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Full Length Article

Oxidative desulfurization of model fuel in the presence of molecular oxygen over polyoxometalate based catalysts supported on carbon nanotubes

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ABSTRACT

With the emergence of environmental problems such as acid rain and haze, the study on fuel desulfurization has become an important subject of environmental protection. Oxidative desulfurization (ODS) becomes the promising method due to its mild reaction condition, low cost and high efficiency. In this work, two series of catalysts supported by carbon nanotubes (CNTs) are prepared by two different procedures: a) the polyoxometalate (POM) is impregnated into the channel of CNTs by impregnation method, b) the modified CNTs is wrapped by polyoxometalate through ion exchange method. The novel catalysts are investigated by FT-IR, XRD, XPS, SEM and N_2 adsorption–desorption isotherms. The desulfurization performance of all catalysts is carried out under a certain condition, and the catalysts have positive effects on dibenzothiophene (DBT) conversion. The effect of factors on desulfurization is evaluated, and the favorable conditions are determined. Based on optimal conditions, the DBT conversion reached up 99.4%, and the desulfurization system could be recycled 8 times without noticeable decrease in activity. In addition, the impact of the critical parameters (temperature, mass of catalyst and oxygen quantity) was investigated using Box–Behnken experimental design. The optimum simulation condition is consistent with the experimental investigation, which further proves the accuracy of the experimental conclusion.

1. Introduction

In recent years, the heavy use of sulfur-containing fuel has brought a series of environmental problems, such as acid rain [1–3]. With the use of oil continue to increase, the problem of fuel desulfurization arouse people's attention [4,5]. Oil desulfurization is dominating technology measure to control acid rain and sulfur dioxide pollution. Hence, oil desulfurization has become the important method which will improve the environment. How to resolve deep desulfurization under effective, green and safe conditions has become the key point. The traditional method of desulfurization is hydrodesulfurization (HDS) [6]. Hydrodesulfurization has some excellences like high efficiency and short reaction time; however, its operating conditions are tough and costly [7,8]. Hence, it is urgent to find an improved method. At present, oxidative desulfurization (ODS) becomes the hot research subject which is researched extensively due to its moderate reaction condition, high efficiency, less equipment invest and low cost [9,10]. The main research contents of the oxidative desulfurization are the preparation of catalyst and the choice of oxidant. Molecular oxygen, as a green oxidant, is widely used in oxidative desulfurization. The oxidant include inorganic material and organic matter, including heteropolyacid [11], phthalocyanine [12], metallic oxide [13] and so on.

Polyoxometalates (POMs) are a class of transition metal–oxygen clusters with unique properties, which have drawn people's attention [14]. Polyoxometalates with special advantages, such as strong activity, unique redox property, good stability, and those advantages are widely used in various aspects. Currently, the structure of polyoxometalate is mainly divided into five types: Keggin, Dawson, Anderson, Waugh and Silverton type [15]. Of these, Dawson type polyoxometalates are extensively investigated in catalysis due to fast reversible multi-electron redox *trans*-formation under mild conditions [16]. Graciela Baronetti and the coworkers obtained silica supporting Wells-Dawson heteropolyacid by sol–gel technique, the catalysts showed high activity in the esterification of levulinic acid with ethanol [17]. Dehghani et al. reported that vanadium substituted Dawson type emulsion catalyst has positive effects on extractive catalytic oxidative desulfurization (EODS),

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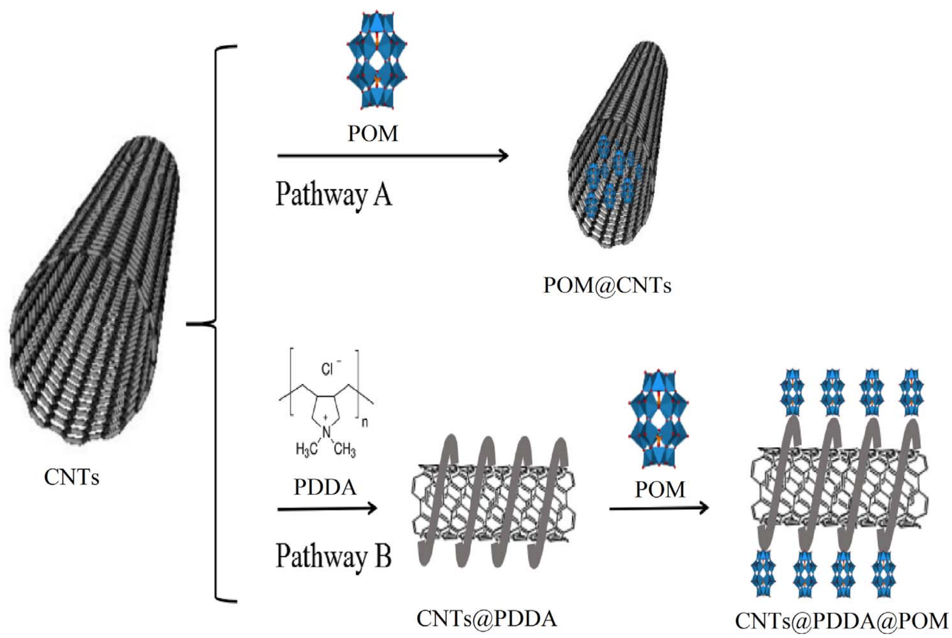

Scheme 1. Preparation of novel catalysts.

