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Communication

Oxidation of dibenzothiophene using oxygen and a vanadophosphate catalyst for ultra-deep desulfurization of diesels

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ABSTRACT

A bicapped Keggin structure vanadophosphate showed high catalytic activity in the oxidation of dibenzothiophene (DBT) to sulfone using molecular oxygen as oxidant under mild reaction conditions. This is a promising approach to the ultra-deep desulfurization of fuels (e.g. diesel) as sulfones can be removed from the fuel by extraction or selective adsorption.

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Sulfur-containing compounds are undesirable in fuels because they contribute to acid rain and cause deactivation of catalysts in automotive applications. The Environmental Protection Agency regulations and EU Euro V standards require the S level in diesel fuels to be less than 15 and 10 ppm, respectively. The current technology is conventional hydrodesulfurization (HDS), which shows high efficiency for the removal of thiols, sulfides, and disulfides. However, it is difficult to reduce refractory sulfur-containing compounds such as dibenzothiophene (DBT) and its derivatives, especially 4,6-dimethyldibenzothiophene (4,6-DMDBT), to an ultra-low level using only conventional HDS. This process requires severe operating conditions such as high temperatures, high pressures, and high hydrogen consumption to achieve the ultra-deep desulfurization of diesel. From an economic and environmental point of view, it is necessary to develop an alternative ultra-deep desulfurization processes [1,2]. One promising strategy to re-

move sulfur-containing compounds from fuel oils (e.g. diesel) is oxidative desulfurization (ODS). ODS avoids the use of hydrogen and allows the process to be conducted under ambient conditions. Moreover, refractory compounds, mainly 4,6-DMDBT, can be removed efficiently, which are difficult to remove with conventional HDS [3].

H₂O₂ is the highly reactive oxidant mostly used for ODS. It has been used with catalysts like Ti molecular sieves [4], vanadium oxide [5], WO_x/ZrO₂ [6], polyoxometallates [7,8], and amphiphilic catalysts in emulsions [9,10]. Other oxidants like organic and inorganic peroxyacids, NO₂, *tert*-butyl-hydroperoxide, and O₃ have also been reported for ODS [11–13]. Taking into account environmental and economic concerns, the utilization of O₂ as the oxidant for ODS is most desirable [14,15]. In this communication, we report a highly efficient oxidation of refractory compounds DBT using molecular oxygen catalyzed by tetradeccavanadophosphate [C₈H₁₇N(CH₃)₃]₅H₄PV₁₄O₄₂

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Fig. 1. ^{31}P and ^{51}V NMR spectra of tetradecavanadophosphate.

($\text{Q}_5\text{H}_4\text{PV}_{14}\text{O}_{42}$) under mild conditions.

$\text{Q}_5\text{H}_4\text{PV}_{14}\text{O}_{42}$ was isolated by treating a mixture of meta-vanadate and orthophosphate ($\text{V}:\text{P} = 4:1$, $\text{pH} = 2.3$) with $\text{C}_8\text{H}_{17}\text{N}(\text{CH}_3)_3\text{Cl}$. The Fourier transform infrared (FT-IR) spectrum of $\text{Q}_5\text{H}_4\text{PV}_{14}\text{O}_{42}$ showed four intense bands from 700 to 1100 cm^{-1} , which served as the signature of the Keggin anion. The band at 1060 cm^{-1} was assigned to the stretching of the P–O bond of the central PO_4 . According to studies by Rocchiccioli-Deltcheff et al. [16,17], the vibrational motion of the phosphate group is independent of the remaining “cage” of the Keggin anion. The band at 946 cm^{-1} was assigned to the stretching of the terminal V–O_t bond. The two bands at 866 and 804 cm^{-1} were the asymmetrical V–O_b–V stretching vibrations. Figure 1 shows the ^{31}P and ^{51}V NMR spectra of tetradecavanadophosphate, which were well explained by the “bicapped Keggin” structure of the anion. The ^{31}P NMR spectrum showed a single peak at 0.12 ppm. The ^{51}V NMR spectrum showed three broad peaks with the relative intensity ratio of 2:8:4. The peak at -529 ppm was assigned to the “capping” 5-coordinated vanadium. The two peaks at -580 and -596 ppm were assigned to the 6-coordinated vanadium in the Keggin unit [18,19].

The oxidation of the DBT-containing model oil was conducted in a flask at $90\text{ }^\circ\text{C}$ with O_2 gas bubbled in. Samples were periodically taken by a pipette and quantified using an external

Fig. 2. FT-IR spectra of DBT before (a) and after (b) reaction.

calibration curve. The sulfur-containing compounds present in the diesel were analyzed by a gas chromatograph coupled to a flame photometric detector (GC-FPD). A white needle-shaped crystal was obtained when the reaction system was cooled down to room temperature. The product was determined to be crystallized dibenzothiophene sulfone (DBTO_2) by FT-IR (Fig. 2) and ^1H NMR (δ 8.20 (2 H), 7.98 (2 H), 7.80 (2 H), 7.65 (2 H)). The band at 1293 cm^{-1} corresponded to the asymmetrical stretching vibration of S=O while the symmetrical stretch was at 1165 cm^{-1} . The bands at 571 and 540 cm^{-1} were assigned to the bending vibration of S=O. The mass spectrum of product showed the molecular ion peak at 216 (m/z), which agreed with the molecular weight of DBTO_2 [20].

