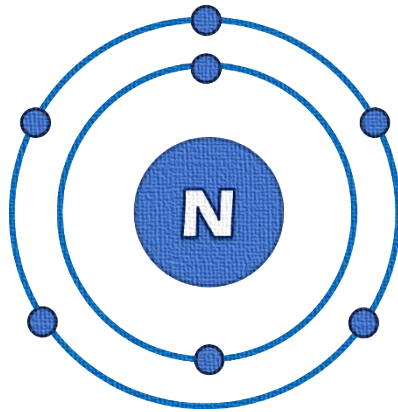


Annotated Bibliography on
Recent Advancements and Technologies in Nitrogen Separation



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Introduction:

Nitrogen is an essential element that plays a significant role in various natural processes. This annotated bibliography aims to focus on Nitrogen separation. Nitrogen separation is a vital process used to remove nitrogen-containing compounds from various gas streams, such as natural gas or air, to meet specific quality and purity requirements. The separation of nitrogen is particularly crucial in industries like petroleum refining, where nitrogen impurities can negatively impact the quality of refined products. Thus, the annotated bibliography reviews recent and different technologies of N separation, such as cryogenic separation, membrane separation, and Pressure Swing Adsorption (PSA), which are employed to effectively remove nitrogen from gas streams. Cryogenic separation involves cooling the gas to extremely low temperatures to separate nitrogen from other components. Membrane separation, which is the most important and profitable process, utilizes selective membranes to allow nitrogen to pass through while retaining other gases. PSA uses solvents or absorbents to selectively remove nitrogen from gas mixtures. These nitrogen separation technologies play a crucial role in improving the overall efficiency, safety, and environmental impact of various industrial processes and applications.

This annotated bibliography contains 27 articles that focus on reviewing recent advancement and technologies in Nitrogen separation. This annotated bibliography aims to benefit the Petroleum Research Center, particularly Refining Capacity Expansion and Flexibility (RCEF) program. It covers articles' abstracts from 2021-2024.

E-resources used: Scopus and American Chemical Society (ACS)

Contact NSTIC to request full-text articles.

Articles' Abstract:

1. Wang, F., Li, H., Gao, J., Geng, N., Jiang, E., Xia, F., Xiang, M., Jia, L., & Ning, P. (2024). High efficiency removal of NO using waste calcium carbide slag by facile KOH modification. *Journal of Environmental Sciences (China)*, 139, 182-192

Abstract: Waste calcium carbide slags (CS), which are widely applied to desulfurisation, are not typically used in denitration. Herein, to well achieve waste control by waste, a facile and high-efficiency denitration strategy is developed using KOH to modify the calcium carbide slags (KCS). Various KCS samples were investigated using a series of physical and chemical characterisations. The performance test results showed that the KOH concentration and reaction temperature are the main factors affecting the denitration efficiency of KCS, and CS modified with 1.5 mol/L KOH (KCS-1.5) can achieve 100% denitration efficiency at 300°C. Such excellent removal efficiency is due to the catalytic oxidation of the oxygen-containing functional groups derived from the KCS. Further studies showed that KOH treatment significantly increased the concentration of oxygen vacancies, nitro compounds, and basic sites of CS. This study provides a novel strategy for the resource utilisation of waste CS in the future.
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2. Wang, L., Ma, B., Teng, Y., Ruan, W., Cheng, G., Zhang, X., Li, Z., Li, Z., Han, C., Ibhaddon, A. O., & Teng, F. (2023). Boosting photocatalytic nitrogen reduction reaction by Jahn-Teller effect. *Journal of Colloid and Interface Science*, 650, 426-436.

Abstract: Compared with traditional the Haber-Bosch process, photocatalytic ammonia production has attracted a considerable attention due to its advantages of low energy consumption and sustainability. In this work, we mainly study the photocatalytic nitrogen reduction reaction (NRR) on $\text{MoO}_3 \cdot 0.55\text{H}_2\text{O}$ and $\alpha\text{-MoO}_3$. Structure analysis shows that compared to $\alpha\text{-MoO}_6$, the $[\text{MoO}_6]$ octahedrons in $\text{MoO}_3 \cdot 0.55\text{H}_2\text{O}$ obviously distort (Jahn-Teller distortion), leading to the formation of Lewis acid active sites that favors the adsorption and activation of N_2 . X-ray photoelectron spectroscopy (XPS) further confirms the formation of more Mo^{5+} as Lewis acid active sites in $\text{MoO}_3 \cdot 0.55\text{H}_2\text{O}$. Transient photocurrent, photoluminescence and electrochemical impedance spectra (EIS) confirmed that $\text{MoO}_3 \cdot 0.55\text{H}_2\text{O}$ has a higher charge separation and transfer efficiency than $\alpha\text{-MoO}_3$. Density functional theory (DFT) calculation further confirmed that the N_2 adsorption on $\text{MoO}_3 \cdot 0.55\text{H}_2\text{O}$ is more favorable thermodynamically than that on $\alpha\text{-MoO}_3$. As a result, under

visible light irradiation ($\lambda \geq 400$ nm) for 60 min, an ammonia production rate of 88.6 $\mu\text{mol}\cdot\text{gcat}^{-1}$ was achieved on $\text{MoO}_3\cdot 0.55\text{H}_2\text{O}$, which is about 4.6 times higher than that on $\alpha\text{-MoO}_3$. In comparison to other photocatalysts, $\text{MoO}_3\cdot 0.55\text{H}_2\text{O}$ exhibits an excellent photocatalytic NRR activity under visible light irradiation without using sacrificial agent. This work offers a new fundamental understanding to photocatalytic NRR from the viewpoint of crystal fine structure, which benefits designing efficient photocatalysts. © 2023 Elsevier Inc.

