



Optimization of Bimetallic Ni–Cr/ZSM-5 Catalysts for Enhanced Oxidative Desulfurization: The Superior Performance of Ni5/Cr3 Formulation

Safa Al-deen A. Juboori, Gholamreza Moradi 

Catalyst Research Center, Faculty of Chemical Engineering and Petroleum, Razi University,
Kermanshah 671441497, Iran

ARTICLE INFO

Article type:
Research article

Article history:

Received: 2026-06-10

Revised: 2026-07-04

Accepted: 2026-08-13

Available online: 2026-08-23

Keywords:

Oxidative desulfurization,
ZSM-5 zeolite,
Nickel,
Chromium

ABSTRACT

Sulfur compounds pose significant challenges for environmental pollution. This issue has led to the application of various methods for sulfur detection and removal, which differ depending on the sulfur content. Among these methods is oxidative desulfurization, which has attracted considerable attention due to its mild operating conditions, ambient pressure, and relatively low temperature. In this study, a combination of chromium and nickel metals supported on ZSM-5 zeolite was used for oxidative desulfurization. Initially, nickel (3–8 wt.%) and chromium (1–8 wt.%) were separately loaded onto the zeolite to investigate the effect of each metal individually. Subsequently, a combination of 5 wt.% nickel and 1–8 wt.% chromium was simultaneously loaded onto the zeolite. The material containing 3 wt.% chromium and 5 wt.% nickel exhibited the highest efficiency within two hours. The synthesized catalysts were thoroughly characterized using FTIR, XRD, FESEM, EDX, and BET techniques. ZSM-5 zeolite with 5 wt.% nickel and 3 wt.% chromium showed 63% sulfur removal in the oxidative desulfurization process over two hours, indicating the favorable performance of this catalyst for the process.

DOI: 10.22034/ijche.2026.586108.1597 URL: https://www.ijche.com/article_251429.html

1. Introduction

Pollution in the atmosphere originates from both natural processes and human activities. Carbon, hydrogen, and sulfur are the common elements found in the petroleum industry. Among these elements, sulfur plays a

significant role in environmental systems. Sulfur is found in terrestrial environments in the form of sulfide and sulfate minerals, in marine environments as soluble sulfates, and in the atmosphere as hydrogen sulfide and sulfur dioxide [1, 2]. Given that the energy

*Corresponding author: gmoradi@razi.ac.ir



required by humans in the modern world is supplied by petroleum and its derivatives—including gasoline, diesel, aviation fuel, and fuel oil, which mainly contain various sulfur compounds—the conversion of this sulfur into harmful gases such as sulfur oxides (SO_x) has become one of the major sources of environmental pollution [3, 4].

To reduce pollutants resulting from sulfur in fuels, various techniques, including the following, have been developed.

- Oxidative desulfurization [5, 6, 7]
- Hydrodesulfurization [8, 9, 10]
- Biodesulfurization [11, 12, 13, 14]
- Extractive desulfurization [15, 16, 17]
- Adsorption desulfurization [18, 19]

The selection of an appropriate desulfurization technique largely depends on the sulfur content and the nature of the fuel. Not all of these methods are applicable to every type of fuel. For instance, heavy oils pose specific challenges due to their high sulfur content, high viscosity, and high boiling point. Consequently, specific methods must be employed to remove sulfur from them. Figure 1 presents a visual representation of the recommended desulfurization methods based on the concentration of sulfur [20].

As mentioned earlier, one of the methods for sulfur removal is oxidative desulfurization. This method has attracted significant attention as an efficient approach for sulfur removal under mild operating conditions, typically at ambient pressure and relatively low

temperatures. In this method, sulfur-containing molecules are selectively oxidized by one or two oxygen atoms using a suitable oxidizing agent, leading to the formation of sulfones and sulfoxides. Due to their higher polarity, compared to that of the original sulfur compounds, these oxidized species are easily removed from light petroleum fractions through extraction or adsorption techniques [21, 22, 23, 24]. Several parameters, the most important of which are the catalyst, the type of the oxidizing agent, and the operating conditions, influence the efficiency of the desulfurization process [25].

As mentioned earlier, one of the parameters affecting oxidative desulfurization is the type of the catalyst. The catalyst plays a crucial role in the performance of ODS. Incorporating metal species onto suitable supports significantly increases the number of active sites available for the reaction. Catalysts enhance the conversion rate through specific chemical interactions or bonding with sulfur-containing molecules and improve the stability of the oxidative desulfurization process. In this work, the effect of adding chromium and nickel metals to ZSM-5 zeolite was investigated. According to the literature, systematic investigations into the synergistic effects of Ni and Cr co-supported on ZSM-5 for oxidative desulfurization (ODS) are scarce, particularly with respect to the role of Ni in suppressing the formation of crystalline Cr₂O₃. Therefore, in the present study, we investigated the effect of their combination.

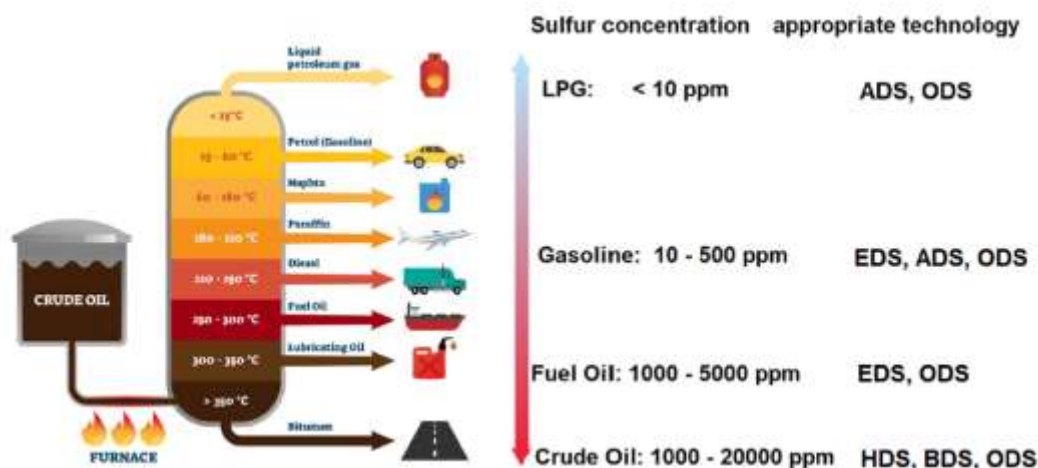


Figure 1. Desulfurization technologies for various petroleum fractions based on the concentration levels of sulfur [20].

2. Materials and methods

The ZSM-5 zeolite used in this study, with a Si/Al ratio of 23, was supplied by Sigma. NaOH (Merck) served as the activating agent for the zeolite. Additional reagents, namely nickel nitrate, dibenzothiophene (DBT), n-hexane, hydrogen peroxide (H_2O_2), and acetonitrile (CH_3CN), were all procured from Merck.

