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Catalytic characterization of mesoporous Ti–Silica hollow spheres

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Titanium–silica hollow spheres (TSHS) with a mesoporous shell were synthesized using an inverse multiple oil–water–oil (O/W/O) emulsion. These novel materials show interesting potential for catalysis. Excellent catalytic performance was found in the epoxidation of cyclohexene with *tert*-butylhydroperoxide. The investigation of the titanium environment by UV–vis, Raman and FTIR spectroscopy showed that at low Ti loading only isolated species are present and catalytic measurements demonstrated that these species are the active sites for this reaction. At higher loading Ti–O–Ti microdomains are present and they do not exhibit any significant catalytic activity.

KEY WORDS: titanium; silica; catalysis; epoxidation; cyclohexene and active sites.

1. Introduction

The direct oxidation of hydrocarbons to form epoxides is one of the most important reactions in organic synthesis because of its applications in food, agrochemical and pharmaceutical industries [1,2]. Catalysts based on Ti and Si belong to the most powerful heterogeneous epoxidation catalysts known today [3]. A variety of titanium-containing nanoporous materials such as TS-1, Ti-MCM41 and Ti-TUD1 have been considered [4–6]. Extensive work has been devoted to the determination of the nature of active sites in crystalline Ti-based catalyst. Elucidating the coordination state of the Ti active sites was a primary goal in several investigations, since this is of primary importance in their catalytic properties. The framework vibrations observed in IR and Raman spectra [7–10], UV measurements [8,11] and X-Ray absorption near the edge structure (XANES) investigations [9,12] revealed a coordination number $n = 4$ for the most intensively studied molecular sieve TS-1. Nevertheless, the Ti environment differs according to the nature of the material as well as the preparation method [13].

Recently, synthesis of functional materials with hollow interiors has attracted much attention because of potential applications in drug storage and release, confined-space catalysis, separation, chromatography and biomolecular release systems [14,15]. Up to now, hollow spheres of various diameters and wall thickness are typically synthesized via layer-by-layer self-assembly of preformed nanoparticles onto spherical particles such as polystyrene beads or silica sol, which are used as templates [16]. Another approach consists in the direct synthesis of intact inorganic shells around soft templates such as vesicles and emulsion droplets [17]. However, the various pathways to prepare spherical nanostructured particles have so far resulted in rather irregular shaped particles, lacking structural stability [18].

In this communication we extend our recently reported method to synthesize and characterize Ti–silica hollow spheres (TSHS) [19] and focus on their application as a catalyst for the liquid phase epoxidation of cyclohexene using *tert*-butyl hydroperoxide (TBHP).

2. Experimental

2.1. Catalyst

TSHS with a mesoporous shell were fabricated according to an inverse multiple oil–water–oil emulsion technique. The detailed synthesis procedure and a description of the characterization techniques are presented elsewhere [19]. Briefly, a homogeneous mixture of Ti–Si precursors was obtained by pre-hydrolyzing tetraethyl orthosilicate (TEOS) with various volumes of a $TiO(NO_3)_2$ solution (50 g/L Ti). By adding the surfactant Span-80 (sorbitan monooleate, $C_{24}H_{44}O_6$) and stirring vigorously, the aqueous solution is uniformly dispersed as fine droplets in an oil phase (kerosene, Span 80). Furthermore, the homogenizer causes each aqueous droplet in the oil phase to also contain many smaller oil droplets, which eventually coalesce to form a concentric oil droplet inside each aqueous droplet, leading to an oil–water–oil emulsion. The oil phase, including surfactants, was removed after filtration, washing, drying and calcination. This led to hollow microspheres with a permeable shell of controllable thickness, traversed by mesopores of a unique size. The spheres range from a few to several tens of micrometers in diameter [19].

