LETTER

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Combination of two catalytic sites in a novel nanocrystalline TiO_2–iron tetrasulfophthalocyanine material provides better catalytic properties

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Mesoporous titania nanocrystals containing iron tetrasulfophthalocyanine (FePcS) have been synthesised by a one-pot hydrolytic process from a modified Ti alkoxide; the novel hybrid catalyst was efficient in heterogeneous oxidation of 2,3,6-trimethylphenol and β-isophorone suggesting a cooperative effect between TiO_2 and FePcS catalytic sites.

Nano-sized functional hybrid materials have become a highly innovative research field. The ability to tailor the organic part combined with the properties of the nano-sized inorganic matrixes is of great interest for potential applications in electronics, optics and catalysis. In particular, an association of a metal complex with a catalytically active inorganic support could provide a catalyst having improved catalytic properties due to the combination of two different catalytic sites in one material.

Recently we reported the synthesis of nanocrystalline particles of titania at low temperature (100 °C) by a sol–gel process using titanium alkoxide and bromide ammonium salts as catalysts.[1] This synthetic approach could allow to introduce acid-containing compounds into TiO_2 particles *via* the synthesis of hybrid nanoparticles from modified titanium alkoxides. Taking into account the catalytic properties of FePcS in the selective oxidation of alkynes[2] and aromatic compounds[3] as well as in the oxidative degradation of organic pollutants[4] this complex containing four sulfonic groups seemed to be a suitable candidate. Photocatalytic degradation studies of pollutants using either Co(II)-tetrasulfophthalocyanine grafted on TiO_2 *via* a silane reagent[5] or polycrystalline TiO_2 samples impregnated with Cu(II)-phthalocyanine[6] were reported in the literature. However, to the best of our knowledge, none stemmed from direct covalent bonding of functionalized phthalocyanine on nanoparticulate TiO_2 material. In this work, we report a practical one-pot sol–gel preparation of surface-modified nanocrystalline titania particles from heteroleptic alkoxide and their catalytic activities in the aerobic oxidation of β-isophorone.

Iron(III) tetrasulfophthalocyanine chloride $[FePc(SO_3H)_4]Cl$ was used to substitute alkoxide ligands (Fig. 1). The reaction between $[FePc(SO_3H)_4]Cl$ and excess of $Ti(OPr^i)_4$ in refluxing 2-propanol for 12 h resulted in a blue-green crystalline material **1** (yield = 60% based on $[FePc(SO_3H)_4]Cl$). Elemental analysis gave a ratio Ti/Fe = 40. UV–Vis and FT-IR spectra indicated that the structure of phthalocyanine is retained upon modification. **1** was hydrolysed in pure water in the presence of tetrabutylammonium bromide salt to give material **2** which was characterised by elemental analysis, FT-IR, XRD, TEM, BET, UV–Visible and XPS techniques.

The FT-IR analyses of **2** showed the absorption peaks related to νOH and new νSO_3 stretching vibrations between 1260 and 1000 cm^{-1} (in comparison to $[FePc(SO_3H)_4]Cl$). This reveals that sulfonic acid groups are chemisorbed as sulfonates onto the TiO_2 nanoparticles. XPS spectra recorded from 0 to 1200 eV indicated that the hybrid material contained iron [Fe2p 3/2 = 709.1 eV], titanium [Ti2p 3/2 = 458.8 eV], nitrogen [N1s = 400.3 (50%), 398.8 (50%) eV], sulfur [S2p = 167,3 eV], oxygen [O1s = 532.1 (18%), 530.2 (82%) eV], carbon [C1s = 284.6 eV] and an atomic ratio Ti2p/Fe2p = 23. The two O1s peaks at 532.1 and 530.2 eV are ascribed to the O^{2-} contributions of sulfonate and oxide ligands, respectively. The binding energy values of the O1s and S2p peaks of the sulfonate groups are different in comparison to the free ligand [O1s = 531.1 eV, S2p = 168,1 eV], suggesting SO_3 covalent bonding onto TiO_2. According to the assignment made by Gosh *et al.*,[7] based on all-electron *ab initio* HF calculations on the metal-free phthalocyanine, the N1s peak at 400.3 eV is assigned to the four pyrrolic nitrogens (the inner ones bonded with two carbons and the central Fe atom). The absence of a chlorine peak indicates that under sol–gel conditions it was replaced by hydroxo or oxo ligands. Diffuse reflectance UV–Vis spectroscopy of **2** confirmed the presence of intact tetrasulfophthalocyanine. The intense Q-band at 641 nm suggests that phthalocyanine exits predominantly in dimeric form while the shoulder at 696 nm could be attributed to the monomer form. Such dimerisation has already been observed for aluminium tetrasulfophthalocyanine chloride in sol–gel processing.[8] The loading of the hybrid material (214 μmol g^{-1} or 19.2 wt% of phthalocyanine), determined by ICP-MS on iron, is high and could be easily modulated by adding various equivalents of $Ti(OPr^i)_4$ during the hydrolysis. XRD patterns, obtained at the scan rate of 0.02° 2θ s^{-1}, show that **2** contains anatase (around 85%) as the main crystalline phase along with brookite. Average particle sizes, estimated from line-broadening according to the Scherrer equation, gave 5.4 and 12 nm, for anatase and brookite phases, respectively. The morphology of the particles was examined by transmission electron microscopy and revealed highly agglomerated nanocrystals of 6–8 nm in length (Fig. 2).

