Facile heterogenisation of molecular $Ti(OSiPh_3)_4$ to form a highly active epoxidation catalyst

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The simple grafting procedure of $Ti(OSiPh_3)_4$ onto the internal surface of MCM-41 to produce an epoxidation catalyst of high activity and selectivity is described. The presence of the phenyl groups on each titanium centre increases the longevity of their catalytic activity towards attack from atmospheric moisture. The conversion of the catalytically inactive titanium centre of the precursor compound to an active centre is followed using XANES.

Keywords: epoxidation catalyst, titanium-grafted mesoporous MCM-41, X-ray absorption spectroscopy

1. Introduction

The incorporation of titanium into silica materials, be they amorphous or crystalline porous materials, is of considerable importance in heterogeneous catalysis [1,2]. These catalysts are used on an industrial scale for processes that include the epoxidation of propylene and styrene. Research into this area is still of intense interest with many workers looking at ways to enhance the activity, selectivity, ease of preparation and durability of the catalyst. Improvements in catalytic activity and selectivity have been achieved by the post-synthetic grafting of the titanium centres onto the silica surface instead of incorporation during the initial synthesis of the host material [3,4], inclusion of activity enhancing elements, for example, germanium [5], and by lining the catalyst surface with hydrophobic organic groups [6–8].

Recent work has shown that molecular $Ti(OSiPh_3)_4$ can be reacted with the silsesquioxane species $[(c\text{-}C_5H_9)_7Si_7O_9(OH)_3]$, via the silanol groups, to form the active homogeneous epoxidation catalyst $[(c\text{-}C_5H_9)_7Si_7O_{12}TiOSiPh_3]$ [9]. Formation of a heterogeneous catalyst in a similar fashion by replacing the silsesquioxane with a readily available silica support is beneficial as it removes the problems associated with homogeneous catalysis and drastically reduces the cost of producing such a catalyst. We are particularly interested in using all-silica mesoporous MCM-41 as the catalytic support because this material has an extremely high internal surface area and a sharply defined pore size distribution. This allows for the possibilities of performing shape selective catalysis for bulkier substrates that do not fit into the small pores of microporous materials [10].

In this letter we report a facile method to graft the molecular precursor $Ti(OSiPh_3)_4$ onto the internal surface of all-silica MCM-41 to produce an epoxidation catalyst of comparable activity and selectivity to other high-performance laboratory catalysts. This method also presents the possibility of introducing a hydrophobic group on each titanium site as shown in figure 1, thus increasing the hydrophobicity of the catalytic site and the catalyst. Comparable control is not achievable by other post-synthetic organosilylating procedures. The formation of the catalytic titanium site is monitored by the use of XANES spectroscopy.

2. Experimental

2.1. Catalyst preparation

The all-silica MCM-41 used as the grafting support was prepared following the procedure of Grun et al. [11]. The

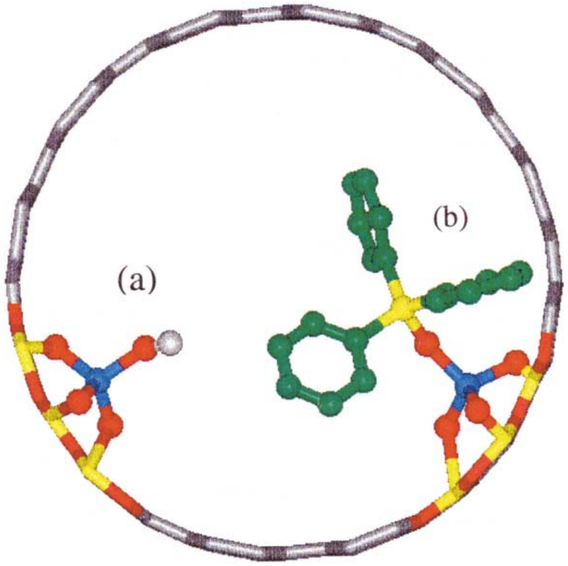

Figure 1. Representation of a catalytic titanium centre tripodally attached to the silica surface of MCM-41 with (a) a hydrophilic HO– group and (b) a hydrophobic Ph_3SiO– group attached to the titanium centre (colour index: C green, Si yellow, O red, Ti blue, H grey and non-bonding silica support atoms grey).

resulting templated material was calcined at 550 °C for 1 h under nitrogen and 6 h under oxygen to remove the surfactant present in the mesopores. The molecular precursor titanium species, $(Ph_3SiO)_4Ti$, was synthesised following the procedure described elsewhere [12,13].

