Applied Catalysis B: Environmental 138–139 (2013) 79–83

Contents lists available at SciVerse ScienceDirect

Applied Catalysis B: Environmental

journal homepage: www.elsevier.com/locate/apcatb

Aerobic oxidative desulfurization of model diesel using a B-type Anderson catalyst $[(C_{18}H_{37})_2N(CH_3)_2]_3Co(OH)_6Mo_6O_{18}\cdot 3H_2O$

Hongying Lü*, Wanzhong Ren, Weiping Liao, Wei Chen, Yang Li, Zhanghuai Suo

College of Chemistry and Chemical Engineering, Yantai University, 32 Qingquan Road, Yantai 264005, China

ARTICLE INFO

Article history:
Received 17 September 2012
Received in revised form 15 January 2013
Accepted 18 February 2013
Available online 26 February 2013

Keywords:
Oxidative desulfurization
Diesel
Dioxygen
Anderson-type polyoxomolybdates

ABSTRACT

A B-type Anderson polyoxomolybdates with mixed-valence molybdenum ions, $[(C_{18}H_{37})_2N(CH_3)_2]_3Co(OH)_6Mo^{(V,VI)}{}_6O_{18}$, was prepared and characterized by Fourier transform infrared spectroscopy(FT-IR), UV–vis diffuse reflectance spectroscopy (UV–vis DRS), differential thermal analysis (DTA) and X-ray photoelectron spectrum (XPS). The polyoxometalate shows high catalytic activity in aerobic oxidative desulfurization of model diesel and the turnover number (TON) can reach about 4200 in absence of any sacrificial agent under mild conditions. The quaternary ammonium cations in the catalysts play a vital role in the aerobic oxidative desulfurization system. The catalytic activity for the oxidation of sulfur-containing compounds decreases in the order of 4,6-DMDBT > DBT > BT.

1. Introduction

The deep removal of sulfur-containing compounds from fuel oils has attracted wide interests due to the stringent environmental regulations imposed on sulfur level in diesel [1–5]. Current technology of hydrodesulfurization (HDS) requires harsh conditions (e.g., high temperature, high pressure, and high hydrogen consumption), which result in high operating cost. Therefore, it is highly desired to develop non-HDS methods to produce clean diesel containing extremely low concentration of sulfur under mild conditions and also with low cost. Among ways that has been under investigation, oxidative desulfurization has received much attention because of its advantages of mild operating conditions and no consumption of H_2 [5–11]. Many types of oxidative systems have been attempted, using hydrogen peroxide and non-hydrogen peroxide compounds (e.g., t-butyl hydroperoxide, etc.) as oxidizing agent [6–12].

It has been expected that molecular oxygen or air instead of peroxides can be used as oxidizing agent under mild conditions for the oxidation of these refractory sulfur-containing compounds due to their characteristics of low price and green chemistry [13–18]. However, the presence of oxygen induced high activation barrier results in the huge difficulty in oxidative desulfurization of diesel under mild conditions. It has been proved [13–17] that the oxidation of these refractory compounds by molecular oxygen is only achieved at high temperatures or in the presence of a sacrificial agent. Therefore, it is a challenge to seek an active catalyst for aerobic oxidative desulfurization under mild temperature and pressure.

