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Oxidative Desulfurisation of Model Oil and Real Sample Using MoO_3/g-C_3N_4 Catalyst and Optimization of Operating Conditions by Box-Benken Method

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INTRODUCTION

Oil pollution is an undesirable phenomenon with serious and destructive effects on human health and environment. As sulfur compounds are one of the most important pollutants in the Oil cuts, the removal of these compounds from them is very important due to the production of SO_x gases in the course of combustion, and subsequently, air pollution, acid rain production, and corrosion of metals [1].

To enhance deep desulfurization, the MoO_3/g-C_3N_4 was selected as catalyst and H_2O_2 as an oxidant. The study was carried out on the removal of DBT from model oil. The effects of MoO3 loading, temperature, H_2O_2/DBT ratio, catalyst weight, and reaction time were investigated using the Box-Behnken Design (BBD) method in experimental design. Also, the performance of the catalysts was evaluated in the removal of sulfur compounds of gasoline and gas oil at the optimum conditions. The MoO_3/g-C_3N_4 catalyst was characterized by XRD, EDX, FE-SEM, and BET analyses.

EXPERIMENTAL PROCEDURE

CATALYST PREPARATION

MoO_3/g-C_3N_4 was prepared according to the reported procedure [2]. Pure MoO_3 was prepared by directly calcining at 500 °C for 4 h. Pure g-C_3N_4 powder was prepared by directly calcining melamine powder at 520 °C for 4 h with a heating rate of 10 °C min^{-1}. After cooling to room temperature, yellow g-C_3N_4 was obtained in a powder form. The MoO_3/g-C_3N_4 composites were prepared by mixing MoO_3 and g-C_3N_4 and grinding in an agate mortar for 20 min. Then, the mixtures were calcined at 400 °C for 2 h to obtain MoO_3/g-C_3N_4 catalysts.

CATALYTIC ACTIVITY TEST

MODEL OIL PREPARATION

Model oil was prepared by dissolving DBT in n-hexane with corresponding S-content of 1000 ppm.

OXIDATION DESULFURIZATION

5 ml the model oil with similar amount of acetonitrile as an extractant and a certain amount of catalyst was poured in a balloon. This balloon was placed in a water bath at a specific temperature while it was connected to the condensation system. At the end of the reaction time, the content of the balloon was poured into the test tube, and the top phase, which was a transparent liquid, was discarded for determining the total sulfur. The amount of sulfur in the model oil was detected by Antek instruments Model 9000F Sulfur Analyzer.

EFFECT OF MOO_3 LOADING

In the synthesis of the catalyst, different quantities of metal loading were investigated. Results are shown in Fig. 1.

in addition, all reactions were carried out under operating conditions of T=55 °C, t=45 min, H_2O_2/DBT =8, and catalyst amount of 0.02 g. As shown in Fig. 1, the efficiency of DBT removal first increased up to 79% at 10% MoO_3 loading, but when metal loading was increased to 15%, no significant difference of DBT removal efficiency was observed. As a result, 10% of metal loading was used for following experiments.

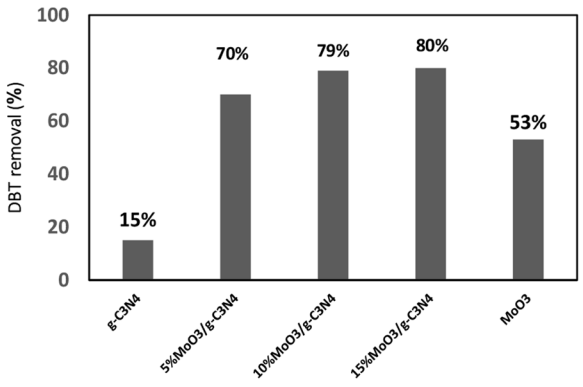

Figure 1: effect of MoO_3 loading.

