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# Metal modified heteropolyacid incorporated into porous materials for a highly oxidative desulfurization of DBT under molecular oxygen

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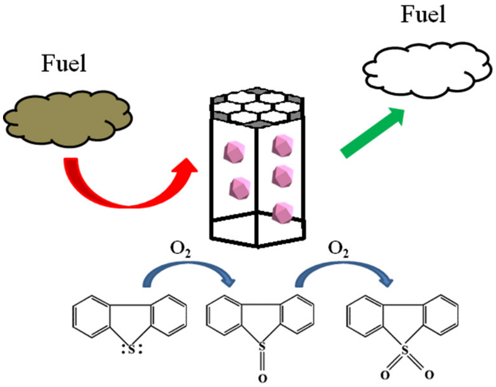
## HIGHLIGHTS

- Mesoporous Metal-POM@MOF-199@MCM-41 was prepared for oxidative desulfurization.
- The hybrid catalyst leads to the deep DBT conversion with $O_2$ as oxidation.
- Stability is mainly correlated with MOF-199 and MCM-41.
- The oxidation of DBT followed pseudo-first-order kinetics.

## GRAPHICAL ABSTRACT



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## ABSTRACT

A kind of composite catalytic materials, Metal-POM@MOF-199@MCM-41 (Metal-PMM), were obtained by confining MOF-199 encapsulating metallic Keggin POM into mesoporous MCM-41. The catalyst was designed on the stability and efficiency, which MCM-41 could act as a stable cavy for the heterogeneous metallic POM-based catalyst in the oxidative desulfurization process. The structure characteristics of the catalysts were elucidated through XRD, IR, XPS, $N_2$ adsorption-desorption, SEM and TEM. The reaction rate could be greatly enhanced, up to 99.1%, under Co-PMM as catalyst and $O_2$ as oxidant. After reaction, the catalyst can be simply recovered and reused more than 5 times without the change of its structure, for the strongly fixation of MOF-199 and MCM-41 to the metallic modified Keggin POM materials.

## 1. Introduction

Due to the constant close attention of environmental and health concerns, the use of friendly fuels has been a common aspiration worldwide [1–4]. Organic sulfur-containing compounds from crude oil are converted to $SO_2$, which have a negative impact on the environment, contributing to air pollution, damaging the exhaust after-treatment devices [5–7]. The clean fuels including less than 10 ppm of sulfur content, is currently a challenging subject, which need the introduction of advanced ultra-deep desulfurization technologies [8].

The conventional process for the removal of organosulfur, catalytic hydrodesulfurization (HDS), is limited by the less efficient in removing dibenzothiophene (DBT) and its derivatives with steric hindrance on the sulfur atom. What is more, the high temperature, high pressure and high hydrogen consumption are also inevitably required for the low fuel level [9–11]. To overcome these

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disadvantages for HDS, potential deep desulfurization processes, such as adsorption [12], extraction [13], oxidation and bioprocesses [14], have been rise. Among them, the oxidative desulfurzation (ODS) has attracted extensive attention for the mild conditions to remove the refractory sulfur compounds, DBT and its derivatives, which could easily achieve the ultra deep desulfurization. During the ODS process, the sulfur compounds could be transformed effectively into the corresponding sulfoxides and sulfones, which could be removed by solvent extraction or solid adsorption for the different chemical and physical properties from hydrocarbons in fuel [15].

The commonly used oxidant in ODS are hydrogen peroxide, ozone, organic hydroperoxides, molecular oxygen and others. Owing to the low cost, wide range of source and environmental compatibility, molecular oxygen gains increasing attention, which could be an ideal oxidant for ODS [16,17]. Polyoxometalate (POM), especially Keggin structure type, have been applied as effective oxidative catalysts for the ODS process [18–20]. POM, belong to a large class nanosized metal-oxygen cluster anions, forms by a self-assembly process typically in an acidic aqueous solution. Owing to the low recovery rate and small surface area (<10 $m^2\ g^{-1}$), immobilization of POMs shows a potential advantage during the ODS reactions [6,21,22]. M. Chamack et al. [23] reported a Cs salts of W-substituted $H_3[PM_{O12}O_{40}]$ catalysts supported on platelet SBA-15 for oxidative desulfurization of dibenzothiophene, which showed higher catalytic activity after 80 min under TBHP as extracting agent. Jose Luis Garcia-Gutierrez et al. [24] prepared catalysts by equilibrium adsorption of tungsten from solution of tungsten(VI) oxide, tungstic acid, ammonium tungstate, ammonium metatungstate and phosphotungstic acid in supports. After comparing the different system, the sulfur removal from diesel fuel was achieved up to 93.8 ppm (70.7%) under the ammonium metatungstate/titania catalyst. Jing Xiao et al. [25] investigated a deep desulfurization process under phosphotungstic acid/activated carbon catalyst with $H_2O_2$, the sulfur conversion rate could reach to 90% in 2 h at 90 °C.