2.1. Washing zeolites with sodium hydroxide (NaOH)

Alkaline treatment of the zeolite with sodium hydroxide (NaOH) solution promotes the development of mesopores throughout its structure. Typically, 1 g of zeolite is suspended in 10 mL of 0.55 M NaOH. This suspension is transferred to a 100 mL round-bottom flask fitted with a condenser and held at 50 °C for 160 min. Upon completion of the treatment, the mixture is cooled to ambient temperature, and the solid is washed multiple times with distilled water until neutrality is achieved. The resulting product is subsequently dried overnight at 110 °C. Finally, calcination was performed in air at 550 °C for 5 h using a ramp rate of 5 °C min⁻¹ [26].

2.2. Adding metal to zeolites

Incorporation of nickel, chromium, or a combination of both into the zeolite was achieved by dissolving the required amounts of nickel nitrate, chromium nitrate, or both salts in 30 mL of distilled water. After stirring the solution for 15 min, the NaOH-treated zeolite was added. The resulting suspension was kept under continuous agitation on a hot plate at approximately 50 °C until a gel-like consistency formed. The material obtained was then dried overnight at 110 °C and subsequently calcined in air at 550 °C for 5 h. In this study, the metal-modified zeolites were denoted as NX or CX, where X indicates the weight percent of nickel or chromium. Zeolites containing 5 wt.% nickel along with varying chromium loadings were named accordingly; for instance, the sample with 5 wt.% Ni and 1 wt.% Cr was designated as N5-C1.

2.3. Model fuel

A 1000 ppm dibenzothiophene solution in n-hexane served as the model fuel. To prepare it, 5 mg of dibenzothiophene was dissolved in 50 cc of n-hexane, and the mixture was stirred for 1 h to ensure uniformity.

2.4. Oxidative experiments

The oxidation reaction setup comprised a 50 mL flask fitted with a condenser and immersed in a water bath set to the desired temperature to provide the required thermal conditions. Heating and magnetic stirring were supplied by a heater-stirrer placed beneath the vessel (rpm = 50), while the bath temperature was continuously monitored with a thermometer. For all experiments, 100 mg of catalyst was added to 10 mL of the model fuel together with 5 cc of acetonitrile, and the H₂O₂-to-DBT molar ratio was 8.44. Tests were performed at 55 °C for 2 h, and the sulfur content was determined by UV-Vis spectrophotometry at 316 nm. Acetonitrile served as a polar solvent, an oxidation promoter (through peroxyimide acid formation with H₂O₂), and an extracting agent for the oxidized sulfur compounds. Each catalytic experiment was run in triplicate, and the results are expressed as mean ± standard deviation (SD).

2.5. Characterization of catalysts

FTIR spectroscopy was employed to identify the functional groups in the synthesized catalysts, using a Thermo AVATAR instrument (Germany) across a wavenumber range of 400–4000 cm⁻¹. XRD analysis was conducted on a PHILIPS PW1730 diffractometer (Netherlands) with CuK α radiation ($\lambda = 1.54056 \text{ \AA}$), operating at 40 kV and 30 mA. FESEM imaging was performed with a TESCAN MIRA III instrument (Czech

Republic). EDX mapping was carried out on a TESCAN MIRII system equipped with a SAMX detector (France). BET surface area measurements were obtained using a BELSORP MINI II analyzer (BEL, Japan), with sample degassing performed on a BEL PREP VAC II unit under vacuum while heating to 450 °C. Dibenzothiophene absorption was determined by UV-Vis spectrophotometry using a UNICO SQ-4802 spectrophotometer.

3. Results and discussion

3.1. XRD

XRD patterns of samples SA23, Ni5, and Cr3 are shown in Figure 2a. According to JCPDS card No. 44-003, the reflections at 2θ values of 9°, 23.3°, 24°, and 24.3° correspond to the (200), (051), (033), and (313) crystallographic planes of the zeolite framework, respectively. The presence of nickel oxide is confirmed by additional reflections at 37.3° and 43.2°, which are assigned to the (111) and (200) planes based on JCPDS card No. 00-024-216. Figure 2b illustrates the XRD patterns of the nickel–chromium samples, where a characteristic NiO peak is detected in all samples [27]. Furthermore, the reflections at 2θ angles of 33.6°, 36.3°, 41.6°, and 54.9° are attributed to chromium oxide phases, and their intensity increases with rising chromium content, reaching a maximum at 8% chromium[28].

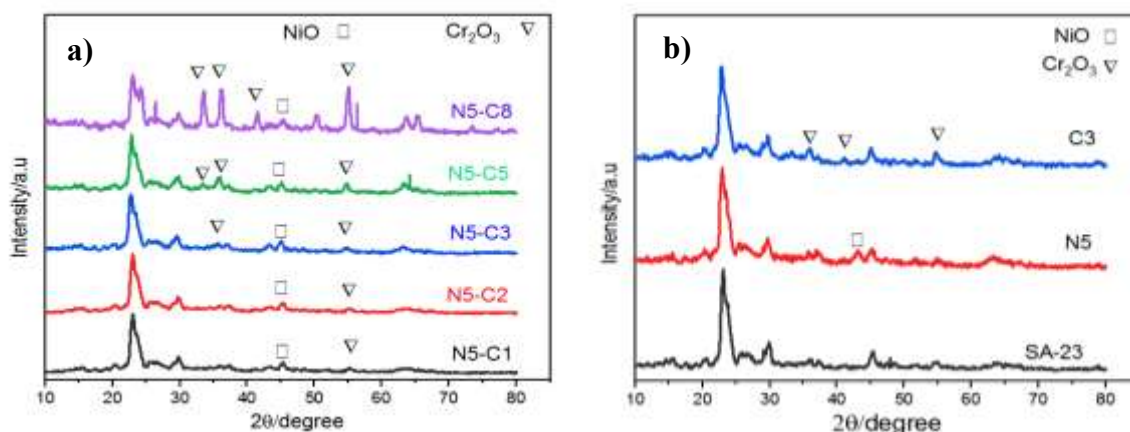


Figure 2. XRD pattern of a) SA-23, Ni5,Cr3 b) Ni5% with Cr 1%-8%.

The crystallinity percentage of the samples was determined using the Scherrer equation (1):

$$DP = (K\lambda) / (\beta \cos\theta) \quad (1)$$

where DP represents the crystallite size in nanometers, K is a constant equal to 0.94, β is the full width at half maximum (FWHM) of the crystalline peak, θ is the diffraction angle, and λ denotes the X-ray wavelength.

The crystallinity percentages obtained for samples SA23, Ni5, Cr3, Ni5/Cr1, Ni5/Cr2, Ni5/Cr3, Ni5/Cr5, and Ni5/Cr8 were 68%, 56%, 60%, 61%, 63%, 70%, 57%, and 45%, respectively.