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2.2. Characterization

The titanium content of all samples was measured by inductively coupled plasma optical emission spectroscopy (ICP-OES). Nitrogen adsorption/desorption isotherms were measured on a Micromeritics ASAP2000 sorption analyser, utilizing the Barrett–Joyner–Halenda (BJH) method to evaluate the pore volume, the surface area and the pore size distributions from the adsorption portion of the isotherm. High-resolution transmission electron micrographs (TEM) were recorded using a Philips CM30T electron microscope with a LaB_6 filament as the electron source, operated at 300 kV. Samples were mounted on a microgrid carbon polymer, supported on a copper grid, followed by drying at ambient conditions. Scanning electron microscopy (SEM) images were recorded using a Philips XL20. Diffuse reflectance UV/vis/NIR spectra were recorded using a Perkin–Elmer Lambda 19 spectrometer. Raman spectra were obtained using a micro Raman spectrograph, the JY Horiba lab Raman HR 800, excited by a Coherent I-308 argon ion laser 200 mW of power at 488 nm.

2.3. Catalytic experiments

The catalytic activity of these materials was measured in the epoxidation reaction of cyclohexene with *tert*-butylhydroperoxide (TBHP) at 40 °C in nitrogen, under similar conditions as described by Kosege and Singh [20]. The TSHS samples calcined at 750 °C were utilized in the epoxidation experiments without further pretreatment. Before the reaction, 25 mmol of cyclohexene were mixed with 20 mL of decane as solvent and 0.05 g of catalyst; the mixture was stirred at 40 °C for 1 h. The reaction was initiated by adding 5.5 mmol of TBHP solution in decane (5.5 M, Aldrich). Liquid samples were withdrawn from time to time and analysed by gas chromatography (Chromopack, Wax 52CB).

3. Results and discussion

The dispersed hollow microspheres with a smooth external surface can be clearly identified by scanning electron microscopy (SEM, figure 1a, b). The spheres remained intact and preserved their spherical shape even after calcination at temperatures up to 750 °C. The mesoporous structure of the shells is confirmed by transmission electron microscopy (TEM). Figure 1c shows that the pores in the shell are randomly oriented. The porosity of the shell was investigated by measuring the nitrogen adsorption and desorption isotherms at 77 K. As a typical value, the TSHS sample with 1.3 wt% titanium has a specific surface area of 479 m^2/g, and a pore volume of 0.29 cm^3/g, distributed around a pore diameter of 2.4 nm. This is similar to previously reported pure silica hollow spheres [21].

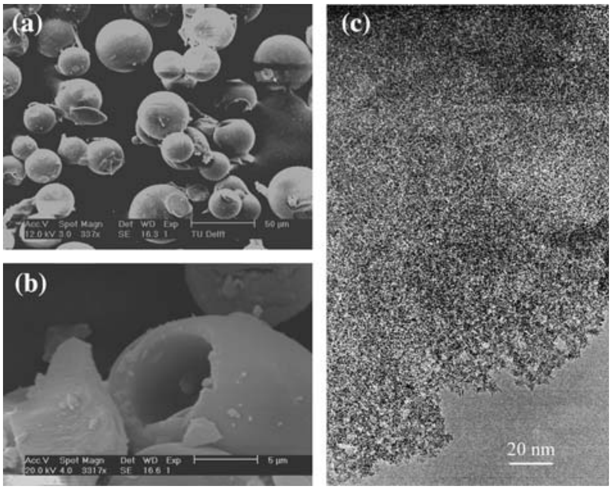

Figure 1. SEM image of non-crushed TSHS (a), crushed TSHS after calcinations at 750 °C (b), and its corresponding TEM (c). Samples contain 1.3 wt% Ti.

