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Hydrophobicity induced vapor-phase oxidation of propene over gold supported on titanium incorporated hybrid mesoporous silsesquioxane

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Received (in Cambridge, UK) 25th September 2002, Accepted 17th October 2002
First published as an Advance Article on the web 5th November 2002

Gold nanoparticles supported on highly hydrophobic ethane bridged Ti incorporated mesoporous organosilica are reported for enhanced vapor phase epoxidation of propene using H_2 and O_2.

The synthesis of a new class of hybrid silsesquioxane mesophases with integral organic functionality has become a rapidly expanding area because of their potential applications especially in optoelectronics, sensing, enantioselective separation, catalysis and adsorption.[1–4] This class of material necessarily incorporates the organic fragment into the framework as molecularly dispersed bridging ligands that enlarge the synergistic properties derived from the molecular-scale mixing of organic and inorganic components.[5,6] This opens a new route for the engineering of mesoporous materials with hydrophobic properties wherein the concentration of hydrophobic species are not limited as in the case of conventional mesoporous materials (M41s-type). The main objective of the present work is to take advantage of the hydrophobicity of the material in the well-known catalytic reaction of the vapor phase epoxidation of propene (C_3H_6) to highly commercially viable propene oxide (PO) using hydrogen and oxygen. Industrially PO is produced using the chlorohydrin and hydroperoxide processes. The first is not environmentally friendly while the other has the disadvantage of producing an equimolar amount of by-products.[7] So, extensive efforts have been made to develop an alternative direct gas-phase epoxidation process. Gold catalyzed epoxidation of propene using H_2 and O_2 opened a new stage of the PO synthesis. In a series of papers, the vapor phase epoxidation of propane over highly dispersed nanosize Au particles supported on TiO_2, TiO_2/SiO_2, TS-1(2), Ti-β , Ti-MCM-41 and Ti-MCM-48 is reported with effective utilization of hydrogen.[8–13] However, the strong constraint is low conversion of propene and rapid deactivation with PO selectivity (> 90%).

We report here for the first time the vapor phase epoxidation of propene over gold supported on titanium containing hydrophobic hybrid mesoporous ethane bridged silsesquioxane for enhanced catalytic activity accompanied with improved PO selectivity and considerably lower H_2 consumption.

Highly ordered titanium-containing mesoporous hybrid silsesquioxane was synthesized according to our modified procedure.[1] BTMSE [1,2-bis(trimethoxysilyl)ethane] (8 g) was first added to a mixture of octadecyltrimethylammonium chloride [C_{18}TMACl] (6 g) surfactant, NaOH (2.9 g) and water (194 g) under continuous stirring at room temperature. The requisite amount (Si/Ti = 48) of titanium butoxide [TBOT] was then introduced very slowly with vigorous stirring. The clear suspension was stirred for 18 h at ambient temperature followed by refluxing and heating for 30 h at 92 °C. The precipitate obtained was filtered and washed with distilled water and finally dried under vacuum. Surfactant was removed from the as-synthesized material by HCl/ethanol extraction.[1,14] For comparison, several other supports such as TS-1, Ti-MCM-41 and Ti-MCM-48 were also synthesized (Si/Ti = 50) according to the procedure already available in literature.[8–13]

DOI: 10.1039/b209392h

The X-ray powder diffraction (PXRD) patterns of surfactant free titanium incorporated (1.96% Ti by ICP) ethane bridged mesoporous silsesquioxane showed the clear diffraction peaks characteristic of a 2d-hexagonal phase with lattice constants *a* = 57.6 Å. The *d* spacings and intensity were slightly lower compared to the ethane bridged hybrid mesoporous materials.[1] Transmission electron microscope (TEM) images also confirmed the high degree of mesoscopic order.[14] The deconvoluted diffuse reflectance UV-spectra (Fig. 1a) indicates that most of the titanium is present as isolated tetrahedral {TiO_4} units in the solid framework. The intensity is mainly due to the electronic transition from O^{2-}(2p) to Ti^{4+} (3d) orbitals. The peak 1 (Abs. 220–245 nm) is assigned to tetrahedral coordination of titanium in the framework (~ 62%), while the peak 2 (Abs > 300 nm) is typical of titanium present in extra framework (~ 38%) of the material (*i.e.* five and six coordinated).