3.2. FTIR

FTIR analysis was performed to confirm the structural characteristics of the samples, and the resulting spectra are presented in Figure 3. In both spectra, absorption bands appear at 1224 cm^{-1} , corresponding to external asymmetric stretching; in the 1050–1150 cm^{-1} range, attributed to internal asymmetric stretching; and at 795 cm^{-1} , assigned to external symmetric stretching; and at 445 cm^{-1} , indicative of T–O bending vibrations. These features are characteristic of zeolite frameworks. The band at 3640 cm^{-1} is assigned to silanol groups (Si–OH), while the

peak at 3454 cm^{-1} corresponds to Al–OH species within the framework, indicating the presence of Brønsted acid sites. Additionally, the band at 546 cm^{-1} is attributed to double five-membered rings in the zeolite structure, confirming that a regular and crystalline framework was preserved after NaOH washing and the incorporation of nickel and chromium metals [26,29].

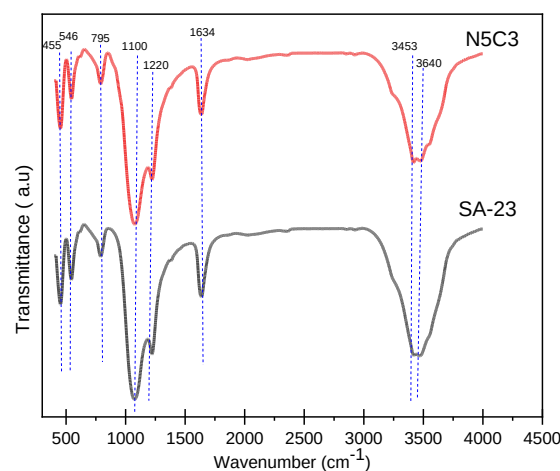


Figure 3. FTIR patterns of SA-23 and Ni5/Cr3

3.3. BET

Figure 4 presents the adsorption and desorption isotherms. All samples exhibit type IV isotherms with hysteresis loops, which are characteristic of mesoporous materials [28, 29]. The hysteresis loops are particularly pronounced in samples C3 and SA-23, indicating a well-developed

mesoporous structure. Although sample C3 shows the highest surface area and nitrogen adsorption capacity, this does not directly result in the formation of efficient active sites. By contrast, sample Ni5/Cr3, despite its lower nitrogen uptake, benefits from synergistic interactions between nickel and chromium that enhance its structural properties.

Specifically, π - π interactions between nickel and aromatic pollutants such as dibenzothiophene, together with increased surface polarity and chromium-induced van der Waals forces, collectively improve the material's suitability for pollutant adsorption [30].

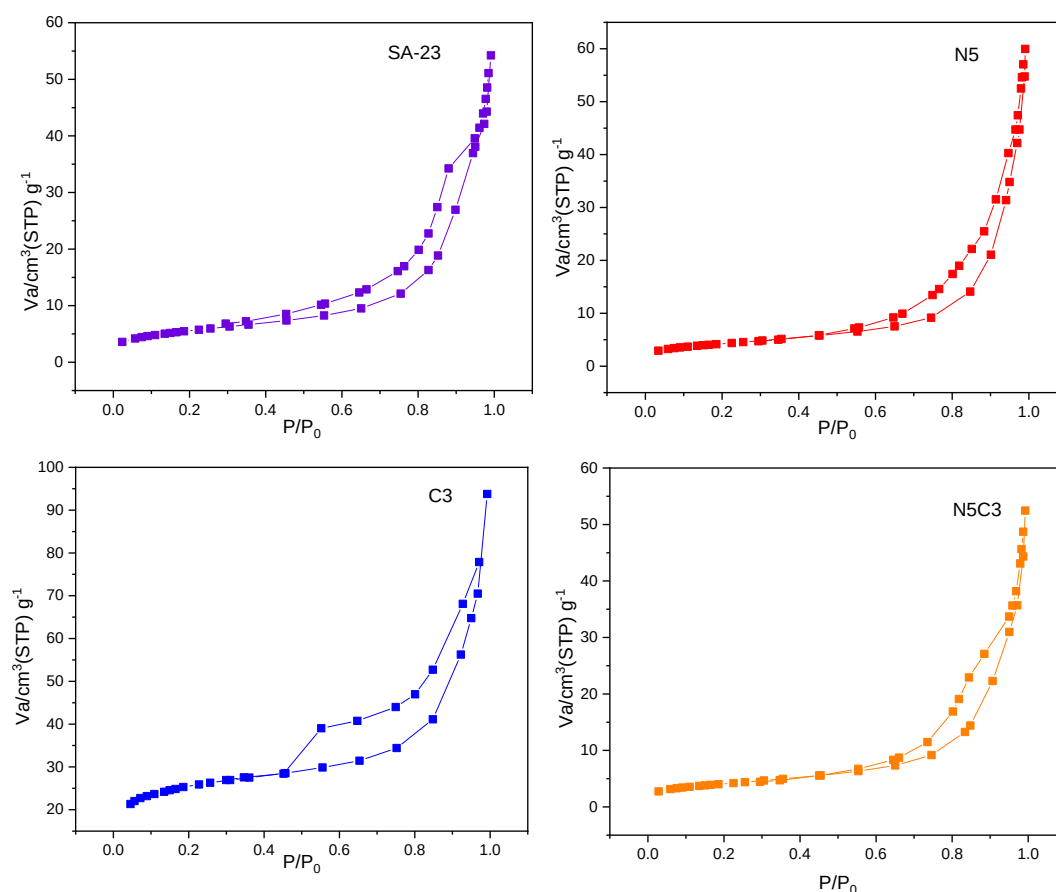


Figure 4. Nitrogen adsorption-desorption isotherms at 77 K for SA-23, Ni5, Cr3, Ni5/Cr3

3.4. FESEM

The catalytic properties and stability of the catalysts are largely governed by their morphology. NaOH treatment of the zeolite causes surface roughening and partial degradation of the zeolite framework, consistent with the reported results [28]. The nickel-modified zeolite shows smaller nanoparticles than its chromium-modified counterpart, in good agreement with previous literature indicating successful encapsulation of nickel nanoparticles within the zeolite

structure [31]. In contrast, chromium incorporation leads to a more cohesive structure that reduces the available surface area for pollutant adsorption [32, 33]. Bright spots in the microscopic images confirm the accumulation of heavy chromium particles on the external zeolite surface. The zeolite containing both nickel and chromium nanoparticles exhibits a hybrid morphology combining the features of both metals. The small, dispersed particles suggest nickel encapsulation, whereas the smooth, reflective

surfaces indicate chromium deposition on the outer surface of the zeolite.