3. Niemann, V. A., Benedek, P., Guo, J., Xu, Y., Blair, S. J., Corson, E. R., Nielander, A. C., Jaramillo, T. F., & Tarpeh, W. A. (2023). Co-designing Electrocatalytic Systems with Separations to Improve the Sustainability of Reactive Nitrogen Management. *ACS Catalysis*, 13(9), 6268-6279.

Abstract: Humans have altered the nitrogen cycle to produce nitrogen commodities like fertilizers and chemicals while releasing anthropogenic reactive nitrogen (Nr) contaminants into the environment. These contaminants endanger human and environmental health, but nitrogen commodities are necessary for quality of life. One approach to solving this global challenge is to remove and recover Nr contaminants as commodities; this approach has caught the attention of the electrocatalysis and separations communities alike. In this perspective we propose co-design, or the integration of typically disparate Nr separations and electrocatalytic technologies. We consider real Nr contaminant waste streams and Nr commodity purity requirements. Considering these criteria in electrocatalytic system design reveals fundamental gaps in understanding as well as opportunity for developing co-designed technology that is uniquely tailored to address a challenge in nitrogen management. We focus on three representative challenges in nitrogen management (nitrate, nitrogen oxides, and nitrous oxide), identify their sources and conditions, highlight accomplishments in the fields of electrocatalysis and separations, and explore ways to address each challenge with a co-design approach. We note that this approach will benefit from advancements in related fields such as nitrogen sensing and environmental policy, especially because transformative solutions for the nitrogen challenge lie at the confluence of multiple fields. The final goal is to transition to a circular nitrogen economy that secures a food-safe, environmentally friendly future. © 2023 American Chemical Society

4. Yu, X., Qiu, P., Wang, Y., He, B., Xu, X., Zhu, H., Ding, J., Liu, X., Li, Z., & Wang, Y. (2023). Defect-induced charge redistribution of MoO_{3-x} nanometric wires for photocatalytic ammonia synthesis. *Journal of Colloid and Interface Science*, 640, 775-782.

Abstract: Photocatalytic ammonia synthesis technology has become one of the effective methods to replace the Haber method for nitrogen fixation in the future for its low energy consumption and green environment. However, limited by the weak adsorption/activation ability of N₂ molecules at the photocatalyst interface, the efficient nitrogen fixation still remains a daunting job. Defect-induced charge redistribution as a catalytic site for N₂ molecules is the most prominent strategy to enhance the adsorption/activation of N₂ molecules at the interface of catalysts. In this study, MoO_{3-x} nanowires containing asymmetric defects were prepared by a one-step hydrothermal method via using glycine as a defect inducer. It is shown that at the atomic scale, the defect-induced charge reconfiguration can significantly improve the nitrogen adsorption and activation capacity and enhance the nitrogen fixation capacity; at the nanoscale, the charge redistribution induced by asymmetric defects effectively improved the photogenerated charge separation. Given the charge redistribution on the atomic and nanoscale of MoO_{3-x} nanowires, the optimal nitrogen fixation rate of MoO_{3-x} reached 200.35 μmol g⁻¹h⁻¹. © 2023 Elsevier Inc.

5. Wu, H., Singh-Morgan, A., Qi, K., Zeng, Z., Mougel, V., & Voiry, D. (2023). Electrocatalyst Microenvironment Engineering for Enhanced Product Selectivity in Carbon Dioxide and Nitrogen Reduction Reactions. *ACS Catalysis*, 13(8), 5375-5396.

Abstract: Carbon and nitrogen fixation strategies are regarded as alternative routes to produce valuable chemicals used as energy carriers and fertilizers that are traditionally obtained from unsustainable and energy-intensive coal gasification (CO and CH₄), Fischer-Tropsch (C₂H₄), and Haber-Bosch (NH₃) processes. Recently, the electrocatalytic CO₂ reduction reaction (CO₂RR) and N₂ reduction reaction (NRR) have received tremendous attention, with the merits of being both efficient strategies to store renewable electricity while providing alternative preparation routes to fossil-fuel-driven reactions. To date, the development of the CO₂RR and NRR processes is primarily hindered by the competitive hydrogen evolution reaction (HER); however, the corresponding strategies for inhibiting this undesired side reaction are still quite limited. Considering such complex reactions involve three gas-liquid-

solid phases and successive proton-coupled electron transfers, it appears meaningful to review the current strategies for improving product selectivity in light of their respective reaction mechanisms, kinetics, and thermodynamics. By examining the developments and understanding in catalyst design, electrolyte engineering, and three-phase interface modulation, we discuss three key strategies for improving product selectivity for the CO₂RR and NRR: (i) targeting molecularly defined active sites, (ii) increasing the local reactant concentration at the active sites, and (iii) stabilizing and confining product intermediates. © 2023 The Authors. Published by American Chemical Society.

6. Sun, Y., Gao, Y., Geng, C., Zhang, Z., Qiao, Z., & Zhong, C. (2023). Improved CO₂/N₂ separation performance by relatively continuous and defect-free distribution of IL-encapsulated ZIF-67 in ion gel membranes. *Journal of Membrane Science*, 683

Abstract: Metal-organic frameworks (MOFs), as a typical type of porous materials, are widely used as fillers in mixed matrix membranes (MMMs) to enhance the gas separation performance. However, non-selective interface defects are prone to appear in MMMs under high MOF loading conditions, meanwhile, the discontinuous dispersion of MOF particles in polymeric matrices makes the gas molecules diffuse along the MOF-polymer-MOF intersection path and difficult to achieve efficient molecular transfer. These factors greatly compromise the ability of MOF to enhance membrane separation performance. Herein, the [C5min][BF₄] encapsulated ZIF-67 (IL@ZIF) composites were embedded into the defect-free IL/Pebax ion gel matrix to form a mixed matrix ion gel membrane without interface defects. On the basis of good interfacial compatibility, the relatively continuous and highly selective CO₂ transmission channels were constructed via increasing the filler loading up to 80 wt%. In this context, the typical IL@ZIF/IL/Pebax membrane with 80 wt% IL content and 70 wt% IL@ZIF doping amount exhibits a CO₂ permeability of 408.2 Barrer and CO₂/N₂ selectivity of 97.2, surpassing the latest upper line. This work may have high reference value in the construction and preparation of MOF-based MMMs with high performance in gas separation. © 2023 Elsevier B.V.

