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Ammoximation of ketones catalyzed by titanium-containing ethane bridged hybrid mesoporous silsesquioxane

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The first example of ammoximation of bulky ketones over highly hydrophobic titanium incorporated ethane bridged hybrid mesoporous silsesquioxane with high selectivity of oximes is presented.

Since its discovery, silicic titanium incorporated MCM-41 mesoporous materials[1] have often been employed as a catalyst in eco-friendly liquid-phase oxidation catalysis in various organic reactions (*viz.* alkane oxidation, epoxidation, hydroxylation, *etc.*) using dilute H_2O_2 as an oxidant.[2] However, the material was found to be hydrophilic due to the presence of excessive Si–OH groups on the surface, which is detrimental for their catalytic applicability to liquid phase oxidation reactions in the presence of water. Extensive work has been carried out to improve the hydrophobicity of these mesoporous silica in recent times by post-synthesis silylation[3] or direct synthesis with a mixture of TEOS and organotrialkoxy silanes[4] as the silica source. Although the catalytic activity of such materials improved with such organic modification,[4,5] the reactivity of Ti-MCM41 has been solely restricted to epoxidation reactions for the last decade[4,5] *i.e.* other attractive catalyses *e.g.* the ammoximation reaction,[6] have not been possible on these Ti-containing mesoporous materials.

Recently, we have synthesized a new class of titanium containing hybrid silsesquioxane mesophases with integral organic functionality[7] from a single organosilane source.[8–10] The materials have a homogeneous distribution of organic fragments and silica moieties within the framework and show hydrophobic surface properties including the high activity to oxidize bulky organics in the presence of dilute H_2O_2 as oxidant.[7] In a previous report,[11] we have demonstrated the hydrophobicity induced vapor-phase oxidation of propene over gold supported on titanium incorporated hybrid mesoporous silsesquioxane.

Here, we report for the first time the outstanding catalytic activity of this titanium containing ethane bridged hybrid mesoporous silsesquioxane in the ammoximation of ketones under liquid phase conditions. Dilute aqueous H_2O_2 and ammonia (25% in water) was used as the other reagents. Thus the potential utility of the ammoximation of a variety of bulky organic ketones that have not been catalyzed by either titanium silicates (TS-1) or Ti-MCM-41, can be made possible.

Titanium containing ethylene bridged mesoporous silsesquioxane was synthesized using a mixture of 1,2-bis-(trimethoxysilyl)ethane (BTME) and tetraethylorthosilicate (TEOS) as the silica precursor. In a typically improved synthesis from the mixed silica sources, 33.6 g of TEOS and 7.2 g of BTME were added to a mixture of 17.5 g octadecyltrimethyl ammonium chloride (C_{18}TMACl) dissolved in 180 g of water with a surfactant to Si molar ratio of 0.5. Then 36.0 g (Si/TMAOH molar ratio = 2) of tetramethylammonium hydroxide (TMAOH, 25% aqueous) was added under vigorous stirring. After 15 min, 2.45 g of tetrabutylorthotitanate (TBOT) dissolved in 5 ml isopropyl alcohol was added into the mixture and stirring was continued for another 2 h at room temperature, followed by aging/hydrothermal treatment at an elevated temperature for 24 h. The white precipitate obtained was collected by filtration and washed with copious amount of water and air-dried. The as-synthesized titanium containing hybrid mesoporous material (Ti-HMM) was treated with HCl/EtOH solution to remove the surfactant (Ti-HMM-Ext). Also, the material was calcined at 823 K for 4 h in air to remove both of the surfactant and ethylene fragments in the pore-wall (Ti-HMM-Cal).

The materials were characterized by powder X-ray diffraction, N_2 adsorption, ^{29}Si MAS NMR, FT-IR, and wet chemical analysis. Detailed textural characteristics are shown in Table 1. The X-ray diffraction patterns of as-synthesized, extracted and calcined titanium containing ethane bridged hybrid mesoporous silsesquioxane are shown in Fig. 1A. Upon calcination of the as-synthesized material at 823 K for 4 h in air to remove the organic surfactant and the ethylene fragments from the organic–inorganic composite, this material retained its XRD pattern (Fig. 1A-c) although lattice contraction as well as the decrease in the long range ordering was observed.