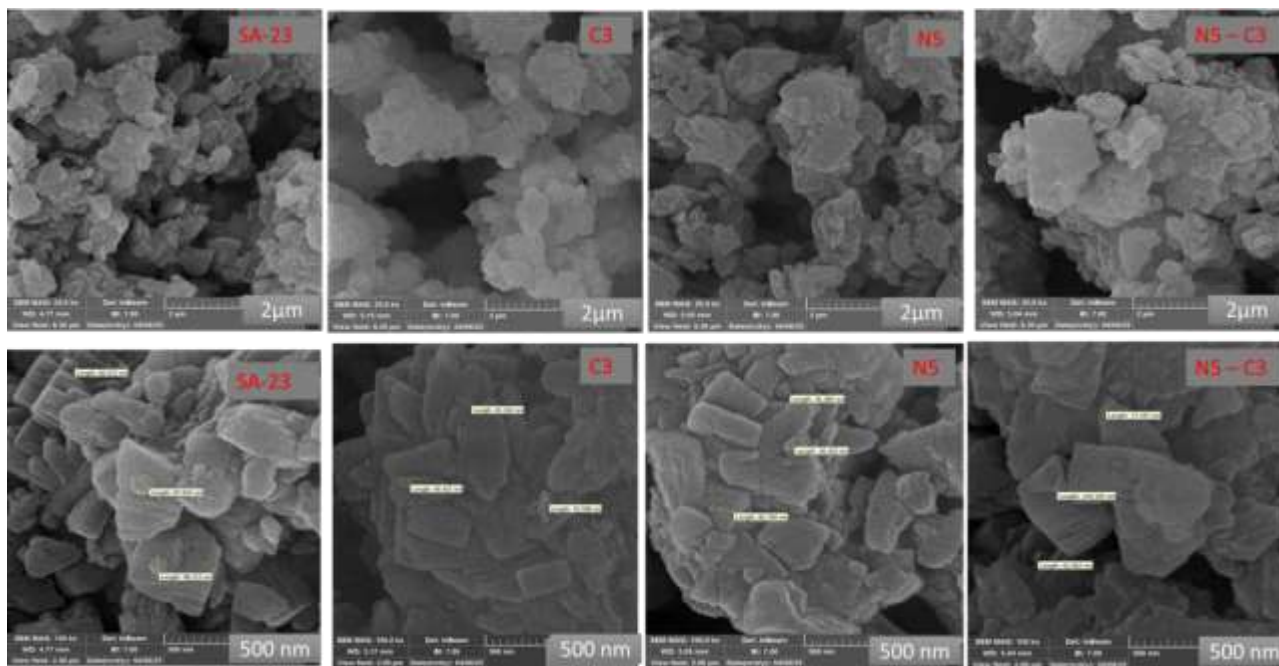


Figure 5. FESEM of SA-23,C3,Ni5 and Ni5-Cr3

3.5. EDX

X-ray spectroscopy combined with elemental mapping analysis was employed to determine the elemental composition of the samples. The index spectrum of all samples shows a prominent peak corresponding to silicon, indicating a high concentration of this element within the zeolite framework. A second intense peak, attributed to oxygen, together with the silicon signal, confirms the presence of SiO_4 tetrahedral units, which are characteristic of zeolite structures. In addition, a minor signal associated with carbon was detected, likely originating from surface contamination or residues from the sample preparation process. The low noise

level in the high-energy region of the index spectrum across all samples suggests the absence of heavy elements. Elemental mapping performed across the matrix of all samples revealed a homogeneous distribution of components throughout the zeolite. The percentage of each element, derived from the index analysis for all four samples, is presented in the tables in Figure 5. As shown, the measured percentages of chromium and nickel are lower than their initially calculated values, a discrepancy that may be attributed to experimental error.

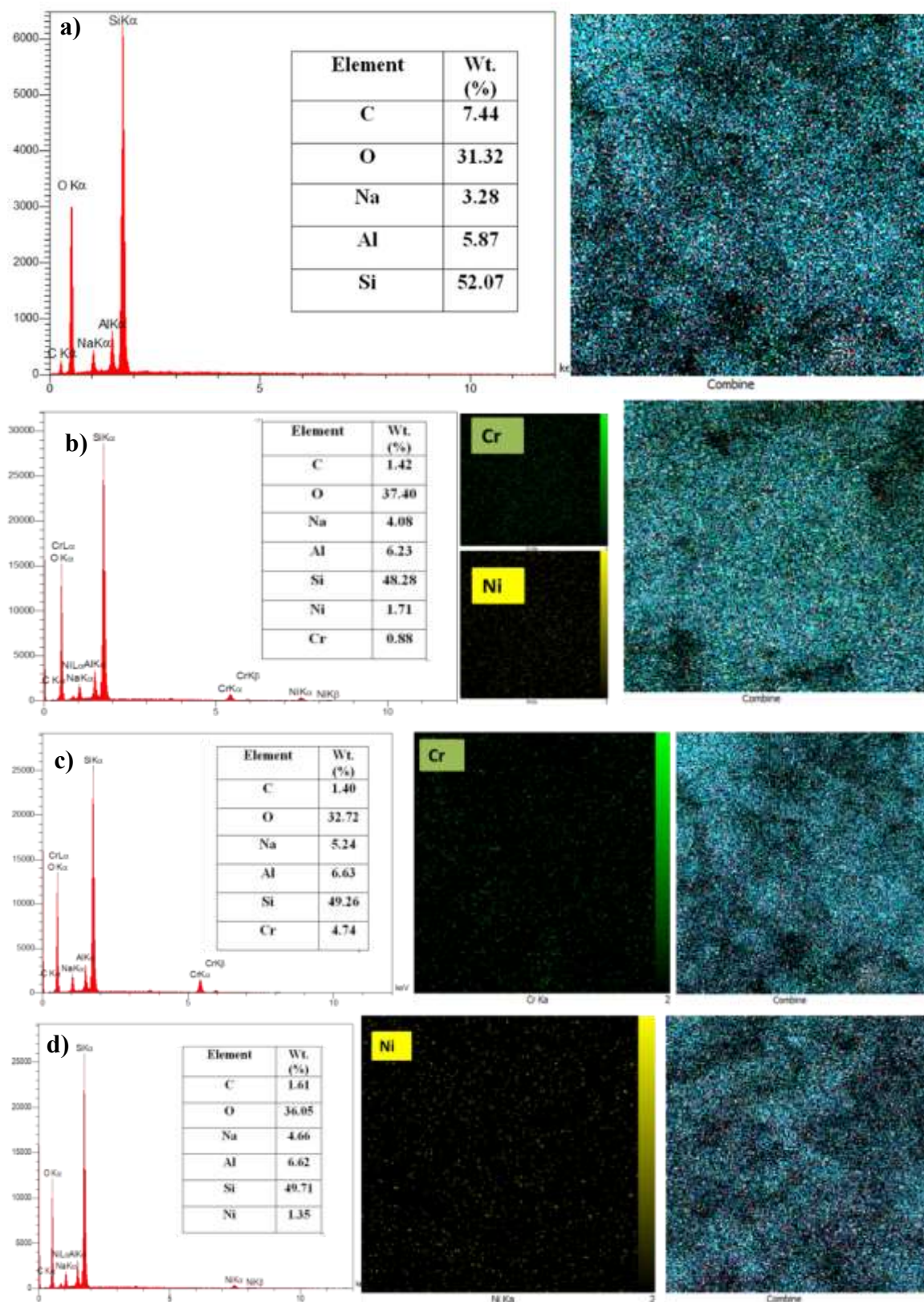


Figure 6. EDX-Mapping of: a) SA-23, b) Cr3, c) Ni5, and d) Ni5/Cr3.