7. Pasichnyk, M., Stanovsky, P., Polezhaev, P., Zach, B., Šyc, M., Bobák, M., Jansen, J. C., Příbyl, M., Bara, J. E., Friess, K., Havlica, J., Gin, D. L., Noble, R. D., & Izák, P. (2023). Membrane technology for challenging separations: Removal of CO₂, SO₂ and NO_x from flue and waste gases. *Separation and Purification Technology*, 323

Abstract: The major gaseous pollutants emitted during the combustion of fossil fuels, during energy-intensive production of materials, and during waste processing are CO₂, SO₂, and NO_x. The combined efforts of industry and the research community aim to intensify their capture and decrease their emissions, with the final objective of meeting stricter emission limits, which is becoming more challenging with conventional technologies. Membrane separation technology is a particularly significant environmental protection application because it can be effectively combined with other separation technologies and generally uses much less energy. As membrane processes represent an energy-efficient alternative to traditional separation processes, in view of today's emissions policy, they have become economically competitive to purify flue gases emitted from small point sources, such as waste incineration units and steel or cement production facilities. Different membrane types with various specific functions, such as high solubility for certain gases, thermal and mechanical stability, and ease of manufacturing, are presented as perspective technologies for flue gas purification. Unique systems are also discussed, including facilitated or retarded transport of permeants in membranes and mixed-matrix membranes. We first describe the basic operating mechanism based on their structure and material properties to compare the advantages and disadvantages of suitable membranes. This review presents state-of-the-art membrane technologies in CO₂, SO₂, and NO_x separation from flue gases and discusses the potential applications of the most promising membranes. © 2023 The Author(s)

8. Surmi, A., Shariff, A. M., & Lock, S. S. M. (2023). Modeling of Nitrogen Removal from Natural Gas in Rotating Packed Bed Using Artificial Neural Networks. *Molecules*, 28(14)

Abstract: Novel or unconventional technologies are critical to providing cost-competitive natural gas supplies to meet rising demands and provide more opportunities to develop low-quality gas fields with high contaminants, including high carbon dioxide (CO₂) fields. High nitrogen concentrations that reduce the heating value of gaseous products are typically associated with high CO₂ fields. Consequently, removing nitrogen is essential for meeting

customers' requirements. The intensification approach with a rotating packed bed (RPB) demonstrated considerable potential to remove nitrogen from natural gas under cryogenic conditions. Moreover, the process significantly reduces the equipment size compared to the conventional distillation column, thus making it more economical. The prediction model developed in this study employed artificial neural networks (ANN) based on data from in-house experiments due to a lack of available data. The ANN model is preferred as it offers easy processing of large amounts of data, even for more complex processes, compared to developing the first principal mathematical model, which requires numerous assumptions and might be associated with lumped components in the kinetic model. Backpropagation algorithms for ANN Lavenberg–Marquardt (LM), scaled conjugate gradient (SCG), and Bayesian regularisation (BR) were also utilised. Resultantly, the LM produced the best model for predicting nitrogen removal from natural gas compared to other ANN models with a layer size of nine, with a 99.56% regression (R²) and 0.0128 mean standard error (MSE). © 2023 by the authors.

9. Lim, J., Chen, Y., Cullen, D. A., Lee, S. W., Senftle, T. P., & Hatzell, M. C. (2023). PdCu Electrocatalysts for Selective Nitrate and Nitrite Reduction to Nitrogen. *ACS Catalysis*, 13(1), 87-98.

Abstract: Electrocatalytic conversion of nitrate in waste can enable efficient waste remediation (NO₃-to N₂) or waste valorization (NO₃-to NH₄⁺) depending on the selectivity of the catalyst. Palladium and copper electrocatalysts typically exhibit ideal nitrate and nitrite binding properties, allowing for effective destruction of nitrate. However, rational steering of selectivity through material design remains a critical challenge for PdCu electrocatalyst. Here, we use the electrochemical underpotential deposition method to synthesize palladium nanocube electrocatalysts with controlled copper surface coverage (e.g., partial and full copper coatings). We then examine the potential for NO₃-destruction (conversion) and NO₂-reduction reaction. We identify that partial copper-coated Pd nanocubes not only effectively facilitate the reduction of 95% of NO₃-but also increase the reduction of NO₂-to N₂with 89% selectivity over 20 consecutive cycles (80 h). We also show that under these conditions, the Pd(100) surface facet is exposed. Complete copper-covered Pd nanocubes effectively facilitate the reduction of ~ 99% of NO₃-. Complete coverage of copper; however, prevented exposure of Pd(100) surface facet, promoting the selective reduction of NO₂-to NH₄⁺ with a 70%

selectivity over 20 consecutive cycles (80 h). Density functional theory (DFT) calculations show that NO₃- and NO₂-adsorb more strongly on the Cu(100) surface compared to the Pd(100) surface, while the NO* intermediate generated from NO₃- or NO₂-reduction adsorbs more strongly on the Pd surface. Barrier calculations show that NO* can readily migrate from the Cu domain to the Pd domain and that the N-N coupling barrier on Pd is significantly diminished at high NO* coverage. Together, these results suggest that the high N₂ selectivity observed on the PdCu electrocatalyst is caused by the spillover of NO* from the Cu domains to the Pd domains. © 2023 American Chemical Society. All rights reserved.

