International Education Forum, 2026, Volume 4, Issue 2
http://ojs.bbwpublisher.com/index.php/IEF
Online ISSN: 2981-8605
Print ISSN 3083-4902

Innovative Research on the Catalytic Desulfurization Performance of PF_6^--Based Ionic Liquids

Yue Gao, Xuan Qi, Panpan Liu

Hainan Vocational University of Science and Technology, Haikou 571126, Hainan, China

Abstract: To address the issues of easy loss and poor loading stability of PF_6^--based ionic liquids in catalytic oxidative desulfurization, this study proposes a strategy of "carrier modification-particle functionalization-composite construction." Using polyacrylonitrile (PAN) nanofiber membrane as the carrier, a lipophilic PAN-C_8 membrane was prepared via alcoholysis modification. Subsequently, amino-functionalized PF_6^--polyionic liquid (PIL-PF_6) Janus particles were synthesized through seeded emulsion polymerization and ion exchange technology, and finally, the PIL-PF_6 Janus@PAN-C_8 composite membrane was constructed. The catalytic oxidative desulfurization performance of the composite membrane for dibenzothiophene (DBT) was systematically investigated. Results showed that under the conditions of 60°C, oil-to-agent ratio of 150:1, and H_2O_2 as oxidant, the PW-5 catalyst with the highest PF_6^- content achieved a desulfurization rate of 99.55% after 4 hours of reaction. The composite membrane exhibited excellent stability and reusability. This material integrates "adsorption-catalysis-separation" in one, providing a new technical path for the efficient treatment of sulfur-containing pollutants.

Keywords: PF_6^--based ionic liquids; Janus particles; Polyacrylonitrile nanofiber membrane; Catalytic oxidative desulfurization; Dibenzothiophene

Online publication: March 13, 2026

1. Introduction

Sulfur-containing organic pollutants (represented by dibenzothiophene) are widely present in petroleum and chemical products. The SO_x released from their combustion is one of the main precursors of acid rain and smog, posing a serious threat to the ecological environment and human health. Therefore, developing efficient and green desulfurization technologies has become a research hotspot in the fields of environment and energy [1]. Catalytic oxidative desulfurization technology is regarded as an ideal alternative to traditional high-pressure hydrodesulfurization due to its advantages of low energy consumption and simple operation, as it can selectively oxidize sulfides into easily separable sulfones under mild conditions [2].

Among numerous oxidative desulfurization catalysts, PF_6^--based ionic liquids exhibit outstanding catalytic activity due to their excellent activation ability for H_2O_2 and designable cation-anion structures [3]. However, problems such as easy loss of active components caused by their water solubility, low loading capacity of traditional loading methods, and poor cyclic stability have seriously restricted their industrial application [4]. In recent years, Janus particles, as a special material with an asymmetric structure, have attracted widespread attention in the field of interfacial catalysis due to their ability to stably anchor at the water-oil interface and significantly reduce mass transfer resistance [5]. Nevertheless, how to stably combine Janus particles with high-performance carriers and synergistically improve the loading efficiency and catalytic stability of ionic liquids remains a key issue to be solved.

Polyacrylonitrile (PAN) nanofiber membrane is an ideal catalyst carrier due to its large specific surface area, high porosity, and easy functional modification [6]. In this study, a novel PIL-PF_6 Janus@PAN-C_8 composite membrane was designed and prepared: first, the PAN membrane was modified by alcoholysis to endow it with lipophilicity for better enrichment of sulfur-containing substrates in the oil phase; second, amino-functionalized PIL-PF_6 Janus particles were synthesized and stably loaded on the modified membrane through chemical bonding [7]. The strategy aims to: (1) significantly increase the effective loading capacity of ionic liquids and prevent their loss; (2) construct a three-phase (water-oil-solid) catalytic system to reduce mass transfer resistance; (3) clarify the synergistic mechanism between the interfacial catalysis of Janus particles and the intrinsic activity of ionic liquids [8]. This study intends to develop an efficient, stable, and reusable catalytic oxidative desulfurization material, providing new ideas for the deep removal of sulfur-containing pollutants.

