



# Adsorption desulfurization by hierarchical porous organic polymer of poly-methylbenzene with metal impregnation



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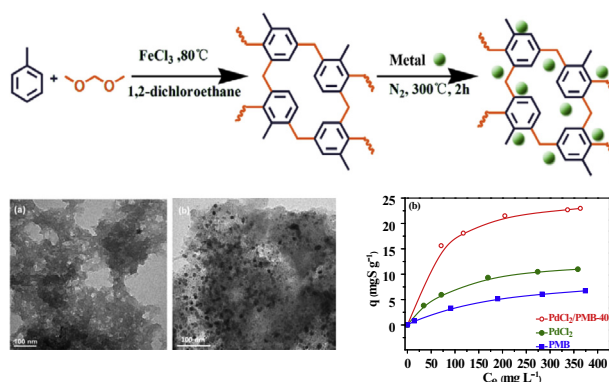
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## HIGHLIGHTS

- A cost-effective hierarchical porous polymer PMB was produced.
- Metal/polymer composites were obtained by metal impregnation.
- PdCl<sub>2</sub>/PMB-40 showed a high DBT capacity of 25.97 mgS/g.
- FTIR measurements confirmed the formation of S–M binding and  $\pi$ -complexation.
- The composite showed a high capacity even in low DBT concentration.

## GRAPHICAL ABSTRACT



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## ABSTRACT

A cost-effective hierarchical porous polymer poly-methylbenzene (PMB) was produced using the most common organic compound methylbenzene via a simple one-step Friedel–Crafts reaction. The large surface area as well as the proper mesoporosity ensured it to be a good substrate for loading metal species. After the impregnation of various metal species including PdCl<sub>2</sub>, Ag<sup>+</sup>, Fe<sup>3+</sup>, Ni<sup>2+</sup>, Zn<sup>2+</sup>, Cu<sup>2+</sup> and Mg<sup>2+</sup>, a series of efficient desulfurization adsorbents of metal/PMB-x were fabricated. Among them, the PdCl<sub>2</sub>/PMB-40 adsorbent showed a most promising desulfurization performance with the DBT adsorption capacity as high as 25.97 mgS/g and a second-order desulfurization rate. Fourier transform infrared spectra (FTIR) measurements confirmed the desulfurization mechanism as the formation of S–M binding and  $\pi$ -complexation. Both high surface area of PMB and highly dispersed PdCl<sub>2</sub> nanoparticles contributed to the good desulfurization performance.

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## 1. Introduction

Desulfurization is a vitally important unit operation in petroleum refining since the combustion of sulfur containing fuels can

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produce toxic SO<sub>x</sub> compounds which cause serious environment pollutions [1–4]. The types and contents of S-compounds in the real diesel oils vary from different operations, ranging from 300–5000 ppm. And many countries publicize the limitations of S-compounds, such as the U.S. Environmental Protection Agency (EPA) restricted the total sulfur content of diesel to 15 and that of gasoline to 30 ppmwS. European standard organization also limited the total sulfur content of diesel and gasoline to 10 ppmwS.

Therefore, the final target for total sulfur content in the real diesel oil for deep desulfurization down to value of 10 ppmS or even lower. Currently, hydrodesulfurization (HDS) is one of the most widely used industrial technology, in which the sulfur compounds are converted into H<sub>2</sub>S and corresponding hydrocarbon [5,6]. Although HDS process is highly efficient and technologically important, the operation conditions of the high hydrogen pressure and the high temperature, the non-selective hydrogenates, as well as the deactivation of the catalysts seriously prohibit its widespread use [7,8]. Moreover, HDS process is less effective for removing thiophene and its derivatives, which limits its application in the deep desulfurization [9,10].

Among various novel technologies proposed for the deep desulfurization, adsorption desulfurization appears to be a promising technology because the process operates at ambient temperature and pressure and there is no hydrogen and catalyst requirements [11–13]. So far, various types of adsorbents have been reported for the desulfurization for fuels [14], such as carbon, alumina, zeolites, mesoporous silica and metal–organic frameworks (MOF) [15–21]. However, the selective adsorption for organosulfur compounds still remains as a great challenge. To meet the selectivity requirements, special attention has been given to improve the interaction between the thiophene-type S-compounds and modified adsorbents via  $\pi$ -complexation [22,23], van der Waals' interaction [24,25], electrostatic interaction [13,26], and (or) reactive chemisorption [27,28]. It has been reported that incorporating transition metal ions, such as Cu<sup>+</sup> and Ag<sup>+</sup>, into the porous materials could result in both high adsorption capacity and high selectivity for desulfurization [6,29,30]. For the porous substrates, mesoporous silicas have been approved to be a type of promising materials because not only the large surface area can provide great space for loading active metal species, but also the relatively large pore size can provide enough space for the adsorption and transportation of bulky sized organosulfur molecules. Yang et al. [30] investigated MCM-41 and SBA-15 supported CuCl and PdCl<sub>2</sub> salts as adsorbents for the desulfurization of a JP-5 light fraction from 841 ppmwS to below 50.0 ppmwS by using a fixed-bed adsorption. Tran et al. [31] impregnated silver on mesoporous material MCM-41 and mesoporous silica nanoparticles (MSN) displayed adsorption capacities of 24.5 mgS/g and 32.6 mgS/g, respectively. Therefore, to develop various mesoporous materials with suitable metal impregnated is desirable for upgrading the desulfurization adsorbents.