Figure 3(a) shows the DBT conversion and $\ln(C_t/C_0)$ vs. reaction time, which revealed the catalytic reaction kinetics. C_t/C_0 was defined as the ratio of the concentration of final and initial sulfur-containing compounds. Increasing reaction temperature from 80 to $100\text{ }^\circ\text{C}$ led to a remarkable enhancement of the

Fig. 3. (a) Conversion of DBT and $\ln C_t/C_0$ vs. reaction time at different temperatures; (b) Apparent activation energy for the ODS of DBT. Reaction conditions: $\text{Q}_5\text{H}_4\text{PV}_{14}\text{O}_{42}$ 40 mg, DBT (S: 500 ppm) in 20 ml decalin, oxidant O_2 1 atm.

Fig. 4. In situ ESR spectra obtained in the oxidative desulfurization process. (1) Sample tested without catalyst at 60 °C; (2) Sample tested without catalyst at 25 °C; (1') Sample tested with catalyst at 60 °C; (2') Sample tested with catalyst at 25 °C.

conversion of DBT. At 100 °C, the conversion of DBT was 100% in 3 h. The linear fit of $\ln(C_t/C_0)$ against reaction time demonstrated pseudo-first order kinetics for the oxidation of DBT on $\text{Q}_5\text{H}_4\text{PV}_{14}\text{O}_{42}$. The apparent activation energy for the ODS of DBT on $\text{Q}_5\text{H}_4\text{PV}_{14}\text{O}_{42}$ was 97.7 kJ/mol (Fig. 3(b)). At 100 °C, the conversion of 4,6-DMDBT was 100% in 4 h.

To study the mechanism of the activation of sulfur-containing compounds, an ESR spin-trap technique with DMPO as a trap for O_2^- was employed. Figure 4 shows the ESR signals obtained from the in situ ODS process. No ESR signals were observed at 25 and 60 °C for the reaction system without $\text{Q}_5\text{H}_4\text{PV}_{14}\text{O}_{42}$. With the introduction of $\text{Q}_5\text{H}_4\text{PV}_{14}\text{O}_{42}$, no ESR signal was observed at 25 °C. When the reaction system was heated to 60 °C, a broad, 8-line ESR signal appeared. The ESR signal was centered at $g = 2.0088$, and can be assigned to oxygen species [21]. The 8-line ESR signal was attributable to the superposition of O_2^- and O^- [22]. These results indicated that active oxygen species were produced through the reaction of $\text{Q}_5\text{H}_4\text{PV}_{14}\text{O}_{42}$ with O_2 . Therefore, we proposed a mechanism where first, O_2 was activated to form an active species when O_2 coordinated to $\text{Q}_5\text{H}_4\text{PV}_{14}\text{O}_{42}$; then, the active species oxidized DBT to DBTO_2 .

In conclusion, we synthesized a “bicapped Keggin” structure vanadophosphate which showed high catalytic activity in the oxidation of DBT to sulfone using oxygen. This provides a new pathway for the ODS of diesel with oxygen as oxidant.

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Graphical Abstract

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Oxidation of dibenzothiophene using oxygen and a vanadophosphate catalyst for ultra-deep desulfurization of diesels

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Oxygen was by interaction with a vanadophosphate, and it oxidized dibenzothiophene to sulfone.

分子氧为氧化剂磷钒酸盐为催化剂超深度氧化脱除柴油中的二苯并噻吩

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摘要: 一种“双帽Keggin型”磷钒酸盐在温和的反应条件下以分子氧为氧化剂氧化二苯并噻吩至二苯并噻吩砒的反应中表现出很高的催化活性。用溶剂萃取或者选择吸附等方法可轻易地将反应产生的二苯并噻吩砒从油品中除去。这提供了一种新型的分子氧为氧化剂的超深度氧化脱硫方法。

关键词: 氧化脱硫; 分子氧; 磷钒酸盐; 二苯并噻吩

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燃料油中含硫化合物可导致酸雨和发动机尾气三效催化剂失活, 是急需除去的物质。美国环境保护局和欧洲欧V标准分别要求燃油中的硫含量低于15和10 ppm。目前, 广泛使用的传统的加氢脱硫技术(HDS)能够高效地脱除燃油中的硫醇、硫醚和二硫醚等硫化物。但很难将二苯并噻吩(DBT)及其衍生物4,6-二甲基二苯并噻吩(4,6-DMDBT)脱除以达到超低硫标准。HDS操作条件苛刻, 需要高温、高压和高氢耗来达到超深度脱硫的目标。从经济和环保的角度去考虑, 急需开发新型的超深度脱硫技术^[1,2]。氧化脱硫(ODS)是一种很有前景的超深度脱硫技术, 它不使用昂贵的氢源, 操作条件温和, 能够高效地氧化脱除加氢脱硫难以脱除的含硫化合物^[3]。

