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Oxidation of olefins using atmospheric oxygen atoms initiated by tert-butylhydroperoxide or hydrogen peroxide with silver nanoparticles deposited on MCM-41 as catalysts

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Silver nanosized particles were grown on the surface and in the channels of mesoporous silica (MCM-41) by stirring a mixture of AgNO₃ and polyvinylpyrrolidone (PVP) in ethylene glycol in a 1:20 weight ratio with MCM-41 for 1h. The heterogeneous product was analysed by BET surface area and X-ray powder diffraction measurements, as well as TEM images which indicated that 5- to 20-nm sized Ag particles were on the surface of MCM-41. The dried material, suspended in a mixture of 1,2-dichloroethane and acetonitrile and in the presence of ¹BuOOH held at 80 °C for 24 h, was capable of the oxidation of the olefins (Z)-cyclooctene, cyclohexene, styrene and indene resulting in a variety of oxidized products. Comparable oxidation was also accomplished in a green solvent mixture consisting of 3%NaCl dissolved in H₂O and ¹BuOH (1:1 by volume). The catalyst was active for five sequential cycles. After the first cycle, H₂O₂ instead of ¹BuOOH could be used as the radical initiator as the Ag nanoparticles were passivated by the formation of AgCl on the surface. This research illustrates a method of oxygen activation allowing for the transfer of an oxygen atom from the atmosphere onto an olefin, presumably via the formation of a peroxide radical.

Introduction

The use of *tert*-butylhydroperoxide (TBHP) and H_2O_2 to form epoxides from olefins using various homogenous catalysts such as $MoO_2(OPR_3)_2$, M = Mo or W,¹⁻³ and tetranuclear $Mo_4O_4(O_2PR_2)_4$ and heterogenous systems such as nano-sized particles of titaniumcontaining mesoporous molecular sieves⁴ and two-dimensional, hydrogen bonded cross-linked molybdenum(VI) network polymers have been previously reported.⁵ In this article, an oxygen atom transfer reaction where atmospheric oxygen is used to react with olefins to form epoxides in the presence of a heterogenous catalyst consisting of silver nanoparticles deposited inside of and on the surface of MCM-41 is detailed.

There are many literature examples of oxygen atom transfer (OAT) reactions using transition metal catalysts and H_2O_2 and N_2O as oxygen sources.⁶ Recently, other more complex molecules have been utilized to effect OAT such as iodosobenzene (PhIO),⁷ dimethyldioxirane (DMDO),⁷ 2-tert-butylsulfonyliodosobenzene (sPhIO),⁸ all requiring various iridium catalysts, and AcOOH and KHSO₅ which require a manganese based metalloenzyme to accomplish benzylic oxygenation and olefin epoxidation.⁹ In these cases, the nature of the OAT agent and/or the catalyst is complex and certainly cannot be considered suitable from a "green" chemistry¹⁰ perspective. Epoxidations with gold particles supported on graphite, TiO₂ and SiO₂ surfaces^{11, 12} and on polyoxometalates¹³ have also been reported. There have also been many publications recently utilizing TBHP as an oxygen source but these have all been accomplished stoichiometrically.¹⁴⁻²² It is clearly not efficient to have to synthesize TBHP in order to effect stoichiometric oxygen atom transfer, though this consideration is not restricting if that is the only way to synthesize the desired compound.

This report details the synthesis and characterization of Ag nanoparticles deposited onto MCM-41 and studies on their use as oxidation catalysts with TBHP. Previous studies demonstrated the synthesis of Ag nanoparticles using PVP²³ and the formation of Ag wires inside of mesoporous silica including MCM-41.²⁴⁻²⁷ Interestingly, the adventitious formation of AgCl on the surface of recycled Ag nanoparticle catalyst permitted the use of H₂O₂ as an initiator.