The state of titanium was further confirmed by Ti K-edge XANES analysis (Fig.1b). A sharp pre-edged peak at 4968 eV corresponding to 1s–3d excitations involving transition to the $2t_{2g}$ and $3e_g$ energy levels[15,16] confirms the presence of tetrahedrally coordinated titanium species along with very little five or six coordinated titanium. The XANES experiments were performed in transmission mode at EXAFS facilities installed on BL-7C of the Photon Factory (KEK, Tsukuba, Japan) with a ring energy of 2.5 GeV and storage positron current of 180–260 mA with a double-crystal Si (111) monochromator. The proton energies were calibrated using the edge of pure Ti foil.

The IR band at 962 cm^{-1} also confirms the presence of tetrahedral framework titanium which can be attributed to SiO-defects in the silica patches, indicating the substitution of Ti^{4+} for Si^{4+} in the SiO_2 domain.[17] The two signals at −57.8 ppm [corresponding to trifunctional (T^2) silicons; $SiC(OH)(OSi)_2$]

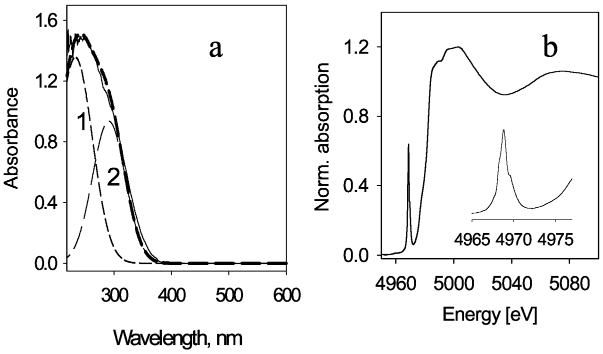

Fig. 1 a) Deconvoluted diffuse reflectance UV-Vis spectrum, b) Ti K-edge XANES spectrum of titanium containing ethane bridged mesoporous silsesquioxane.

and −66.7 ppm [T^{3}silicons; $SiC(OSi)_3$] in the ^{29}Si MAS NMR spectrum reveal that organic fragments (ethane) are covalently bonded to Si at the both sides as in $SiO_{1.5}–CH_2CH_2–SiO_{1.5}$ network. There was no evidence of tetra-functional Q silicons at –102 or –108 ppm, implying complete retention of bridging ligands after extraction. The ^{13}C NMR spectrum shows a signal at 5.2 ppm corresponding to the $Si–CH_2CH_2–Si$ fragment. The BET surface area, BJH pore diameter and mesopore volume were 860 m^2g^{-1}, 33.1 Å and 0.76 cm^3g^{-1}, respectively.[14]

The gold nanoparticles were deposited on all the supports by deposition–precipitation (DP) method.[18] The actual gold loading on the resultant materials was comparable to those reported for reference materials.[10–13] The catalyst was placed in the vertical fixed bed U-shape quartz reactor (i.d. 10 mm) and pretreated in a flow of 10 vol.% H_2 diluted in argon, followed by 10 vol.% O_2 in argon for 30 min each at 150 °C. Then a feed containing 10 vol.% each C_3H_6, H_2 and O_2 diluted in argon was fed (space velocity; 4000 cm^3 $h^{-1}g^{-1}$.cat) over the catalyst at desired temperatures. The details of the pretreatment of reference samples, reaction conditions and products analysis are available elsewhere.[8–13]

