International Journal of Natural Sciences: Current and Future Research Trends (IJNSCFRT)
ISSN: 2790-7929

https://ijnscfrtjournal.isrra.org/index.php/Natural_Sciences_Journal/index

Catalytic Oxidative Desulfurization of Model Oil Fuels by Novel Bifunctional Molecular Sieve NbFeAPSO-5

Mominou Nchare[a*], Moctar Iyami Bintou[b], Albertine Alarba Sam-Tunsa[c], Elvis Kah[d]

[a,b,c,d]Department of Mining & Extractive Metallurgy, School of Geology & Mining Engineering, Meiganga BP 115, Cameroon
[a]Email: nmominou@yahoo.com
[b]Email: iyammimoktar@gmail.com
[c]Email: albertinealarba@yahoo.fr
[d]Email: kah_elvis@yahoo.fr

Abstract

In this work, novel bifunctional NbFeAPSO-5 molecular sieve was synthesised and used in oxidative desulfurization of model oil with hydrogen peroxide (H_2O_2, 25 wt%) as an oxidant. It was observed that ICP-EAS analysis confirmed the incorporation of silicon (12.9%), aluminium (15.4%), phosphorous (21.9%), iron (5.62%) and niobium (0.39%) into AlPO-5 framework**.** Furthermore, the NbFeAPSO-5 can be reused for at least six cycles without noticeable changes in desulfurization performance, thus revealing its good reusability. Used in the catalytic oxidative desulfurization of model diesel oil, the sulfur content can be reduced from 559.7 ppm to 4.8 ppm with 99.2% sulfur removal via a one-step process under mild conditions.

Keywords: Bifunctional molecular sieve; Oxidative desulfurization; Model diesel oil; Dibenzothiophene.

Received: 5/1/2025
Accepted: 6/28/2025
Published: 7/7/2025

---

* *Corresponding author.*

1. Introduction

In the last few years, sulfur and nitrogen oxides produced by burning fuels are one of the causes of air pollution, especially hazy weather and acid rain [1,2]. Therefore, strict regulations on the permissible sulfur content in fuel have been performed, which presented a challenge for the removal of S-compounds in fuel. The competitive adsorption of sulfides and nitrides on the active center in the hydrodesulfurization (HDS) could lead to a decrease in removal ratios of the sulfur compounds and catalyst poisoning. Besides, the reaction between basic nitrogen and acid sites led to inhibition effects on HDS. Laredo and his colleagues [3] considered that nitrides had a restrained effect on the removal of sulfides at a concentration of 5 μg/g. Also, there was a negative effect of pyrrolic compounds on fuel stability due to the pyrrolic autoxidation. Therefore, desulfurization with the simultaneous denitrogenation of diesel fuel is necessary. In the past literature, many researchers have described desulfurization and denitrogenation of transport fuel [4]. Alternative methods of HDS have been studied, including selective adsorption, extraction, oxidation, and their combination. Mohammadian and his colleagues [5–7] studied the process of desulfurization and denitrogenation of fuel oil by adsorption with mesostructure adsorbent and its modified one by metallic oxide. Rezvani and his colleagues [8,9] have synthesized novel organic–inorganic hybrid materials with superior performances for oxidation desulfurization (ODS) of fuel oil. Li and his colleagues [10] described oxidative desulfurization and denitrogenation of fuel using metal–organic framework-based/-derived catalysts under oxygen as an oxidant. Some studies have shown that the ODS process can effectively oxidize sulfur compounds to sulfones in diesel oil under the action of catalyst [11–13]. However, removing the oxides of sulfides and nitrides of fuel needed polar solvents because of the low water solubility of the oxidized products, which reduced the yield of refined diesel fuel. Therefore, selective oxidation was combined with in-situ hydrogenation to improve the removal efficiency of sulfides and nitrides [14,15], and it is carried out at low pressure and temperature compared with the other desulfurization and denitrogenation. Nitrides and sulfides were oxidized to N-oxides and sulfones, and then hydrogenated to hydrocarbon compounds [16].

In this work, bifunctional NbFeAPSO-5 molecular sieve syntsized previously [17]., is used to investigate the catalytic oxydative desulfurization of fuel.

2. Experimental Procedures

2.1. Synthesis of NbFeAPSO-5 Molecular Sieve [7,8,17]

In 50 ml Erlern Mayer, a fixed amount of deionized water was added with 85% phosphoric acid and just after aluminum source was slowly added under stirring which took 20 minutes.

After adding the template (Triethylamine), the temperature was rised to 40˚C and the whole mixture was then stirred for another 30 minutes. The resulting mixture was then placed into a Teflon-line stainless steel autoclave and heated at 200˚C for 24 hours. After quenching to the room temperature, the product was washed repeatedly with deionized water, and then dried at 100˚C for 4 hours. The resulting product was calcined at 600˚C for 4 hours.

For the niobium solution preparation, a fixe quantity of niobium hydroxide was put in 80 g oxalic acid and 500 ml deionized water under stirring, and the temperature was rised to 70˚C - 80˚C. After a period of time, a clear solution of niobium complexed in oxacilic acid was obtained.

For the synthesis of NbFeAPSO-5, niobium solution was added just after putting silicon source.

The raw materials for different synthesized catalysts are found in **table 1**.