RESULTS AND DISCUSSION PHASE COMPOSITION ANALYSIS

The typical XRD pattern of the MoO_3/g-C_3N_4 composite is shown in Fig.2. Two prominent peaks at 2θ =27.5° and 13.1° match with the (002) and (100) diffraction planes of the layered g-C_3N_4, respectively. The most intense peak at 27.5° corresponds to the interlayer stacking of the aromatic compound. The other peak observed at 13.1° refers to an in-plane structural packing motif (JCPDS No: 87-1526). The diffraction peaks of pure MoO_3 at 2θ =2.8°, 23.4°, 25.7°, 27.3°, 33.6° and 39.0° can be indexed as the (020), (110), (040), (021), (111) and (060) planes of the orthorhombic crystal of MoO_3, respectively (JCPDS No: 05-0508).

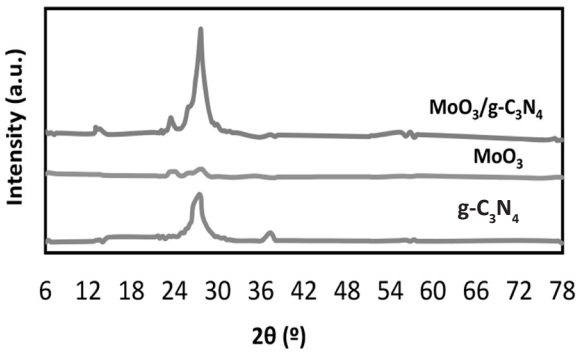

Figure 2: XRD patterns of MoO_3/g-C3N_4.

CATALYTIC PERFORMANCES

GRAPHICAL DESCRIPTION

In Fig. 3 (a), the effect of interaction between temperature and H_2O_2/DBT molar ratio in the fixed amounts of catalyst and time is shown. As can be seen at the temperature range of 60 °C to 70 °C and a H_2O_2/DBT molar ratio between 4 and 13, the highest efficiency is achieved. Moreover, the simultaneous effect of the temperature and amount of catalyst in the fixed values of the H_2O_2/DBT=8 molar ratio and 45 minutes is shown in Fig. 3 (b).

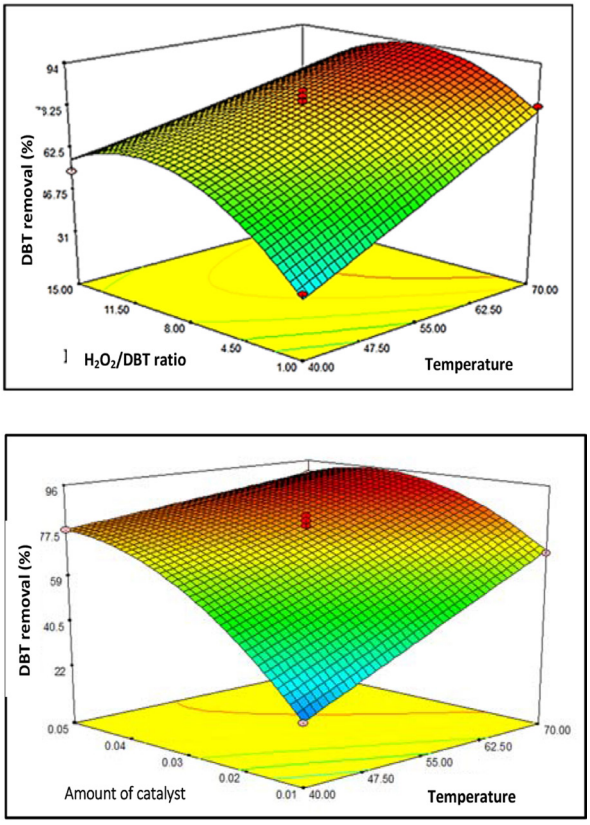

Figure 3: The 3D surface plots (a) the interaction between temperature and H_2O_2/DBT ratio, (b) the interaction between amount of catalyst and temperature.

CONCLUSIONS

In this paper, the performance of the MoO_3/g-C_3N4 composites in ODS process has been studied. The results of characterization analysis showed that the catalysts were synthesized correctly. Then, the effect of operating conditions on the ODS process efficiency was investigated and by using the BBD method the optimal operation point was identified. Finally, at the optimum point, at 70 °C, the catalyst amount of 0.04 g, H_2O_2/DBT=8.44 molar ratio, and the duration of 55 min, 97.7% DBT removal from the model oil was obtained.

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