Fig. 3 shows the nitrogen adsorption–desorption isotherms and the corresponding pore size distribution curve (inset) for desorbed sample **2** (200 °C/6 h). The BET surface area was 250 m g^{-1} (243 m g^{-1} for TiO_2 obtained by the same procedure) and the total pore volume was 0.33 cm^3 g^1 (determined by BJH method). The isotherm, a type IV with a hysteresis of type H2, shows that **2** is a well-characterised ordered mesoporous system with interconnected particles, different from TiO_2 (less

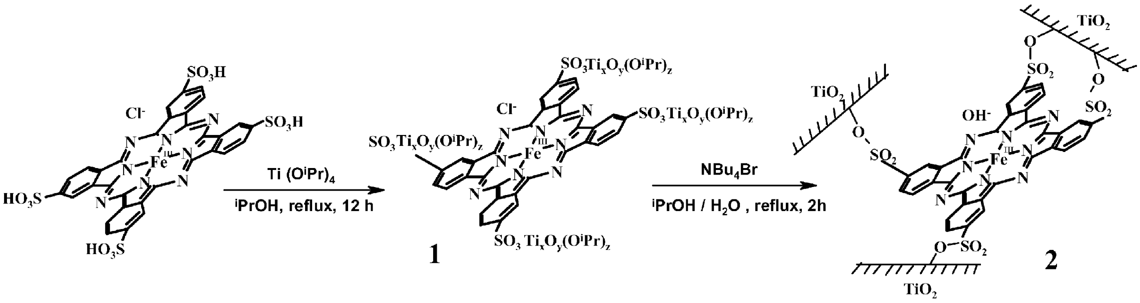
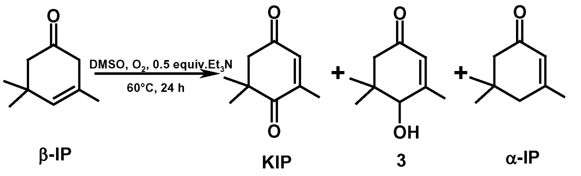


Fig. 1 Preparation of FePcS–TiO$_2$ (**2**).

rigid texture). This self-assembly process gave an average pore diameter with a narrow distribution of about 5 nm, comparable with the size of the phthalocyanine ligand (2 × 2 nm).

The catalytic activity of **2** has been determined in the TBHP oxidation of 2,3,6-trimethylphenol (TMP) into 2,3,6-trimethylquinone (TMQ), a precursor of vitamin E industrially obtained by *p*-sulfonation with H_2SO_4 followed by stoichiometric oxidation with MnO_2. While only 20% conversion and 1% TMQ yield were obtained with TiO_2 after 2 h, **2** provided 96% conversion and 57% yield of TMQ under identical reaction conditions.[9] Using H_2O_2, **2** was less active (44% conversion) but high selectivity (84%) was achieved. In the presence of TiO_2, TMP conversion was only 15%. It should be noted that conventional FePcS–SiO_2 catalysts were not active in oxidation of TMP using H_2O_2 as oxidant.[3] These data show that combination of two catalytically active FePcS and Ti-based sites in one material could result in co-operative catalysis providing an improved catalyst.