Experimental

General method

A Scintag XDS2000 powder diffractometer was used to confirm the formation of MCM-41 and the deposition of silver particles. The BET surface area of MCM-41 and its derivatives were measured on an ASAP 2000 physisorption analyzer. TEM images were taken with a JEOL-JEM-2010 transmission electron microscope. The thermal stability of Ag_{np} -MCM-41 was tested using a Shimadzu TGA-50. A Shimadzu GCMS-QP5050 was used to identify substrates and their oxidation products resulting from catalysis. Infrared spectra were obtained on a PerkinElmer Frontier FTIR. Most chemicals including polyvinylpyrrolidone (PVP, mw=55000), silver nitrate (99%),

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tetraethyl orthosilicate (TEOS, 98%), hexadecyltrimethylammonium bromide (CTAB, 99%), cyclohexene (99%), styrene (99%), indene (99%), dodecane (99%) were purchased from Sigma-Aldrich. Ethylene glycol (EG) and sodium hydroxide (NaOH, 98.0%) were purchased from Fisher Scientific. (Z)-cyclooctene (95%), tert-butyl hydroperoxide (TBHP, 70% solution in water), and sodium chloride were purchased from Alfa Aesar, Acros Organics and Macron respectively. All solvents were used as received.

Preparations

Synthesis of MCM-41. MCM-41 was synthesized with CTAB as the template in the compositional ratio: 1.0 TEOS/0.1 CTAB/0.3 NaOH/60 H_2O as reported previously.²⁸ The mixture was kept unstirred in a Parr bomb at 110 °C for 96h, filtered, washed with deionized water and dried in an oven at 80 °C. MCM-41 was obtained by calcining the solid at 550 °C for 24h.

Synthesis of Ag_{np}-**MCM-41.** The nano-sized Ag particles were prepared, eqn 1, based on an adaptation to a literature procedure²⁹ where instead of preparing solutions of Ag nanoparticles, Ag⁺ was reduced with PVP in ethylene glycol in the presence of already formed MCM-41.^{30, 31} The reaction of Ag⁺ and PVP in solution is believed to result in PVP-capped Ag nanoparticles.³² 0.047g AgNO₃ (0.27 mmol) were dissolved in 20 mL of ethylene glycol, to which 0.98 g PVP (0.018 mmol) and 0.30 g MCM-41 were subsequently added. The mixture was stirred at room temperature for 30 min and then heated at 180 °C for 1h. Upon filtration and washing, a brownish yellow powder (0.39 g) was obtained which was dried at 100 °C in a furnace. This material referred to as Ag_{np}-MCM-41 was used as the catalyst. The cured Ag_{np}-MCM-41 (0.34g) was prepared by calcination at 500 °C under air for 4 hours.

AgNO₃ +
$$N = 0$$
 (PVP) \xrightarrow{EG} Ag_{ap}-MCM-41-PVP (1)

Catalytic epoxidation reaction. 0.05 g Ag_{np} -MCM-41 were placed in a two-neck flask fitted with a condenser, and 4.6 mmol of substrate in a 1,2-dichloroethane (5.0 mL) and acetonitrile (0.5 mL) solution were added. Next, 0.3 mL dodecane (2.9 mmol) which is the internal standard and 0.03 mL 70% TBHP (0.24 mmol) in H₂O were added. The mixture was heated to 80 °C and kept there for three days. For each reaction, two samples, after 24h and then 72h were collected for GC-MS measurements. The catalyst was recovered by filtration and washed first with 1,2-dichloroethane and then acetonitrile. A white solid was obtained and dried in a furnace at 100 °C for 4-5 hours. The recycled catalyst was then used under the conditions mentioned above with freshly loaded reactants. This recycling procedure was repeated four times. A comparison reaction using (Z)-cyclooctene as the substrate was conducted under pure nitrogen instead of air.

Results

Catalysts characterization. The synthesis of MCM-41 followed a literature procedure²⁸ but the deposition of the Ag_{np} consisted of an

adaptation. Ag⁺ was reduced by ethylene glycol with the added PVP regulating the size of the nanoparticles, the reduction growth rate and hindering agglomeration.²⁹ A TGA curve on the almost dried material, Fig. S1, revealed a small weight loss of 1.2% up to 150 °C due to solvent residue and then decomposition from 250 to 470 °C, resulting in a weight loss of 18.8% presumably due to organic combustion.

