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Template method for a hybrid catalyst material POM@MOF-199 anchored on MCM-41: Highly oxidative desulfurization of DBT under molecular oxygen

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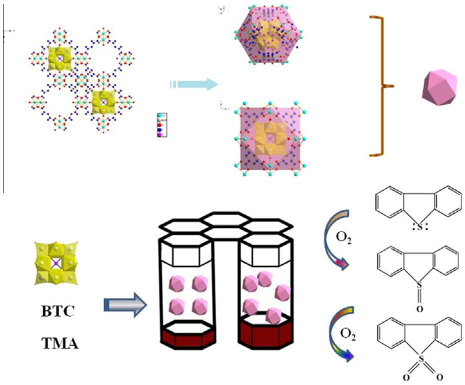
HIGHLIGHTS

- A kind of novel heteropolyacid-loaded catalyst POM@MOF-199@MCM-41 was synthesized.
- The structure of MOF-199 with POM encapsulated in is clear under crystal analysis.
- Under O_2, PMM exhibits excellent catalytic performance for deep desulfurization.
- The oxidation of DBT followed pseudo-first-order kinetics.

GRAPHICAL ABSTRACT



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ABSTRACT

A catalyst system designed by a kind of hybrid material POM@MOF-199@MCM-41 (PMM) was found by a one pot and POM template self-construction of MOF-199 in the pore of MCM-41. This catalyst was exploited to act as a stable heteropolyacid-based one in the direct oxidative desulfurization process with a feedstock of model oil under O_2 as oxidant. Based on optimal conditions, the DBT conversion reached up to 98.5% and the PMM could be recycled ten times with a slight decrease, which was compared with heteropolyacid only based on MOF-199 and MCM-41, respectively. Additionally, the structure of ordered nano-sized pores of MOF-199 with POM encapsulated in was clear under crystal analysis, which offered strong evidences for the further movement into the MCM-41.

1. Introduction

Ultra low sulfur diesel (DLSD) with 10–15 ppm sulfur, which has been implemented during the last several years in Europe, Japan and USA [1], has been a stringent need for the rest of world to satisfy the upcoming pieces of legal requirements and environmental concerns. Today, hydrodesulfurization (HDS) is mainly relied on by refineries [2], but this traditional process entails some inherent problems in treating sulfur-containing aromatic hydrocarbon compounds, operating at high temperature (300–400 °C) and high hydrogen pressure (3–6 MPa) to convert organosulfur compounds to hydrogen sulfide (H_2S). To avoid these problems, a variety of alternative technologies e.g. adsorptive

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desulfurization (ADS), extractive desulfurization (EDS) and oxidative desulfurization (ODS) have been investigated to remove sulfur to a low level. Among them, for the extra complementary chemistry, ODS shows great promise in lowering the sulfur level from a few hundred to less than 10 ppm, which has received massive research interests [3–9].

During the ODS, organosulfur compounds can be oxidized by the electrophilic addition of oxygen atoms to form sulfoxide (DBTO) and further sulfone ($DBTO_2$), in which the choice of oxidant is one of key factors. For the significantly different from the chemical and physical properties of hydrocarbons in the fuel oil, DBTO and $DBTO_2$ can be easily removed by solvent extraction or solid adsorption. Up to now, different catalytic systems have been used in ODS, such as organic acid, polyoxometalate, ionic liquids, a Fenton reagent, and so on [10,11]. As an economic and environment-friendly catalyst due to fast reversible multi-electron redox transformation under mild conditions, thermal and hydrolytic stability and polyoxometalates (POMs) have been proposed as a potential catalyst for deep oxidative desulfurization. Qiu et al. studied phosphomolybdate catalysts treated by amphiphilic quaternary ammonium, whose ODS conversion can be up to 84.4% on the straight-run diesel [12]. Gall et al. reported that the oxidation reactivities of the representative thioethers may be governed by the steric effects after studying the ODS of thioethers using $H_5PV_2Mo_{10}O_4$ [13]. Wang et al. found $H_3PW_6Mo_6O_{40}$ has high desulfurization efficiency in many Keggin-type POMs for catalytic oxidation of DBT with H_2O_2 as oxidant [14]. Yazu et al. used the 12-tungstophosphoric acid as the catalyst in the *n*-octane/acetonitrile biphase system for the catalytic oxidation of the DBT [15]. However, pure POMs used as the catalysts are hindered by their low specific area ($<10\ m^2\ g^{-1}$) and high solubility in polar reaction systems, which leads to the difficulty in separation and recovery. Immobilization of POMs, such as supporting POMs onto a solid porous substrate, heteropolyacid-encapsulated self-assembled materials and so on, has been proposed as a potential strategy. Li et al. synthesized phosphotungstic acid on a mesoporous silicate, which yielded a 98–99% of DBT conversion rate but the low re-utilizing gave its relative little practicality [16]. Xiong et al. reported a heterogeneous catalyst system was synthesized by immobilizing phosphotungstic acid on ionic liquid-modified mesoporous silica SBA-15 applied in oxidative desulfurization and the removal of BT could reach 81.3% within 60 min [17].