In order to confirm the superior catalytic properties of **2** we studied the aerobic oxidation of β-isophorone (β-IP), an important intermediate for the preparation of flavors and fragrances fine chemicals. The transformation of β-IP to epoxide has been described.[10] Several homogeneous[11] and heterogeneous[12] catalysts for the oxidation of β-IP to ketoisophorone (KIP) have been published. Homogeneous phthalocyanine and porphyrin complexes of different transition metals were used for aerobic β-IP oxidation in the presence of Et_3N.[13] With 1.3 mol% of FePc 55% yield of KIP was obtained. Manganese porphyrin complexes were the most efficient catalysts to provide 93% KIP yield. Recently, Murphy and Baiker reported an efficient homogeneous oxidation of β-IP in the presence of Cu(salen) (100% conversion, 67% yield of KIP).[11] However, only 52% conversion and less than 6% KIP yield was obtained in the best case with the Cu(salen) catalyst supported on SiO_2. This very low activity and poor selectivity in the heterogeneous oxidation were explained by the different reaction pathways imposed by the isolated immobilised catalytic sites.[12b] Additionally, metal(salen) complexes were not stable against leaching of the metal from the solid silica matrix.

We were delighted to observe that β-IP was successfully oxidised by O_2 to give KIP, allylic alcohol **3** and α-IP, the isomerisation product formed from the enolate intermediate.[14] In the presence of FePcS–SiO_2 β-IP was oxidised by dioxygen to afford 38% yield of KIP (Table 1). In the presence of TiO_2 only 2% yield of KIP was obtained, α-IP being the main product. FePcS supported on TiO_2 performed much better than FePcS supported on SiO_2 or TiO_2 alone giving 57% KIP yield. It is notable that the combined yield of KIP and **3** was 78% for **2** (FePcS–TiO_2) compared to 45% for FePcS–SiO_2 suggesting cooperativity of the two catalytic sites in the oxidation.

Taking into account the importance of recyclability of heterogeneous catalysts we studied the recycling of **2** and the possibility of metal leaching into solution at 1 mmol β-IP scale and 10 mL reaction mixture. After completing the first run the catalyst **2** was isolated by centrifugation, washed with MeCN (2 × 25 ml) and dried. On reuse, we observed a gradual decrease of catalytic activity, 77 and 64% conversion in runs 2 and 3, respectively (Table 1). The yield of KIP was also lower, 33% (run 2) and 27% (run 3). In order to determine possible Fe leaching in solution we isolated the solution after run 1 by filtration (0.45 μm filter). The residual Fe content in this solution of 7 ppm indicated that 9.9% of fixed FePcS was dissolved in the reaction mixture. However, taking into account the very small particle size of **2** we can not exclude the

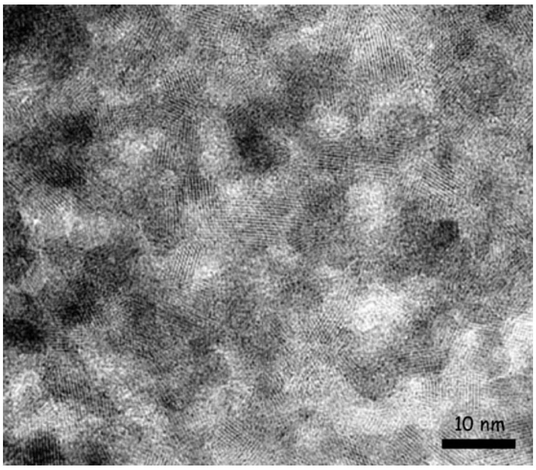


Fig. 2 TEM image of **2** obtained on a JEOL 2010 electron microscope.

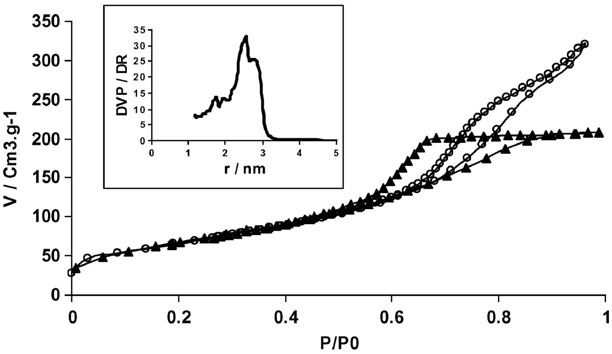


Fig. 3 Nitrogen adsorption–desorption isotherms of samples **2** (▲) and TiO_2 (○) and pore size distribution *vs.* radius (inset).