Tables 1: Catalyst raw materials

Raw materials	Spécifications	Molecular formula	Molecular weight (g/mol)	Purity
Phosphoric acid	AR 500 ml	H3PO4	98.0	85.0%
Boehmite		Al2O3·2H2O	138.0	95%
Triethylamine	AR 500 ml	(C2H5)3N	101.19	≥99.0%
Niobium hydroxide	AR 500 g	Nb(OH)5	177.94	99.9%
Ferric nitrate	AR 500 g	Fe(NO3)3·9H2O	404.00	98.5%
Ethyl orthosilicate	AR 500 ml	(C2H5O)4Si	208.33	40.45%

2.2. NbFeAPSO-5 Characterization

X-ray powder diffraction data were obtained on a Rigaku D/max diffractometer using Cu ka radiation at 40 kv and 60 Ma. Elemental composition of the catalysts was accessed using ICP-AES performed on IRIS 1000 and the acidity by mean of infrared spectrometry performed on Nicolet Magna-IR 550.

2.3. Desulfurization of the model oils

Model oils were prepared by dissolving different S-compounds such as BT, 4,6-DMDBT and DBT in n-octane with a corresponding sulfur content of 500 and 1000 ppm, respectively. The sulfur removal was calculated as follows:

Sulfur removal $\mathbf{(\%) = (1 - C_t/C_0) \times 100\%}$

where $\mathbf{C_0}$ (ppm) is the initial sulfur concentration at the beginning and $\mathbf{C_t}$ (ppm) is the sulfur concentration at certain time.

3. Results and discussion

3.1. Effect of Nb Content in NbFAPSO-5 Molecular Sieve

Two sources of niobium were tested, niobium pentaoxide and niobium hydroxide. The first resulted in low solubility; niobium hydroxide complexed easily in oxalic acid as described in experimental section. The XRD patterns of NbFAPSO-5 is shown in **Figure 1**. Compositional analysis of the synthesized NbFeAPSO-5 showed that 39% of niobium was confirmed to be incorporated while maintaining AIPO-5 type structure.

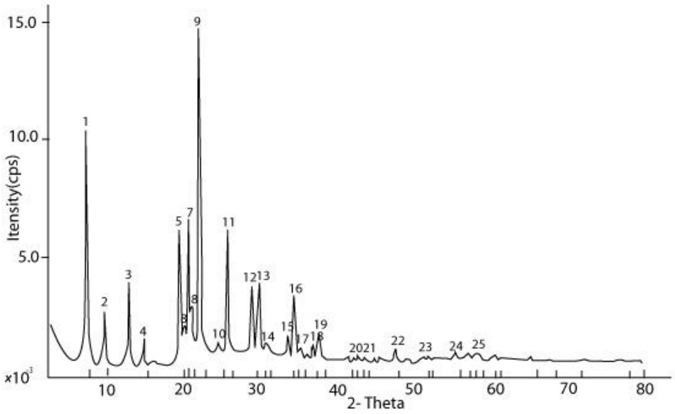

Figure 1: XRD patterns of niobium containing NbFAPSO-5.

The synthesis of NbFeAPSO-5 exhibits many similarities to that of aluminosilicate molecular sieves. All are synthesized from reactive gels under the pH of 4 to 7, with the presence of organic additives helping to promote crystallization of a specific phase. Temperature plays an important role in the crystallization of these synthesized samples. At lower temperature (100˚C - 125˚C) AFI type structure was not obtained; this structure occurred only for temperature ranging from 150˚C to 200˚C. At higher crystallization temperature (200˚C), other non-zeolitic phases are observed to crystalllize with increased crystallization time. The optimum time needed to promote crystallization of these phases appears to be dependent on both the temperature and the nature of the organic species used in the reaction mixture.

The organic additives appear to promote crystallization of a specific aluminophosphates structure, although it is unclear if it is in the same way that the organic additive promotes crystallization of a specific structure in the synthesis of the aluminosilicates. Many organic amines have been claimed to promote the crystallization of the AIPO4-5 structure; but there appears to be little correlation among them. A wider range of neutral organic amines have been found to aid in crystallization of aluminophosphates structures, compared to the aluminosilicate

system; however, this may be a result of the initially acidic environment of the aluminophosphates gel, which would encourage the formation of a protonated amine, thus generating the cationic form in situ. The preparation of several structures from a given organic amine is a result of changing other synthesis conditions. Incorporation of Nb into FAPSO-5, leading to NbFAPSO-5 molecular sieve, infrared spectrum is shown in **Figure 2**

