaction rate of silane oxidation.

To elucidate the role of water as the prominent oxygen source, we carried out the oxidation reaction of phenyldimethylsilane using D_2O instead of H_2O and confirmed with the help of mass spectroscopy that D atom was transferred to the product. The same reaction was also run with CD_3OD which afforded the corresponding deuteriated methoxysilane and these observations revealed that water acts as oxidant in the silane oxidation reaction (see ESI). Based on the above results, it is proposed that the reaction occurs through the insertion of Si-H bond on AuNPs, followed by nucleophilic attack of water molecule producing silanol together with the generation of H_2. Oxygen adsorbed on to the surface of AuNPs enhances the silane oxidation by increasing the electron deficiency of AuNPs through charge transfer from AuNPs to O_2 for Si-H bond activation of silanes.[37]

The generality of the silane-silanol oxidation reaction using Au-MPBen was established and the details are presented in table 3. The sterically hindered triisopropylsilane was quantitatively oxidized to triisopropylsilanol in 2 h. Benzyl dimethylsilanol was obtained by the reaction of benzyl dimethylsilane in 99 % yield within 1 h. Diphenylmethylsilane was also converted to the corresponding silanol in 97 % yield within 3 h. Oxidation of deactivated triphenylsilane afforded triphenylsilanol in excellent yield (95 %) in 5 h. In addition, diphenylsilane was quantitatively transformed to diphenyl silanediol and 1,4-bis(dimethylsilyl)benzene was doubly oxidised into the corresponding bis-silanol within 1 h in excellent yield (99 %). Moreover no disiloxane was detected as by-product for all of the examples.

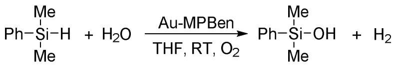
Table 3 Au-MPBen catalysed oxidation of various silanes



Reaction conditions: silane (0.37 mmol), Au-MPBen (1 mg, 52 μmol %), THF:H_2O / 7:3 (1 mL), O_2 (1 atm), RT.

The recyclability of Au-MPBen for the silane oxidation was investigated by performing five consecutive reactions (Table 4) using the same catalyst which was recovered by simple centrifugation (see ESI). After fifth run, TEM analysis showed that the morphology of the catalyst remained unchanged (see ESI, SFig. 3). These observations confirmed the higher efficacy and stability of Au-MPBen nanohybrid catalyst.

Table 4 Recycling experiments of Au-MPBen catalyst



$$\mathrm{Ph{-}\overset{Me}{\underset{Me}{Si}}{-}H} + H_2O \xrightarrow[\text{THF, RT, } O_2]{\text{Au-MPBen}} \mathrm{Ph{-}\overset{Me}{\underset{Me}{Si}}{-}OH} + H_2$$

Catalyst	Fresh	Reuse 1	Reuse 2	Reuse 3	Reuse 4
Yield (%)	99	94	95	94	96

Reaction conditions: phenyldimethylsilane (0.37 mmol), Au-MPBen (1 mg, 52 μmol %), THF:H_2O / 7:3 (1 mL), 30 min, O_2 (1 atm), RT.

This catalytic system was also found applicable to the gram scale synthesis of silanol (Scheme 1). 1 g of dimethyl phenyl

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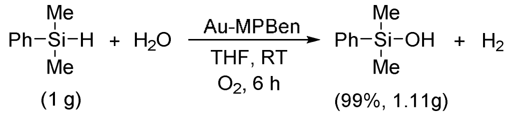
silane was successfully transformed to dimethylphenylsilanol in 99% yield (1.11 g) where the turn over number (TON) and turn over frequency (TOF) were calculated as 1990 and 332 h^{-1} respectively. But based on the fraction of gold nanoparticles that are exposed to the substrate, the TON and TOF values reached 8844 and 1475 h^{-1} respectively (see ESI). Moreover the reaction is 98.7% atom economic and environmentally benign.



$$\mathrm{PhSiMe_2H} + H_2O \xrightarrow[\text{THF, RT, } O_2\text{, 6 h}]{\text{Au-MPBen}} \mathrm{PhSiMe_2OH} + H_2$$

Scheme 1 Gram scale oxidation of phenyldimethylsilane using Au-MPBen.

In conclusion we have successfully developed a new, green and reusable, heterogeneous bentonite-gold nanohybrid catalyst, Au-MPBen which can be prepared from readily available cheap reagents, under mild reaction conditions through simple processes. This nanohybrid catalyst effectively oxidised various aromatic, aliphatic and sterically hindered silanes to silanols in excellent yields without the formation of disiloxanes. The present silane oxidation with Au-MPBen catalyst is environmentally benign, 98.7% atom economic and proceeded with low catalyst loading. This catalyst was also applicable for the gram scale preparation of silanols. We are currently investigating the applicability of the catalyst for other organic transformations.

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