The catalyst was prepared by grafting the $(Ph_3SiO)_4Ti$ molecules onto the silanol groups of the internal surface area of the MCM-41. In a typical synthesis a 1 g sample of MCM-41 was dehydrated at 200 °C under vacuum for 4 h. To this, 0.6141 g of $(Ph_3SiO)_4Ti$ and then 70 ml of anhydrous toluene were added under a dry argon atmosphere. The mixture was then refluxed for 7 days under flowing argon. The resulting material was recovered by suction filtration, washed in 500 ml of hot toluene, to dissolve and remove any residual $(Ph_3SiO)_4Ti$ and dried in air by suction filtration. The ICP chemical analysis showed that the final catalyst had a Si/Ti ratio of 72.

A standard catalyst was also prepared by grafting titanocene dichloride (Cp_2TiCl_2) onto the internal surface of MCM-41, using a method developed earlier in our laboratory [3], to give a catalyst with the Si/Ti ratio of 73 (determined by ICP chemical analysis).

2.2. XAS data collection

Room temperature Ti K-edge X-ray absorption spectra were collected at station 8.1 at Daresbury Laboratory (which operates at an energy of 2 GeV with an average beam current of ca. 190 mA) on raw catalyst samples and samples evacuated *in situ* to 400 °C. The station was equipped with a Si(111) monochromator, two Ar/He filled ion chambers to measure the incident and transmitted beam intensities and a Canberra 13-element solid-state detector to measure the fluorescence. The data were processed using the EXCALIB and EXBROOK programs that form part of the EXAFS analysis suite of programs at the Daresbury Laboratories.

2.3. Catalysis

Time-resolved catalytic studies were performed at 50 °C for the catalysts using cyclohexene as the substrate, TBHP in decane (52 or 59 wt%) and mesitylene (as a GC standard) in the ratio 20 : 1 : 1. Aliquots of 0.1 ml were periodically removed from the reaction vessel and filtered through a 0.2 μm syringe filter to remove the catalyst. The filtrate was analysed by Varian 8000 GC fitted with a HP column. All reagents were used without any pre-drying or purification. A time gap of 2 months occurred between the catalytic testing in batch A and that in B and C; during this time the catalysts were kept at room temperature in air. The catalysts in batches A and B (see table 1) were pre-dried under vacuum at 100 °C for 15 min before catalysis, and the catalysis was performed under an argon atmosphere. The catalysts in batch C were not predried before catalysis and the catalysis was performed in air.

Table 1
Catalytic performance of Ti-grafted species for epoxidation of cyclohexene.

Catalyst	TON for the conversion of TBHP to cyclohexene oxide per mole of Ti after 5 min ($mmol^{-1}$)		
	A[a]	B[b]	C[b]
(1) (HO)Ti↑MCM-41	28.9	10.93	8.3
(2) $(Ph_3SiO)Ti$↑MCM-41	25.9	20.0	22.1

[a] Catalytic conditions: 75 mmol cyclohexene : 3.75 mmol TBHP : 3.75 mmol mesitylene, amount of catalyst: (1) 89 and (2) 107 mg, selectivity to epoxide >95%.

[b] Catalytic conditions: 75 mmol cyclohexene : 3.75 mmol TBHP : 3.75 mmol mesitylene, 50 mg of catalyst used for all catalysis, selectivity to epoxide >95%, catalysis performed 2 months after reactions in A.

3. Results and discussion

The formation of active titanium centres can be followed by the use of X-ray absorption near-edge structure (XANES) which can be used as an element specific probe. XANES is known to be sensitive to local coordination geometry, oxidation state and electronic effects of the chosen probed atom centre [14,15]. In particular, the pre-edge peak is extremely sensitive to the local coordination geometry around the metal centre under investigation. For example, titanium-containing MCM-41, zeolite-β and TS-1 all show an intense pre-edge peak in their dehydrated form which decreases dramatically upon hydration or exposure to other coordinating molecules [3,16–19]. This change in intensity of the pre-edge peak results from a change of the coordination of the titanium centre from a four-coordinated tetrahedral site to a six-coordinated distorted octahedral site.