The type IV nitrogen adsorption isotherm (Fig. 1B) clearly illustrates the mesoporous nature of titanium containing ethylene bridged hybrid silsesquioxane. The calcined materials have an effective BET surface area of 1288 $m^2 g^{-1}$ and a pore volume of 0.89 $cm^3 g^{-1}$. TEM analysis supports the PXRD and sorption results and confirms the highly mesoscopic ordering of the mesoporous silsesquioxane. ^{29}Si MAS NMR spectra of the extracted material show two peaks each in the -58 to -67 ppm

Table 1 Textural properties of Ti-HMM[a]

Material	Si/Ti in product[b]	BET/m^2 g^{-1}	D_p/Å	V_p/cm^3 g^{-1}	Wall thickness/ Å
Ti-HMM-Ext	26.0	612	30.0	0.43	16.2
Ti-HMM-Cal[c]	24.5	1288	27.2	0.89	15.6

[a] HMM = hybrid mesoporous silsesquioxane material. [b] Determined by XRF. [c] Calcined at 823 K for 4 h; wall thickness = $a_0 - D_p$, $a_0 = 2d_{100}/\sqrt{3}$.

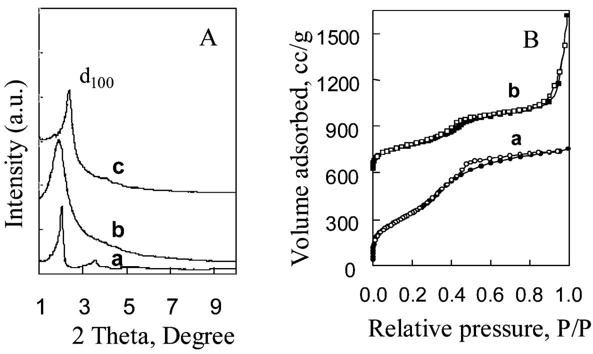

Fig. 1 (A) X-ray diffraction patterns of Ti-HMM (a) as-synthesized, (b) HCl/EtOH extracted and (c) calcined at 823 K; (B) Nitrogen adsorption (●)-desorption (○) isotherms for (a) calcined and (b) extracted Ti-HMM. (The *y*-axis of plot **b** is enhanced by 600.)

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and -98 to -111 ppm range, corresponding to the T_2–T_3 and Q_3–Q_4 species, confirming that organic fragments were bonded covalently in the silicate network. The calcined material shows only one broad peak centered at -110 ppm, indicating that organic fragments were removed completely from the silicate framework. FT-IR spectra of the calcined material showed a very strong band at 960 cm^{-1} attributable to the framework Ti–O–Si vibrations similar to other titanium silicates and is a clear indication of the incorporation of an isolated tetrahedral Ti species in the silicate framework.[12] The material also showed a strong UV-Visible absorption band in the 240–260 nm region indicating the presence of isolated tetrahedral Ti species in the silicate framework. The characteristics of similar materials have already been reported in detail in our earlier report.[7,11]

Titanium containing ethane bridged hybrid mesoporous silsesquioxane and its calcined analog were tested for the ammoximation of cyclohexanone and cyclododecanone substrates using aqueous hydrogen peroxide as oxidant. The conversion and the selectivity of oximes formation are listed in Table 2. The reactions were performed in a magnetically stirred round-bottomed flask fitted with a condenser and placed in a temperature controlled oil bath. Typically, 0.01 mol of the substrate was dissolved in 10.0 ml *tert*-butanol (solvent), and to this was added the required amount of liquid ammonia (2.5 times the substrates added at different reaction times) and catalyst (20 wt.% with respect to the substrate) and then the mixture was preheated to 353 K. The reaction was started when 30 wt.% H_2O_2 was added very slowly for a period of 8 h. The substrate : H_2O_2 : NH_3 mole ratio was kept at 1 : 1.25 : 2.5 for all reactions. 0.5 ml n-heptane was introduced in each of the reaction mixtures as internal standard. Samples of the reaction aliquots were taken at regular intervals and after cooling and filtration the reaction was monitored by GC.