Table 1 Heterogeneous oxidation of β-IP[a]

Catalyst	Conversion (%)	KIP	Yield[b] (% **3**)	α-IP
2 (FePcS–TiO_2)	99	57	21	10
2 (run 2)	77	33	9	16
2 (run 3)	64	27	6	20
2[c]	68	29	7	15
2[d]	77	40	9	17
TiO_2	97	2	4	46
FePcS–SiO_2	92	38	7	22

[a] Reaction conditions: substrate (0.1 mmol), catalyst (15 mg, 1 mol% to substrate), triethylamine (0.05 mmol), dimethyl sulfoxide (1 mL), 60 °C, O_2 atmosphere, 24 h. [b] Determined by GC. [c] After 5 h of reaction, the solid catalyst was separated by filtration and the solution was allowed to react for 19 h (total reaction time = 24 h). [d] Subsequent oxidation run with the catalyst separated after 5 h of reaction.

presence of the smallest catalyst particles in the solution after filtration. In a separate experiment the catalyst was filtered after 5 h of reaction when the conversion was 48%, KIP yield was 25% and α-IP yield was 4%. The solution was allowed to react further. After 19 h (24 h total reaction time) the conversion was 68% (+20% as compared with 5 h reaction time). The yield of KIP increased from 25 to only 29% (+4%) while the yield of α-IP increased from 4% to 15% (+11%). Comparison of these data with those obtained from standard oxidation (Table 1, run 1) shows significant decreases of catalytic activity (−31%) and KIP yield (−28%) after removal of the supported catalyst, and 5% increase in α-IP yield. The recycled catalyst was used for the subsequent cycle. Similarly to run 2, in this second oxidation the conversion was 77%, the yield of KIP was 40% and the yield of α-IP was 17% thus demonstrating a good reproducibility of recycling. These results suggest that the oxidation of β-IP to KIP occurs mainly at the supported catalyst and the reaction of isomerisation of β-IP to α-IP occurs in solution containing triethylamine base. The FePcS–TiO_2 catalyst recovered after three successive oxidations exhibited practically the same diffuse reflectance (DR) UV–Vis spectrum as that of the initial supported catalyst indicating no significant degradation (Fig. 4).

Although further work is still required to understand the mechanism of synergistic action, to optimise this novel oxidation catalyst in terms of selectivity and scope and to improve its recyclability, the KIP yield already obtained with **2** provides the basis for a heterogeneous oxidation of such an important substrate as β-isophorone.

In summary, iron(III) phthalocyanine was successfully covalently grafted onto crystalline TiO_2 nanoparticles by a simple one-pot sol–gel process. This method avoids preliminary modifications of either the support or the metal complex that are usually necessary in conventional procedures. Tetrasulfophthalocyanine acts as a bridging ligand and controls the molecular self-assembly hydrolytic process which results in a new hybrid material with well-ordered mesoporous structure and high surface area. This catalyst containing two different catalytic sites exhibited promising results in heterogeneous aerobic oxidation of cyclic olefins exemplified by β-isophorone.

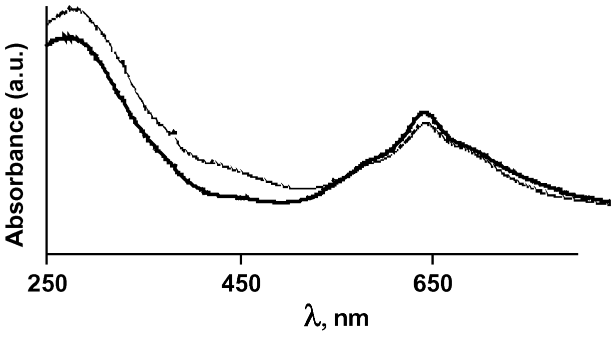


Fig. 4 DR UV–Vis spectra of initial FePcS–TiO_2 (bold line) and after 3 oxidations (light line).

Experimental

All manipulations were performed under dry argon using Schlenk tube techniques. $Ti(OPr^i)_4$ was purchased from Aldrich. Solvents were purified by standard methods and stored over molecular sieves. FT-IR spectra were recorded as Nujol mulls on a Perkin-Elmer Paragon 500 FT-IR spectrometer. UV–Visible spectra were carried out on an UNICAM UV2-100 spectrometer. The DR UV–Vis spectra were recorded on a Lambda 35 Perkin-Elmer spectrophotometer. BET measurements were performed on a Micromeritics ASAP 2010. Powder X-Ray diffraction data were obtained with a Siemens D 5000 diffractometer using the CuKα radiation. XPS experiments were performed with an Escalab 200R (VG Scientific) spectrometer using the monochromated AlKα radiation as excitation source. TEM images were collected on a JEOL 2010 microscope. Analytical data were determined by an inductively coupled plasma–mass spectrometry method.