3.6. Adding Ni and Cr metals

In this study, nickel and chromium metals were introduced into the SA-23 zeolite structure at various concentrations ranging from 1 to 8 wt.%. As shown in Figures 7a and 7b and Table 1, the highest oxidation capacity for dibenzothiophene was achieved with the samples containing 5% nickel and 3% chromium. The notable decrease in adsorption capacity for the sample with 8% nickel can be ascribed to three main factors: pore blockage caused by metal aggregation, a reduction in the number of accessible active sites for adsorption, and the formation of inactive NiO oxide phases that do not participate in the adsorption process [34–36]. The BET analysis results for this particular sample confirmed a pore size of 23.7 nm and a specific surface area of 15.16 m²/g, indicating a decrease in effective surface area relative to samples with lower metal loading.

Table 1.

Oxidative desulfurization efficiency of all catalysts. Data are expressed as mean $\pm$ SD (n = 3).

Catalyst	Oxidative desulfurization activity (%)
N3	33.7 $\pm$ 1.5
N5	57.2 $\pm$ 0.8
N8	28.8 $\pm$ 0.8
C1	36.5 $\pm$ 0.5
C2	48.3 $\pm$ 0.6
C3	53.3 $\pm$ 1.2
C5	27.3 $\pm$ 1.2
C8	18.7 $\pm$ 0.6
N5-C1	43 $\pm$ 1
N5-C2	46.3 $\pm$ 1.5
N5-C3	63.7 $\pm$ 0.6
N5-C5	32.3 $\pm$ 2.5
N5-C8	19.7 $\pm$ 1.5

With respect to chromium, earlier studies have shown that the optimal loading range, depending on operating conditions such as

temperature and contact time, generally falls between 1 and 3 wt.%. Loadings above this range lead to a decline in adsorption performance owing to factors including the tendency to form Cr₂O₃ crystalline structures (trivalent chromium oxide) and a marked reduction in the number of acidic sites within the zeolite framework [37]. For the sample containing 3% chromium, which lies within the optimal range, BET analysis revealed a pore size of 5.9 nm and a specific surface area of 95.3 m²/g, indicating favorable metal dispersion and preservation of the porous zeolite structure.

3.7. Simultaneous addition of nickel and chromium metals.

Because the zeolite sample loaded with 5 wt.% nickel showed high oxidative desulfurization efficiency, this nickel content was held constant, and chromium was loaded onto the zeolite alongside the nickel in amounts ranging from 1 to 8 wt.%. The experimental results of the oxidative desulfurization process using these catalysts are presented in Figure 7c and Table 1. As can be seen, the Ni5/Cr3 catalyst—containing 5% nickel and 3% chromium—exhibits the highest oxidative desulfurization efficiency. The BET analysis results for these samples are listed in Table 2. These results indicate that all catalysts possess a mesoporous structure, with pore diameters ranging from 16.4 to 22.47 nm. Although variations in specific surface area, pore volume, and pore diameter influence the accessibility of reactants to active sites, comparison of the oxidative desulfurization results reveals no direct correlation between the BET parameters and sulfur removal efficiency. The decrease in oxidative desulfurization efficiency observed for the Ni5/Cr5 and Ni5/Cr8 samples relative to Ni5/Cr3, despite their increased pore volume and diameter, can

be attributed to the aggregation of chromium metal and the resulting reduction in the

number of active sites. The FESEM results further confirm this aggregation [38, 39].

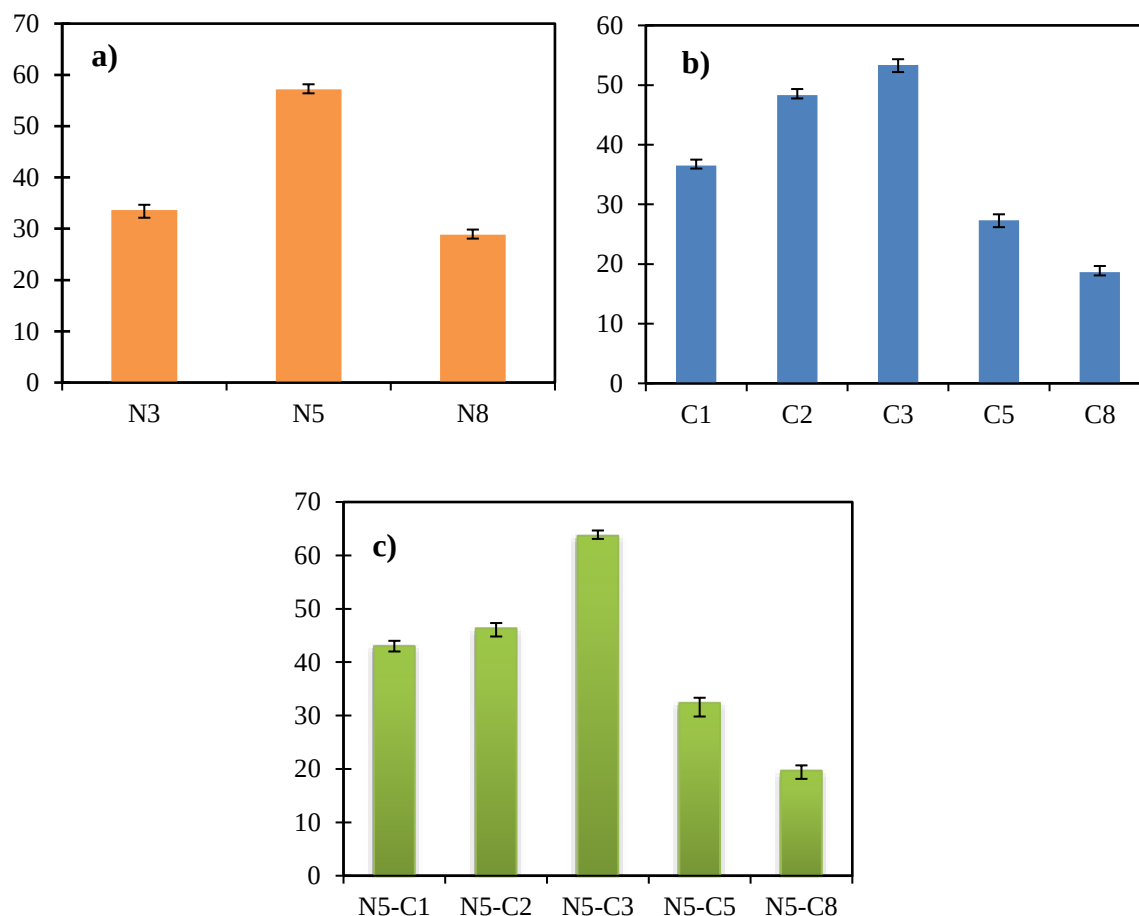


Figure 7. Results of oxidative desulfurization experiments for: (a) nickel metal, (b) chromium metal, (c) 5% nickel and 1–8% chromium. All data are expressed as the mean $\pm$ standard deviation (SD) from three independent replicates ($n = 3$). Error bars represent SD.

Table 2.