As noted previously, the nature of the particles can be controlled by varying the reduction time, Ag⁺ and PVP concentrations, and temperature²⁹ and our synthetic conditions produced the most active catalyst. The final cured product did contain some PVP sticking to the surface of the desired Ag_{np} -MCM-41 as the product mass of 0.34 g (i.e., for the cured product) was slightly more than the theoretical of 0.33 g. Calcining at 550 °C for 24h did not remove this but the product did change color after use as a catalyst suggesting that adsorbed PVP could be removed by washing. Transmission electron microscope. The TEM images of synthesized Agnp-MCM-41 indicated that spherical silver particles were found deposited inhomogeneously on the surface of MCM-41 with diameters mostly ranging from 5 nm to 20 nm as shown in the particle size distribution displayed as the inset in Figure 1. However, some particles are at 100 nm (Figure 1b). The MCM-41 channels were measured to be around 3.1 nm wide which is consistent with literature results. Silver particles were also found inside the MCM-41 channels (Figure 1c). The recycled Agno-MCM-41 material has larger particles (50-200 nm) with a few particles found under 50 nm in diameter (Figure 1d). This is probably due to the agglomeration of silver particles during the 72h reaction.³³

Powder X-ray diffraction. The formations of MCM-41 and silver particles were also confirmed by powder X-ray diffraction spectroscopy. The signals from MCM-41 are much stronger than those of silver particles as only 10% of silver to MCM-41 by weight was used in the reduction process (Figure 2). The signal-to-noise ratio is weak for Ag_{np} -MCM-41 probably due to organics (PVP) from the reduction reaction. This ratio can be slightly enhanced by calcination at 500 °C for 4h which results in the removal of organics. The 2-theta signals at 38.1°, 44.5°, 64.4° and 77.5° are the (1,1,1), (2,0,0), (2,2,0) and (3,1,1) indexed planes for Ag particles.³⁴

After the catalytic reaction, the spectrum for recycled Ag_{np} -MCM-41 indicated formation of AgCl with 2-theta peaks at 27.8° (1,1,1), 32.2° (2,0,0), 46.1° (2,2,0).^{35, 36} There was also a peak at 18.1° which is not observed in the spectrum when the reaction is conducted in a mixture of 3%NaCl in H₂O/^tBuOH as solvent, Fig. S2. Additionally, only the FTIR spectrum of the solid catalyst recycled from the dichloroethane/acetonitrile solvent mixture contains two absorptions at 1151 and 1206 cm⁻¹ perhaps indicating the presence of C-O bonds, Fig. S3. It is possible that a polyether compound formed in the reaction, perhaps PEG, coating the Ag_{np}. A study on the synthesis of silver nanoparticles in PEG assigned a 20 peak at 19° to PEG on the silver surface.³⁷

The presence of AgCl was also confirmed by a qualitative analysis method. A white suspension was observed upon addition of a few drops of HNO₃ to the filtrate from recycled Ag_{np} -MCM-41 and an ammonia solution mixture. Silver chloride has been reported to



Figure 1. TEM image of Ag_{np}-MCM-41 (a, b, c) and recycled Ag_{np}-MCM-41 (d).

form on silver particles during catalytic ethylene epoxidation reactions.³⁸ Therefore, AgCl formation, evident at the end of a catalytic cycle, is due to the presence of chlorinated solvents reacting with Ag_{np}.

BET surface area test. BET measurements on the initially prepared MCM-41 established a surface area of 925 m²/g which is consistent with literature results.²⁸ With Ag_{np}-MCM-41, silver particles in the mesoporous channels and on the surface decreased the surface area to 338 m²/g. It has been reported that 1% Ag nanowires in MCM-41 channels decreased the surface area from 965 m²/g to 751 m²/g.³⁹ The possibility that organics from the silver reduction process, coating the surface or deposited within the channel in Ag_{np}-MCM-41, also contributed to the surface area decrease cannot be ruled out. The surface area further decreased to 208 m²/g for the recycled Ag_{np}-MCM-41 material.



Figure 2. Powder X-ray diffraction of Ag_{np} -MCM-41 (top), cured Ag_{np} -MCM-41 (middle) and recycled Ag_{np} -MCM-41 from 1,2-Dichloroethane-acetonitrile (10:1) solvent (bottom). \blacktriangle : peaks of Ag, \bigstar : peaks of AgCl.