10. Zhao, H., Song, T., Ding, X., Cai, R., Tan, X., & Zhang, Y. (2023). PIM-1 mixed matrix membranes incorporated with magnetic responsive cobalt-based ionic liquid for O₂/N₂ separation. *Journal of Membrane Science*, 679

Abstract: Membrane technology for O₂/N₂ separation is a mature industrial unit. Membranes with excellent permeation-separation performance are still one of the critical requirements. The cobalt-based compounds have been well known for their good affinity for O₂, which can facilitate O₂ transfer and improve the O₂/N₂ selectivity in membranes. The cobalt-based compounds, moreover, have a magnetic responsive effect, which can lead to a further improvement in O₂/N₂ separation under a magnetic field. A class of PIM-1 mixed matrix membranes (MMMs), containing cobalt-based ionic liquid (CILs)@polyarylate (aromatic polyester) (PAR) (core-shell) composite nanospheres (CILs@PAR (c-s) CNPs), were prepared. Chemical compositions of CILs@PAR (core-shell) CNPs were determined by Fourier transform infrared spectroscopy (FTIR). Morphologies and structures of CILs@PAR (core-shell) CNPs were observed by transmission electron microscopy (TEM). Gas adsorption properties of CILs@PAR (core-shell) CNPs were tested. Thermal properties of the (CILs@PAR (c-s) CNPs)/PIM MMMs were investigated by simultaneous thermal analysis (TGA-DSC). Gas permeation-separation performances of the (CILs@PAR (c-s) CNPs)/PIM MMMs were also reported. Compared with the original PIM-1 membrane, the (CILs@PAR (c-s) CNPs)/PIM MMMs display higher O₂/N₂ selectivity because of cobalt-based ionic liquid as O₂ carrier, coupled with a reduction in O₂ permeability. With increasing the content of the CILs@PAR (c-s) CNPs, the O₂/N₂ selectivity increases, and the O₂ permeability decreases. It is also found that, as a magnetic field on the MMMs, the O₂/N₂ selectivity further increases; and it increases more, as a higher content of CILs@PAR (c-s) CNPs. Therefore, the

(CILs@PAR (c-s) CNPs)/PIM MMMs exhibit excellent O₂/N₂ selectivity of ~5 coupled with good O₂ permeability of ~140 Barrer under a 180 mT magnetic field and show great potential for air separation. © 2023 Elsevier B.V.

11. Ma, C., Li, N., Xue, W., Guo, X., Qiao, Z., & Zhong, C. (2023). Polarization enhanced CH₄/N₂ separation in bromine functionalized ZIF-62 based mixed-matrix membranes. *Journal of Membrane Science*, 683

Abstract: Owing to the similarities in polarity, kinetic size, and boiling point, CH₄ and N₂ separation remains difficult and energy-consuming. However, the difference in polarizability offers an opportunity for boosting the separation by differentiating their interactions with the metal-organic framework (MOF). Herein, bromine (Br) functional group is rationally introduced into ZIF-62 to strengthen CH₄/N₂ separation through the polarization effect. The anisotropic charge distribution on Br atom can induce electron cloud deformation of gas molecules, especially CH₄ molecules with higher polarizability, thus generating differentiated interactions. As a result, ZIF-62-Br exhibits a 69.7% increase in CH₄ adsorption capacity and obviously improved selectivity compared with the ZIF-62, and embedding ZIF-62-Br in the polyethyleneimine (PEI) matrix endows the obtained mixed-matrix membranes (MMMs) with good CH₄/N₂ separation performance (CH₄ permeance of 3157 GPU and CH₄/N₂ ideal selectivity of 7.6 for single gas permeations, and CH₄ permeance of 2235 GPU and CH₄/N₂ selectivity of 4.2 for mixed gas tests). The good separation performance and stability suggest that MMMs fabricated with ZIF-62-Br in this work can be a promising candidate for facilitating the exploration of CH₄/N₂ membrane separation. © 2023 Elsevier B.V.

12. Li, T., An, X., & Fu, D. (2023). Review on Nitrogen-Doped Porous Carbon Materials for CO₂ Adsorption and Separation: Recent Advances and Outlook. *Energy and Fuels*, 37(12), 8160-8179.

Abstract: One of the most serious environmental problems is the global warming brought by CO₂ and other greenhouse gases. Thus, the development of Carbon Capture, Utilization, and Storage Technology (CCUS) is urgent. Thereinto, the merits of porous carbon adsorption materials are their substantial specific surface area, stable physical and chemical properties, adjustable pore structure, etc., and they are considered to be good adsorbents for CO₂. The

adsorption properties of porous carbon material are capable of being directionally controlled by regulating the collocation of carbonization and activation methods and setting the technological parameters used in the preparation process. In addition, nitrogen doping can enhance the effect between adsorbent and adsorbate, leading to higher CO₂ adsorption capacity. After in-depth studies, although there is still no clear explanation on the mechanism of nitrogen-doped enhancement of the adsorption properties of the adsorbent, it can be confirmed that the main reason is not the traditional acid-base theory, but a large number of micropores, specific surface area, and induction forces are more likely to be the root cause. The porous carbon materials preparation methods, pore structure adjustment strategies, and the types of functionalization and mechanism between nitrogen-doped sites and adsorbents are highlighted in this Review. Finally, the future development direction and existing challenges of this emerging field are also discussed. © 2023 American Chemical Society. All rights reserved.

- Izelaar, B., Ripepi, D., Asperti, S., Dugulan, A. I., Hendrikx, R. W., Böttger, A. J., Mulder, F. M., & Kortlever, R. (2023). Revisiting the Electrochemical Nitrogen Reduction on Molybdenum and Iron Carbides: Promising Catalysts or False Positives? *ACS Catalysis*, *13*(3), 1649-1661.

