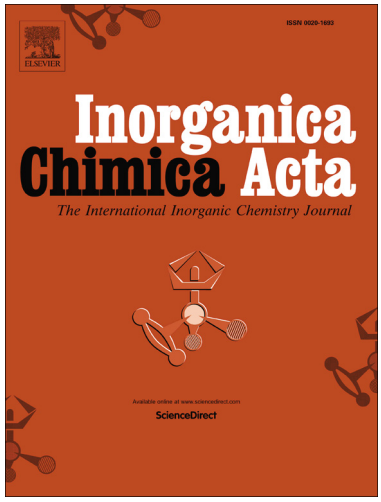

Research paper

Oxidative Desulfurization of Dibenzothiophene by Central Metal Ions of Chlorophthalocyanines-Tetracarboxyl Complexes

Min Gao, Gai Zhang, Min Tian, Bulei Liu, Weixing Chen

PII: S0020-1693(18)31085-5
DOI: https://doi.org/10.1016/j.ica.2018.09.079
Reference: ICA 18537

To appear in: *Inorganica Chimica Acta*

Received Date: 15 July 2018
Revised Date: 27 September 2018
Accepted Date: 27 September 2018

Please cite this article as: M. Gao, G. Zhang, M. Tian, B. Liu, W. Chen, Oxidative Desulfurization of Dibenzothiophene by Central Metal Ions of Chlorophthalocyanines-Tetracarboxyl Complexes, *Inorganica Chimica Acta* (2018), doi: https://doi.org/10.1016/j.ica.2018.09.079

Oxidative Desulfurization of Dibenzothiophene by Central Metal Ions of Chlorophthalocyanines-Tetracarboxyl Complexes

Min Gao, Gai Zhang*, Min Tian, Bulei Liu, Weixing Chen

School of Materials and Chemical Engineering, Xi'an Technological University, 710021, Xi'an

Abstract: Oxidative desulfurization (ODS) is one of the most promising methods of ultra low sulfur diesel(ULSD). Herein, metallophthalocyanine($MPc(COOH)_4Cl_8$, M= Mn(Ⅱ), Fe(Ⅱ), Co(Ⅱ), Ni(Ⅱ), Cu(Ⅱ), Zn(Ⅱ)) composites are synthesized by a facile in situ solid method and characterized by elemental analysis, UV-Vis, XPS and IR spectra. The simulated bionic catalytic system is composed of $MPc(COOH)_4Cl_8$ and molecular O_2, which exhibited great activity for ultra-deep removal of dibenzothiophene (DBT) from the model oil containing n-octane. The catalytic activity of $MPc(COOH)_4Cl_8$ for the degradation of DBT in fuel was significantly improved at room temperature with natural light irradiation. After 90 minutes of catalytic reaction, the sulfur content in the model fuel decreased from (800ppm) to 20 ppm. Catalytic activity studies revealed that the central metal ions of phthalocyanine structures presented a significant influence in the catalytic activity for the degradation of DBT. Additionally, mechanistic studies revealed that the '$*O_2$-$MPcTcCl_8^+$' species was the key active intermediate. The metallophthalocyanine composites as active photocatalysts offer great potential for degradation of thiophene derivatives in fuel

Keywords: metallophthalocyanine; molecular oxygen; dibenzothiophene; Oxidative desulfurization

Introduction

The research and production of ultra low sulfur diesel(ULSD) has been of great concern universally in various countries worldwide. Some macromolecular substances such as thiophene and its alkylated derivatives are converted into SO_2 and sulfate particles during fuel combustion, which has negative health and environmental effects[1-7]. It is urgent to develop a new method of ultra-deep desulfurization of fuel oil. Oxidative desulfurization (ODS) is one of the most potential approaches to produce ultra low sulfur diesel(ULSD) [8-10].

Oxidants presented a significant influence for the performance of ODS. It is widely known that H_2O_2 in aqueous solution is commonly used as oxidant for ODS. However, the technology can cause fuel losses. When the by-product H_2O were removed by distillation[11-15]. Molecular oxygen is an ideal oxidant for ODS due to economical, practical and environmentally friendly. Metallophthalocyanine(MPCs) have proved to be effective bionic catalysts due to their oxygen carrier functions similar to the naturally occurring heme proteins. The triplet oxygen($^3O_2$) bonded on MPcs materials could be converted into singlet oxygen ($^1O_2$). singlet oxygen ($^1O_2$) was the main active intermediate for oxidizing organic pollutants[20]. O_2/iron tetranitrophthalocyanine ($FePc(NO_2)_4$) oxidative system has been investigated in oxidation of dibenzothiophene in hydrocarbon solvent for ultra-deep