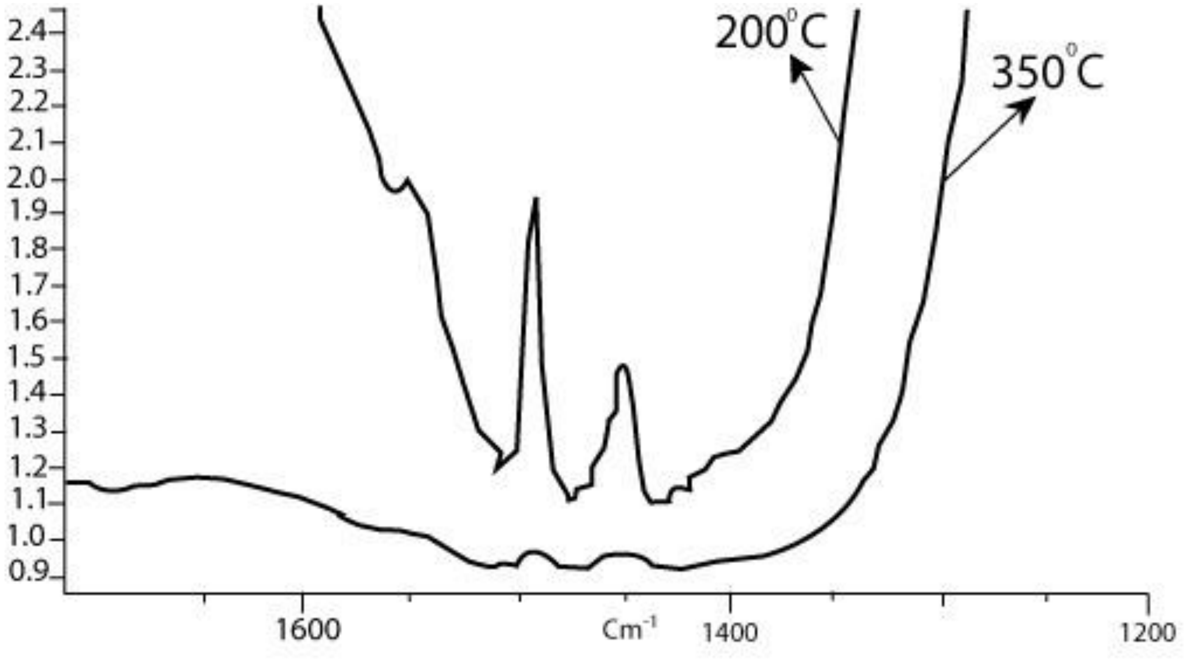

Figure 2: Infrared spectrum of NbFAPSO-5.

3.2. Effect of NbFeAPSO-5 on oxydative desulfurization of model oil

In order to evaluate the desulfurization performance of NbFeAPSO-5 with different proportion of Nb contening FeAPSO-5, the ODS experiments of model oil were conducted. As shown in Table 1, with the increasing of NbFeAPSO-5 proportion, the ODS performance was firstly enhanced and then basically unchanged, the Nb contain of 2ml exhibited the best ODS performance by achieving 93.8% sulfur removal.

In a typical ECODS process, the reaction between oxidants and sulfides occurs in the catalytic activity, affecting mostly the ODS performance.[52].

Table 1: Comparison of different Nb containing NbFeAPSO-5 on DBT removal

Entry	NbFeAPSO-5	Sulfur removal %	Viscosity/cp
1	[Nb]/NbFeAPSO-5 (0.5 ml)	12.4± 0.3	163± 2.1
2	[Nb]/NbFeAPSO-5 (1ml)	14.5± 0.7	286± 2.4
3	[Nb]/NbFeAPSO-5 (2ml)	15.1± 0.5	342± 2.1
4	[Nb]/NbFeAPSO-5 (3ml)	15.6± 0.3	614± 3.6

Conditions: T=40 °C, m/oil=1/10, initial S-content=1000 ppm, t=60 min.

3.2. Effect of reaction temperature on oxydative desulfurization of model oil

To investigate the influence of reaction temperature on the sulfur removal, ODS experiments were carried out at 30, 40, 50 and 60 °C with the results illustrated in Fig.3. When the operation temperature was 30 °C, the removal of DBT could only reach 76.1%, which indicated that the catalyst could not catalyse the reaction efficiently at the relatively low temperature. When the temperature increased to 40, 50 and 60 °C, the sulfur removal was remarkably increased to 93.8, 98.5 and 99.3%, respectively. The sulfur removal was limited by kinetics at low temperature, while it might also be restricted by the unproductive decomposition of H_2O_2 at high temperature. Therefore, the desulfurization efficiency was not significantly improved when the temperature raised from 50 to 60 °C. Thus, in the current work, the optimal reaction temperature was chosen as 50 °C.