Abstract: The electrochemical dinitrogen reduction reaction (NRR) has recently gained much interest as it can potentially produce ammonia from renewable intermittent electricity and replace the Haber-Bosch process. Previous literature studies report Fe- and Mo-carbides as promising electrocatalysts for the NRR with activities higher than other metals. However, recent understanding of extraneous ammonia and nitrogen oxide contaminations have challenged previously published results. Here, we critically assess the NRR performance of several Fe- and Mo-carbides reported as promising by implementing a strict experimental protocol to minimize the effect of impurities. The successful synthesis of α -Mo₂C decorated carbon nanosheets, α -Mo₂C nanoparticles, θ -Fe₃C nanoparticles, and χ -Fe₅C₂ nanoparticles was confirmed by X-ray diffraction, scanning and transmission electron microscopy, and X-ray photoelectron and Mössbauer spectroscopy. After performing NRR chronoamperometric tests with the synthesized materials, the ammonia concentrations varied between 37 and 124 ppb and are in close proximity with the estimated ammonia background level. Notwithstanding the impracticality of these extremely low ammonia yields, the observed ammonia did not originate from the electrochemical nitrogen reduction but from unavoidable extraneous

ammonia and NO_x impurities. These findings are in contradiction with earlier literature studies and show that these carbide materials are not active for the NRR under the employed conditions. This further emphasizes the importance of a strict protocol in order to distinguish between a promising NRR catalyst and a false positive. © 2023 The Authors. Published by American Chemical Society.

14. González-Revuelta, D., Fallanza, M., Ortiz, A., & Gorri, D. (2023). Thin-Film Composite Matrimid-Based Hollow Fiber Membranes for Oxygen/Nitrogen Separation by Gas Permeation. *Membranes*, 13(2)

Abstract: In recent years, the need to reduce energy consumption worldwide to move towards sustainable development has led many of the conventional technologies used in the industry to evolve or to be replaced by new alternatives. Oxygen is a compound with diverse industrial and medical applications. For this reason, obtaining it from air is one of the most interesting separations, traditionally performed by cryogenic distillation and pressure swing adsorption, two techniques which are very energetically expensive. In this sense, the implementation of membranes in a hollow fiber configuration is presented as a much more efficient alternative to carry out this separation. The aim of this work is to develop cost-effective multilayer hollow fiber composite membranes made of Matrimid and polydimethylsiloxane (PDMS) for the separation of oxygen and nitrogen from air. PDMS is used as a cover layer but can also enhance the performance of the membrane. In order to compare these two materials, three different configurations are studied. First, integral asymmetric Matrimid hollow fiber membranes were produced using the spinning method. Secondly, by using dip-coating method, a PDMS dense selective layer was deposited on a self-made polyvinylidene fluoride (PVDF) hollow fiber support. Finally, the performance of a dual-layer hollow fiber membrane of Matrimid and PDMS was studied. Membrane morphology was characterized by SEM and separation performance of the membranes was evaluated by mixed-gas permeation experiments. The novelty presented in this work is the manufacture of hollow fiber membranes and the way Matrimid is treated. This makes it possible to develop much thinner dense layers than in the case of flat-sheet membranes, which leads to higher permeance values. This is a key factor when implementing this technology on an industrial scale. Membranes prepared in this work were compared to the current state of the art, reporting quite good performance for the dual-layer membrane, reaching O₂ permeance of 30.8 GPU and O₂/N₂ selectivity of 4.7, with a

thickness of about 5–10 μm (counting both selective layers). In addition, the effect of operating temperature on the membrane permeances has been studied experimentally; we analyze its influence on the selectivity of the separation process. © 2023 by the authors.

15. Yu, Z., Gu, Z., Lei, J., & Zheng, G. (2023). Vacuum treated amorphous MOF mixed matrix membrane for methane/nitrogen separation. *Journal of Solid State Chemistry*, 320

Abstract: CH₄/N₂ separation is considered a feasible method for reducing the greenhouse effect, but its utility in industrial applications has limited by the low permselective performance. In this work, a novel method for enhancing CH₄/N₂ separation performance using amorphous UIO-66-NH₂ with a carbonized structure (ACU) via high vacuum resistance calcination is proposed. Owing to the presence of carbonized framework that contains rich Zr⁴⁺ active sites, these vacuum-treated ACU nanoparticles showed high IAST CH₄/N₂ selectivity, good alkaline stability and satisfactory compatibility with polymers. Then, ACU were uniformly dispersed in polyvinyl alcohol (PVA) to obtain defect-free mixed matrix membranes (MMMs), the resulting ACU-based MMMs exhibited an enhanced CH₄ separation performance. Remarkably, the PVA/ACU-120A/MPSf MMM that consisted of 80 wt% ACU-120A exhibited the outstanding CH₄ permselectivity, achieving a CH₄ permeance of 5584 GPU and CH₄/N₂ selectivity of 3.43. © 2023 Elsevier Inc.

16. Ahmadi-Motlagh, M., Amini, Y., & Karimi-Sabet, J. (2022). Experimental study of nitrogen isotope separation by ion-exchange chromatography: effect of process factors. *Journal of Radioanalytical and Nuclear Chemistry*, 331(1), 309-315.

Abstract: Ion-exchange chromatography is known as one of the most important techniques of stable isotope separation such as nitrogen isotopes. This study aims to investigate the effect of initial feed concentration and migration distance on the efficiency of nitrogen isotope separation. A set of 10 columns filled with the ion-exchange resin Dowex- 50 W X8 with 1 cm I.D. and 100 cm height was set up in order to study the isotope accumulation of ¹⁵N by ion-exchange chromatography. The analytical determination of the samples was made by emission spectrometry. The height equivalent to a theoretical plate (HETP) was found to decrease with increasing the migration distance. Results showed that a maximum separation factor of 6.616%

could be obtained at an initial ammonium concentration of 0.5 mol/l, feed flow rate of 1.5 ml/min, and migration distance of 70 m. And also the separation factor decreases slightly with the ammonia concentration. © 2021, Akadémiai Kiadó, Budapest, Hungary.

17. Dias, R. O. M., Ferreira, A. F. P., Cho, K. H., Lee, U. -, Chang, J. -, Rodrigues, A. E., & Ribeiro, A. M. (2022). Methane/nitrogen separation by SMB using UiO - 66(Zr) ₂(COOH) ₂. *Brazilian Journal of Chemical Engineering*, 39(4), 973-990.