Materials synthesis

Synthesis of anhydrous $[FePc(SO_3H)_4]Cl$. Sodium salt of FePcS (600 mg in 50 mL of water), prepared according to the modified Weber–Busch procedure,[15] was converted to the tetrabutylammonium salt by the treatment with 5 mL of a 40% tetrabutylammonium hydroxide aqueous solution followed by the extraction with CH_2Cl_2 (6 × 50 ml). The organic phase was dried and the obtained material was dissolved in 200 mL of acetonitrile. 37% HCl (2 mL, about 6-fold excess with respect to the sulfonate group) was added dropwise under stirring. The precipitate of $[FePc(SO_3H)_4]Cl$ was isolated by centrifugation and dried at 60 °C for 24 h *in vacuo*. $[FePc(SO_3H)_4]Cl$ was further dried by the azeotropic distillation of ethanol. Finally, the product was dried *in vacuo* at 60 °C for 24 h (435 mg, 91% yield). FT-IR (Nujol, cm^{-1}): 3423br, 3173 [νO–H]; 1771w, 1715m, 1604m, 1504m [ν(C=N, C=C)]; 1330w, 1306w; 1258w, 1227m, 1182s, 1169s, 1147s, 1107s, 1089s, 1052m, 1027s [$\nu(SO_3)$]; 963m, 929m, 844w, 762w, 748m, 700s, 677w, 650s, 630s, 598m, 591m, 566m, 543w.

Synthesis of 1. In a typical preparation, 0.74 g (2.6 mmol) of $Ti(OPr^i)_4$ and 0.194 g (0.21 mmol) of $[FePc(SO_3H)_4]Cl$ were refluxed in 2-propanol for 12 h. After filtration, the resultant dark green solution was concentrated under vacuum. Cooling it down to −4 °C resulted in a dark blue-green crystalline material **1** (0.85 g, 60%/Fe). Anal. Found: Fe, 0.45; Ti, 15.15%. FT-IR (Nujol, cm^{-1}): 1775w, 1772m, 1685w, 1606m, 1581w, 1512m, 1463w [ν(C=N, C=C)]; 1336w, 1325m, 1308w; 1263w, 1227w, 1186w, 1161w, 1146m [$\nu(SO_3)$]; 702w, 696w, 648m, 632m, 601w, 595w, 567w, 524w, 508w, 468w [ν(M–O, M–N)].

Synthesis of 2. In a typical hydrolysis process, 1 g of **1** (83.1 μmol) in 5 mL of 2-propanol was added dropwise to 25 mL of a $N(^nBu)_4Br$ (0.4 g, 1.24 mmol) aqueous solution under vigorous stirring at boiling temperature. The mixture was heated under reflux for 2 h and was centrifuged to give a dark blue-green solid. The as-prepared precipitate (denoted **2**) was washed several times with deionised water, until the solution was colorless, and ethanol (25 mL) and was dried at 70 °C overnight. Anal. Found: Fe, 1.20%. FT-IR (KBr, cm^{-1}): 3342br [νO-H]; 1722m, 1617s, 1539m, 1481w, 1401m [ν(C=N, C=C)]; 1254w, 1218w, 1187m, 1141w, 1101w, 1072w, 1032m [$\nu(SO_3)$]; 721s, 553vs, 478vs [ν(M–O, M–N)].

Catalytic tests

The reaction products were identified and quantified by GC-MS (Hewlett-Packard 5973/6890 system; electron impact ionization at 70 eV, He carrier gas, 30 m × 0.25 mm cross-linked 5% PH ME siloxane (0.25 μm coating) capillary column, HP-5MS) and GC (Agilent 4890D system, N_2 carrier gas, 15 m × 0.25 mm crosslinked 5% PHME siloxane (0.25 μm coating) capillary column, HP-5MS) methods.

Typical procedure for the oxidation of TMP. 2 (8 mg, 2 mol%) was added to a solution of TMP (80 μmol) in 1,2-dichloroethane (DCE, 4 mL), then four 15.8 μL portions of a 3.8 M TBHP in DCE were added to the mixture at reaction times of 0, 0.5, 1, 1.5 h (total oxidant amount: 240 μmol). The reaction was carried out at 30 °C for 2 h. The products were identified by GC-MS and quantified by GC using authentic samples.

Typical procedure for the oxidation of β-IP. Catalyst (1 mol%) was added to a solution of β-IP (0.1 mmol) in dimethyl sulfoxide (1 ml) containing 0.05 mmol of triethylamine. The reaction was performed at 60 °C under oxygen atmosphere (2 bar) for 24 h. The products were identified by GC-MS and quantified by GC using authentic samples. Recycling experiments were carried out with 1 mmol β-IP keeping the same reagent ratio.

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