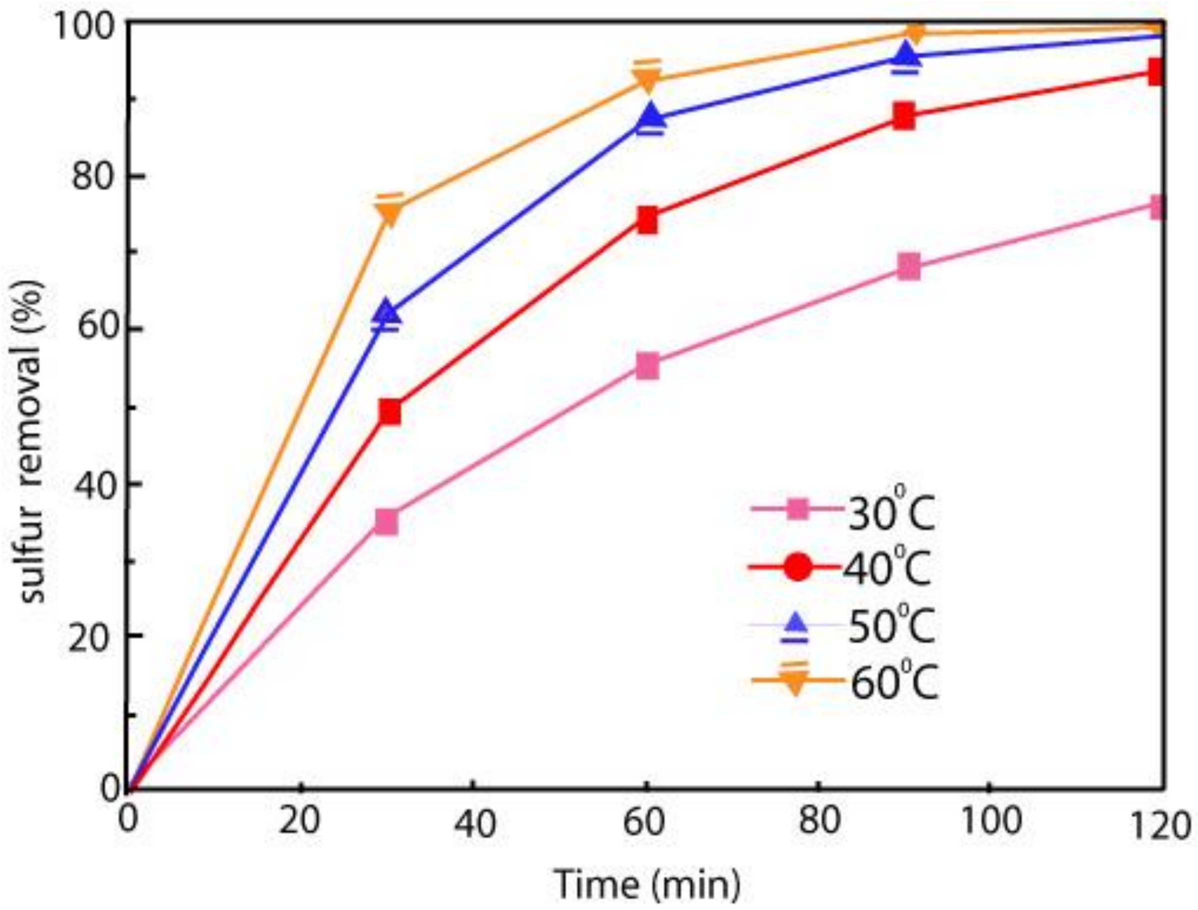

Figure 3: Effects of reaction temperature on sulfur removal performance.

Conditions: Catalyst/oil=1/10, H_2O_2/S=6/1, initial S-content=1000 ppm.

3.3. Kinetic study of oxydative desulfurization of model oil

For a more in-depth study of the relationship between desulfurization efficiency and reaction temperature, the kinetics research of the oxidative reaction was carried out. As shown in Fig.4, the reaction was in accord with the pseudo-first-order kinetics as follows:

$$\mathbf{Ln(C_0/C_t) = k_t} \qquad \mathbf{(1)}$$

Where C_0 (ppm) is the total sulfur concentration and C_t (ppm) is the sulfur concentration at certain reaction time t, and k is the first-order rate constant (min^{-1}). It could be observed that the constant k increased from 0.0125 to 0.0422 when the temperature raised from 30 to 60 °C, which indicates the acceleration of reaction along with the increasing of reaction temperature.

According to the Arrhenius equation:

$$\mathbf{-\ln k = Ea/RT - \ln A} \qquad \mathbf{(2)}$$

The apparent activation energy for the current oxidation of DBT was estimated to be 34.3 kJ mol^{-1}.

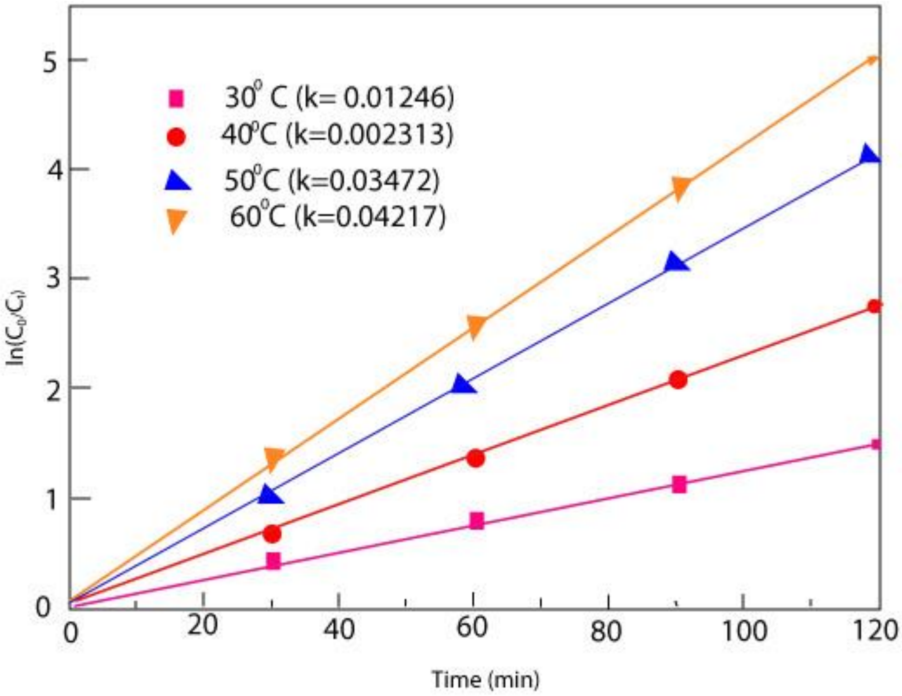

Figure 4: Pseudo-first-order kinetics for the oxidative of DBT under different reaction.

Conditions: Catalyst/oil=1/10, H2O2/S=6/1, initial S-content=1000 ppm.

3.4. Effect of NbFeAPSO-5 usage on oxydative desulfurization of model oil performance

The effect of NbFeAPSO-5 usage was also investigated and the results are shown in Fig.5. It seemed that the increase in the quantity of molecular sieve in the reaction may be an efficient strategy to improve the desulfurization efficiency of NbFeAPSO-5. The removal of DBT obviously increased from 72.3% to 98.7% when the dosage of NbFeAPSO-5 was raised from 0.5 to 1.0 g. As expected, when the usage of Nb increased to 2.0 g and 3.0 g, the sulfur removal both approached 100%. Moreover, the operational time which the complete sulfur removal required decreased to 60 min and 30 min, respectively.

