Study of Oxidative Desulfurization of Jet Fuel Using Molecular Oxygen over $Fe(NO_3)_3.9H_2O$-$FeBr_3$ Catalyst at Room Temperature

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Introduction

Deep desulfurization of liquid hydrocarbon fuels is becoming an important subject worldwide. The sulfur content in the transportation fuels is a very serious environmental concern, because sulfur in the fuels is converted to toxic SOx in combustion and contributes to acid rain. The SOx also poisons the catalysts for exhaust emission treatment in vehicles. Moreover, the development of fuel cells makes the deep desulfurization to be an even more challenging issue for producing fuel-cell grade fuel [1,2].

The major sulfur compounds existing in current liquid hydrocarbon fuels are thiophenic compounds and their alkyl-substituted derivatives. Some of them have been considered to be the refractory sulfur compounds in the fuels due to the steric hindrance of the alkyl groups in HDS [2]. It is necessary to make new approaches to ultra-deep desulfurization of liquid hydrocarbon fuels. Oxidative desulfurization (ODS) methods are of great challenge among the current desulfurization approaches. The current oxidant system in the ODS processes include hydrogen peroxide[3],H_2O_2/formic-acid,H_2O_2/phosphotungstic acid,H_2O_2/12-tungstophosphori-acid, peracid/Co(II), tert-BuOCl/Mo-Al_2O_3, and tert-BuOOH/Mo-Al_2O_3,and others.

Our objective in the present study is to explore a novel ODS method of liquid hydrocarbon fuels, which combines a catalytic oxidation step directly in the presence of molecular oxygen at ambient condition and an adsorption step to removal oxidized sulfur compounds. Fe(III) salts and iron complexes have been reported as the good catalysts for many oxidation reactions at ambient conditions. Rossi and Martin have comparatively studied the catalytic and selective sulfoxidation reaction of methylphenylsulfide in the presence of metallic nitrates and bromides [4]. They found that a combination of Fe(III) nitrate and Fe(III) bromide is favorable for oxidation of sulfides into sulfoxides, and the participation of dissolved atmospheric oxygen in the system. We also reported that ODS –adsorption system of Fe(III) nitrate supported over activated carbon have a good desulfurization performance for jet fuel at 65˚C. In the present study, the mixture of Fe(III) nitrate and Fe(III) bromide without carbon support, denoted as Fe-Fe salts catalyst, were used for ODS of a model jet fuel (MJF) and a commercially available jet fuel (JP-8) in the presence of molecular oxygen in a batch reaction system at room temperature.

Materials and Methods

Fe-Fe salts catalyst were prepared by simple mixing $Fe(NO_3)_3{\cdot}9H_2O$ and $FeBr_3$ at 2:1 in weight, denoted as Fe-Fe. A model jet fuel (MJF) was prepared by adding sulfur compounds into liquid alkanes for the present study. The total sulfur content in MJF was 468 ppmw. a commercial jet fuel, JP-8, which contained 791 ppmw sulfur, was provided by the U,S. Air Force Wright Patterson Laboratory.

The oxidation was conducted by contacting MJF or JP-8 with the catalyst at a fuel-to-catalyst weight ratio of 21 in a 20 ml vial with a magnetic stirrer at 25 ˚C. Oxygen gas was bubbled up through the mixture at a flow rate of ~ 30 ml/min within the reaction. The total sulfur concentration of the treated fuel samples was analyzed by using an ANTEK 9000 series analyzer. The identification and semi-quantification of the various compounds in the treated MJF and JP-8 was analyzed by a HP 5890 gas chromatograph with a capillary column (XTI-5, Restek, 30 m in length, 0.25 mm in internal diameter) and a pulsed flame photometric detector (PFPD).

Results and Discussion

Oxidation of the sulfur compounds in MJF with Fe-Fe was conducted in the batch reaction system with O_2 gas bubbling at 25 ˚C and different reaction times, 5, 10,30, and 120 min, respectively. The PFPD chromatograms of MJF and the oxidized MJF samples with identification are shown in Figure 1. It is clear that the concentration of BT, 2-MBT and 5-MBT decreased with increasing reaction time, but at the same time, there are about 5 new peaks appeared in the retention time range of 10 to 13 min. After 10 min reaction, the area corresponding to some of these new peaks decreased with increase of the retention time, while other new peaks appeared at the retention time higher than 13 min. It indicates that the process of the oxidation reaction might be conducted through two steps, one is the monosulfoxidation and the other is the disulfoxidation. It also can be found that the reactivity of sulfur compounds in MJF is in the order of 2MBT>5MBT>BT>>DBT. The study of mechanism of the oxidation reaction is underway.

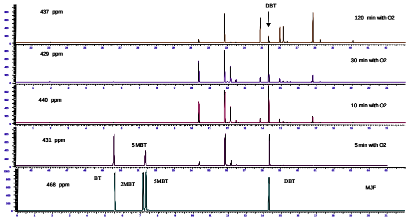

Figure 1. PFPD chromatograms of MJF and the oxidized MJF samples at different reaction times

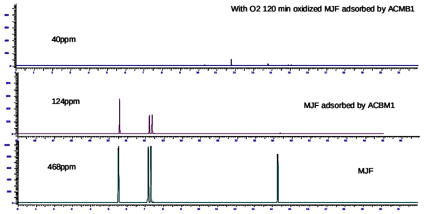

Figure 2. PFPD chromatograms of MJF and activated carbon treated fuels from MJF and the oxidized MJF at 2hours with O_2 over the catalyst

The results in Figure 2 show that the oxidized sulfur compounds in jet fuel can be removed easily by a carbon-based adsorbent in comparison with the initial sulfur compounds in the fuel. Our preliminary results also showed that the present oxidative desulfurization reaction also worked for the real jet fuel.

References

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