The Ti K-edge XANES of the molecular precursor $Ti(OSiPh_3)_4$ under ambient conditions, and the two catalysts, under ambient and dehydrated conditions are presented in figure 2. The XANES of the molecular precursor $Ti(OSiPh_3)_4$ shows an intense pre-edge peak representative of a tetrahedrally coordinated titanium centre which is consistent with the crystal structure of this compound [13]. It is interesting to note that the coordinatively unsaturated titanium centre in this material cannot be accessed by the water in the atmosphere because of the shrouding effect of the twelve phenyl groups surrounding the titanium centre [6]. The shrouding effect makes this precursor material catalytically inactive toward epoxidation reactions using cyclohexene [6] or 1-octene as the substrate [20].

The XANES of the (HO)Ti↑MCM-41 catalyst (where ↑ implies that the titanium atoms are grafted on the surface of the MCM-41) under ambient and dehydrated conditions show an increase in the pre-edge peak intensity on dehydrating the sample. This implies that under ambient conditions the titanium centres are accessible to water molecules in the atmosphere and have a distorted octahedral coordination environment [16]. Upon dehydration, the water molecules are removed and coordinatively unsaturated tetrahedral titanium centres are formed accompanied by an increase in the pre-edge peak intensity. The behaviour ex-

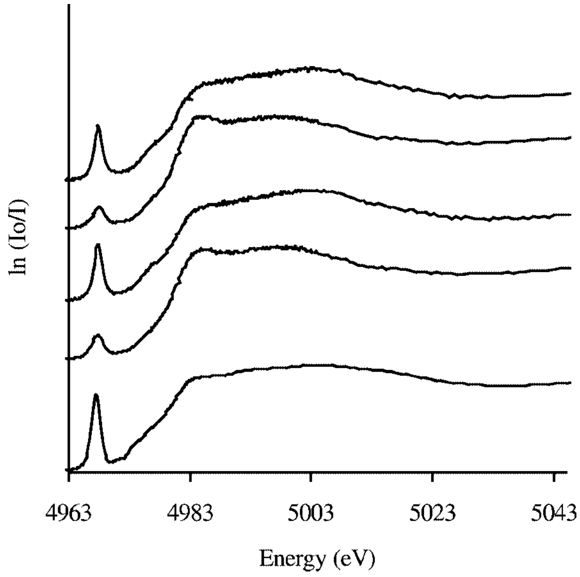

Figure 2. Ti K-edge XANES spectra of (a) molecular $(Ph_3SiO)_4Ti$, (b) hydrated $(Ph_3SiO)Ti\uparrow$MCM-41, (c) dehydrated $(Ph_3SiO)Ti\uparrow$MCM-41, (d) hydrated (HO)Ti$\uparrow$MCM-41 and (e) dehydrated (HO)Ti$\uparrow$MCM-41.

hibited by the titanium centres in this catalyst is indicative for the material to be an active epoxidation catalyst [16].

The XANES of the $(Ph_3SiO)Ti\uparrow$MCM-41 catalyst under ambient and dehydrated conditions follows the same pattern as the aforementioned (HO)Ti$\uparrow$MCM-41 catalyst with an increase in the pre-edge peak intensity on dehydrating the sample. Again, this implies that under ambient conditions the titanium centres are accessible to water molecules in the atmosphere and have a distorted octahedral coordination environment. Upon dehydration, the water molecules are removed and coordinatively unsaturated tetrahedral titanium centres are formed accompanied by an increase in the pre-edge peak intensity. This implies that the grafting procedure used to prepare the $(Ph_3SiO)Ti\uparrow$MCM-41 catalyst has rendered the tetrahedral coordinatively unsaturated titanium centres of $(Ph_3SiO)_4Ti$ accessible to interaction with water and other reactant molecules by replacement of some of the Ph_3SiO– ligands with the silanol groups of the MCM-41 to form catalytic sites of the type shown in figure 1. The XANES results indicate that the titanium centres formed from grafting $(Ph_3SiO)_4Ti$ onto the MCM-41 surface have the necessary properties to be catalytically active.