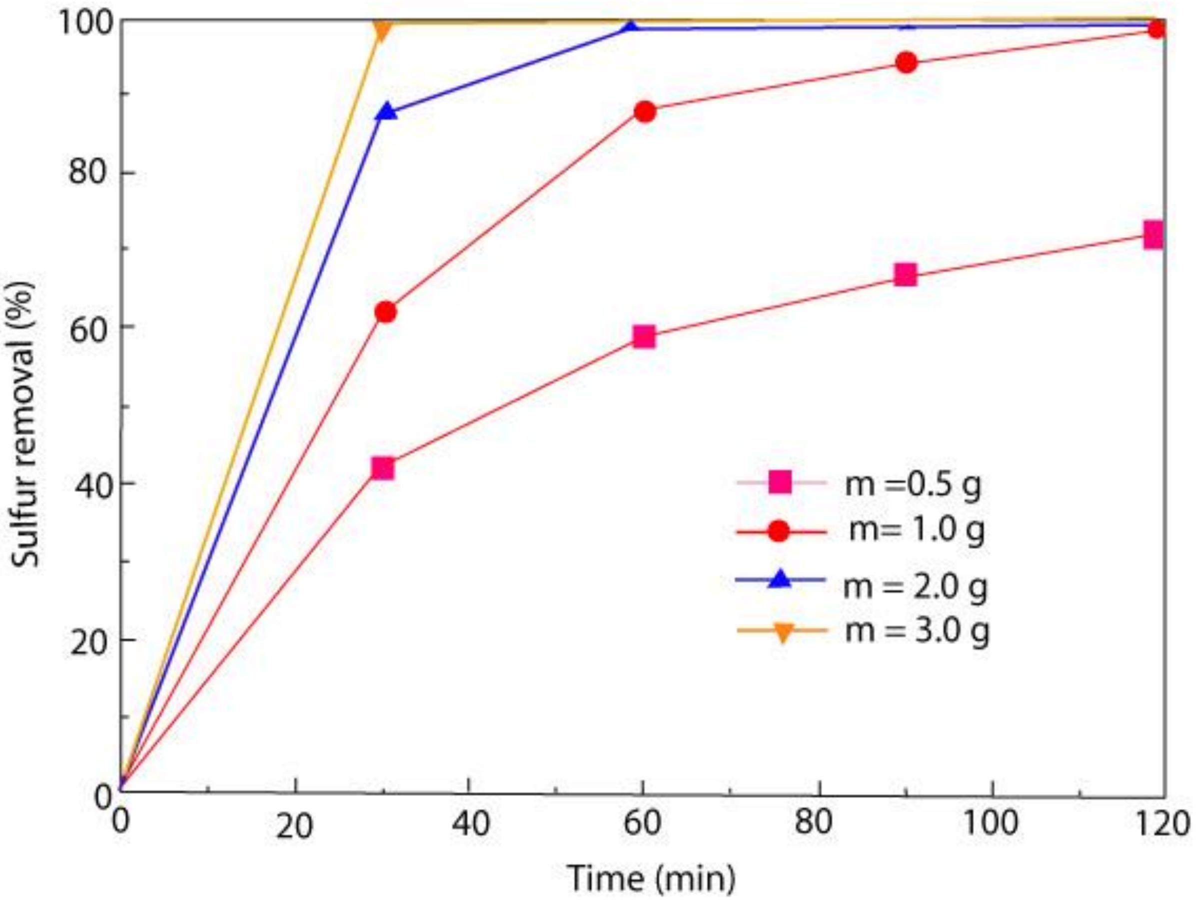

Figure 5: Effects of the dosage amount of catalyst on sulfur removal performance.

Reaction conditions: H_2O_2/S=6/1, T=50 °C, initial S-content=1000 ppm.

3.5. Effect of O/S molar ratio on oxydative desulfurization of model oil performance

The effect of the usage of H_2O_2 on the removal of DBT was also investigated which is shown in Figure 6. When the molar ratio of H_2O_2/S was 2/1, which is in accordance with the stoichiometry of the oxidative reactions, the sulfur removal was not satisfying, which only reached 63.4%.