Surface area and pore size for different percentages of Cr by 5% Ni

Sample name	BET (m ² /g)	Pore size (nm)	Total pore volume($p/p_0=0.990$) [cm ³ g ⁻¹]
N5-C1	20.21	18.15	0.091716
N5-C2	16.15	19.63	0.079305
N5-C3	14.4	20.87	0.075148
N5-C5	17.15	18.94	0.081373
N5-C8	15.67	22.47	0.099283

Table 3 compares the results of this study with those of previous research on oxidative desulfurization. As observed, the sulfur removal efficiency of the catalyst prepared by this research group is lower than the same of some of the previously reported catalysts. This reduction can be attributed to the high oxide content of the metals used in the structure and the lower number of active sites in this synthesized catalyst compared to other catalysts presented in the table. Nevertheless, the reported performance is acceptable for practical applications under similar conditions and could be improved by optimizing the synthesis conditions.

Table 3.

Comparison of the efficiency of the oxidative desulfurization of the synthesized catalyst (this work) with those of previously reported catalysts in the literature.

Catalyst	Temperature (k)	Oxidant	Removal (%)	Ref.
10 % Mn/Nano-Activated Carbon	353	H ₂ O ₂	94.1	[40]
CoMo/reduced graphene oxide (rGO)	333	Citric acide	99	[41]
with an active phase of Co ₃ O ₄ –MoO ₃				
novel POM-based IL	333	tertbutyl	81.9	[42]
ZrXPTA supported on γ -Al ₂ O ₃	313	*	96.5	[43]
CrN-based catalyst supported on porous carbon	303-333	H ₂ O ₂	96	[44]
Potassium ferrate	315	Ferrate	99.6	[45]
2D-0.6TiO ₂ @MWCNT	342	H ₂ O ₂	97.5	[46]
polyoxometalate	*	H ₂ O ₂	*	[47]
Zr-MOFs and SO ₄ 2- / γ -Al ₂ O ₃	313	H ₂ O ₂ , Fe(VI)	100	[48]
γ -Al ₂ O ₃	403-437	Air	*	[49]
dual functional mesoporous catalyst	353	peracetic acid	98.42	[50]
zeolite bimetallic nanocatalyst	433	*	91.8	[51]
Co ₃ O ₄ / γ -Al ₂ O ₃ , MnO ₂ / γ -Al ₂ O ₃	403-437	molecular air	*	[52]
Fe ₂ O ₃ -supported composite	323-353	peracetic acid	98.42	[53]
Ag ₂ O ₃ /Zeolite	353-413	Air	87.4	[54]
nano-catalyst	353	peracetic acid	98.42	[55]
Zeolite ZSM5-5%Ni-3%Cr	323	H ₂ O ₂	63%	This work

4. Conclusions

The release of sulfur compounds from industry continues to rise, underscoring the growing need for efficient sulfur removal methods. In the present study, the oxidative desulfurization process was investigated using a zeolite modified with two metals, nickel and chromium. The obtained results offer new insight into the synergistic performance of these two metals together. Initial evaluations showed that, among the single-metal samples, the optimal loading was 5 wt.% for nickel and 3 wt.% for chromium. Subsequently, when both metals were loaded together onto the zeolite, it was observed that if the nickel content was below 3 wt.%, the dibenzothiophene removal efficiency decreased compared with the case in which only chromium was used. At higher concentrations, however, the performance improved significantly. The reason for this

phenomenon appears to be the role of nickel in suppressing the formation of the crystalline Cr₂O₃ phase, which is regarded as an inactive phase. Ultimately, the best performance belonged to the sample containing 5 wt.% nickel and 3 wt.% chromium. This catalyst was able to remove 63% of the sulfur, which is considered a remarkable achievement. This success provides a clear perspective for the industrial application of this catalyst. In summary, the findings of this research pave the way for the development of desulfurization processes on an industrial scale and offer a practical and promising solution for reducing sulfur pollution in produced fuels.

References

- [1] Robinson E, Robbins RC (1970) Gaseous sulfur pollutants from urban and natural sources. J Air Pollut Control Assoc

- 20(4):233–235.
<https://doi.org/10.1080/00022470.1970.10469396>.
- [2] Saleh TA (ed) (2019) Nanocomposites for the desulfurization of fuels. IGI Global, Hershey. <https://doi.org/10.4018/978-1-7998-2146-5>.
- [3] Srivastava VC (2012) An evaluation of desulfurization technologies for sulfur removal from liquid fuels. RSC Adv 2(3):759–783.
<https://doi.org/10.1039/C1RA00309G>.
- [4] Fox BR, Brinich BL, Male JL, Hubbard RL, Siddiqui MN, Saleh TA, Tyler DR (2015) Enhanced oxidative desulfurization in a film-shear reactor. Fuel 156:142–147.
<https://doi.org/10.1016/j.fuel.2015.04.028>.
- [5] Rajendran A, Cui TY, Fan HX, Yang ZF, Feng J, Li WY (2020) A comprehensive review on oxidative desulfurization catalysts targeting clean energy and environment. J Mater Chem A 8(5):2246–2285.
<https://doi.org/10.1039/C9TA12555H>.
- [6] Di Giuseppe A, Crucianelli M, De Angelis F, Crestini C, Saladino R (2009) Efficient oxidation of thiophene derivatives with homogeneous and heterogeneous MTO/H₂O₂ systems: a novel approach for oxidative desulfurization (ODS) of diesel fuel. Appl Catal B Environ 89(1–2):239–245.
<https://doi.org/10.1016/j.apcatb.2009.02.009>.
- [7] Chica A, Corma A, Dómine ME (2006) Catalytic oxidative desulfurization (ODS) of diesel fuel on a continuous fixed-bed reactor. J Catal 242(2):299–308.
<https://doi.org/10.1016/j.jcat.2006.06.013>.
- [8] Alshammari DA, Obaidullah AJ, Khasawneh MA, El-Sakhawy MA, Elkholi SM, Albaghdadi MF (2023) Theoretical investigations on the purification of petroleum using catalytic hydrodesulfurization process: AI optimization of SO₂ emission and process cost. Eng Appl Artif Intell 126:106828.
<https://doi.org/10.1016/j.engappai.2023.106828>.
- [9] Pham DD, Nguyen TM, Ho TH, Le QV, Nguyen DLT (2024) Advancing hydrodesulfurization in heavy oil: recent developments, challenges, and future prospects. Fuel 372:132082.
<https://doi.org/10.1016/j.fuel.2024.132082>.
- [10] Kokliukhin A, Nikulshina M, Mozhaev A, Lancelot C, Lamonier C, Nuns N, Blanchard P, Bugaev A, Nikulshin P (2021) Bulk hydrotreating MonW12-nS₂ catalysts based on SiMonW12-n heteropolyacids prepared by alumina elimination method. Catal Today 377:26–37.
<https://doi.org/10.1016/j.cattod.2020.07.018>.
- [11] Stylianou M, Samanides CG, Vyrides I, Agapiou A (2023) High biodesulfurization efficiency of oil by aerobic (*Burkholderia* sp. and *Serratia* sp.) and anaerobic bacteria using various additives. Energy 282:128950.
<https://doi.org/10.1016/j.energy.2023.128950>.
- [12] Kalita M, Sangannavar PA, Chutia M, Jha DK, Sathyanarayana K, Kumar JS, Subrahmanyam G (2022) Microbial biodesulfurization: a sustainable technology for refining fossil fuels. In: Microbial Resource Technologies for Sustainable Development. Elsevier, pp 333–351. <https://doi.org/10.1016/B978-0-323-90590-9.00019-5>.
- [13] Dinamarca MA, Ibacache-Quiroga C, Baeza P, Galvez S, Villarroel M, Olivero P, Ojeda J (2010) Biodesulfurization of gas oil using inorganic supports biomodified with metabolically active cells immobilized by adsorption. Bioresour Technol 101(7):2375–2378.
<https://doi.org/10.1016/j.biortech.2009.11.086>.
- [14] Kilbane JJ, Stark B (2016) Biodesulfurization: a model system for microbial physiology research. World J Microbiol Biotechnol 32(8):137.
<https://doi.org/10.1007/s11274-016-2084-6>.
- [15] Khan N, Srivastava VC (2021) Quaternary ammonium salts-based deep

