DEEP OXIDATIVE DESULFURIZATION OF FUELS CATALYZED BY PRISTINE SIMPLE TUNGSTIC ACID

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Abstract

The catalytic system of pristine simple tungstic acid and quaternary ammonium salts has been found suitable for deep removal of sulfur in diesel with $\text{H}_2\text{O}_2$ as oxidant. The longer the length of the carbon chain of the quaternary ammonium salt is, the better its catalytic activity is in desulfurization. By combining oxidation and extraction with dimethylformamide, low sulfur level in diesel could be obtained.

Keywords: Oxidative desulfurization, tungstic acid, quaternary ammonium salt, $\text{H}_2\text{O}_2$

INTRODUCTION

Deep desulfurization is needed stringently as sulfur in fuels has inevitably led to the pollution of the environment. $\text{SO}_x$ emission from automobile exhausts not only pollutes air greatly, but also poisons noble metal catalyst irreversibly in automobiles [1]. Many countries have made environment legislations to limit sulfur content (<10 $\mu$g/mL) in transportation fuels [2]. In the conventional process, hydrodesulfurization (HDS) is used to remove thiols, sulfides and disulfides. However, it is hard to remove refractory sulfur-containing compounds such as dibenzothiophene (DBT) and its derivatives due to steric hinderance in the reactions of these compounds. In order to remove these...
compounds, severe operating conditions and large capital costs are needed [2]. Therefore, alternative desulfurization technologies have attracted wide attention [2-7].

As a post-treatment to the traditional HDS for deep desulfurization, oxidative desulfurization (ODS) is promising, which has a lot of advantages such as ambient pressure, lower temperature, no use of expensive hydrogen, and potential for removal of sterically hindered sulfides (DBT and 4,6-dimethyl-dibenzoanthiophene) [2]. Sulfur compounds are oxidized into their corresponding sulfones or sulfoxides, which can be removed by extraction or adsorption because of higher polarity.

Various ODS systems have been reported, such as acetic acid/H₂O₂ [8], formic acid/H₂O₂ [9], polyoxometalates/H₂O₂ [10-12], aldehyde/O₂ [13], TS-1/H₂O₂ [14]. Besides oxygen, hydrogen peroxide is the most economical and environmentally benign oxidant and its use is attractive in fuel desulfurization. However, a biphasic system forms in the process of the reactions using hydrogen peroxide, which inhibits the reactivity during oxidative desulfurization. For this reason, co-catalysts such as surfactants and organic solvents may be introduced into desulfurization to increase the reactivity. For example, Huang et al. [15] employed phosphotungstic acid and quaternary ammonium salts in the reaction system, by which the deep desulfurization could be achieved.

In present work, pristine simple tungstic acid was employed and introduced into ODS as catalyst. Hydrogen peroxide was chosen as an oxidant and a series of various size of amphiphilic quaternary ammonium cations were tested on desulfurization. In the process of ODS, DBT was oxidized into the corresponding sulfone. The sulfur content in model oil could be lowered from 1000 µg/mL to about 20 µg/mL.

**EXPERIMENTAL**

**Oxidation of DBT in model oil**

The oxidative desulfurization experiments were carried out in a home-made 40 mL flask. The mixture composed of model oil, 30(wt.)% H₂O₂, a quaternary ammonium salt and tungstic acid was stirred vigorously. After the reaction was complete, model oil was withdrawn and analyzed by gas chromatography (internal standard method with nitrobenzene) coupled with a flame ionization detector (GC-FID). A SE-54 capillary column (15 m×0.32 mm inner diameter×1.0 µm film thickness) was used for separation. High purity nitrogen and hydrogen were used as carrier and fuel for FID. A sample volume of 0.4 µL was injected without any solvent dilution. The temperature profile is given in Scheme 1.