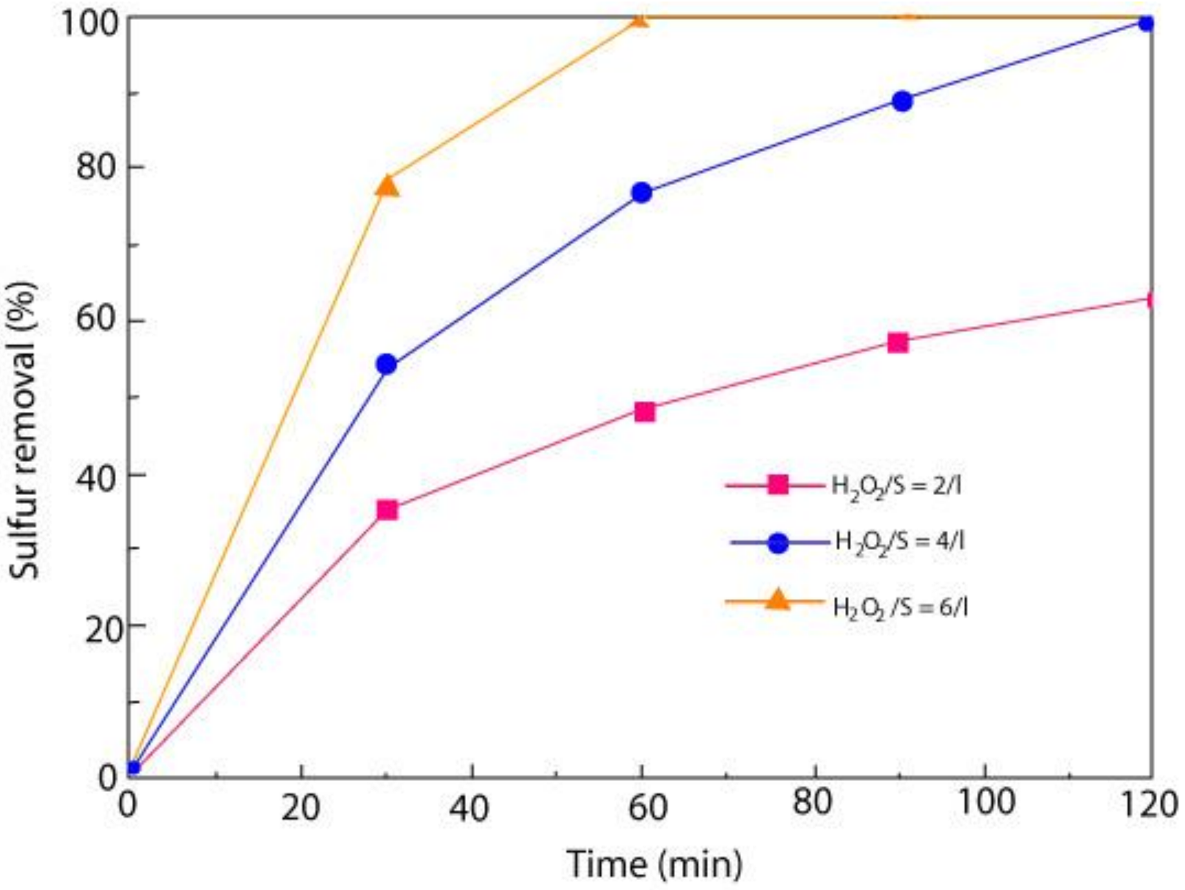

Figure 6: Effects of the usage of oxidant on sulfur removal performance.

Reaction conditions: Oxydant/oil=1/5, T=50 °C, initial S-content=1000 ppm.

3.6. Effect of sulfur species on ODS performance

The sulfur species also play a vital role in affecting the desulfurization efficiency in oxydative desulfurization. As shown in Fig.7, the removal rate of BT, DBT and 4,6-DMDBT in 30 min were 67.9%, 84.7% and 78.1%, respectively. In addition, the three S-compounds can be removed completely within different reaction time, which demonstrated the excellent catalytic activity of the NbFeAPSO-5.

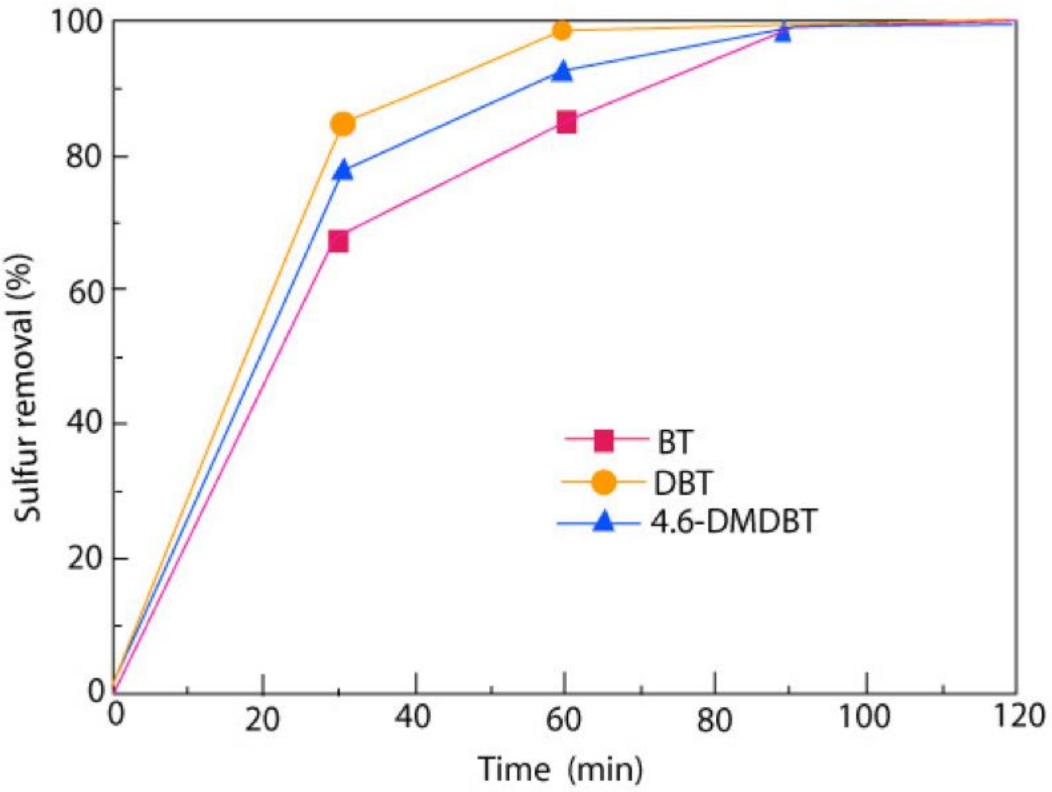

Figure 7: Effects of sulphide species in model oil on sulfur removal performance.