Table 1 lists the results of direct propylene epoxidation at the various reaction temperatures and different reaction times on stream. Under identical reaction conditions, the Au nanoparticles supported on highly hydrophobic mesoporous silsesquioxane showed enhanced catalytic activity for the propylene epoxidation. The propene conversion was >5 times higher compared to TS-1. The propylene conversion increased dramatically at higher temperature while PO selectivity was always above 97%. The highest propylene conversions (3.9%) and PO selectivity ($>97\%$) were observed at 120 °C, while the propene conversions were 2.1% and 2.8% for the conventional Ti-MCM 41 and Ti-MCM 48, respectively with PO selectivity around 92%. Conversions were decreased with reaction time on stream in all the cases but the relatively lower decrease was observed with highly hydrophobic titanium incorporated mesoporous ethane bridged silsesquioxane. This is perhaps due to the slow accumulation of PO on the hydrophobic surface compared to Ti-MCM 41 and Ti-MCM 48 supported catalysts. An enhanced propene conversion and PO selectivity can be assigned to homogeneous distribution of organic fragments and inorganic oxides in the framework with highly ordered structure and uniform pores.

The higher structural integrity and mesoscopic nature of the hybrid mesoporous ethane bridged silsesquioxane helps titanium to be present as an isolated species in its tetrahedral coordination. Also, the hydrogen utilization was very efficient for these materials. For the reaction temperature at 120 °C, the H_2 consumption was nearly half of that observed for conventional Ti-MCM-48. Such substantial decrease in H_2 consumption can be directly attributed to hydrophobicity of the catalyst. Indeed, the presence of organic functionality makes the material more hydrophobic and homogenous distribution of Au nanoparticles resulted in interesting surface properties facilitating diffusion of reactants and products in the propene epoxidation reaction. Therefore, the extent of the hydrophobic character of the material facilitates and enhances the *in situ* generation of hydrogen peroxide from H_2 and O_2 over the gold surface, that first converts into an excessively higher concentration of hydroperoxo-like species[19] on the tetrahedral titanium sites (Ti^{4+}-SiO_2) and in turn reacts with preadsorbed propene on the silica surface to yield propene oxide. The exact role of hydrophobic moieties in the enhanced yield of PO can also be explained by the decrease in charge density that allows the accommodation of the large active tetrahedral species at an easily accessible location, probably around the pore mouth and the inner walls of the hybrid mesoporous materials. This favors the homogeneous and higher dispersion of gold nanoparticles (particle size ~2.6 nm calculated by using Scherrer's equation after mathematical subtraction of diffraction profile of Ti-HMM from Au/Ti-HMM) as well as the better catalytic properties in the propene epoxidation reaction.

In summary, we have successfully demonstrated for the first time that highly dispersed gold nanoparticles supported on a hydrophobic mesoporous surface are an excellent candidate for the propene epoxidation to propene oxide using H_2 and O_2. Further, the extent of hydrophobicity could be controlled by inserting an organic molecule of a different nature as an integral part of the chemical connectivity in the hybrid mesoporous silsesquioxane. This will be the subject of subsequent work wherein more interesting and useful results are anticipated.

Table 1 Propene epoxidation over gold deposited on titanium containing hybrid mesoporous silsesquioxane and reference materials

Materials	Reaction temperature (°C)	TOS (h)	Conversion (%)		PO Selectivity (%)
			C_3H_6	H_2	
Ti-HMM[a]	90	1	2.6	7.1	99.1
	100	1	2.9	10.4	98.0
		3	2.6	9.5	98.2
	120	1	3.9	12.2	97.1
		3	3.2	10.1	97.7
TS-1	100	1	0.58	91.9	95.6
	120	1	0.84	14.2	93.2
Ti-MCM-41	100	1	1.9	11.8	94.3
		3	1.5	9.8	95.4
	120	1	2.1	15.1	91.7
		3	1.7	14.3	92.4
Ti-MCM-48	100	1	2.5	17.8	94.2
		3	1.9	16.5	95.0
	120	1	2.8	21.1	92.2
		3	2.1	19.3	92.8

[a] HMM = Hybrid Mesoporous silsesquioxane material.

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