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# Synthesis and application of different phthalocyanine molecular sieve catalyst for oxidative desulfurization



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## ABSTRACT

$M_2(\text{PcAN})_2$  ( $M = \text{Fe, Co, Ni, Cu, Zn}$  and  $\text{Mn}$ ) anchored onto W-HZSM-5 ( $M_2(\text{PcAN})_2$ -W-HZSM-5) or the  $M_2(\text{PcTN})_2$  doping W-HZSM-5 ( $M_2(\text{PcTN})_2$ -W-HZSM-5) were prepared and their catalytic performances were tested for oxidative desulfurization in the presence of oxygen. Thiophene (T), benzothiophene (BT), and dibenzothiophene (DBT) were considered as sulfur compounds. Among zeolite-based catalysts, the  $\text{Cu}_2(\text{PcAN})_2$ -W-HZSM-5 and  $\text{Cu}_2(\text{PcTN})_2$ -W-HZSM-5 showed superior desulfurization performance and the activity of selectivity followed the order:  $T > BT > DBT$ . The effects of phthalocyanine concentration were studied by UV-Vis and calcination temperature was obtained by TG-DSC for  $\text{Cu}_2(\text{PcTN})_2$ -W-HZSM-5. Catalysts were characterized by EA, IR, XRD, SEM, TEM, ICP, and  $\text{N}_2$  adsorption. Reaction time, temperature and the amount of catalyst were investigated as the important parameters for optimization of the reaction. Furthermore, a possible process of oxidative desulfurization and the reaction products were proposed.

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## 1. Introduction

Sulfur in transportation fuels is a major source of notorious and undesirable air pollution [1], which leads directly to the emission of  $\text{SO}_2$  and sulfate particulates [2]. Namely, the combustion of sulfur-containing fuels has negative health and environmental effects [3]. Although increasingly stringent regulations have been established worldwide to limit the sulfur level, a near-zero sulfur content [4,5] is still a challenging problem not only from a fundamental but also from an applied point of view. Thus, finding new processes for ultra-deep desulfurization of fuel oils has been an urgent need [6,7].

Recently, many efforts have been implemented to develop novel catalysts for desulfurization. A wide variety supports materials such as amphoteric carbon, mixed oxides and mesoporous materials have been studied. Soni et al. [8] prepared the 3-D

ordered mesoporous KIT-6 support for effective hydrodesulfurization. Klimova et al. [9] reported the novel bifunctional NiMo/Al-SBA-15 catalysts for deep hydrodesulfurization. Sarda et al. [4] showed that deep desulfurization of diesel fuel by selective adsorption over Ni/Al<sub>2</sub>O<sub>3</sub> and Ni/ZSM-5 extrudates. Zhang et al. [10] prepared the bifunctional NiPb/ZnO-diatomite-ZSM-5 catalyst for adsorption desulfurization performance. Zhang et al. [11] reported that highly stable and regenerable Mn-based/SBA-15 sorbents for desulfurization. Jabbarnezhad et al. [12] reported that the sonochemical synthesis of NiMo/Al<sub>2</sub>O<sub>3</sub>-ZrO<sub>2</sub> nanocatalyst in hydrodesulfurization reaction. Duan et al. [13] synthesized the porous L-KIT-6 silica-alumina material for hydrodesulfurization of benzothiophene. Razavian et al. [14] reported that the synthesis and application of ZSM-5/SAPO-34 and SAPO-34/ZSM-5 composite systems for propylene yield enhancement.

