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Oxidative Desulfurization of DBT Using Tri-metallic Ni-Mo-W Nanocatalysts Based on Different Natural Zeolites: Mordenite, Ferrierite, and Clinoptilolite

Somaiyeh Alahyari[1], Milad Mehrabi[2], Nader Rahemi[1] and Saeed Tadayyon[1]

1. Chemical Engineering Faculty, Sahand University of Technology, Tabriz, Iran

2. Chemical Engineering Faculty, Kashan University, Iran

alahyari_s_62@yahoo.com

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INTRODUCTION

Most of desulfurization technics have expensive catalysts, need hydrogen and carry out in severe pressure and temperature [1]. But one promising approach to remove S-containing aromatic compounds in fuel is oxidative desulfurization (ODS) in which the organic sulfides are oxidized to the corresponding sulfoxides and sulfones [2]. A catalyst is essential for oxidation of S-bearing compound during ODS. Due to facilitating the separation of the catalyst after ODS, it is necessary to impregnate the active metals over a porous support suitable for ODS. Natural zeolites like clinoptilolite, mordenite and ferrierite are hydrated alumina silicates which have acidic sites. The protons in the bridging hydroxyl groups (Si – OH – Al) make Bronsted acidity in the zeolite structure. Therefore, in this paper natural zeolites of clinoptilolite, ferrierite and mordenite were used as support of trimetallic NiMoW catalysts and were evaluated in oxidative desulfurization of DBT.

EXPERIMENTAL PROCEDURE

CATALYST PREPARATION

Natural zeolites of clinoptilolite, ferrierite and mordenite were used as catalytic support. These zeolites were ion exchanged and base washed before use. Then Mo in 12 wt.% and the W and Ni loadings in 6 wt.%. and 4 wt.% were impregnated over modified zeolites.

CATALYTIC ACTIVITY TEST

Catalysts, DBT and hexane and H_2O_2 were added together and stirred at 60°C and for 1h. Then the solution was mixed with the same volume of acetonitrile. The upper phase was analysed after 30 min. The extraction with acetonitrile was repeated three times and the results were reported using UV-Vis spectroscopy.

RESULTS AND DISCUSSION

CHARACTERIZATION

Figure 1 indicates the XRD patterns of NiMoW catalysts over clinoptilolite, mordenite, and ferrierite. Among these catalysts, just clinoptilolite preserve its crystalline nature. In all three studied catalysts, a very small reflection was observed at 2θ=43° which is the characteristic peak of NiO. This means NiO exists as a very small crystallite in nanometric scale in all studied catalysts.

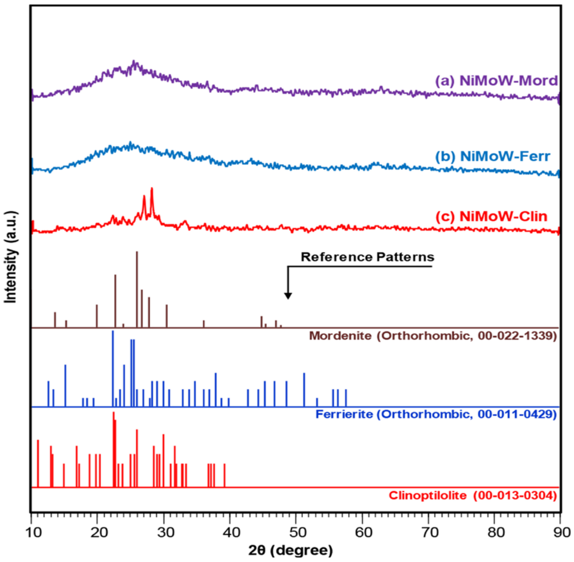


Figure 1: XRD patterns of synthesized samples.

FESEM pictures of NiMoW catalysts over clinoptilolite, mordenite and ferrierite have been indicated in Figure 2. The catalyst of NiMoW-Mord has a uniform morphology. In addition, all the particles in this catalyst are spherical and in nano-scale. NiMoW-Ferr has a higher porosity in comparison with NiMoW-Mord and proper distribution of particles integrated agglomerate leads to lower porosity and surface area of the catalyst. Furthermore, the smallest particle size was observed in NiMoW-Clin catalyst but this led to high agglomeration which reduces the surface area.