Abstract: Nowadays, natural gas (NG) has been widely studied as an alternative to petroleum-based fuels. However, when extracted from unconventional sources, it is contaminated with N₂. Its removal is industrially done by cryogenic distillation, which is an extremely energy-intensive process. Therefore, adsorption-based methods are of particular interest, and the application of metal-organic frameworks (MOFs) in adsorption-based processes focus on separating different mixtures. This way, the goal of this work was to test a functionalized zirconium-based MOF, the UiO-66(Zr) ₂(COOH) ₂, to be used in a gas-phase simulated moving bed (SMB) process for the purification of nitrogen contaminated methane streams, which is the case of methane obtained from shale gas, landfill gas and coalbeds. The adsorbent material was supplied by KRICT (Korea Research Institute of Chemical Technology) as granules. Firstly, the adsorption isotherms of pure C₂H₆ were determined at 303, 333, and 373 K. The dual-site Langmuir (DSL) isotherm was used to fit the experimental results. The equilibrium data for ethane was compared with previously measured data for CH₄, N₂, and CO₂. The affinity of the gas towards the adsorbent has the following order, CO₂>C₂H₆>>CH₄>N₂, from the most adsorbed to the less adsorbed at 303 K and 1.5 bar. At 333 K and 1.5 bar, C₂H₆ exhibits the highest uptake. Single, binary, and pseudo-ternary breakthrough curves were performed at 333 K and 1.5 bar. These experimental results allowed experimental validation of adsorption equilibrium predicted by the multicomponent extension of the DSL isotherm and the validation of the fixed-bed mathematical model, as well as the evaluation of the ability of the eluent of displacing the mixture and its own displacement by the mixture. Lastly, a gas-phase SMB process was designed, based on the simulation of the separation regions for each one of the target desorbents, operating at 303 K and 1.5 bar, using four-zone unit configuration (2-3-2-1), in a closed-loop. This process allows the production of a methane stream with 99.56% purity and 99.65% recovery and a nitrogen stream with

99.73% purity and a recovery of 99.58%, showing the potential of this technology for the separation of CH₄/N₂ mixtures. © 2021, Associação Brasileira de Engenharia Química.

18. Dias, R. O. M., Ferreira, A. F. P., Rodrigues, A. E., & Ribeiro, A. M. (2022). Gas-Phase Simulated Moving Bed for Methane/Nitrogen Separation Using a Commercial Activated Carbon. *Industrial and Engineering Chemistry Research*, 61(34), 12739-12753.

Abstract: This work focuses on designing and developing a simulated moving bed (SMB) process for the separation of methane and nitrogen mixtures, using a commercial activated carbon (BPL) as the adsorbent material and two potential desorbent gases: argon and carbon dioxide. As such, the material performance was evaluated by measuring the adsorption equilibrium data and the dynamic behavior of single and multicomponent adsorption through fixed-bed experiments. The pure component isotherms of N₂, CH₄, Ar, and CO₂ were measured at 303, 323, and 343 K in a pressure range of 0-2.5 bar using a volumetric apparatus, with CO₂ exhibiting the highest affinity to the stationary phase and Ar the lowest. The data was regressed against the dual-site Langmuir (DSL) model. Single, binary, and ternary breakthrough curves were also assessed, allowing the validation of the proposed mathematical model. Two SMB cycles were employed to separate an equimolar CH₄/N₂ mixture using each desorbent gas to evaluate the impact of the desorbent strength in the process. The respective separation regions were drawn. Both cycles were capable of producing a high-purity methane stream (96.2 and 97.4% for the Ar and CO₂ experiment, respectively) with high recovery (>92%). When argon is used as the desorbent gas, the extract product stream is obtained with productivity of 14.1 kg·m⁻³·ads·h⁻¹ © 2022 American Chemical Society. All rights reserved.

19. Zhou, Y., Yuan, Y., Cong, S., Liu, X., & Wang, Z. (2022). N₂-selective adsorbents and membranes for natural gas purification. *Separation and Purification Technology*, 300

Abstract: Conventional natural gas confronts the growing supply shortage due to the fewer formation reserves. As a powerful replenishment, the nitrogen-rich unconventional natural gas, mainly including shale gas and coalbed methane, has attracted much attention in recent years and stimulated the efficient separation processes for N₂-CH₄ system. Benefiting from the boom in materials science, a large number of advanced adsorbents and membranes have been

used for N₂-CH₄ separation. In this paper, the recent advances in the design and fabrication of N₂-selective adsorbents and membranes for N₂ removal from unconventional natural gas are reviewed. The physicochemical characteristics of N₂-selective adsorption and membrane materials are briefly introduced, and the internal commonalities between different materials are analyzed to identify the underlying reasons for the specific performance. Additionally, the challenges and directions for the future development of N₂/CH₄ separation materials are discussed. © 2022 Elsevier B.V.

20. v, M. -, Li, S. -, Mao, H., Feng, Y. -, Zhang, A. -, Xu, L. -, Wang, S., Xie, W. -, & Zhao, Z. -. (2022). Promoted propylene/nitrogen separation by direct incorporating 2-methylimidazole into PDMS membranes. *Journal of Membrane Science*, 661

Abstract: Polymeric membrane separations have been used for hydrocarbon recovery in some polyolefin plants due to the low energy consumption and easy operation, but the relatively low separation factor and hydrocarbon permeance block their ways to popularization. In this study, membranes with high propylene permeance and sufficient separation factor for propylene/nitrogen separation were prepared by direct incorporating 2-methylimidazole (MIM) into polydimethylsiloxane (PDMS), which manifested simultaneous promotion of separation factor and propylene permeance. Interestingly, MIM simultaneously acted in promoting the crosslinking process of PDMS and tetraethyl orthosilicate. A series of tests and characterizations were conducted to investigate the microstructure, morphology, thermal property, and mass transfer property of the membranes. The gas separation performance of the MIM-incorporated PDMS membrane with a separation factor of 20.2 and propylene permeance of 440.9 GPU outperformed many other propylene-selective membranes reported in the literature. Molecular dynamics simulations revealed that MIM had a preferential affinity for propylene rather than nitrogen, which was similar to PDMS, but the propylene-affinity of MIM was significantly higher than that of PDMS, accounting for the promoted separation of propylene/nitrogen upon the incorporation of MIM. The MIM-incorporated PDMS membranes with readily available, cheap materials and straightforward manufacturing procedures should be a promising alternative for hydrocarbon recovery. It is also enlightening for the study and design of membrane materials for gas separation. © 2022 Elsevier B.V.