Among different catalysts, HZSM-5 molecular sieve seems to be more suited to be modified because of its uniform and ordered micropores [15], high extensive surface area, as well as charged framework [2,16]. However, a variety of modification techniques are the key factor to improve the shape-selectivity of molecular sieve and catalytic activity [17,18]. Tungsten has received considerable attention due to its unique physical-chemical properties [19]. Thus, tungsten-containing HZSM-5 molecular sieve is a kind

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of potential catalyst which has highly reactivity for desulfurization [20,21]. Besides, metal phthalocyanines and their symmetrically substituted derivatives possess high sensitivity, fast response, and ease of processability [22–24]. Currently, modified phthalocyanines are of much interest for oxidative desulfurization processes in the oil industry and many scientists have explored their gripping feature [25,26]. In the previous study, Gedeon et al. [17] have reported that the ZSM-5 zeolite was synthesized in the presence of a copper-phthalocyanine complex by hydrothermal treatment. Zhang et al. [27] have prepared the ZSM-5-Ln (Pc)<sub>2</sub> by chemical bond for catalytic oxidation of thiophene. However, HZSM-5 zeolite catalysts promoted both by metal ions and phthalocyanine are not yet available.

Herein, we report the oxidation of model sulfur compounds with O<sub>2</sub> as the oxidant using the W/HZSM-5 modified with metal phthalocyanines as catalyst to get a superior performance for desulfurization. Three model sulfur compounds were used: thiophene (T), benzothiophene (BT), and dibenzothiophene (DBT).

## 2. Experimental

### 2.1. Materials

HZSM-5 powder (SiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> ≥ 500, H-type) was purchased from Shanghai Novel Chemical Technology Co. Ltd. (China). 3-Chloropropyltriethoxysilane and 4-NitroPhthalimide were obtained from Aladdin Reagent Co. Ltd. (Shanghai, China). Model compounds including T, BT, and DBT were bought from J&K technology Co. Ltd. (Beijing, China). All solvents and reagents were used without any further purification.

### 2.2. The synthesis of catalyst

#### 2.2.1. Preparation of W-HZSM-5 catalyst

Incorporation of W into the HZSM-5 zeolite was prepared by impregnation method. It was performed by adding the HZSM-5 powder to the certain amounts of sodium tungstate solution, which was prepared by dissolving Na<sub>2</sub>WO<sub>4</sub> in distilled water. Afterwards, the required amount of HCl was added to deposit tungsten acid on the surface of HZSM-5. The mixture was thoroughly stirred and left for 5 h at ambient temperature. The solid, after filtration, was washed with distilled water until no white precipitate was generated by adding silver nitrate solution. The sample was dried at 120 °C for 24 h and calcined in air at 500 °C for 4 h with a heating rate of 5 °C/min. The content of tungsten component was 1.056 ppm by ICP analysis. IR (KBr)  $\nu_{\max}/\text{cm}^{-1}$ : 790 ( $\nu_{\text{Si-O}}$ ); 1099 ( $\nu_{\text{Si-O}}$ ); 450; 550.

#### 2.2.2. Synthesis of M<sub>2</sub>(PcTN)<sub>2</sub> (M=Fe, Co, Ni, Cu, Zn and Mn)

4-NitroPhthalimide, urea, NH<sub>4</sub>Cl, (NH<sub>4</sub>)<sub>6</sub>Mo<sub>7</sub>O<sub>24</sub>·4H<sub>2</sub>O, pyromellitic dianhydride and CuCl<sub>2</sub>·2H<sub>2</sub>O were ground in a mortar. Then the mixture was placed in a three-neck flask in which about 150 mL of aviation kerosene was added. Afterwards, the mixture solution was heated in a thermostatic oil bath at 180 °C for 5 h and violently stirred until the reaction was completed. The crude product was purified successively with 150 mL deionized water, 2% hydrochloric acid, methyl alcohol, acetone, and trichloromethane, respectively. After filtration, the precipitate was dried in the oven. Similarly, M<sub>2</sub>(PcTN)<sub>2</sub> (M=Fe, Co, Ni, Zn and Mn) were synthesized (Scheme 1).

Anal. Calc. for C<sub>58</sub>H<sub>20</sub>O<sub>12</sub>N<sub>22</sub>Cu<sub>2</sub> C, 51.82; H, 1.49; N, 22.93. Found: C, 51.90; H, 1.50; N, 22.83. Yield: 4.05 g, 75.41% m.p > 300 °C IR (KBr)  $\nu_{\max}/\text{cm}^{-1}$ : 1606 ( $\nu_{\text{C=N}}$ ); 1523, 1334 ( $\nu_{\text{NO}_2}$ ); 1140, 1087, 846, 726, 657 ( $\nu_{\text{PC}}$ ).