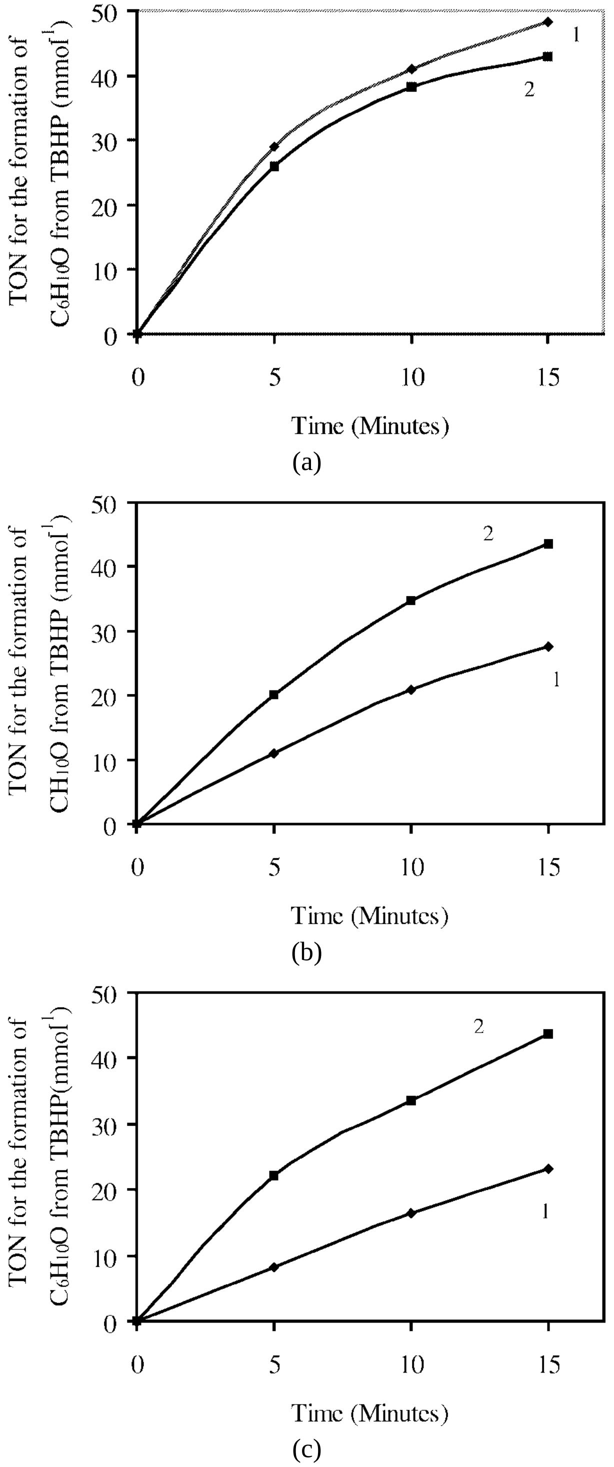

Figure 3. Time-resolved profiles of the turnover number for the cyclohexene oxide formation from TBHP for catalysts (HO)Ti$\uparrow$MCM-41 (1) and $(Ph_3SiO)Ti\uparrow$MCM-41 (2) under conditions (a) A, (b) B and (c) C (referring to table 1).

The catalytic results are presented in table 1 and time-resolved profiles for the catalysis reactions are shown in figure 3. The results indicate that the molecular precursor $(Ph_3SiO)_4Ti$ has successfully been grafted onto the inner surface of MCM-41 to produce a catalyst of comparable activity and selectivity to that produced by the surface grafting of titanocene dichloride to MCM-41 (column A, table 1 and figure 3(a)). The catalytic results also show that the $(Ph_3SiO)Ti\uparrow$MCM-41 catalyst retains its activity and selectivity after storage in air for two months while the activity of the (HO)Ti$\uparrow$MCM-41 catalyst, after similar storage, is reduced significantly (columns B and C, table 1 and figure 3 (b) and (c)). It is apparent that the presence of phenyl groups in the $(Ph_3SiO)Ti\uparrow$MCM-41 catalyst enhance the stability of the Ti catalytic centres and MCM-41 framework with respect to atmospheric moisture. This is presumably due to the protective action of the Ph_3SiO– groups on the Ti centres, which is hydrophobic in origin.

4. Conclusion

We have presented a facile method for grafting molecular $(Ph_3SiO)_4Ti$ onto the internal surface of the mesoporous material MCM-41 to produce an epoxidation catalysis of comparable activity and selectivity to previously described high performance titanium-containing MCM-41 catalysts. The conversion of the catalytically inactive titanium centre of the precursor compound $(Ph_3SiO)_4Ti$ to a catalytically active grafted titanium centre on the internal surface of the MCM-41 is clearly followed using XANES. Finally, the presence of the phenyl groups on each titanium centre of the catalyst increases the longevity of the activity of the catalytic centres towards attack from atmospheric moisture.

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