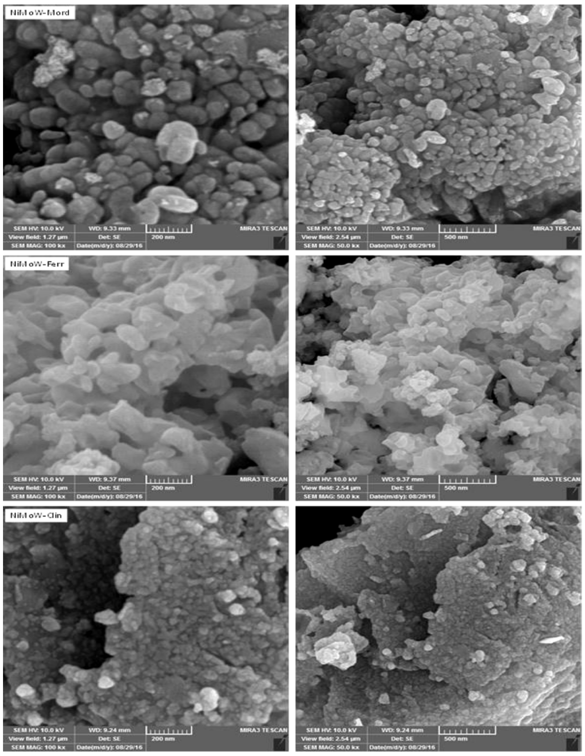
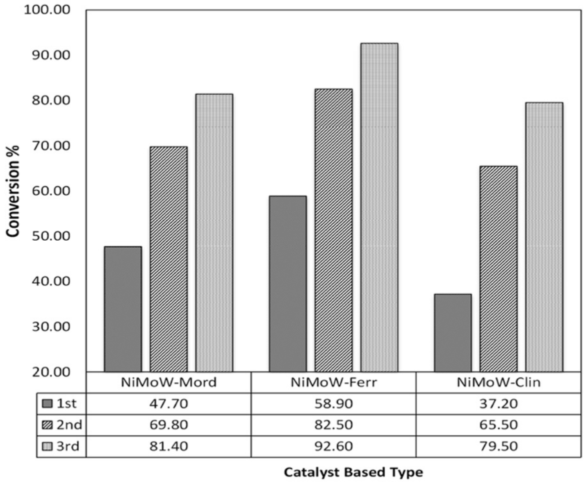


Figure 2: FESEM pictures of synthesized samples.

ODS TESTS

Desulfurization performances of NiMoW catalysts with different supports of clinoptilolite, mordenite, and ferrierite after three times of extraction with acetonitrile, were studied and summarized in Figure 3. Among the supported NiMoW catalysts, NiMoW-Ferr shows the superior performance and the DBT conversion up to near 92.8% after three times of extraction. The NiMoW-Clin showed the lowest DBT conversion among studied catalysts. By increasing the extraction times, amount of converted DBT was enhanced which showed the importance of extraction in extractive ODS. NiMoW-Ferr indicated lowest Si/Al ratio (FTIR, not shown) which causes higher adsorption capacity of the catalyst. Moreover, a number of acid sites are higher over this catalyst. Furthermore, the surface area of this catalyst is larger (not shown) which enhances a number of effective functional groups. FTIR confirmed the existence of higher amounts of metal active sites over ferrierite which leads to more active sites per gram of catalyst. According to these results, NiMoW-Ferr was selected as the best catalyst among studied ones.



	NiMoW-Mord	NiMoW-Ferr	NiMoW-Clin
■ 1st	47.70	58.90	37.20
▨ 2nd	69.80	82.50	65.50
▤ 3rd	81.40	92.60	79.50

Figure 3: ODS activity of synthesized samples.

CONCLUSIONS

Different natural zeolites of ferrierite, mordenite, and clinoptilolite which are abundant zeolites in Iranian mines, were studied as support of NiMoW and used for ODS of dibenzothiophene. Three times of extraction with acetonitrile was carried out after each run of ODS. Also, more extraction increases the DBT conversion. Finally, NiMoW over ferrierite showed the highest DBT conversion due to lower Si/Al ratio, higher surface area, and populated essential functional groups.

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