H₂O₂具有较高的反应活性, 是一种常用的ODS氧化剂, 可用于多种催化剂体系, 如Ti分子筛体系^[4]、钒氧化物体系^[5]、WO_x/ZrO₂体系^[6]、杂多酸盐体系^[7,8]和乳液催化剂体系^[9,10]。文献中报道的氧化脱硫体系也使用其他的氧化剂如, 有机和无机过氧酸、NO₂、叔丁基过氧化氢和臭氧^[11–13]。从环保和经济性去考虑, 分子氧是最理想的ODS氧化剂^[14,15]。本文报道了一种在温和反应条件下, 采用分子氧做氧化剂, 磷钒十四酸盐[C₈H₁₇N(CH₃)₃]₅H₄PV₁₄O₄₂ (Q₅H₄PV₁₄O₄₂)为催化剂高效地催化氧化加氢脱硫难以脱除的含硫化合物(DBT)的体系。

将偏钒酸钠和磷酸的混合溶液(V:P = 4:1, pH = 2.3)和C₈H₁₇N(CH₃)₃Cl混合制得磷钒十四酸盐Q₅H₄PV₁₄O₄₂。磷钒十四酸盐Q₅H₄PV₁₄O₄₂的红外光谱(FT-IR)谱中, 700–1100 cm⁻¹之间的四个强吸收峰是Keggin型阴离子的特征吸收峰; 1060 cm⁻¹处的吸收峰可归属为中心PO₄

的P-O振动。Rocchiccioli-Deltcheff等^[16,17]研究发现磷酸基团的振动独立于Keggin阴离子。946 cm⁻¹处的吸收峰可归属为端位V–O_t振动。866和804 cm⁻¹两处的吸收峰可归属为V–O_b–V的不对称振动。³¹P和⁵¹V的NMR谱图很好地解释了磷钒十四酸盐阴离子的双帽Keggin型结构(图1)。³¹P NMR谱有一个位于0.12 ppm处的单峰。⁵¹V NMR谱呈现出三个相对强度为2:8:4的宽峰; –529 ppm处的峰可归属为“帽位”5配位的钒原子; –580和–596 ppm的峰可归属为Keggin单元中6配位的钒原子^[18,19]。

模型油DBT的氧化在90 °C, 鼓入氧气的三口烧瓶中进行的。每隔一定时间用吸管取样, 用外标曲线法测定油品中的硫含量。采用GC-FPD分析检测含硫化合物。当反应体系冷却至室温, 有白色针状晶体析出。通过IR (图2)和¹H NMR(δ 8.20 (2 H), 7.98 (2 H), 7.80 (2 H), 7.65 (2 H))表征得出该产物为二苯并噻吩砒(DBTO₂)。129和1165 cm⁻¹处吸收峰可分别归属为S=O的不对称伸缩振动和S=O的对称伸缩振动。571和540 cm⁻¹处吸收峰可归属为S=O的弯曲振动。GC-MS结果也表明216 (m/z)分子离子峰在处为DBTO₂, 与文献结果一致^[20]。

图3(a)给出了DBT转化率和ln(C/C₀)对反应时间的关系可以看出, 该反应为准一级反应。当温度从80 °C上升至100 °C时, DBT的转化速率大幅提高; 100 °C反应3 h, DBT完全被氧化成DBTO₂。该反应的表现活化能为97.7 kJ/mol (图3(b))。100 °C反应4 h, 4,6-DMDBT完全被氧化成DBTO₂。

我们使用原位ESR自旋-捕获技术, 用DMPO作为氧自由基捕获剂来考察反应体系硫化物氧化的机理。图4给出了在催化剂Q₅H₄PV₁₄O₄₂存在下, 原位分子氧氧化

DBT的特征ESR谱图. 可以看出, 在不加催化剂, 无论是室温还是加热都没有活性氧物种的信号; 当加入催化剂后, 在室温也未出现活性氧物种; 当加热到60 °C时, 有一八重峰的出现, 峰信号集中在中心场 $g = 2.008$, 这归属为活性氧物种信号^[21]. 该八重峰可认为是超氧自由基 $O_2^{\cdot-}$ 和 $O^{\cdot-}$ 信号叠加而成^[22]. 这表明催化剂 $Q_5H_4PV_{14}O_{42}$ 和 O_2 相互作用可产生活性氧物种. 由此, 我们推测出该

过程可能的反应机理: 首先, O_2 和催化剂 $Q_5H_4PV_{14}O_{42}$ 相互作用产生活性氧物种; 然后, 该活性氧物种将DBT氧化成DBTO₂.

综上, 我们合成了一种“双帽Keggin型”磷钒酸盐. 该磷钒酸盐在以分子氧为氧化剂氧化DBT至DBTO₂的反应中表现出很高的催化活性. 这为以分子氧为氧化剂氧化脱除柴油中含硫化合物提供了一种新的方法.

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