Table 1. (Z)-cyclooctene epoxidation catalyzed by Ag _{np} -MCM-41 or cured
Ag _{nn} -MCM-41 with TBHP as initiator

Sub				
Period	Catalyst	Weight (mg)	Conversion (%)	Selectivity (%)
24h	Ag _{np} -MCM-41 (1 st cycle)	51	16.9	86.2
	Ag _{np} -MCM-41 (2 nd cycle)	48	35.2	85.1
	cured Agnp-MCM-41	50	27.8	86.6
72h	Ag _{np} -MCM-41 (1 st cycle)	52	74.8	96.8
	Ag _{np} -MCM-41 (2 nd cycle)	49	67.3	99.4
	Ag _{np} -MCM-41 (3 rd cycle)	42	63.6	96.1
	Ag _{np} -MCM-41 (4 th cycle)	37	67.7	98.9
	Ag _{np} -MCM-41 (5 th cycle)	26	61.8	97.2
	cured Ag _{np} -MCM-41	50	59.7	96.1

Catalysis

Epoxidation of (Z)-cyclooctene to (1S,8S)-9-

oxabicyclo[6.1.0]nonane. (Z)-cyclooctene, in the presence of the Ag_{np} -MCM-41 catalyst under the stated experimental conditions, reacted to form epoxide products (16.9% conversion, 86.2% selectivity) after a 24h period (Table 1). These values increased to 74.8% and 96.8% respectively after 72 hours. Since insufficient TBHP (5%) was used in the reaction, molecular oxygen from the air is the major oxygen atom source for the formation of epoxides as noted previously with studies on gold nanoparticles.¹³ Chlorine atoms can also serve as promoters for ethylene epoxidation by modifying the electronic environments and number of active sites on the surface of a silver nanopowder catalyst.⁴⁰ This could explain the better conversion (35.2%) observed for the recycled Ag_{np} -MCM-41.

The Ag_{no}-MCM-41catalyst was recycled four times and remained active with a noteworthy selectivity to epoxide of over 95% after a 72h period. The decrease in conversion is likely due to the loss of catalytic particles during the recycling process. The experimental conditions utilized to recycle the catalyst, specifically drying in a furnace at 100 °C for 4-5 hours, are not sufficient to remove organics adsorbed either on the surface or within the channels of Ag_{nn}-MCM-41 as observed by the 25.3% decrease in weight measured by TGA, see Fig. S4. Reductions in weight due to adsorbed molecules within MCM-41⁴¹ and also on functionalized MCM-41⁴² have been previously described. The cured Ag_{no}-MCM-41 sample resulted in a lower conversion (59.7%) during a 72h period probably because the silver particles sintered upon calcination at 500 °C. An attempt to use H₂O₂ instead of TBHP as the initiator was not successful with freshly prepared Ag_{np} -MCM-41 since H_2O_2 decomposed immediately upon addition of the catalyst. However, the H₂O₂ initiated reaction worked with recycled catalyst resulting in a 76.7% conversion and 88.1% selectivity to (1S,8S)-9oxabicyclo[6.1.0]nonane. As confirmed by powder X-ray diffraction and qualitative analysis of the recycled material, silver chloride forms and may have covered the surface of the silver nanoparticles, preventing H_2O_2 decomposition on a pure silver atom surface.

There is a great difference in the rates of the reaction depending on if they are conducted under oxygen or nitrogen as a plot of

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unerent solvents"		
Solvents	Conversion (%)	Selectivity (%)
1,2-Dichloroethane- acetonitrile (10:1)	16.9	86.2
1,2-Dichloroethane	17.1	89.9
Hexane	0.2	88.9
Ethanol	0.2	82.0
T-butanol	0.1	75.5
Toluene	2.5	67.6
3% NaCl in water-tert- butanol (1:1)	16.2	86.3

*Reaction condition: 4.6 mmol (Z)-cyclooctene, 0.05 g Ag_np-MCM-41, 0.24 mmol TBHP, 5.5 mL solvent, 80 °C, air, 24h.

conversion rate for the production of (1S,8S)-9-

oxabicyclo[6.1.0]nonane illustrates, Fig. S5. Essentially, oxidation products under nitrogen were not detected in the first 1h of reaction and only a 1.1% conversion resulted after 5h. In comparison, the reaction under air is faster with a 3.3% conversion during a 5h period. This suggests that (15,85)-9-

oxabicyclo[6.1.0]nonane is mostly generated through the proposed free radical mechanism, Scheme 1, which requires atmospheric oxygen. The decomposition of THBP to generate free radicals is usually considered the rate determining step.⁴³ Conducting thereaction under pure nitrogen for longer periods resulted in 5.8% (24h) and 6.5% (72h) conversions, conclusively demonstrating that oxygen molecules from the air participate and oxidize (Z)-cyclooctene in the reaction.