Metal-organic frameworks (MOFs), obtained by connecting metal ions with organic linkers through coordinative bonding, are nowadays on top of research in materials chemistry [18]. The success of these kinds of high surface area, crystalline materials comes from the diversity of metal or metallic clusters that are interconnected with various functionalized organic linkers leading to further tailoring [19,20]. Such superiorities endowed their potential applications spread over gas adsorption, storage, separation, and recently catalysis. By means of covalent or electrostatic interaction, POMs can be surely encapsulated into appropriate metal organic frameworks. Recently, a 3D porous MOF material, MOF-199, has shown important capacities for catalyst engineering. Hill et al. studied and proposed a synergistic effect between $PW_{11}Cu$ and MOF-199 in the oxidation of H_2S which could obviously increase the reaction rate [21]. Yang et al. have proved PMoV@MOF-199 as an efficient catalyst for the exceptional activity for the phenol from benzene [22]. MOF-199 is a kind of micropore MOF with Cu(II) dimmers linked into paddlewheels by BTC, owning two types of cages of cuboctahedral symmetry. The porous structure allows the introduction of nanoparticles, molecular inorganic species and drugs within its cages due to the correlation between their size and the accessible dimensions of the windows of each cage. While only one of the large cages in MOF-199 could be suited for encapsulation of POMs, the POMs added to go through hydrothermal synthesis process are found in the cavities afterward, which discovered strong interaction between Cu(II) and POMs ions leading to spontaneous self-assembly of MOF. The POMs act as a kind of template species guiding the synthesis and stabilizing the structure [23,24].

Aiming to solve the easy-solubility of heteropolyacid in solvent, we anchored them into the suitable porous materials. For the little times re-usability of POM@MOF-199 and much mobility for heteropolyacid in the MCM-41 for POM@MCM-41, in this work, a new kind of hybrid material POM@MOF-199@MCM-41(PMM), which is by an one pot and POM template self-construction of MOF-199 in the pore of MCM-41, was synthesized and used in the oxidation of model sulfur compounds with O_2 as oxidant to get a superior performance for desulfurization [25]. The obvious increased stability and desulfurization performance of this material were also investigated after the introduction of MCM-41. Additionally, the structure of ordered nano-sized pores of MOF-199 with POM encapsulated in was clear, which offered strong evidences for the further movement into the MCM-41.

2. Experimental

2.1. Materials

All the reagents were analytical purity and were used as received. DBT was bought from J&K technology Co., Ltd. (Beijing, China). Disodium hydrogen phosphate (AR) was from Xi'an Chemical Works. Tetramethylammonium hydroxide and sodium tungstate were obtained from Aladdin Reagent Co., Ltd. (Shanghai, China). Sodium molybdate was purchased from Adamas Reagent Co., Ltd. (Beijing, China) and 1,3,5-benzenetricarboxylic was from Acros Organics. Cupric nitrate (AR), concentrated H_2SO_4 (AR), and cetyltrimethylammonium bromide (AR) were the products of Tianjin Chemical Works.

2.2. Catalyst preparation

2.2.1. Preparation of $PMo_{12-x}W_xO_{40}\cdot nH_2O$

The solution of disodium hydrogen phosphate (2.15 g, 6 mmol) and sodium molybdate (8.71 g, 36 mmol) was fully dissolved in 12.5 ml, 25 ml deionized water, respectively. After refluxed at 90 °C for 30 min, was added sodium tungstate (11.88 g, 36 mmol) and concentrated H_2SO_4 dropwise to adjust pH = 1.5. The temperature of the mixture was then increased to 90 °C again and stirred for another 8 h. Extracted by diethyl ether 3 times, the yellow powders $PMo_6W_6O_{40}\cdot nH_2O$ could be achieved by evaporating to dryness. The other products of $PMo_{12-x}W_xO_{40}\cdot nH_2O$ (X = 2, 4, 6, 8 and 10) were similarly prepared followed by the different molar ratio of sodium molybdate and sodium tungstate.

2.2.2. Preparation of MCM-41

MCM-41 was prepared according to the reported method [26]. After stirring the two solutions at 40 °C for 0.5 h, 3.3 g cetyltrimethylammonium bromide (CTAB) in 50 ml distilled water and 28.4 g sodium silicate into 300 ml, they all totally rendered transparent. Mixing the above two parts and stirring another 0.5 h, let it stand to crystallization in flask at 90 °C for 25 h. Followed by adjusting the pH = 10.5, the mixture continued stand at the same temperature for 96 h. The white powders were obtained after dried at 75 °C for 50 h and calcined at 550 °C for 6 h.

2.2.3. Preparation of PMM

$PMo_{12-x}W_xO_{40}$@MOF-199@MCM-41 was achieved by the hydrothermal method [27]. 0.1815 g (0.75 mmol) of