21. Shen, B., Zhao, S., Yang, X., Carta, M., Zhou, H., & Jin, W. (2022). Relation between permeate pressure and operational parameters in VOC/nitrogen separation by a PDMS composite membrane. *Separation and Purification Technology*, 280

Abstract: Transmembrane driving force, which can be produced by permeate pressure, is a significant element in the design of VOC/nitrogen separation processes. Studies on the impact of the pressure on the membrane performance and the separation mechanism can provide important information for the design of new membranes and separation processes. In this work, the effect of permeate pressure on membrane performance was studied for the separation of a cyclohexane/nitrogen mixture using a polydimethylsiloxane (PDMS)/polyamide (PA) composite membrane. The changing trends of the separation performance for the separation of VOCs with different saturated vapor pressures under different permeate pressures were analyzed. The variation in the transmembrane driving force for cyclohexane and nitrogen with different parameters, such as membrane thickness, were also investigated under various permeate pressures. The reason for the decrease in selectivity with increasing permeate pressure was discussed. It was demonstrated that permeate pressure affects the membrane performance mainly by weakening the cyclohexane flux, while having little influence on the nitrogen flux in the studied range due to their different saturated vapor pressures. Lastly, the energy consumption for the VOC/nitrogen separation, which provides fundamental insight for industrial membrane-based VOC recovery, was simulated keeping in consideration all the obtained experimental data. © 2021 Elsevier B.V.

22. Mousavi, S. H., Chen, K., Yao, J., Zavabeti, A., Liu, J. Z., & Li, G. K. (2022). Screening of Alkali Metal-Exchanged Zeolites for Nitrogen/Methane Separation. *Langmuir*,

Abstract: Methane (CH₄) is the primary component of natural gas and must be purified to a certain level before it can be used as pipeline gas or liquefied natural gas (LNG). In particular, nitrogen (N₂), a common contaminant in natural gas needs to be rejected to increase the heating value of the gas and meet the LNG product specifications. The development of energy-efficient N₂ removal technologies is hampered by N₂'s inertness and its resemblance to CH₄ in terms of kinetic size and polarizability. N₂-selective materials are so rare. Here, for the first time, we screened 1425 alkali metal cation exchange zeolites to identify the candidates with the best potential for the separation of N₂ from CH₄. We discovered a few extraordinary zeolite frameworks capable of achieving equilibrium selectivity toward N₂. Particularly, Li⁺-RRO-3

zeolite with a specific two-dimensional structure demonstrated a selective N₂ adsorption capacity of 2.94 mmol/g at 283 K and 1 bar, outperforming the capacity of all known zeolites. Through an ab initio density functional theory study, we found that the five-membered ring of the RRO framework is the most stable cationic site for Li⁺, and this Li⁺ can interact with multiple N₂ molecules but only one CH₄, revealing the mechanism for the high capacity and selectivity of N₂. This work suggests promising adsorbents to enable N₂ rejection from CH₄ in the gas industry without going for energy-intensive cryogenic distillations. © 2023 American Chemical Society.

23. Merukan Chola, N., Gajera, P., Kulkarni, H., Kumar, G., Parmar, R., Nagarale, R. K., & Sethia, G. (2022). Sorption of Carbon Dioxide and Nitrogen on Porous Hyper-Cross-Linked Aromatic Polymers: Effect of Textural Properties, Composition, and Electrostatic Interactions. *ACS Omega*,

Abstract: Porous hyper-cross-linked aromatic polymers are one of the emerging classes of porous organic polymers with the potential for industrial application. Four different porous polymeric materials have been prepared using different precursors (indole, pyrene, carbazole, and naphthalene), and the composition and textural properties were analyzed. The materials were characterized in detail using different physicochemical techniques like scanning electron microscopy, transmission electron microscopy, nitrogen adsorption at 77 K, Fourier transform infrared spectroscopy, X-ray diffraction, etc. The effect of textural properties and nitrogen species on carbon dioxide and nitrogen adsorption capacities and selectivity was studied and discussed. The carbon dioxide and nitrogen adsorption capacities were measured using a volumetric gas adsorption system. The adsorption data were fitted into different adsorption models, and the ideal adsorbed solution theory was used to calculate adsorption selectivity. Among the studied samples, POP-4 shows the highest carbon dioxide and nitrogen adsorption capacities. While POP-1 shows maximum CO₂/N₂ selectivity of 78.0 at 298 K and 1 bar pressure. It is observed that ultra-micropores, which are present in the prepared materials but not measured during conventional surface area measurement via nitrogen adsorption at 77 K, play a very important role in carbon dioxide adsorption capacity and determining the carbon dioxide selectivity over nitrogen. Surface nitrogen also increases the CO₂ selectivity in the dual mode by increasing carbon dioxide adsorption via the acid-base interaction as well as by

decreasing nitrogen adsorption due to N-N repulsion. © 2023 The Authors. Published by American Chemical Society.