Compared with conventional Ti-MCM-41[5,13] and TS-1,[14] these novel materials exhibited outstanding catalytic performance along with very high yield towards oxime products with 100% selectivity. The highest loading of Ti reported in Ti-MCM-41 materials have a Si/Ti mole ratio of 48 in the product. This sample shows no catalytic activity in the ammoximation reaction. The ethane-bridged hybrid mesoporous materials reported in this study contain a large amount of Ti in the silica framework (Si/Ti mole ratio of ~25). This reveals that the reduction of the charge density of the inorganic phase due to the introduction of the hydrophobic ethane groups of BTME can accommodate active tetrahedral Ti species (possibly Ti(O–Si)$_3$(OH)[7,12] at the interface of inorganic and surfactant micelle phases. This probably helps to locate the large amount of tetrahedral Ti species around the pore mouth rather than amorphous thick pore wall. Location of such active tetrahedral Ti species may be responsible for the enhanced catalytic activity (Table 2).

Table 2 Ammoximation of ketones over Ti-HMM[a]

Material	Substrate	Conversion (mol%)	Oxime[b] selectivity (mol%)
Ti-HMM-Ext	Cyclohexanone	63.2	100
	Cyclododecanone	42.0	100
Ti-HMM-Cal[c]	Cyclohexanone	90.0	95.2
	Cyclododecanone	72.5	100
	Cyclohexanone[d]	84.2	94.6
TS-1[e]	Cyclododecanone	0.8	100
Ti-MCM41[f]	Cyclohexanone	No reaction	
	Cyclododecanone	No reaction	

[a] HMM = hybrid mesoporous silsesquioxane material. [b] Oximes refers to cyclohexanoneoxime and cyclododecanoneoxime. [c] Calcined at 823 K for 4 h. [d] Isopropylalcohol as solvent instead of *tert*-butanol. [e] Si/Ti = 27. [f] Si/Ti = 48.

Interestingly, it is seen that the material obtained after removal of ethylene groups upon calcination is the more active catalyst. The cyclohexanone and cyclododecanone conversions were reached at 90.0 mol% and 72.5 mol% respectively. However, the oximes selectivity was almost comparable in both cases. This is attributable to the higher surface area, selective incorporation of isolated tetrahedral titanium atoms at the internal surface of the silicate framework and uniform pore-size distribution of the calcined samples. Although the ethane fragment was completely decomposed at 823 K, the more hydrophobic features remained and led to improved catalytic activity. In addition, It is believed that the generation of more hydrophobic centers *via* organic ethylene fragments, which should be an advantage to oxidize bulky organic compounds which has not been possible in the presence of TS-1 and Ti-MCM-41 catalysts. The hydrophobic feature was further confirmed by noticeable uptake of H_2O vapor during water adsorption measurements at 298K. Compared with pure Ti-MCM-41 (V_m = 2.73 molecules nm^{-1}) a little uptake (V_m = 1.45 molecules nm^{-1}) was observed for this calcined silsesquioxane at monolayer adsorption (P/P_0 of 0.3), confirming more hydrophobic nature of the material.

In summary, the first example of ammoximation of bulky ketones over highly hydrophobic titanium incorporated ethane bridged hybrid mesoporous silsesquioxane with high selectivity of oximes is presented. The most remarkable features of this titanium containing organic–inorganic hybrid mesoporous silica were its high activity and retention of the mesostructure as well as hydrophobic nature after removal of the organic ethylene bridge by calcination at high temperature. 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. These ammoximation reactions are very important industrially for the production of caprolactam nylon 6 and nylon 66.

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