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Oxidative desulfurization of dibenzothiophene with dioxygen and reverse micellar peroxotitanium under mild conditions

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ABSTRACT

The reverse micellar peroxotitanium-containing catalyst $[C_{18}H_{37}N(CH_3)_3]_7[PW_{10}Ti_2O_{38}(O_2)_2]$ was assembled in the organic solvent and the structure was characterized by Fourier transform infrared spectroscopy(FT-IR), Diffuse reflectance UV–vis spectrum (DR-UV–vis), X-ray photoelectron spectrum (XPS), transmission electron microscopy (TEM), Energy dispersive X-ray analysis (EDAX), and Matrix-assisted laser desorption ionization time-of-flight (MALDI-TOF) mass spectrometry. Direct oxidation of dibenzothiophene (DBT) using O_2 was performed by this reverse micellar catalyst with ~100% selectivity in the oxidation of DBT to sulfone. By this catalyst, it could catalytically decrease sulfur level in diesel from 500 ppm to 1.0 ppm at ambient pressure and moderate temperature.

1. Introduction

Deep desulfurization from fuel oils has been paid more attention due to urgently environmental problem. More and more stringent regulation limits the sulfur content to be about 10 ppm in diesel in many countries by 2010. The conventional method for removing sulfur in industry is catalytic hydrodesulfurization (HDS) process, which can desulfurize aliphatic and acyclic sulfur compounds. This process, however, is limited for treating some refractory sulfur compounds such as dibenzothiophene (DBT) or its derivatives. In order to achieve deep desulfurization, severe operating conditions such as high temperature ($T > 623$), high pressure (3–10 Mpa) and high hydrogen consumption are required, leading to high instrumental cost [1]. Therefore, an essential demand for developing alternative non-HDS methods to achieve deep desulfurization is to produce clean diesel containing low sulfur concentration. Among them, oxidative desulfurization (ODS) combined with extraction is considered to be one of the most promising process, because it can remove the refractory sulfur compounds [2–4] under mild conditions. In ODS, the choice of oxidant is one of the key factors for deep desulfurization. In aqueous solution, hydrogen peroxide (H_2O_2) and peroxyacids are very known oxidants for ODS [5–7] when using different catalysts such as polyoxometalates (POMs) [5,6,8], metal oxide [9] or Fenton-like reagents in ionic liquids [10]. Besides peroxides, molecular oxygen is the most economical and environmental benign oxidant which might be used in desulfurization of fuels [11–13]. In these processes, the sulfur compounds can be oxidized to corresponding sulfones using O_2 and heterogeneous catalysts involving aldehydes as co-oxidants, which transfer O_2, from gas-phase to liquid-phase, to peroxyacids by itself oxidation. The two major disadvantages are the cost of co-oxidants and the loss of fuel during the separation of organic acids. To date, there are only few reports [14] on directly catalytic oxidation of DBT using O_2 in non-polar hydrocarbon solvent without a sacrificial agent at 100 °C and 0.3 MPa for 2 h, in which 500 μg/g of DBT could be decreased to less than 4 μg/g. And more recently, Li reported that aerobic oxidative desulfurization could be catalyzed by Anderson-type polyoxometalates under 80 °C and 10 h [15]. The oxidation of DBT by oxygen instead of H_2O_2 under rather mild conditions would be of great significance in industry due to its lower costs and green chemical advantages. In order to achieve this, the main task is to seek an active and durable catalyst under mild temperature and atmospheric pressure.