Anal. Calc. for C<sub>58</sub>H<sub>20</sub>O<sub>12</sub>N<sub>22</sub>Fe<sub>2</sub> C, 52.41; H, 1.51; N, 23.19. Found: C, 52.34; H, 1.50; N, 22.20. Yield: 2.88 g, 54.18% m.p > 300 °C IR (KBr)  $\nu_{\max}/\text{cm}^{-1}$ : 1608 ( $\nu_{\text{C=N}}$ ); 1518, 1334 ( $\nu_{\text{NO}_2}$ ); 1134, 1087, 845, 726, 660 ( $\nu_{\text{PC}}$ ).

Anal. Calc. for C<sub>58</sub>H<sub>20</sub>O<sub>12</sub>N<sub>22</sub>Co<sub>2</sub> C, 52.17; H, 1.50; N, 23.09. Found: C, 52.01; H, 1.50; N, 23.15. Yield: 1.90 g, 35.54% m.p. > 300 °C IR (KBr)  $\nu_{\max}/\text{cm}^{-1}$ : 1607 ( $\nu_{\text{C=N}}$ ); 1522, 1335 ( $\nu_{\text{NO}_2}$ ); 1137, 1072, 848, 728, 666 ( $\nu_{\text{PC}}$ ).

Anal. Calc. for C<sub>58</sub>H<sub>20</sub>O<sub>12</sub>N<sub>22</sub>Ni<sub>2</sub> C, 51.20; H, 1.50; N, 23.10. Found: C, 51.08; H, 1.52; N, 23.01. Yield: 3.87 g, 72.57% m.p. > 300 °C IR (KBr)  $\nu_{\max}/\text{cm}^{-1}$ : 1606 ( $\nu_{\text{C=N}}$ ); 1517, 1333 ( $\nu_{\text{NO}_2}$ ); 1138, 1092, 847, 729, 676 ( $\nu_{\text{PC}}$ ).

Anal. Calc. for C<sub>58</sub>H<sub>20</sub>O<sub>12</sub>N<sub>22</sub>Zn<sub>2</sub> C, 51.71; H, 1.49; N, 22.88. Found: C, 51.68; H, 1.50; N, 22.95. Yield: 3.07 g, 57.07% m.p. > 300 °C IR (KBr)  $\nu_{\max}/\text{cm}^{-1}$ : 1603 ( $\nu_{\text{C=N}}$ ); 1519, 1330 ( $\nu_{\text{NO}_2}$ ); 1137, 1090, 844, 726, 675 ( $\nu_{\text{PC}}$ ).

Anal. Calc. for C<sub>58</sub>H<sub>20</sub>O<sub>12</sub>N<sub>22</sub>Mn<sub>2</sub> C, 51.49; H, 1.51; N, 23.23. Found: C, 51.48; H, 1.51; N, 23.23. Yield: 2.66 g, 50.10% m.p. > 300 °C IR (KBr)  $\nu_{\max}/\text{cm}^{-1}$ : 1607 ( $\nu_{\text{C=N}}$ ); 1521, 1334 ( $\nu_{\text{NO}_2}$ ); 1138, 1090, 847, 725, 675 ( $\nu_{\text{PC}}$ ).

#### 2.2.3. Synthesis of M<sub>2</sub>(PcAN)<sub>2</sub>-W-HZSM-5

M<sub>2</sub>(PcAN)<sub>2</sub> (M=Fe, Co, Ni, Cu, Zn, and Mn) and functionalization of W-HZSM-5 were obtained according to the procedure reported by Zhang et al. [20] (Scheme 2).

IR (KBr) for functionalization of W-HZSM-5:  $\nu_{\max}/\text{cm}^{-1}$ : 2928, 2850 ( $\nu_{\text{CH}_2}$ ).