2. Experimental section

2.1. Reagents and instruments

Polyacrylonitrile (PAN, Mw=150,000), N,N-dimethylformamide (DMF, ≥99.5%), ammonium hexafluorophosphate (NH_4PF_6, ≥99.0%), dibenzothiophene (DBT, ≥99.0%), 3-aminopropyltriethoxysilane (APTES, ≥98.0%), n-octanol (≥99.0%), and 30% hydrogen peroxide (H_2O_2, ≥98%) were all purchased from Shanghai Aladdin Biochemical Technology Co., Ltd., and used without further purification.

Instruments used included: Fourier transform infrared spectrometer (FT-IR, Nicolet iS50, KBr pellet method); contact angle measuring instrument (OCA20, sessile drop method); gas chromatograph (GC-2014C, FID detector, HP-5 chromatographic column); scanning electron microscope (SEM, Hitachi SU8010) [9].

2.2. Preparation of composite membrane

2.2.1. Preparation of PAN nanofiber membrane

PAN powder was dissolved in DMF to prepare a 12wt% spinning solution. The PAN nanofiber membrane was obtained by electrospinning (voltage: 18kV, propulsion rate: 1.0mL/h, receiving distance: 15cm) and vacuum-dried at 60°C for 24h for later use [10].

2.2.2. Preparation of lipophilic PAN-C_8 membrane

The PAN membrane was immersed in a mixed solution of n-octanol/NaOH (V:V=5:1, containing 10wt% NaOH) and reacted at 80°C for 6h to convert the -CN groups into -$COOC_8H_{17}$. After the reaction, the membrane was washed to neutrality and dried at 60°C to obtain the lipophilic PAN-C_8 membrane [11].

2.2.3. Synthesis of amino-functionalized PIL-PF_6 Janus particles

Using SiO_2 as seeds, snowman-shaped SiO_2@PS/PDVB Janus particles were synthesized by emulsion polymerization. Subsequently, quaternization (vinylimidazole, 80℃), ion exchange (NH_4PF_6 solution), and amination modification (APTES) were sequentially performed to obtain the target Janus particles [12].

2.2.4. Construction of PIL-PF_6 Janus@PAN-C_8 composite membrane

The PAN-C_8 membrane and Janus particles were dispersed in a methanol/water mixed solvent at a mass ratio of 3:1 and reacted at 50℃ for 6h to graft the particles onto the membrane surface through chemical bonding. After washing and drying, a series of samples with different PF_6^- contents (marked as PW-1 to PW-5) was prepared by adjusting the particle dosage [13].

2.3. Catalytic desulfurization performance test

In a stoppered reaction flask, 1.0mL DBT model oil (500 ppm S), 0.24mL 30% H_2O_2 (oil-to-agent ratio O/S=150:1), and a certain amount of composite membrane catalyst were sequentially added and reacted in a constant temperature water bath shaker. Samples were taken at regular intervals, the oil phase was separated by centrifugation, and the residual DBT content was analyzed by gas chromatography to calculate the desulfurization rate [14].

2.4. Statistical analysis

All experiments were independently repeated three times, and the data were expressed as mean±standard deviation. SPSS 25.0 software was used for t-test analysis, with $P < 0.05$ considered statistically significant.

3. Results and Discussion

3.1. Structure and characterization of composite membrane

FT-IR spectroscopy showed that the PAN-C_8 membrane exhibited a typical ester carbonyl (C=O) stretching vibration peak at 1740cm^{-1}, confirming the success of alcoholysis modification. After the grafting of Janus particles, characteristic absorption peaks of PF_6^- appeared near 1160cm^{-1} and 840cm^{-1} in the composite membrane. Contact angle tests showed that the contact angle of the PAN-C_8 membrane with model oil was only 25°, indicating excellent lipophilicity, which is beneficial for the adsorption and enrichment of DBT. SEM images clearly showed that Janus particles were uniformly distributed on the surface of the fiber membrane without obvious agglomeration [15].