Solvents effect. Solvents were found to affect the efficiency of (Z)-cyclooctene epoxidation. Similar results were reported for a gold catalyst.¹³ Catalytic reactions carried out in pure 1,2-dichloroethane or the 1,2-dichloroethane-acetonitrile (10:1) solvent mixture showed higher conversions compared to reactions conducted in hexane, ethanol and t-butanol (Table 2). The use of toluene is not appropriate as approximately 1.6% of toluene was oxidized to benzaldehyde (68.3%) and benzyl alcohol (28.0%) during a 24h

period. These reactions can also be efficiently conducted in a more green solvent⁴⁴ mixture consisting of 3%NaCl in a $H_2O/^tBuOH$ (1:1 by volume) solvent mixture (Table 2).

Ag_{np}-MCM-41 catalysis on other substrates containing C=C bonds. Given the high selectivity to form the oxidized product with (Z)cyclooctene, reactions with other substrates containing C=C bonds were also explored, namely cyclohexene, styrene and indene. The results indicate that the selectivity of the products, obtained from oxidation reactions catalysed by Ag_{np}-MCM-41, vary depending on the substrate (Table 3). A high conversion (93.6%) in a 24h period

was observed for cyclohexene with 68.3% selectivity to 2cyclohexen-1-one and 24.8% to 2-cyclohexen-1-ol. The desired epoxide, 7-oxabicyclo[4.1.0]heptane, accounted for 3.2% of the products obtained, a much lower desired selectivity than that for the (Z)-cyclooctene reaction. Benzaldehyde (50.8%) and benzeneacetaldehyde (38.4%) were the two major products from oxidation of styrene under similar conditions. The oxidation of indene catalysed by Ag_{np} -MCM-41 resulted in a decent yield of 1,3dihydro-2H-inden-2-one in a 24h period with a high selectivity (84.6%) determined by GC-MS.

Mechanism

A radical mechanism for (Z)-cyclooctene epoxidation catalysed by the MCM-41 supported silver nanoparticles catalyst (Scheme 1) similar to what was noted previously is proposed.^{11, 45, 46} The reaction is initiated by t-BuO· or t-BuOO· radicals resulting from the thermolysis of TBHP on the surface of silver particles.⁴⁷ A hydrogen atom is then abstracted from (Z)-cyclooctene by the radical to form an allylic radical 1, followed by an oxidation reaction with atmospheric oxygen atoms to form radical 2. Radical 2 can abstract a hydrogen atom from (Z)-cyclooctene, resulting in a cyclooctene hydroperoxide 3 and regenerating radical 1. Cyclooctene hydroperoxide could decompose to form an enone product,¹² or to form an HO· radical and a radical 4 on the surface of the silver nanoparticles. 2-Cycloocten-1-ol product forms via hydrogen abstraction from (Z)-cyclooctene by radical 4. Radical 4 could also attack the C=C bond of (Z)-cyclooctene to form an intermediate 5, resulting in the desired epoxide product via cleavage.

Table 3. Ad MCM-41	catalysis on	different substrates	containing	C=C bonds initiated by TB	SHP*
	cataly 515 Off	annerent Substrates	contraining		