Recently, porous organic polymers (POPs), a new type of porous materials constructed by organic building blocks, have attracted numerous attentions because of their good porosity, diversity, specific functions, and good physicochemical properties [32–35]. Various POPs with excellent adsorption capacity have been prepared via different polymerization reactions [32–35]. Qiu et al. [36] reported the synthesis of a microporous aromatic framework PAF-1 by metal catalyzed Yamamoto coupling reaction. With the surface area as exceptionally high as 7100 m<sup>2</sup> g<sup>-1</sup>, PAF-1 showed high uptake capacities for H<sub>2</sub>, CO<sub>2</sub>, as well as benzene and toluene vapors. Ying et al. [37] reported the synthesis of a mesoporous poly-melamine–formaldehyde (mPMF), with a high surface area of 1099 m<sup>2</sup> g<sup>-1</sup>, it showed high selectivity toward toxic metals, including lead, cadmium, copper and palladium. Therefore, POPs with suitable mesoporous structure would be a good support for metal loading. However, most monomers of the reported POPs and the polymerization catalysts were usually expensive, so far, the cost-effective synthesis of mesoporous POPs and applied as the support for metal loading have remained largely unexplored. Moreover, the aromatic networks of POPs could exhibit desired  $\pi$ - $\pi$  interaction with thiophene type S-compounds, however, their applications as the desulfurization adsorbent are still seldom developed.

As suggested above, a hierarchical POP with metal impregnation would be a good adsorbent for the desulfurization, because the aromatic networks of POPs is expected to exhibit desired  $\pi$ - $\pi$  interaction with thiophene type S-compounds; and the impregnated metals are expected to exhibit S-M binding and  $\pi$ -complexation to enhance the desulfurization performance. Herein, we used methylbenzene, the most common organic compound, and a conventional cross-linker of Formaldehyde dimethylacetal (FDA) to produce a cost-effective porous polymer (PMB) via a simple one-step Friedel–Crafts reaction with a very cheap catalyst of FeCl<sub>3</sub>. With a high surface area and micro-mesoporous porosity, the desulfurization properties of PMB was preliminarily tested. After loading PdCl<sub>2</sub>, the enhanced desulfurization performance of PdCl<sub>2</sub>/PMB was investigated in both thermodynamic and kinetic ways. Moreover, various metal ions including Ag<sup>+</sup>, Ni<sup>2+</sup>, Mg<sup>2+</sup>, Fe<sup>3+</sup>, Cu<sup>2+</sup>, Zn<sup>2+</sup> were loaded on PMB, respectively. Through the investigation of their desulfurization performance, the adsorption mechanism of metal supported POPs was further illustrated.

## 2. Experimental section

### 2.1. Chemicals

Most reagents, including FeCl<sub>3</sub>, NiCl<sub>2</sub>, Zn(NO<sub>3</sub>)<sub>2</sub>, Cu(NO<sub>3</sub>)<sub>2</sub>, Mg(NO<sub>3</sub>)<sub>2</sub>, AgNO<sub>3</sub> etc. were reagent grade. Methylbenzene ( $\geq 99.5\%$ ), 1, 2-dichloroethane (DCE) ( $\geq 99\%$ ), Formaldehyde dimethylacetal (FDA) ( $\geq 98\%$ ), n-Octane ( $\geq 95\%$ ), dibenzothiophene (DBT) ( $\geq 98\%$ ), benzothiophene (BT) ( $\geq 98\%$ ), thiophene (99%) were purchased from Sigma–Aldrich Co. All chemicals were used as purchased without further purification.

### 2.2. Synthesis hierarchical porous PMB

As illustrated in Scheme 1, porous organic polymer of PMB was prepared by a one-step Friedel–Crafts reaction. Briefly, methylbenzene (1.84 g, 0.02 mol), FDA (3.04 g, 0.04 mol) and 20 mL DCE were mixed together under stirring at ambient conditions. Then FeCl<sub>3</sub> (anhydrous 6.5 g, 0.04 mol) was added into the mixture. After continuous stirring for 5 h at 45 °C, an initial PMB network was formed. Then increasing the temperature to 80 °C, the complete polymerization resulted a brown precipitate. The resulting product was washed three times with methanol, extracted by a Soxhlet for 24 h to remove the residual methanol, and dried at 60 °C in a vacuum oven overnight, the final product of porous PMB was obtained.

### 2.3. Loading metal on PMB

Metal species were loaded on PMB by a wet impregnation method (J. M. Palomino et al., 2014) [31]. Briefly, a suitable amount of salt including NiCl<sub>2</sub>, Zn(NO<sub>3</sub>)<sub>2</sub>, FeCl<sub>3</sub>, Cu(NO<sub>3</sub>)<sub>2</sub>, Mg(NO<sub>3</sub>)<sub>2</sub> and AgNO<sub>3</sub> were dissolved in 10 ml ethanol aqueous solution ( $V_{\text{H}_2\text{O}}:V_{\text{ethanol}} = 2:1$ ) to prepare the salt solution with the concentration of 0.1 mol/L, respectively. Drip the solution dropwise onto the PMB powder until it was just wetted, then the sample was moved into a vacuum oven at 110 °C overnight. The dripping and drying steps were repeated for several times till the desired amount of the metal ion was loaded. The final products were denoted as M/PMB-*x*, in which *M* represented the type of metal ions, and *x* was the weight percentage of metal ions.

Because PdCl<sub>2</sub> is an insoluble salt, we prepared PdCl<sub>2</sub>/PMB adsorbent by the solid impregnation method (Wang et al., 2008) [30,38]. Briefly, PMB (0.2 g) and PdCl<sub>2</sub> were grinded and mixed thoroughly, and then the mixture was placed in a quartz tube for the heat treatment at 300 °C in N<sub>2</sub> flow for 2 h, with the temperature increasing rate of 2 °C/min. After cooling down, the products

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