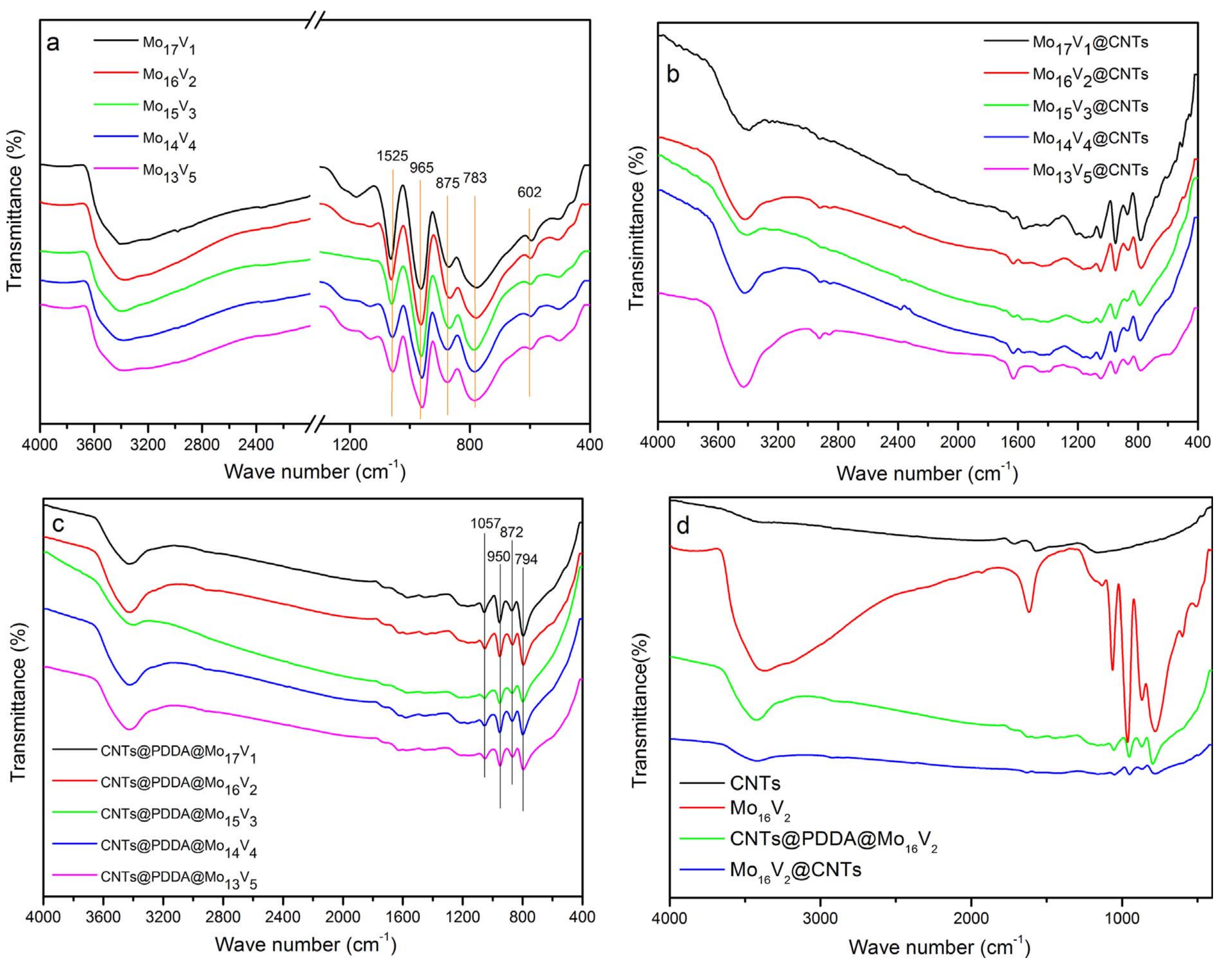

Fig. 1. FT-IR spectra of (a) POM, (b) POM@CNTs, (c) CNTs@PDDA@POM and comparison figure (d) of CNTs, $Mo_{16}V_2$, CNTs@PDDA@$Mo_{16}V_2$ and $Mo_{16}V_2$@CNTs.

the desulfurization rate can reach 94% under the optimized conditions [18]. Mohammad et al. used vanadium-substituted Dawson-type polyoxometalate $[cetronium]_{11}P_2W_{13}V_5O_{62}$ as the catalyst for oxidative desulfurization with H_2O_2 as oxidant; they found that materials have potential application in the oxidation desulfurization process, the system can remove 90% sulfur from 500 ppmw fuel [19]. However, the application of pure polyoxometalate is restricted for the shortcomings of low specific area and reclamation difficulty [20]. Selecting proper