24. Li, L., Liu, D., Zhen, D., Ge, Z., Zhang, X., Xiong, B., Li, Z., Zhang, K., Xing, T., Xu, W., Zhang, F., Gu, X., Dai, P., & Zhao, X. (2022). Thermodynamic-Kinetic Synergistic Separation for O₂/N₂ and CO₂/CH₄ on Nanoporous Carbon Molecular Sieves. *ACS Applied Nano Materials*,

Abstract: Carbon molecular sieves (CMSs) are the key adsorbents for gas separation through pressure swing adsorption (PSA), a promising technique that has found many applications in air separation and natural gas purification. However, the current process of preparing CMSs with finely tuned nanopores based on the repeated CVD process is technically challenging and energy-consuming. In this work, we report a facile method of preparing CMSs through the one-step carbonization of a metal-organic framework. The direct carbonization of an rht-type metal-organic framework (MOF) affords a type of CMSs with an ultramicro-nanoporous structure that is comparable with the kinetic diameter of small gases (N₂, O₂, CO₂, and CH₄). As a result, this type of CMSs shows significant differences in both equilibrium adsorption properties and diffusion rates for O₂/N₂ and CO₂/CH₄. The kinetic separation coefficient for O₂/N₂ and CO₂/CH₄ is high up to 47 and 105, respectively. In addition to excellent equilibrium and kinetic selectivity, this MOF-CMS shows compatibility between equilibrium and kinetic adsorption properties, giving rise to a thermodynamic-kinetic synergistic effect for O₂/N₂ and CO₂/CH₄ separation. These outstanding separation performances can be attributed to the ultramicro-nanopores of CMSs, which are modulated by the uniform pore structure of the MOF precursor. The high selectivity combined with the facile preparation process for this CMS may open an avenue of preparing nanoporous CMSs with desired functionalities. © 2022 American Chemical Society.

25. Malekzadeh Dirin, A., Saljoughi, E., Kiani, S., & Mousavi, S. M. (2022). Zein Protein Obtained from Maize as a Novel Biodegradable Membrane Material for Oxygen/Nitrogen Separation: Membrane Fabrication and Characterization. *Journal of Polymers and the Environment*, 30(12), 5069-5083.

Abstract: In this study, biodegradable zein protein obtained from maize was used as a novel material to prepare a membrane for oxygen/nitrogen separation. Scanning electron microscopy (SEM), thermogravimetric analysis (TGA), tensile test, X-ray diffraction (XRD) spectroscopy, differential scanning calorimetry (DSC), biodegradability test, and attenuated total reflectance Fourier transform infrared (ATR-FTIR) spectroscopy were conducted for characterizing the zein membrane, and membrane properties was compared with that of the polymeric membranes reported in the literature. The developed zein membrane showed a significantly high thermal stability. The mechanical properties of the zein membrane were higher or comparable to those of the previously reported dense membranes. In addition, biodegradation in compost was significantly higher than the other membranes reported in the literature. The developed zein membrane provided a significantly high oxygen/nitrogen selectivity at 2 bar, which was superior to most of the previously reported data on the neat biodegradable polymers with dense structure. The permeability of oxygen and nitrogen at 2 bar was 0.67 and 0.12 barrer, respectively, which brought about the selectivity of 5.45 for oxygen/nitrogen separation. © 2022, The Author(s), under exclusive licence to Springer Science+Business Media, LLC, part of Springer Nature.

26. Lemaoui, T., Benguerba, Y., Darwish, A. S., Hatab, F. A., Warrag, S. E. E., Kroon, M. C., & Alnashef, I. M. (2021). Simultaneous dearomatization, desulfurization, and denitrogenation of diesel fuels using acidic deep eutectic solvents as extractive agents: A parametric study. *Separation and Purification Technology*, 256

Abstract: Based on the literature, deep eutectic solvents (DESs) have been proven to be promising candidates for the separation of aromatics or heteroaromatics (“sulfur-/nitrogen-containing aromatics”) from fuels. However, most studies investigated the separation of a single fuel impurity (aromatics or heteroaromatics) from n-alkanes. Thus, to realistically represent a process that simulates the treatment of both types of aromatics, this work investigated the application of DESs in simultaneous dearomatization, desulfurization, and denitrogenation of fuels, particularly “diesel” using an arbitrary fuel model consisting of {5 wt% toluene + 5 wt% thiophene + 5 wt% pyridine + 5 wt% pyrrole + 80 wt% n-decane}. The selected DES was comprised of tetrapropylammonium bromide and acetic acid at a 1:4 M ratio. The DES performance was evaluated based on single-stage liquid–liquid extraction, the Liquid-Liquid Equilibrium (LLE) data of each impurity, multi-stage, and multi-cycle

extraction of the diesel model. Furthermore, the influence of initial concentration and mixing effects of impurities were also studied. The results showed that complete removal of pyrrole and pyridine (“≈100%”) can be achieved in 2 stages only, while extraction efficiencies of 68% and 89% for toluene and thiophene, respectively, were achieved after the 5th stage. Based on the obtained results, it was concluded that acidic DESs could be considered as potential solvents for the simultaneous dearomatization, desulfurization, and denitrogenation of diesel fuels. © 2020 Elsevier B.V.

27. Javani, R., Maghsoudi, H., Darvishi Gilan, S., & Majidpour, M. (2021). Study on adsorption performance of different adsorbents in nitrogen/methane separation. *Separation Science and Technology (Philadelphia)*, 56(15), 2562-2577.

Abstract: Equilibrium adsorbed amount and selectivity of adsorbents are investigated using the Ideal Adsorption Solution Theory (IAST) to determine suitable adsorbents for nitrogen/methane separation. The results revealed that among the nitrogen selective adsorbents, Sr-ETS-4 has the highest nitrogen/methane selectivity and among the selective adsorbents toward methane, CMS-3 K and Cu-MOF have the highest adsorbed amount and selectivity, respectively. It was found that MOFs have great potential for methane adsorption and separation. However, carbon-based adsorbents have the highest adsorption capacity for methane. Finally, a novel trade-off plot of adsorbed amount versus selectivity was constructed as a simple guide for researchers and industrial applications. © 2020 Taylor & Francis Group, LLC

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