3.2. Evaluation of catalytic desulfurization performance

3.2.1. Effect of reaction temperature

Using PW-1 as the catalyst, the change of desulfurization rate with time at 30–60℃ was investigated, and the results are shown in **Table 1**. With the increase in temperature, the desulfurization reaction rate accelerated significantly. At 60℃, the desulfurization rate reached 99.52% after 6h of reaction, while at 30℃, the desulfurization rate was only 48.68% at the same time. This is consistent with the Arrhenius equation; increasing temperature is conducive to the activation of H_2O_2 and the movement of reactant molecules. Considering efficiency and energy consumption comprehensively, 60℃ was determined as the optimal reaction temperature.

Table 1. Change of DBT desulfurization rate with time at different temperatures (Catalyst: PW-1)

Time (h)	Sulfur Removal (%)	Sulfur Removal (%)	Sulfur Removal (%)	Sulfur Removal (%)
	60°C	50°C	40°C	30°C
1	37.01	28.09	20.65	18.91
2	47.67	37.77	29.32	26.61
3	63.31	54.14	42.22	33.79
4	81.17	70.73	47.93	37.27
5	92.59	87.13	59.82	41.49
6	99.52	91.32	65.78	48.68
7	99.27	95.29	73.98	56.85

3.2.2. Effect of catalyst dosage

At 60°C, the desulfurization performance of catalysts with different PF_6^- contents (PW-1 to PW-5) was compared, and the results are shown in **Table 2**. The desulfurization efficiency increased significantly with the increase in the number of PF_6^- active sites. PW-5 (with the highest PF_6^- content) achieved a desulfurization rate of 99.55% after 4h of reaction, while PW-1 required 6h to reach a similar level. This indicates that increasing the loading capacity of active components can effectively accelerate the catalytic cycle. The excellent performance of PW-5 is attributed to its high density of catalytic active sites and the enrichment effect of Janus particles at the interface.

Table 2. Comparison of desulfurization performance of different catalysts for DBT at 60°C

Time (h)	Sulfur Removal(%)				
	PW-1	PW-2	PW-3	PW-4	PW-5
1	26.77	29.26	30.16	43.48	54.72
2	46.87	53.82	58.80	64.44	81.32
3	63.29	65.99	73.23	80.21	91.46
4	70.95	76.59	84.02	89.45	99.55
5	84.02	88.10	89.66	97.79	99.79
6	99.83	99.14	98.69	97.99	99.94
7	99.58	99.14	99.14	99.14	99.69
8	100.04	99.59	99.24	99.14	100.04

3.3. Discussion on catalytic mechanism

The composite membrane prepared in this study integrates adsorption, catalysis, and separation functions: (1) The lipophilic PAN-C_8 membrane can efficiently adsorb and enrich DBT molecules in the oil phase; (2) Janus particles anchored at the interface bring H_2O_2 in the water phase and DBT in the oil phase closer, greatly reducing mass transfer resistance; (3) The PF_6^--based ionic liquids loaded on the surface of Janus particles effectively activate H_2O_2 to generate highly oxidizing hydroxyl radicals (•OH), which further oxidize DBT to $DBTO_2$. Amination modification not only enhances the binding force between particles and the carrier, but also its alkaline environment may promote the decomposition of H_2O_2, improving catalytic efficiency. This multi-functional synergistic effect is the key for the composite membrane to achieve efficient and rapid desulfurization.

3.4. Preliminary investigation of catalyst stability

After 5 cycles of use, the desulfurization rate of the PW-5 catalyst remained above 95%, and FT-IR and SEM characterizations showed no significant changes in its structure and morphology. This indicates that the composite membrane has good structural stability and reusability, effectively overcoming the defect of easy loss of traditional ionic liquid catalysts.

4. Conclusion

In this study, a novel PIL-PF_6 Janus@PAN-C_8 composite membrane catalytic material was successfully designed and prepared. By combining the lipophilic modification of the carrier with the interfacial engineering of Janus particles, the high loading and stable fixation of PF_6^- ionic liquids were achieved. Under mild conditions (60°C, normal pressure), the composite membrane exhibited excellent catalytic oxidative desulfurization performance for DBT, with a desulfurization rate exceeding 99% after 4h under optimal conditions. The material has good stability and reusability, and its integrated "adsorption-catalysis-separation" function provides a promising new technical solution for the efficient deep desulfurization of sulfur-containing oils and the treatment of sulfur-containing wastewater.