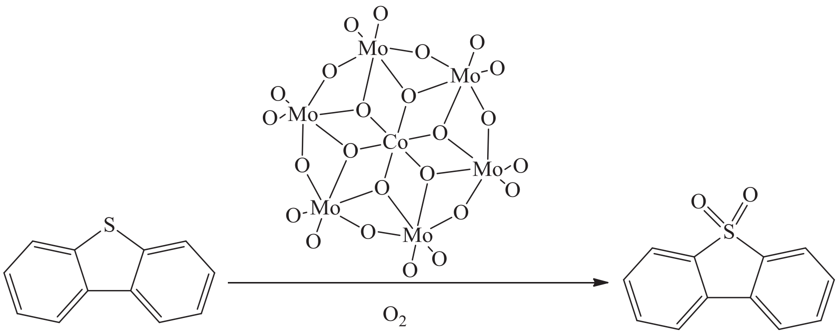
Polyoxometalates (POMs) have attracted much attention in the fields of acid and oxidation catalysis, because their acidic and redox properties can be designed and tuned at molecular or atomic level. However, the Anderson-type POMs are not well known as catalysts [19,20]. Anderson-type heteropolyanions ($[YM_6O_{24}H_x]^{n-}$) possess a heteroatom (Y) in a central octahedral cavity of the crown by edge-sharing six octahedral MO_6 (M = Mo or W) [21]. These polyanions become a family for a number of 2+, 3+, 4+, 6+ and 7+ ions as the heteroatom. They are classified into types of A ($x = 0$) and B ($x = 6$) by the number of attached protons [22]. In our previous work [23], an A-type Anderson catalyst ($[(C_{18}H_{37})_2N(CH_3)_2]_5IMo_6O_{24}$) was reported, which can oxidize the sulfur-containing compounds in diesel under mild conditions to their corresponding sulfones using molecular oxygen as oxidant. We assumed that the other Anderson-type of polyoxomolybdates may also catalyze the oxidative desulfurization of diesel with similar reactivity, which led to further research into the type polyoxometalate in this study.

In this paper, aerobic oxidative desulfurization of diesel was developed, which was catalyzed by a B-type Anderson polyoxomolybdate with mixed-valence molybdenum ions ($[(C_{18}H_{37})_2N(CH_3)_2]_3Co(OH)_6Mo_6O_{18}$). The catalyst was proved to be effective in aerobic oxidative desulfurization with extremely high TON in absence of any sacrificial agent (Scheme 1). Our study provides an example of the mixed-valence molybdenum ions in the Anderson polyoxometalate and we particularly focus on the positive effect of mixed-valence of molybdenum ions in Anderson structure in the aerobic oxidative desulfurization.

---

* Corresponding author. Tel.: +86 535 6902063.
E-mail address: lhrye@yahoo.com.cn (H. Lü).

0926-3373/$ – see front matter © 2013 Elsevier B.V. All rights reserved.
http://dx.doi.org/10.1016/j.apcatb.2013.02.034



Scheme 1. Aerobic oxidation of DBT to the corresponding sulfone.

2. Experimental

2.1. Catalyst preparation

All the chemicals were of analytical grade and used as received. The Co (III) polyanion $(NH_4)_3Co(OH)_6Mo_6O_{18}$ was prepared according to the procedure reported in literature [22], a mixed aqueous solution ($30\,cm^3$) of $CoSO_4{\cdot}7H_2O$ (0.015 mol) and 30% aqueous H_2O_2 (2 g) were added dropwise into the boiling aqueous solution of heptamolybdate (0.025 mol in $260\,cm^3$ water). The obtained solution was refluxed for 10 min and then filtered while hot. The filtrate was set aside for crystallization.

$[(C_{18}H_{37})_2N(CH_3)_2]_3Co(OH)_6Mo_6O_{18}$ was prepared as following: 10 mL ethanolic solution of quaternary ammonium (3 mmol) was added dropwise into a 40 mL aqueous solution of $(NH_4)_3H_6CoMo_6O_{24}$ (1 mmol) under stirring at room temperature. A light blue-green precipitate was immediately formed. After continuous stirring for 4 h, the resulted mixture was filtered and dried at 60 °C in vacuum for 24 h.

2.2. Characterization of catalysts

The infrared spectrum (IR) of the catalyst, diluted with KBr and pressed into a pellet, was recorded on a Nicolet 470 FTIR spectrometer. UV–vis diffuse reflectance spectroscopy (UV–vis DRS) was recorded on a TU-1901 (Beijing General Analytical Instrument Ltd Co., China) with $BaSO_4$ as the internal standard. The scanning patterns were recorded at 200–800 nm in a step-scan mode with a step of 5 nm. Differential thermal analyses (DTA) and thermogravimetric analyses (TGA) were carried out on NETZSCH STA409PC thermal analyzer with heating rate of $10\,K\,min^{-1}$ from 298 to 873 K under nitrogen atmosphere. A cyclic voltammogram of 1 mM $[(C_{18}H_{37})_2N(CH_3)_2]_3Co(OH)_6Mo_6O_{18}$ was measured on a LK3200A instrument using a glassy-carbon as working electrode versus SCE. The measurement was carried out in a 0.1 M acetonitrile solution of $(C_4H_9)_4NBF_4$ with scan rate of $50\,mV\,s^{-1}$. XPS spectrum was obtained by using Thermo ESCALAB 250Xi with Al Kα X-ray source. Pass energy was 20 eV and base pressure of analysis chamber was greater than 1×10^{-8} Pa. The spectra were calibrated against the reference binding energy of C 1s (284.8 eV).

