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Investigation of Catalytic Oxidative Desulfurization of a Commercial Diesel Using Mo Catalyst Supported on γ-Al_2O_3

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INTRODUCTION

The presence of organic sulfur compounds in fossil fuels such as diesel and gasoline leads to corrosion of equipment, environmental pollution and production of acid rains. Hence, severe environmental regulations have been put in place to reduce sulfur compounds and improve fuel quality [1]. The researchers have been studied various methods having low cost for deep desulfurization. Among all, the known catalytic oxidative desulfurization (ODS) has attracted more attention. Todays, many catalysts have been developed for this process. The supported molybdenum catalysts shows a good performance in ODS. For example, ODS of simulated diesel using MoO_3 on different supports using TBHP oxidant [2] and H_2O_2 [3] were evaluated, and the results showed a high performance. Moreover, deep ODS of model diesel using MoO_3/Al_2O_3 catalyst and hydrogen peroxide oxidant under ultrasound irradiation was stated by Akbari et al [4], and the result indicated over 98% efficiency at the optimal condition. In this work, catalytic oxidative desulfurization of commercial diesel from Tehran oil refinery with sulfur amount of 590 ppmw has been evaluated with MoO_3/γ-Al_2O_3 catalyst for the first time. Also, the effect of various parameters (Loading of Mo, temperature, amount of catalyst and oxidant) have been investigated in oxidative desulfurization of commercial diesel.

EXPERIMENTAL PROCEDURE

CATALYST PREPARATION

The MoO_3/γ-Al_2O_3 catalyst were prepared from Ammonium heptamolybdate tetrahydrate

(($(NH_4)_6Mo_7O_{24}.4H_2O$) as Mo sources and Aluminiumoxide anhydrous as the catalyst support. First of all, a specific amount of Ammonium heptamolybdate was dissolved in a specific volume of distilled water and then slowly added to an appropriate amount of support. Then, the obtained mixture was laid into the vaccum rotary evaporator and dried, after that, calcined at 500°C for 8 h in air. The synthesized catalyst was characterized using Ft-IR, SEM, EDS, BET and XRD analyses.

CATALYTIC OXIDATIVE DESULFURIZATION METHOD

Catalytic oxidative experiments were carried out in a 100 ml glass batch reactor with a condenser and a recirculation water bath for temperature control. In a typical run, the diesel and the catalysts were added to the reactor. After reaching the temperature to 45°C, the H_2O_2 was added as an oxidant and the reaction was started. Acetonitrile was used as a solvent to extracted sulfones from commercial diesel. After a desired reaction time, the oil sample was extracted and the desulfurization efficiency was determined by gas chromatography.

RESULTS AND DISCUSSION

Different characterization analyses confirmed the well immobilization of Mo on the support. Moreover, in Table 1, it is indicated that the highest sulfur removal in both commercial and simulated diesel was obtained at 10 wt.% of Mo loading.

Due to the presence of many aromatic sulfur and non-sulfur compounds in commercial diesel, an extraction solvent was necessary to extract sulfones from diesel. Fig 1. showed the effect of solvent type on the ODS yield.

Also, the influence of different reaction parameter (Temperature, amount of catalyst, reaction time and H_2O_2/sulfur molar ratio) have been evaluated.

The results showed that the maximum sulfur removal of 89.8% was reached in the optimal condition of 45°C, H_2O_2/Sulfur molar ratio of 12, Mcatalyst/Voil of 0.2 g/mL and reaction time of 90 min.

Table 1: influence of molybdenum loading on the catalyst.

Mo loading on the catalyst	Desulfurization efficiency of commercial diesel using $MoO_3/\gamma\text{-}Al_2O_3$ (%)[a]	Desulfurization efficiency of model diesel using $MoO_3/\gamma\text{-}Al_2O_3$ (%)[b]
0	3.82	21.9
5	74.24	71.35
10	84.19	99
12	82.8	96.27
15	75.94	96.1
20	70.41	80.5
30	70.01	68.9

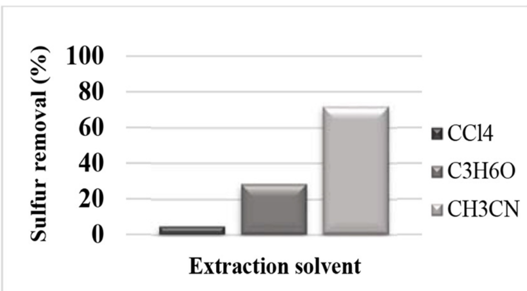

Figure 1: Investigation of extraction solvent in ODS of commercial diesel.

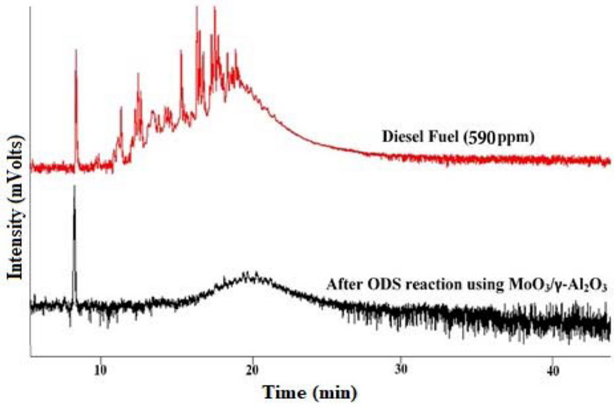

Figure 2: GC-PFPD analysis of commercial diesel.

CONCLUSIONS

In this work, MoO_3(10%)/γ-Al_2O_3 catalyst was synthesized with dry impregnation and then characterized by FT-IR, BET, SEM, EDS and XRD analysis. In addition, catalytic ODS of a diesel fuel was evaluated using MoO_3(10%)/γ-Al_2O_3 catalyst. The effect of different reaction parameters were evaluated and discussed in detail. The high water production and H_2O_2 decomposition at some conditions, reduced process efficiency. Finally, according to the obtained results, the catalyst showed the best performance of 89.8% efficiency in ODS of the diesel at reaction condition of 45°C, H_2O_2/Sulfur molar ratio of 12, reaction time of 90 min and using acetonitrile as a solvent.

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