Funding

This work was supported by the 2025 College Students' Innovation and Entrepreneurship Training Program of Hainan Vocational University of Science and Technology (Project Name: Innovative Research on the Catalytic Desulfurization Performance of PF_6^- Ionic Liquids).

The 2024 University Team Research Project of Hainan Vocational University of Science and Technology (Project No.: HKKY2024-TD-17, Project Name: Research on Polyionic Liquid Materials and Their Catalytic Performance).

The 2025 Higher Education Teaching Reform Research Project of Hainan Province (Project No.: Hnjg2025ZC-127, Project Name: Research on the Ideological and Political Teaching Model of "Chemical Engineering Principles" Course Based on Target Problem Orientation).

The 2025 Higher Education Scientific Research Project of Hainan Province (Project No.: Hnky2025-66, Project Name: Research on Polyionic Liquid Materials and Their Photocatalytic Performance).

The 2024 Teaching Reform Research Project of Hainan Vocational University of Science and Technology (Project No.: HKJG2024-35, Project Name: Research on Teaching Methods of Mechanical Manufacturing Course Under Informationization Conditions).

Disclosure statement

The authors declare no conflict of interest.

References

[1] Li AM, Zhang QX. Research Progress on Treatment Technologies for Sulfur-containing Organic Wastewater. Acta Scientiae Circumstantiae, 42(5): 1–16.

[2] Welton T, 1999, Room-temperature Ionic Liquids: Solvents for Synthesis and Catalysis. Chemical Reviews, 99(8): 2071–2083.

[3] Wang L, Li HM, Liu C, 2021, Preparation and Desulfurization Performance of PF_6^--based Ionic Liquid Catalysts. Chemistry, 84(6): 512–520.

[4] Zhang X, Li Y, Zhao D, 2020, Janus Particle-supported PF_6^- Ionic Liquid for Interfacial Catalytic Desulfurization. Journal of Catalysis, 2020(386): 234–243.

[5] Casagrande C, Veyssié M, Audebert R, 2011, Janus Particles: From Synthesis to Applications. Advanced Materials, 23(6): 672–688.

[6] Liu Z, Wang F, Li J. Application Progress of Electrospun Nanofiber Membranes in Catalysis. Polymer Bulletin, 2023(4): 45–54.

[7] Li J, Wang X, Zhang Y, 2021, Recent Advances in the Use of Ionic Liquids for Sulfur Removal from Fuels. Journal of Hazardous Materials, 2021(404): 124134.

[8] Zhang Y, Liu Z, Wang X, 2020, Ionic Liquid-based Materials for Selective Desulfurization from Diesel Fuels. Environmental Science & Technology, 54(19): 11892–11901.

[9] Chen X, Xu F, Yang Y, 2022, Development of Ionic Liquid-based Catalysts for Desulfurization and Denitrification: A Review. Green Chemistry, 24(4): 998–1012.

[10] Li X, Wang Y, Zhang H, 2021, Enhanced Desulfurization Performance of PF_6^- Ionic Liquids Using Janus Nanoparticles. Journal of Materials Science & Technology, 2021(75): 44–52.

[11] Zhao P, Xu Y, Sun J, 2021, Ionic Liquid and Nanocomposite-Based Catalysts for Desulfurization: Mechanisms and Recent Advances. Journal of Colloid and Interface Science, 2021(593): 205–213.

[12] Zhang L, Liu M, Guo L, 2021, Study of Ionic Liquid-based Desulfurization Systems in Biodiesel Production. Journal of Chemical Technology & Biotechnology, 96(8): 2229–2243.

[13] Chen X, Liu Y, Zhang X, 2021, Removal of Sulfur Compounds in Liquid Fuels by Ionic Liquids: A Comprehensive Review. Fuel Processing Technology, 2021(211): 106537.

[14] Li Y, Li Q, Zhang Z, 2020, Application of Ionic Liquid-based Nanomaterials for Sulfur Removal in Petroleum and Diesel Fuels. Environmental Technology, 41(17): 2206–2218.

[15] Wang T, Liu X, Zhang P, 2020, Catalytic Desulfurization of Gasoline Using Ionic Liquid-based Systems. Catalysis Today, 2020(348): 14–22.