2.3. Oxidation of model sulfur-containing compounds

In a typical experiment, the sulfur concentration was kept at 500 ppm by dissolving model sulfur-containing compound (BT, DBT or 4,6-DMDBT) in 25 mL Decalin. After this solution was heated to 80 °C and bubbled by molecular oxygen, catalyst was added. The solution in reaction was stirred vigorously and sampled periodically. The obtained samples were placed into an ice chamber for the termination of reaction and precipitation of most sulfones. The sulfur content in the upper clear solution was determined by microcoulometry after the catalyst and sulfones were precipitated by centrifugation.

3. Results and discussion

3.1. Characterization of the B-type Anderson catalyst

The IR spectrum of $[(C_{18}H_{37})_2N(CH_3)_2]_3Co(OH)_6Mo_6O_{18}$ is shown in Fig. 1. The spectrum of the catalyst reveals the characteristic bands of bridged Mo—O—Mo bonds in the molecule of hetropolyanione around 572, 653 cm^{-1}, The bands at 890, 912 and 938 cm^{-1} are attributed to the terminal group of Mo═O bond and the band at 431 cm^{-1} is assigned to central Mo—O···Co modes [24,25]. In addition, the other peaks at 1470, 2852, 2922 and 3027 cm^{-1} belong to the vibrations of the quaternary ammonium cations.

UV–vis spectrum of $[(C_{18}H_{37})_2N(CH_3)_2]_3Co(OH)_6Mo_6O_{18}$ shows intense absorption in the range of 200–330 nm (Fig. 2), which is the characteristic of polymer Mo–O–Mo structures induced by charge transfer processes from O^{2-} to Mo^{6+} in octahedral coordination[24,26]. The two bands at 410 and 600 nm are the characteristic of Co^{3+} in the regular octahedral configuration, which are registered in the spectrum of cobalt heteropolymolybdate [24].

The weight loss was 2.1% around 160 °C in TG curves of $[(C_{18}H_{37})_2N(CH_3)_2]_3Co(OH)_6Mo_6O_{18}$ (Fig. 3). It suggests the molar ratio of water molecules to heteropolyanions is 3.1:1. The weight loss of 61.1% between 160 and 600 °C was resulted from the loss of quaternary ammonium cations. The total weight loss (63.2%) of the sample agrees with the calculated value of 64.7%.

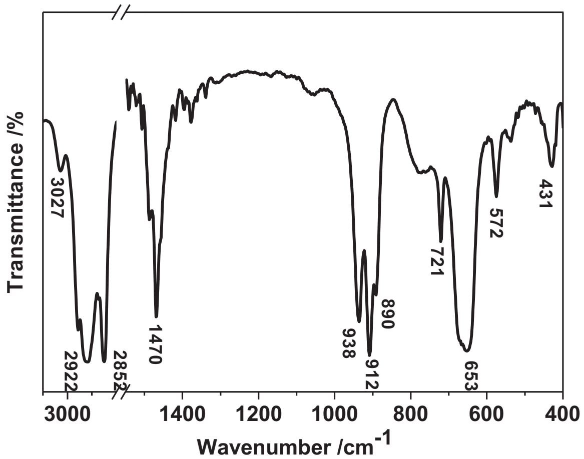


Fig. 1. The IR spectrum characterization of catalyst $[(C_{18}H_{37})_2N(CH_3)_2]_3Co(OH)_6Mo_6O_{18}$.