Reaction conditions: Catalyst/oil=1/5, H_2O_2/S=6/1, T=50 °C, initial S-content= 500 ppm.

3.7. Recycling of the NbFeAPSO-5

As is shown in Fig.8, the desulfurization performance just decreased from 100% to 97.4% without showing significant decline after six repeated cycles. Judging from the experimental results, the NbFeAPSO-5 exhibited a satisfactory recyclability through a low-cost regeneration approach, and may be prospective for industrial application.

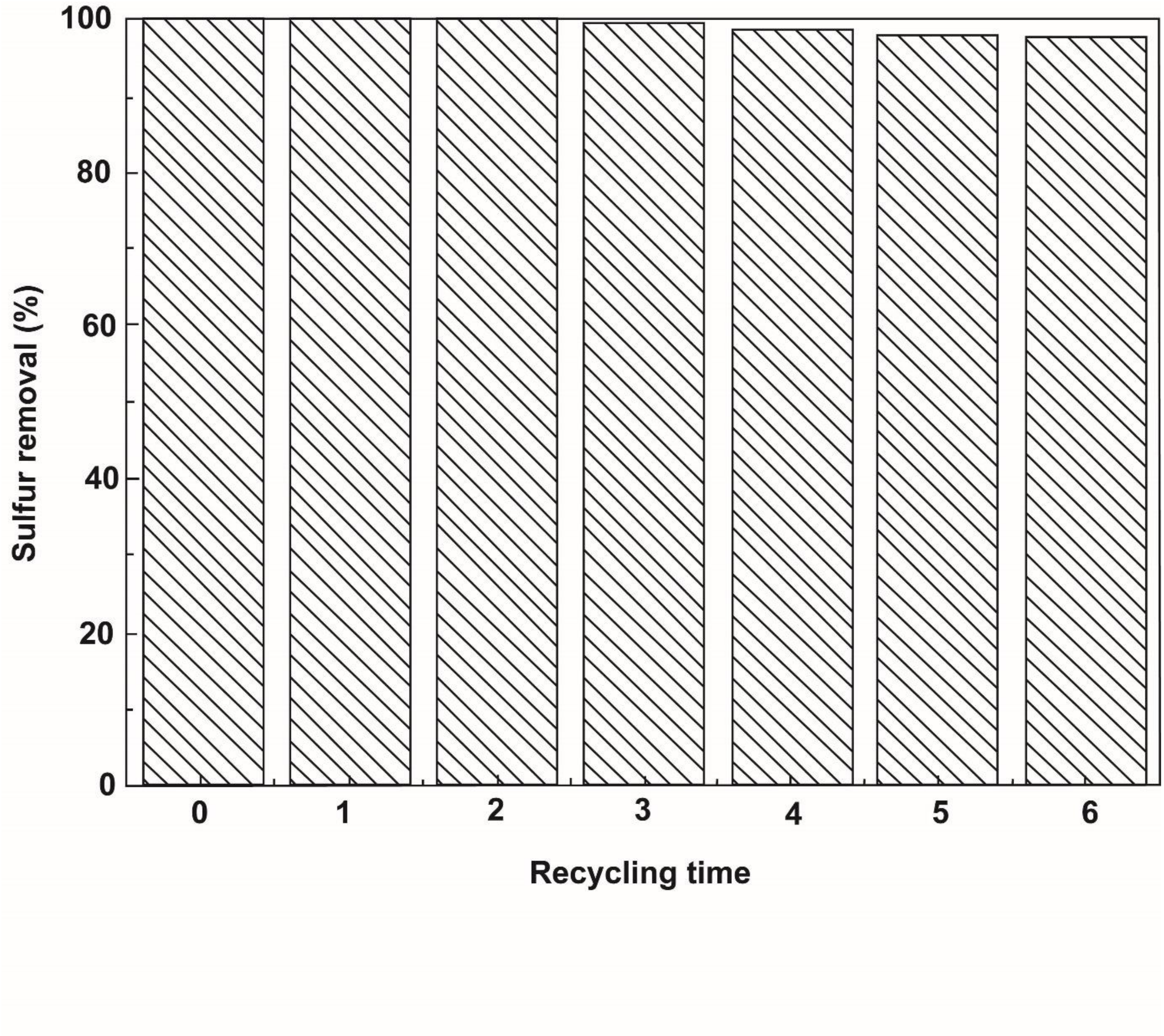

Figure 8: Recycling of NbFeAPSO-5 for DBT removal.

Reaction conditions: Catalyst/oil=1/5, H_2O_2/S=6/1, T=50 °C, initial S-content= 1000 ppm.

4. Conclusion

Bifunctional NbFeAPSO-5 molecular sieve were synthesized and used in the catalytic oxydative desulfurization of model diesel fuel, with hydrogen peroxide (H_2O_2, 25 wt%) as the oxidant. Both Lewis and Brönsted acidity were found in the synthesized NbFeAPSO-5 catalyst. The optimal desulfurization performance can be obtained by achieving complete sulfur removal under quiet mild conditions. The sulfur species also play a vital role in affecting the desulfurization efficiency in oxydative desulfurization. It seemed that the increase in the quantity of molecular sieve in the reaction may be an efficient strategy to improve the desulfurization efficiency of NbFeAPSO-5. The removal of DBT obviously increased from 72.3% to 98.7% when the dosage of NbFeAPSO-5 was raised from 0.5 to 1.0 g. As expected, when the usage of Nb increased to 2.0 g and 3.0 g, the sulfur removal both approached 100%. Judging from the experimental results, the NbFeAPSO-5 exhibited a satisfactory recyclability through a low-cost regeneration approach, and may be prospective for industrial application.