- eutectic solvents: utilization in extractive desulfurization. *Energy Fuels* 35(15):12734–12745.
<https://doi.org/10.1021/acs.energyfuels.1c01220>
- [16] Jha D, Maheshwari P, Singh Y, Haider MB, Kumar R, Balathanigaimani MS (2023) A comparative review of extractive desulfurization using designer solvents: ionic liquids & deep eutectic solvents. *J Energy Inst* 110:101313.
<https://doi.org/10.1016/j.joei.2023.101313>
- [17] Li H, Ran H, Zhang Y, Yin J, Zhang J, He J, Jiang W, Zhu L, Li H (2023) Atomically dispersed aluminum sites in hexagonal boron nitride nanofibers for boosting adsorptive desulfurization performance. *Inorg Chem* 62(43):17883–17893.
<https://doi.org/10.1021/acs.inorgchem.3c02703>
- [18] Tian F, Shen Q, Fu Z, Wu Y, Jia C (2014) Enhanced adsorption desulfurization performance over hierarchically structured zeolite Y. *Fuel Process Technol* 128:176–182.
<https://doi.org/10.1016/j.fuproc.2014.07.018>
- [19] Dehghan R, Anbia M (2017) Zeolites for adsorptive desulfurization from fuels: a review. *Fuel Process Technol* 167:99–116.
<https://doi.org/10.1016/j.fuproc.2017.06.015>
- [20] Sarda KK, Bhandari A, Pant KK, Jain S (2012) Deep desulfurization of diesel fuel by selective adsorption over Ni/Al₂O₃ and Ni/ZSM-5 extrudates. *Fuel* 93:86–91.
<https://doi.org/10.1016/j.fuel.2011.10.020>
- [21] Humadi JI, Nawaf AT, Jarullah AT, Ahmed MA, Hameed SA, Mujtaba IM (2023) Design of new nano-catalysts and digital basket reactor for oxidative desulfurization of fuel: experiments and modelling. *Chem Eng Res Des* 190:634–650.
<https://doi.org/10.1016/j.cherd.2022.12.043>
- [22] Hasannia S, Kazemeini M, Rashidi A, Seif A (2020) The oxidative desulfurization process performed upon a model fuel utilizing modified molybdenum-based nanocatalysts: experimental and density functional theory investigations under optimally prepared and operated conditions. *Appl Surf Sci* 527:146798.
<https://doi.org/10.1016/j.apsusc.2020.146798>
- [23] Ding Y, Wang J, Liao M, Li J, Zhang L, Guo J, Wu H (2021) Deep oxidative desulfurization of dibenzothiophene by novel POM-based IL immobilized on well-ordered KIT-6. *Chem Eng J* 418:129470.
<https://doi.org/10.1016/j.cej.2021.129470>
- [24] Wang Q, Wang H, Zhong J, Qi Z, Chen J, Ye C, Qiu T (2023) Novel high-activity Al₂O₃@ZrXPTA catalysts and their catalytic oxidative desulfurization, mechanism, and molding. *Ind Eng Chem Res* 62(6):2525–2535.
<https://doi.org/10.1021/acs.iecr.2c03730>
- [25] Luna ML, Alvarez-Amparán MA, Cedeño-Caero L (2019) Performance of WO_x–VO_x based catalysts for ODS of dibenzothiophene compounds. *J Taiwan Inst Chem Eng* 95:175–184.
<https://doi.org/10.1016/j.jtice.2018.06.010>
- [26] Li H, Dong L, Zhao L (2017) Enhanced adsorption desulfurization performance over mesoporous ZSM-5 by alkali treatment. *Ind Eng Chem Res* 56(14):3813–3821.
<https://doi.org/10.1021/acs.iecr.6b05053>
- [27] Garba ZN, Hamza SA, Ratanatamskul C (2024) A novel copper modified microcrystalline cellulose (Cu-MCC) for treatment of crude oil-contaminated water. *J Water Process Eng* 67:106293.
<https://doi.org/10.1016/j.jwpe.2024.106293>
- [28] Shi Y, Wang J, Wang Y, Kong F, Zhou R (2022) Synergistic effect in bimetal Cr-Pt/ZSM-5 catalysts with high activity for CVOCs low-temperature removal. *J Environ Chem Eng* 10(3):107629.