Metal-Organic Frameworks (MOFs), known as hybrid crystalline porous materials, have been noticed yielding novel functional materials with remarkable potential for catalysis, separation, drug delivery, nonlinear optical studies, magnetism properties and gas storage [26–29]. The diversity of metal or metallic clusters that are interconnected with various functionalized organic linkers, leading to 3D porous structures with large and accessible cages and tunnels, endowed the success of these materials. MOF-199 has been shown high porosity combined with high thermal and chemical stability, in which Cu(II) dimmers linked into paddle-wheels by BTC and owning two types of cages of cuboctahedral symmetry [30,31]. The special structure makes it an excellent candidate to support catalytic species. The attempt of incorporating POMs in porous MOFs arises as a novel pathway to exploit new catalytic system, transferring the cheap materials into valuable products. A few papers have been reported the immobilization of catalytically active POMs in MOFs [32]. Carlos M. Granadeiro et al. [33] tried to incorporate monovacant polyoxometalates into MIL-101(Cr) for liquid phase oxidation, in which found MOF has a relevant influence in the stability of POM. Diana Juliao et al. [34] used a zinc-substituted polyoxometalate as catalyst under homogeneous and heterogeneous (MIL-101(Cr) encapsulated) condition for the desulfurization of model diesel, gaining the short time usage to complete desulfurization and without loss of activity after reuse several times. We supposed the catalytic activity of the well performed catalysts POM encapsulated in MOF-199 could be better in the oxidative desulfurization.

In the previous work [35], considering the right size of pores, we have introduced the POM@MOF-199 into the MCM-41, increasing the stability of catalyst to obtain the several times repeat usage. The composite catalyst was synthesized by adding the POM, MCM-41 and the raw materials of MOF-199 in a one pot, POM template self-construction of MOF-199 in the pores of MCM-41. In the current work, we aimed to modify the POM with different metal ions. The metal heteropoly acid salts could easily appear a kind of Fake-Liquid phase, which show a relative soft structure to promote the entrance. What is more, the more POM catalytic species into the system, the higher ODS rate. These metal-POMs were uniformly encapsulated in the order nanoscale pores of MOF-199, further into a suitable large molecular sieve MCM-41 to obtain the more stability, namely Metal-PMM, leading to improvements for deep oxidative desulfurization.

## 2. Experimental

### 2.1. Materials

All the reagents used in the preparation of the composite materials were analytical purity, namely Disodium hydrogen phosphate (Xi'an Chemical Works), sodium tungstate (Aldrich), Sodium molybdate (Adamas), Tetramethylammonium hydroxide (Aldrich), 1, 3, 5-benzenetricarboxylic (Acros Organics), Cupric nitrate (Tianjing Chemical Works), concentrated $H_2SO_4$ (Tianjing Chemical Works), cetyltrimethylammonium bromide (Tianjing Chemical Works) , Barium hydroxide (Shanghai Chemical Works) and other sulfate (Cr, Mn, Fe, Co, Ni, Cu, Zn and Cd, Xi'an Chemical Works). The chemicals for desulfurization experiments, DBT (J&K technology) and n-octane (Tianjing Fuchen chemical reagent factory), were used as received.

### 2.2. Catalyst preparation

#### 2.2.1 Preparation of metal loaded POM (Metal-POM, M = Cr, Mn, Fe, Co, Ni, Cu, Zn, Cd)

Pure POM was prepared following the method in our previous work [36]. The M-POM was synthesized by substitution method according to the Ref. [37]. Adding 1.5 mmol $Ba(OH)_2$ to the aqueous solution containing 1.0 mmol of $H_3PMo_6W_6O_{40}$, in which Ba $(OH)_2$ to neutralize protons. Then, 1.5 mmol metal sulfate was added to replace the Barium ion with metal above and eliminated it as BaSO4 precipitate. The product was recovered from the solution by recrystalization.

#### 2.2.2 Preparation of Metal-POM@MCM-41 (Metal-PMC)

The pure MCM-41 was synthesized also followed the reported method [38]. Metal-PMC, which was obtained by adding 2.5 g MCM-41 into the aqueous solution with 1.0 mmol of Metal-POM, was constant stirred for 16 h. After filtration, the white solid products were dried under 110 °C overnight and calcined under 300 °C for 2 h.

#### 2.2.3 Preparation of Metal-POM@MOF-199@MCM-41 (Metal-PMM)

Metal-PMM was achieved by the hydrothermal method. 0.1815 g (0.75 mmol) of $Cu(NO_3)_2{\cdot}3H_2O$ and 0.1 g Metal-POM were added into 5 ml distilled water containing 0.1 g MCM-41. Then, 0.2718 g (1.5 mmol) $(CH_3)_4NOH{\cdot}5H_2O$ (TMA) and 0.0946 g (0.75 mmol) 1, 3, 5-benzenetricarboxylic (BTC) were added to stir for addition 30 min. Transferring the mixture into an autoclave equipped with 10 ml of PTEF lined and heated to 180 °C for 16 h, the light green powders could be obtained.

Preparation of Metal-POM@MOF-199 (Metal-PMO): The same synthesis procedure above to obtain the Metal-PMO, just no MCM-41 was added. The olive drab crystals could be collected.