Polyoxometalates (POMs), represent an increasingly important class of environmentally benign catalysts that can be used even under rather mild conditions for the oxidation of a number of organic substrates in the presence of either O_2 or other donors [16–18]. The properties of titanium-containing POMs are of great interest that can lead to interesting applications in catalysis and medicine [19,20]. Especially in H_2O_2-based oxidation catalysis, titanium-containing POMs could react with hydrogen peroxide for forming peroxo complexes—actual active species toward organic

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substrates [21], which are widely used to promote the epoxidation of the oleinic substrates [22] and are responsible for sulfide oxidation [23]. On the basis of these findings, we proposed that the peroxo-titanium complexes could provide reactive peroxo species, and oxygen could be transferred from $Ti(O_2)$ species to the substrates, leading to the oxidation of organic substrates with O_2 as oxidant instead of H_2O_2. In addition, the most often used strategy is to utilize surfactants to form micelles or reverse micelles for significantly accelerating the reaction rate in a micellar medium [24]. Amphiphilic quaternary ammonium micelles of POMs, with a surfactant surface and a POM core, can form supramolecular reverse micellar assemblies ranging from nanoscale to microscale sizes in non-polar solvents [25]. This structure could possibly afford high local reactant concentrations near the catalysts, helping to enhance the catalytic rate. Amphiphilic POM catalysts have been successfully used in various organic synthesis reactions with hydrogen peroxide [5,6,26–29] as an oxidant in an emulsion or microemulsion system. Thus far, only Li and co-workers [13] have reported on the oxidative desulfurization of dibenzothiophene with O_2 using amphiphilic POM emulsion catalysts and aldehyde as the sacrificial agent at 60 °C for 8 h. Few studies have been conducted to develop peroxotitanium POM reverse-micellar catalysts for O_2 desulfurization of organic sulfur by now [15].

Here, we report the oxidation of DBT with O_2 as the oxidant using reverse micellar system under natural daylight, where an amphiphilic catalyst $[C_{18}H_{37}N(CH_3)_3]_7[PW_{10}Ti_2O_{38}(O_2)_2]$ (abbreviated as $C_{18}PW_{10}Ti_2(O_2)_2$) acts as both the surfactant and the catalyst. The catalyst $C_{18}PW_{10}Ti_2(O_2)_2$ in decalin could form an reverse micelle with POM core and surfactant surface. As result, sulfur-containing molecules could assemble on surfactant ends of reverse-micellar droplets and oxygen molecules could assemble inside the reverse-micellar droplets. So the oxidation rate of DBT could accelerate and could be completely oxidized by O_2 into sulfone in this reverse micellar system under mild conditions within short time.

2. Experimental

2.1. Materials

All reagents were of AR grade and used without further purification. $K_7PW_{10}Ti_2O_{40}$ and $K_7PW_{10}Ti_2O_{38}(O_2)_2$ were prepared according to the literature methods [30,31], and were characterized by IR spectroscopy.

2.2. Physical measurements

Elemental analysis was carried out using a Leeman Plasma Spec (I) ICP-ES and a P-E 2400 CHN elemental analyzer. IR spectra (4000–400 cm^{-1}) were recorded in KBr discs on a NicoletMagna 560 IR spectrometer. DR-UV–vis spectra (200–600 nm) were recorded on a Cary 500 UV–vis-NIR spectrophotometer. XPS were recorded on an Escalab-MK II photoelectronic spectrometer with Al Kα (1200 eV). Dynamic light scattering (DLS) was employed in order to study the sizes of the reverse-micelles in the Microtrac S3500 Particle Analyzer in terms of the hydrodynamic radius. TEM image was determined by JEM-2100F instrument. Energy dispersive X-ray analysis (EDAX) was performed to take into account of the C, P, W and Ti elements. The identification and quantification of DBT in decalin were performed by Gas Chromatography (GC) equipped with an OV1701 capillary column (30 m × 0.32 mm × 0.25 μm) using Flame Ionization Detector (SHIMADZU GC-14C). Analysis conditions were as follows: injection port temperature, 280 °C; detector temperature, 250 °C; oven temperature program, 280 °C, hold for 8 min; split ratio, 1/100; carrier gas, ultra-purity nitrogen; column flow, 0.9 mL/min; reagent gases, air flow of 100 mL/min, hydrogen flow of 75 mL/min; the injection volume of sample was 1 μL. The leaching concentrations of $C_{18}PW_{10}Ti_2(O_2)_2$ during the reaction were also measured through analyzing the dissolved concentration of W in solvent using a Leeman Plasma Spec (I) ICP-ES. The positive-ion MALDI-TOF mass spectra of $[PW_{10}Ti_2O_{38}(O_2)_2]^{7-}$ were recorded by using Bruker autoflex III smartbeam MALDI-TOF/TOF (smartbeam laser with 355 nm wavelength, Germany). In the experiments the mass spectrometer was tuned in the linear mode by using delayed extraction of 200 ns. The acceleration voltage was set to +20 kV. The samples were dissolved in $CHCl_3$ and the matrix solution was dithranol.