IR (KBr)  $\nu_{\max}/\text{cm}^{-1}$  C<sub>58</sub>H<sub>32</sub>N<sub>22</sub>Cu<sub>2</sub>: 1606 ( $\nu_{\text{C=N}}$ ); 3254, 3327 ( $\nu_{\text{NH}_2}$ ); 1140, 1082, 822, 737, 644 ( $\nu_{\text{PC}}$ ).

IR (KBr)  $\nu_{\max}/\text{cm}^{-1}$  C<sub>58</sub>H<sub>32</sub>N<sub>22</sub>Fe<sub>2</sub>: 1607 ( $\nu_{\text{C=N}}$ ); 3296, 3301 ( $\nu_{\text{NH}_2}$ ); 1140, 1086, 823, 736, 648 ( $\nu_{\text{PC}}$ ).

IR (KBr)  $\nu_{\max}/\text{cm}^{-1}$  C<sub>58</sub>H<sub>32</sub>N<sub>22</sub>Co<sub>2</sub>: 1604 ( $\nu_{\text{C=N}}$ ); 3257, 3325 ( $\nu_{\text{NH}_2}$ ); 1140, 1089, 823, 744, 642 ( $\nu_{\text{PC}}$ ).

IR (KBr)  $\nu_{\max}/\text{cm}^{-1}$  C<sub>58</sub>H<sub>32</sub>N<sub>22</sub>Ni<sub>2</sub>: 1602 ( $\nu_{\text{C=N}}$ ); 3258, 3331 ( $\nu_{\text{NH}_2}$ ); 1140, 1082, 823, 737, 648 ( $\nu_{\text{PC}}$ ).

IR (KBr)  $\nu_{\max}/\text{cm}^{-1}$  C<sub>58</sub>H<sub>32</sub>N<sub>22</sub>Zn<sub>2</sub>: 1606 ( $\nu_{\text{C=N}}$ ); 3258, 3400 ( $\nu_{\text{NH}_2}$ ); 1140, 1086, 824, 736, 647 ( $\nu_{\text{PC}}$ ).

IR (KBr)  $\nu_{\max}/\text{cm}^{-1}$  C<sub>58</sub>H<sub>32</sub>N<sub>22</sub>Mn<sub>2</sub>: 1603 ( $\nu_{\text{C=N}}$ ); 3274, 3323 ( $\nu_{\text{NH}_2}$ ); 1140, 1085, 823, 737, 644 ( $\nu_{\text{PC}}$ ).

#### 2.2.4. Synthesis of M<sub>2</sub>(PcTN)<sub>2</sub>/W-HZSM-5

The M<sub>2</sub>(PcTN)<sub>2</sub> (M=Fe, Co, Ni, Cu, Zn, and Mn) loaded on W-HZSM-5 complexes were prepared by first impregnating a certain amount of the W-HZSM-5 zeolite were stirred with a calculated amount of M<sub>2</sub>(PcTN)<sub>2</sub> in 20 mL DMF solution. The sample was dried at 90 °C and calcined at 300 °C for 3 h, and subsequently impregnated with the same amount phthalocyanine solution. Finally, the sample was dried for 24 h and calcined at 300 °C for 3 h. The sample was designated as xPc/W-HZSM-5 (x=load of phthalocyanine). A series of nominal load of phthalocyanine had been explored.

### 2.3. Characterization of catalysts

Concentration of W on the W-HZSM-5 catalyst was analyzed using an inductively coupled plasma atomic emission spectrometry (IRIS Advantage) after dissolution of the W-HZSM-5 in the aqua regia and heat treatment. IR spectra were recorded on the EQUINOX-55 FTIR spectrometer from German Bruker Company. Elemental analysis was performed by Vario EL-III CHNOS instrument and the obtained values agreed with the calculated ones. Powder X-ray diffraction patterns were characterized by a D8-advance Advance (Bruker, Germany) using CuK $\alpha$  radiation in the 2 $\theta$  range of 5–80° with a 2 $\theta$  step size of 0.02. The surface morphology of catalyst was analyzed using SEM images (TM3000)

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