Acknowledgements

Special thanks to professor Wang Lei and Dr Li Hong for the collaboration during the last two decades

References

[1]. J. Xue, Z. Yuan, S.M. Griffith, X. Yu, A.K.H. Lau, J. Yu, Sulfate formation enhanced by a cocktail of high NOx, SO_2, particulate matter, and droplet pH during haze-fog events in megacities in China: an observation-based modeling investigation, Environ. Sci. Technol. 50 (2016) 7325–7334.

[2]. X. Zhuang, Y. Wang, H. He, J. Liu, X. Wang, T. Zhu, M. Ge, G. Tang, J. Ma, Hazardous insights and mitigation in China: an overview, J. Environ. Sci. 26 (2014) 2–12.

[3]. G.C. Laredo, J.A. De los Reyes, J.L. Cano, J.J. Castillo, Inhibition effects of nitrogen compounds on the hydrodesulfurization of dibenzothiophene, Appl. Catal. A 207 (2001) 103–112.

[4]. M. Sau, K. Basak, U. Manna, M. Santra, R.P. Verma, Effects of organic nitrogen compounds on hydrotreating and hydrocracking reactions, Catal. Today 109 (2005) 112–119.

[5]. M. Mohammadian, M.R. Khosravi-Nikou, A. Shariati, M. Aghajani, Model fuel desulfurization and denitrogenation using copper and cerium modified mesoporous material (MSU-S) through adsorption process, Clean Technol. Environ. Policy. 20 (2018) 95–112.

[6]. M. Mohammadian, M. Ahmadi, M. R. Khosravi-Nikou, Adsorptive desulfurization and denitrogenation of model fuel by mesoporous adsorbents (MSU-S and CoO-MSU-S), Pet. Sci. Technol. 35(6) 608–614.

[7]. S. Rashidi, M.R. Khosravi-Nikou, B. Anvaripour, Adsorptive desulfurization and denitrogenation of model fuel using HPW and NiO-HPW modified aluminosilicate mesostructures, Microporous Mesoporous Mat. 211 (2015) 134–141.

[8]. M.A. Rezvani, O.F. Miri, Synthesis and characterization of PWMn/NiO/PAN nanosphere composite with superior catalytic activity for oxidative desulfurization of real fuel, Chem. Eng. J. 369 (2019) 783.

[9]. M.A. Rezvani, Z.S. Aghbolagh, H.H. Monfared, Green and efficient organic-inorganic hybrid nanocatalyst for oxidative desulfurization of gasoline, Appl. Organomet. Chem. 32 (2018) e4592.

[10]. S. Li, W. Wang, J. Zhao, Highly effective oxidative desulfurization with magnetic MOF supported WMoO3 catalyst under oxygen as oxidant, Appl. Catal. B 277 (2020) 119224.

[11]. M.A. Rezvani, M. Ali Nia Asli, S. Khandan, H. Mousavi, Z.S. Aghbolagh, Synthesis and characterization of new nanocomposite CTAB-PTA@CS as an efficient heterogeneous catalyst for oxidative desulphurization of gasoline, Chem. Eng. J. 312 (2017) 243–251.

[12]. M. A. Rezvani, M. Ali Nia Asli, M. Oveisi, R. babaei, K. Qasemi, S. Khandan, An organic-inorganic hybrid based on Anderson-type polyoxometalate immobilized on PVA as a reusable and efficient nanocatalyst for oxidative desulphurization of gasoline, RSC Adv. 6 (2016) 53069–53079.

[13]. A.F. Shojaei, M.A. Rezvani, M.H. Loghmani, Comparative study on oxidation desulphurization of actual gas oil and model sulfur compounds with hydrogen peroxide promoted by formic acid: Synthesis and characterization of vanadium containing polyoxometalate supported on anatase crushed nanoleaf, Fuel Process. Technol. 118 (2014) 1–6.

[14]. J. Zhang, J. Xu, J. Qian, L. Liu, Denitrogenation of straightrun diesel with complexing extraction, Pet. Sci. Technol. 31 (2013) 777–782.

[15]. B. Bertleff, M. S. Haider, J. Claußnitzer, W. Korth, P. Wasserscheid, A. Jess, J. Albert, Extractive catalytic oxidative denitrogenation of fuels and their promoting effect for desulfurization catalyzed by vanadium substituted heteropolyacids and molecular oxygen, https://dx.doi.org/10.1021/acs.energyfuels.0c00864.

[16]. E.C. Gaudino, D. Carnaroglio, L. Boffa, G. Cravotto, E.M. Moreira, M.A.G. Nunes, V. L. Dressler, E.M.M. Flores, Efficient H_2O_2/CH_3COOH oxidative desulfurization/ denitrification of liquid fuels in sonochemical flow-reactors, Ultrason. Sonochem. 21 (2014) 283–288.

[17]. Nchare, M., Wang, L. and Anagho, S. Synthesis of NbFAPO-5 and NbFAPSO-5 Molecular Sieve by Hydrothermal Method and Comparison of Their XRD Patterns and Their Acidic Properties Evaluation by Infrared Spectroscopy. Open Journal of Inorganic Chemistry, 6, (2016), 155-162. http://dx.doi.org/10.4236/ojic.2016.63011