- <https://doi.org/10.1016/j.jece.2022.107629>.
- [29] Schmidt R, Stöcker M, Hansen E, Akporiaye D, Ellestad OH (1995) MCM-41: a model system for adsorption studies on mesoporous materials. *Microporous Mater* 3(4-5):443-448. [https://doi.org/10.1016/0927-6513\(94\)00055-Z](https://doi.org/10.1016/0927-6513(94)00055-Z).
- [30] Sabarish R, Unnikrishnan G (2019) Synthesis, characterization and evaluations of micro/mesoporous ZSM-5 zeolite using starch as bio template. *SN Appl Sci* 1(9):989. <https://doi.org/10.1007/s42452-019-1036-9>.
- [31] Kampouraki ZC, Giannakoudakis DA, Nair V, Hosseini-Bandegharai A, Colmenares JC, Deliyanni EA (2019) Metal organic frameworks as desulfurization adsorbents of DBT and 4,6-DMDBT from fuels. *Molecules* 24(24):4525. <https://doi.org/10.3390/molecules24244525>.
- [32] Kassaye S, Gupta D, Pant KK, Jain S (2022) Valorization of microcrystalline cellulose using heterogeneous protonated zeolite catalyst: an experimental and kinetics approach. *Reactions* 3(2):283-299. <https://doi.org/10.3390/reactions3020021>.
- [33] Baamran K, Rownaghi AA (2024) Direct conversion of CO₂ to olefins over a Cr₂O₃/ZSM-5@CaO cooperative and bifunctional material under isothermal conditions. *ACS Sustain Chem Eng* 12:17783-17792. <https://doi.org/10.1021/acssuschemeng.4c0684134>.
- [34] Gao Y, Zheng B, Wu G, Ma F, Liu C (2016) Effect of the Si/Al ratio on the performance of hierarchical ZSM-5 zeolites for methanol aromatization. *RSC Adv* 6:83581-83588. <https://doi.org/10.1039/C6RA17084F>.
- [35] Ding YL, Wang HQ, Xiang M, Yu P, Li RQ, Ke QP (2020) The effect of Ni-ZSM-5 catalysts on catalytic pyrolysis and hydro-pyrolysis of biomass. *Front Chem* 8:790. <https://doi.org/10.3389/fchem.2020.00790>
- [36] Mguni LL, Nkomzwayo T, Yao Y (2024) Effect of support and NiO loading on adsorptive desulfurization of diesel fuel. *Sep Sci Technol* 59(1):122-137. <https://doi.org/10.1080/01496395.2024.2315616>
- [37] Shimura K, Yoshida S, Oikawa H, Fujitani T (2023) Impacts of Ni-loading method on the structure and the catalytic activity of NiO/SiO₂-Al₂O₃ for ethylene oligomerization. *Catalysts* 13:1303. <https://doi.org/10.3390/catal13091303>.
- [38] Hossain MN, Park HC, Choi HS (2019) A comprehensive review on catalytic oxidative desulfurization of liquid fuel oil. *Catalysts* 9(3):229. <https://doi.org/10.3390/catal9030229>.
- [39] Kumar S, Srivastava VC, Badoni RP (2012) Oxidative desulfurization by chromium promoted sulfated zirconia. *Fuel Process Technol* 93(1):18-25. <https://doi.org/10.1016/j.fuproc.2011.08.017>.
- [40] Humadi JI, Nawaf AT, Jarullah AT, Ahmed MA, Hameed SA, Mujtaba IM (2023) Design of new nano-catalysts and digital basket reactor for oxidative desulfurization of fuel: experiments and modelling. *Chem Eng Res Des* 190:634-650. <https://doi.org/10.1016/j.cherd.2022.12.043>.
- [41] Hasannia S, Kazemeini M, Rashidi A, Seif A (2020) The oxidative desulfurization process performed upon a model fuel utilizing modified molybdenum-based nanocatalysts: experimental and density functional theory investigations under optimally prepared and operated conditions. *Appl Surf Sci* 527:146798. <https://doi.org/10.1016/j.apsusc.2020.146798>.
- [42] Ding Y, Wang J, Liao M, Li J, Zhang L, Guo J, Wu H (2021) Deep oxidative desulfurization of dibenzothiophene by novel POM-based IL immobilized on well-ordered KIT-6. *Chem Eng J*

- 418:129470.
<https://doi.org/10.1016/j.cej.2021.129470>.
- [43] Wang Q, Wang H, Zhong J, Qi Z, Chen J, Ye C, Qiu T (2023) Novel high-activity $\text{Al}_2\text{O}_3/\text{ZrXPTA}$ catalysts and their catalytic oxidative desulfurization, mechanism, and molding. *Ind Eng Chem Res* 62(6):2525–2535.
<https://doi.org/10.1021/acs.iecr.2c03730>.
- [44] Hossain MA, Jhung SH (2024) Supported chromium nitride: a new catalyst for oxidative desulfurization of liquid fuel. *Fuel* 372:132178.
<https://doi.org/10.1016/j.fuel.2024.132178>
- [45] Haboc MM, Dugos NP, Choi AES, Wan MW (2024) Enhancing oxidative desulfurization using sludge-derived ferrate (VI) for dibenzothiophene: an optimization study. *J Clean Prod* 470:143307.
<https://doi.org/10.1016/j.jclepro.2024.143307>.
- [46] Mahmoudabadi ZS, Rashidi A, Tavasoli A (2021) Synthesis of two-dimensional $\text{TiO}_2/\text{multi-walled carbon nanotube}$ nanocomposites as smart nanocatalyst for ultra-deep oxidative desulfurization of liquid fuel: optimization via response surface methodology. *Fuel* 306:121635.
<https://doi.org/10.1016/j.fuel.2021.121635>
- [47] Ng SJC, Choi AES, Dugos NP, Wan MW (2024) Driving sustainable solutions: exploring supported polyoxometalate catalysts for enhanced oxidative desulfurization. *Chem Eng Trans* 113:79–84.
<https://doi.org/10.3303/CET24113014>.
- [48] Haboc MM, Dugos NP, Choi AES, Wan MW (2023) A review on the current and potential oxidant-catalyst systems in mixing-assisted oxidative desulfurization. *Chem Eng Trans* 103:559–564.
<https://doi.org/10.3303/CET23103094>.
- [49] Nawaf AT, et al. (2015) Development of kinetic and process models for the oxidative desulfurization of light fuel, using experiments and the parameter estimation technique. *Ind Eng Chem Res* 54(50):12503–12515.
<https://doi.org/10.1021/acs.iecr.5b03289>.
- [50] Nawaf AT, Abdulmajeed BA (2024) Design of oscillatory helical baffled reactor and dual functional mesoporous catalyst for oxidative desulfurization of real diesel fuel. *Chem Eng Res Des* 209:193–209.
<https://doi.org/10.1016/j.cherd.2024.07.032>.
- [51] Abdulateef LT, Nawaf AT, Al-Janabi OYT, Foot PJS, Mahmood QA (2021) Batch oxidative desulfurization of model light gasoil over a bimetallic nanocatalyst. *Chem Eng Technol* 44(9):1708–1715.
<https://doi.org/10.1002/ceat.202100027>.
- [52] Nawaf AT, Gheni SA, Jarullah AT, Mujtaba IM (2015) Improvement of fuel quality by oxidative desulfurization: design of synthetic catalyst for the process. *Fuel Process Technol* 138:337–343.
<https://doi.org/10.1016/j.fuproc.2015.05.033>.
- [53] Nawaf AT, Abdulmajeed BA (2025) A synthesis of a Fe_2O_3 -supported composite for rapid oxidative desulfurization production of environmentally friendly fuel in an OBR. *Int J Environ Sci Technol* 22(6):4923–4950. <https://doi.org/10.1007/s13762-024-05920-1>.
- [54] Nawaf AT, Hameed SA, Abdulateef LT, Jarullah AT, Kadhim MS, Mujtaba IM (2021) A novel synthetic nano-catalyst ($\text{Ag}_2\text{O}_3/\text{Zeolite}$) for high quality of light naphtha by batch oxidative desulfurization reactor. *Bull Chem React Eng Catal* 16(4):716–732.
<https://doi.org/10.9767/bcrec.16.4.11383.716-732>.
- [55] Nawaf A, Abdul Majeed B (2024) Kinetics study of oxidative desulfurization of real diesel fuel over uncoated and coated nano-catalysts in an oscillatory helical baffled reactor. *J Chem Pet Eng* 58(2):359–374.
<https://doi.org/10.22059/jchpe.2024.377539.1522>.