It is well-established that the active species in titanium(IV) containing catalysts, e.g., TS-1, are isolated tetrahedral titanium sites in a silica matrix with every single Ti^{IV} surrounded by siloxane ligands (O–Si–O).[4,22] The high catalytic activity is attributed to the enhanced Lewis acidity of Ti^{IV} and the presence of active monomeric titanyl (Ti = O) species. In our experiments we investigated the titanium environment in TSHS using UV–vis, Raman and FTIR spectra. As shown in figure 2, the broad absorption band centered at 210 nm for the sample containing 1.3 wt% Ti can be assigned to an electronic charge-transfer transition (LMCT) associated with an isolated Ti(IV) framework site in tetrahedral coordination, similar to TS-1 [23]. FTIR also shows a characteristic peak at about 950 cm^{-1}, corresponding to a Ti–O–Si asymmetric stretching mode [24]. However, the UV absorption band at 210 nm is much broader than for TS-1 and similar to previous results for Ti-MCM41 and Ti-TUD1 [25]. This

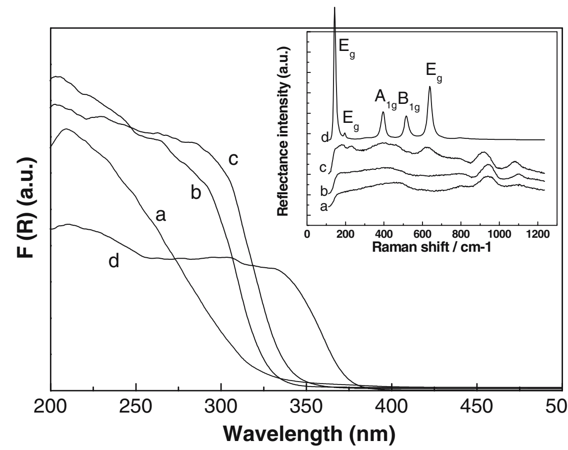

Figure 2. Diffuse reflectance UV–vis spectra of samples of different Ti content (wt%): (a) 1.3, (b) 2.7, (c) 5 and (d) pure anatase TiO_2. The insert shows the corresponding laser-Raman spectra.

Table 1
Catalytic performance in cyclohexene epoxidation

Catalyst	Ti (wt%)	$\mathrm{Conv_{CHXE}}$[a] (%)	$\mathrm{Conv_{TBHP}}$ (%)	TOF[b] (h^{-1})	$\mathrm{S_{CHXE}}$[c] (%)
TSHS	1.3	20 ± 1	91 ± 5	61	89 ± 5
TSHS	2.7	19 ± 1	89 ± 5	28	87 ± 5
TSHS	~5	20 ± 1	90 ± 5	16	82 ± 5
Ti-TUD1[d]	1.4	20 ± 1	91 ± 5	57	92 ± 5

[a] Total conversion of cyclohexene.
[b] Turnover frequency after 6 h of reaction.
[c] Epoxide selectivity with respect to total products after 6 h of reaction.
[d] Ti-TUD1 was synthesized according to the procedure of Shan *et al.* [6].

is an indication of the amorphous character of the pore walls, yielding a wide range of Ti–O–Si bond angles [26]. With increasing Ti content, the absorption edges shift to 300–350 nm (curves b and c in figure 2). The broad band at 300 nm can be attributed to $\mathrm{Ti^{IV}}$ framework sites of titania, in agreement with the literature [26,27]. Apparently, an excess titanium leads to a material in which part of the Ti atoms are not completely isolated in the silica framework but form Ti-rich microdomains with Ti–O–Ti linkages [28]. Meanwhile, no phase separation is observed, as is also supported by Raman spectra (Inset of figure 2), in which none of the three TSHS samples exhibits the characteristic peaks of bulk anatase. The clear bands at 955 and 1100 $\mathrm{cm^{-1}}$ correspond to a symmetric stretching and an asymmetric stretching of the octahedrally bonded titanium with oxygen, respectively [12]. Other evidence for an amorphous structure is given by the Raman intensities of the TSHS samples, which are an order of magnitude lower than for highly crystalline titania.