2.3. Preparation of $[C_{18}H_{33}N(CH_3)_3]_7[PW_{10}Ti_2O_{38}(O_2)_2]$

The preparation of $C_{18}PW_{10}Ti_2(O_2)_2$ was as follows: a 50 mL alcohol solution of $[(C_{18}H_{37})N(CH_3)_3]Br$(7 mmol) was added dropwise into a 20 mL hydrogen peroxide (30%) solution containing $K_7PW_{10}Ti_2O_{38}(O_2)_2$(1 mmol). A yellow precipitate was formed immediately and was stirred for another 2 h. The yellow precipitate was filtered and dried in nitrogen to produce. The resulting $C_{18}PW_{10}Ti_2(O_2)_2$ was obtained with yield 50%. IR(1% KBr pellet, 4000–400 cm^{-1}): 1059(υas P-Oa), 954(υas W-Od), 882(υas W-Ob-W), 804(υas W-Oc-W), 650(Ti-O-O)[32].

The other amphiphilic quaternary ammonium salts of peroxotitanium-POMs were prepared in the same procedure except using $[(C_8H_{17})N(CH_3)_3]Br$, $[(C_{12}H_{25})N(CH_3)_3]Br$, or $[(C_{16}H_{33})N(CH_3)_3]Br$ instead of $[(C_{18}H_{37})N(CH_3)_3]Br$.

2.4. Catalytic procedure

The oxidative desulfurization experiments were carried out in a 100 mL three-necked flask. The model sulfur-containing compound (DBT) was dissolved in 50 mL decalin and a sulfur concentration of 500 ppm. In this typical reaction run, a water bath was heated to 90 °C. Then, the catalyst (0.05 mmol) was added to model oil and molecular oxygen was bubbled through the reaction solution. Keep stirring at 200 rpm and 90 °C for some time. After the reaction, the samples were placed into an ice chamber to stop the reaction. The sulfur content of the upper clear solution was determined by GC. Finally, the catalyst was separated by centrifugation and reused without any treatment.

2.5. Adsorption experiments

Adsorption experiments were carried out to determine the adsorption capacity of catalysts for DBT at 90 °C and atmosphere pressure flowing nitrogen with an agitator. In the simultaneous adsorption experiments, 50 mL of 500 ppm DBT solution and 0.05 mmol of catalyst were loaded in the bottle. At the predetermined time intervals, samples were taken and the concentration of DBT adsorbed on the catalysts were gained by measuring the decrease of the concentration in solution using GC.

3. Results and discussion

3.1. Characterization of the micellar catalyst

The IR spectra of $C_{18}PW_{10}Ti_2(O_2)_2$ were investigated. Peaks in the range of 600–1100 cm^{-1} corresponding to Keggin structural vibrations could be easily distinguished. This indicates that $C_{18}PW_{10}Ti_2(O_2)_2$ maintains the Keggin structure.

From the results of the elemental analyses: W, 38.56; Ti, 2.21; P, 0.58; C, 35.74; H, 6.39; N, 2.43%. Compared with the calculated values W, 38.10; Ti, 1.98; P, 0.64; C, 36.59; H, 6.73; N, 2.03%, the results are satisfactory.