Substrate	24h		72h	
	Conversion (%)	Selectivity (%)	Conversion (%)	Selectivity (%)
(Z)-cyclooctene	16.9	Cis-9-oxabicyclo[6.1.0]nonane: 86.2	74.8	Cis-9-oxabicyclo[6.1.0]nonane: 96.8
		2-Cycloocten-1-ol: 1.5		2-Cycloocten-1-ol: 0.3
		2-Cycloocten-1-one: 9.1		2-Cycloocten-1-one: 2.7
Cyclohexene	93.6	7-Oxabicyclo[4.1.0]heptane: 3.2	99.5	7-Oxabicyclo[4.1.0]heptane: 0.7
		2-Cyclohexen-1-ol: 24.8		2-Cyclohexen-1-ol: 18.1
		2-Cyclohexen-1-one: 68.3		2-Cyclohexen-1-one: 59.7
Styrene	45.7	Benzaldehyde: 50.8	86.5	Benzaldehyde: 35.9
		Benzeneacetaldehyde: 38.4		Benzeneacetaldehyde: 25.3
Indene	24.6	1,3-Dihydro-2H-inden-2-one: 84.6	66.1	1,3-Dihydro-2H-inden-2-one: 62.2
*Reaction condition: 4.6 mmol substrate, 0.05 g Ag _{np} -MCM-41, 0.24 mmol TBHP, 5 mL 1,2-dichloroethane, 0.5 mL acetonitrile, 80 °C, air.				

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To test for the heterogeneity of the reaction and the stability of Ag_{np} on MCM-41 during the reaction, a hot filtration at 80 °C was performed after 24h of reaction.^{48, 49} The filtrate was stirred for another 48h, resulting in a 64.0% conversion which is lower than the 74.8% conversion after 72h for a standard reaction conducted without filtration, Fig. S6. This demonstrates that catalyst particles leached out into the solution during reaction. In comparison, the filtrate from a cold filtration, conducted at room temperature, resulted in a lower conversion of 46.0%. This reveals that the leached silver catalyst nanoparticles can be reabsorbed onto the solid to some extent when the reaction cools down to room temperature.

Conclusion

Silver nanoparticles supported on mesoporous MCM-41 have been synthesized via the reduction of AgNO₃ by ethylene glycol in the presence of PVP. The catalytic particles are found to be located in the channels and on the surface of MCM-41. With substoichiometric TBHP (5%) as the initiator, the catalyst is capable of using oxygen atoms from the atmosphere for the epoxidation of (Z)-cyclooctene. The catalyst is recyclable with selectivity to the desired epoxide cis-9-oxabicyclo[6.1.0] nonane higher than 85% and was found to have AgCl on the surface of the Ag nanoparticles which allowed for the use of H_2O_2 as radical initiator. Other alkenes, such as cyclohexene, styrene and indene, resulted in a variety of oxidized products. Under reaction conditions, silver particles dissociated off of the Ag_{np}-MCM-41 material and these were also capable of catalysis.

Supplementary materials

Fig. S1. TGA curve of freshly prepared Ag_{np}-MCM-41 under air at a heating rate of 10 °C/min. Fig. S2. Powder X-ray diffraction of recycled Ag_{np}-MCM-41 from an H2O/tBuOH (1:1) solvent mixture containing 3% NaCl and a 1,2-dichloroethaneacetonitrile (10:1) solvent mixtures. Fig. S3. Infrared spectra of Ag_{np}-MCM-41, recycled Ag_{np}-MCM-41 from a 1,2dichloroethane-acetonitrile (10:1) solvent mixture and recycled Ag_{np}-MCM-41 from an H2O/tBuOH (1:1) solvent mixture containing 3% NaCl. Fig. S4. TGA curve of recycled Agnp-MCM-41 under air at a heating rate of 10 °C/min. Fig. S5. Comparison of Agnp-MCM-41 catalyzed (Z)-cyclooctene epoxidation rate for the first 5h of reaction conducted under air and under nitrogen. Fig. S6. Comparison of (Z)-cyclooctene epoxidation rates for solutions that were hot filtered and cold filtered to remove solid Ag_{np} -MCM-41 after 24h of reaction, to the rate for a solution which was not filtered.

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Scheme 1. Proposed mechanism for (Z)-cyclooctene epoxidation on MCM-41 supported Ag catalyst.

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Oxidation of olefins using atmospheric oxygen atoms initiated by tertbutylhydroperoxide or hydrogen peroxide with silver nanoparticles deposited on MCM-41 as catalysts

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Graphical Abstract



The 20 word sentence

Silver nanoparticles on MCM-41 oxidize olefins using atmospheric oxygen initiated by peroxides with 3% NaCl in $H_2O/^tBuOH$ as solvent.