The effectiveness of Ti-containing porous silicas for a number of low temperature selective oxidation reactions with organic hydroperoxides has been demonstrated before [29]. One of the best catalysts for selective epoxidation is Ti-TUD1, which is about six times more active than framework-substituted Ti-MCM41 [6]. Table 1 summarizes our results of epoxidation of cyclohexene with TBHP over TSHS samples, together with the performance data of a Ti-TUD1 sample. The turn-over frequency (TOF) is defined as moles of cyclohexene converted per mol of titanium per hour. TSHS with 1.3 wt% Ti exhibits approximately the same performance in terms of conversion and selectivity toward the epoxide as Ti-TUD1 with a similar 1.4 wt% Ti loading. Although the surface area of Ti-TUD1 (600 $\mathrm{m^2/g}$) is much larger than that of TSHS (479 $\mathrm{m^2/g}$), this difference in surface area does not seem to affect the catalytic performance. The catalytic activity of TSHS samples with different Ti content reveals that both activity and selectivity remain rather constant, which is consistent with previous findings [4,11]. This suggests that the active sites are similar in all TSHS samples and that their amount does not increase with loading beyond at least 1.3 wt%. UV–vis spectra indeed showed the formation of Ti–O–Ti microdomains at the expense of isolated $\mathrm{Ti^{IV}}$ sites. Because the isolated environment of $\mathrm{Ti^{IV}}$ is responsible for selective epoxidation reactions, it is a logical consequence that the presence of these microdomains does not lead to an increase in either activity or epoxide selectivity. Nevertheless, according to the catalytic performance the amount of isolated $\mathrm{Ti^{IV}}$ appears to stay the same in all samples. We also performed leaching tests. After one reaction the catalyst was separated for the solution by filtration, dried overnight at room temperature, and re-used as catalyst. Results indicated that the activity of calcined samples stayed constant, barring the slight loss of catalyst during the filtration, and suggested that no leaching occurred (figure 3). Therefore, the whole epoxidation process on calcined TSHS samples proceeds heterogeneously. From kinetic measurements (figure 3), the reaction order was determined to be 0 and the formation of cyclohexene oxide occurred at a constant rate of 0.029 mol/L/h. Under these conditions the conversion of TBHP should be almost complete, which is in very good agreement with experimental data summarized in table 1. Mass transfer limitations are absent, and the data gives unambiguous information on the nature of the active sites.

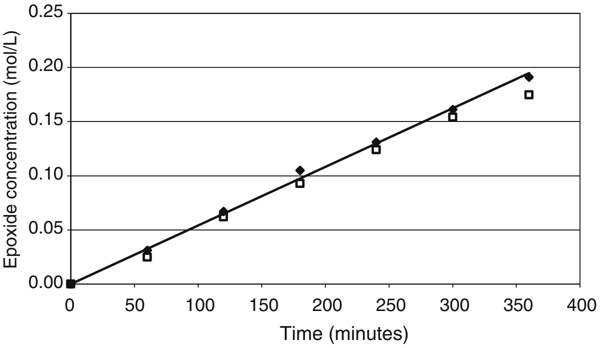

Figure 3. Time course of epoxide formation using 1.3 Ti–TSHS sample as the catalyst. Close marks correspond to fresh catalyst and open marks to re-used catalyst. For the second run, the amount of catalyst was 0.0465 g.

4. Conclusion

Ti–silica mesoporous hollow spheres (TSHS) were studied as catalysts for the epoxidation of cyclohexene with *tert*-butylhydroperoxide. They show excellent, stable catalytic performance for this reaction. UV–vis and Raman spectra indicate that Ti atoms were successfully incorporated as isolated Ti sites into the silica framework at low Ti loading. Catalytic study of TSHS indicates that a Ti loading of 1.3 wt% is enough to obtain a maximum activity and clearly demonstrates that isolated Ti sites are the only active sites for this reaction. Above 1.3 wt% the presence of non-isolated Ti species are detected by UV–vis spectroscopy and they appear to have no influence either on the activity or on the selectivity. Finally, a leaching test shows that the hollow spheres are stable under reaction conditions and that only heterogeneous catalysis takes place.

An *in situ* ATR-FTIR study is currently performed on the use of the TSHS in various epoxidations reactions to further evaluate the role of the Ti-structure and transport phenomena.

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