Adsorption Applications of Electronic Specialty Gases

1. Background

Electronic specialty gases are essential foundational materials in modern electronics manufacturing. These high-purity gases are critical to the production of semiconductors, display panels, LEDs, and photovoltaics. With the explosive growth of the clean energy sector, the market size for electronic specialty gases is expected to increase 140% by 2032.[(1)]

The purity requirements for electronic specialty gases are stringent, typically at the 5N (99.999%) level, with some applications demanding 6N (99.9999%) or even higher. Gas purity and quality directly influence device yield and performance, with purification techniques spanning adsorption, distillation, absorption, and membrane separation.[(2)]

Each major semiconductor process uses specialty gases for critical roles:

- ✓ **Cleaning**: Removes contaminants from wafers and surfaces using gases (SF_6, CF_4)
- ✓ **Coating (CVD/ALD)**: Deposits films through gas-phase reactions (WF_6, SiH_4, NH_3, N_2O)
- ✓ **Lithography**: Plasma formation from mixed gases (Ar/F/Ne, Kr/Ne) to generate stable, high-precision light sources for photomask patterning
- ✓ **Etching**: Selectively removes material using fluorocarbons (CH_3F, CH_2F_2, CF_3H), and halogen gases (Cl_2, HBr) to define intricate microstructures
- ✓ **Doping**: Introduces conductivity to semiconductors (AsH_3, PH_3, B_2H_6, BF_3)

These processes demand precise control and validation of gas delivery, purity, and usage conditions, making gas analysis, gravimetric sorption, and breakthrough testing indispensable tools in quality assurance and process development.

The **adsorption method** leverages the principle that porous materials exhibit selective gas uptake depending on the molecular properties of the gas and the characteristics of the material. For a given gaseous adsorbate, different porous materials exhibit different adsorption capacities. When a gas mixture is passed through an adsorbent bed, gases with stronger affinities to the surface will be preferentially adsorbed, while those with weaker interactions will exit the system, achieving a separation effect. The adsorbed gas can subsequently be desorbed by thermal regeneration or gas purging, allowing for recovery of purified components.

Perfluorinated electronic specialty gases, including NF_3, CF_4, and SF_6, play a critical role in the fabrication of silicon-based semiconductors due to the strong chemical reactivity between fluorine and silicon. However, the conversion efficiency of F-gases in plasma processes is often below 60%, leaving unreacted F-gases and byproducts such as N_2, NO_x, HF, and H_2O in the exhaust stream. As environmental regulations tighten and gas recovery becomes increasingly important, adsorbent-based purification has emerged as a key area of research and development.

Another prominent application of this technique is the separation of xenon (Xe) and krypton (Kr). They are often referred to as "golden gases" due to their scarcity and wide-ranging industrial applications such as semiconductors, medical imaging, aerospace, and lighting. Wang et al. developed a negatively charged coordination ultramicroporous material, NbOFFIVE-2-Cu-i (ZU-62), that demonstrated a breakthrough in Xe/Kr separation performance.[3] ZU-62 features a finely tunable pore size and flexible framework, resulting in a unique inverse size sieving effect—a rare case where the larger atom (Xe) is selectively adsorbed over the smaller atom (Kr).

2. Experiment

For this application note, two metal-organic framework (MOF) materials were selected for adsorption and gas separation studies:

- ✓ MOF-1: Targeted for SF_6/N_2 adsorption and separation
- ✓ MOF-2: Targeted for Xe/Kr adsorption and separation

Competitive adsorption experiments were performed using the **BTSorb-100** breakthrough curve and mass transfer analyzer from **AMI**. A 1 mL stainless steel adsorption column (inner diameter: 0.45 cm; bed height: 5 cm) was used for all tests. MOF-1 was tested at 25 °C, 200 kPa, and total gas flow of 30 mL/min (13.5 mL/min N_2, 1.5 mL/min SF_6, 15 mL He carrier gas). MOF-2 was tested at 25 °C, 100 kPa, and total gas flow of 3mL/min (0.6 mL/min Xe, 2.4 mL/min Kr). Breakthrough curves were recorded and used to assess gas retention times, separation resolution, and dynamic capacity for each system.

Static adsorption isotherms were measured using the **AMI Sync 400** gas physisorption analyzer. For both MOFs, 0.12 grams were degassed under vacuum at 120 °C for 12 hours. The SF_6 and N_2 static isotherms were obtained for MOF-1 at 0 °C, and the Xe and Kr static isotherms were obtained for MOF-2 at 25 °C.

3. Results

To assess adsorption-based purification of SF_6, MOF-1 was tested with the **AMI Sync 400** to determine the adsorption capacity of SF_6 and N_2. As shown in Figure 1a, static adsorption isotherms indicate that MOF-1 exhibits a significantly higher adsorption capacity for SF_6 compared to N_2. This disparity suggests the potential for selective adsorption and separation of SF_6 from nitrogen under controlled conditions.

To evaluate real-world separation behavior, a dynamic breakthrough experiment was conducted using the **BTSorb 100** system. A 10:90 SF_6/N_2 gas mixture was introduced, and the breakthrough curves shown in Figure 3b illustrates clear separation behavior.

- ✓ N_2 began to elute at approximately 50 seconds
- ✓ SF_6 broke through at around 250 seconds

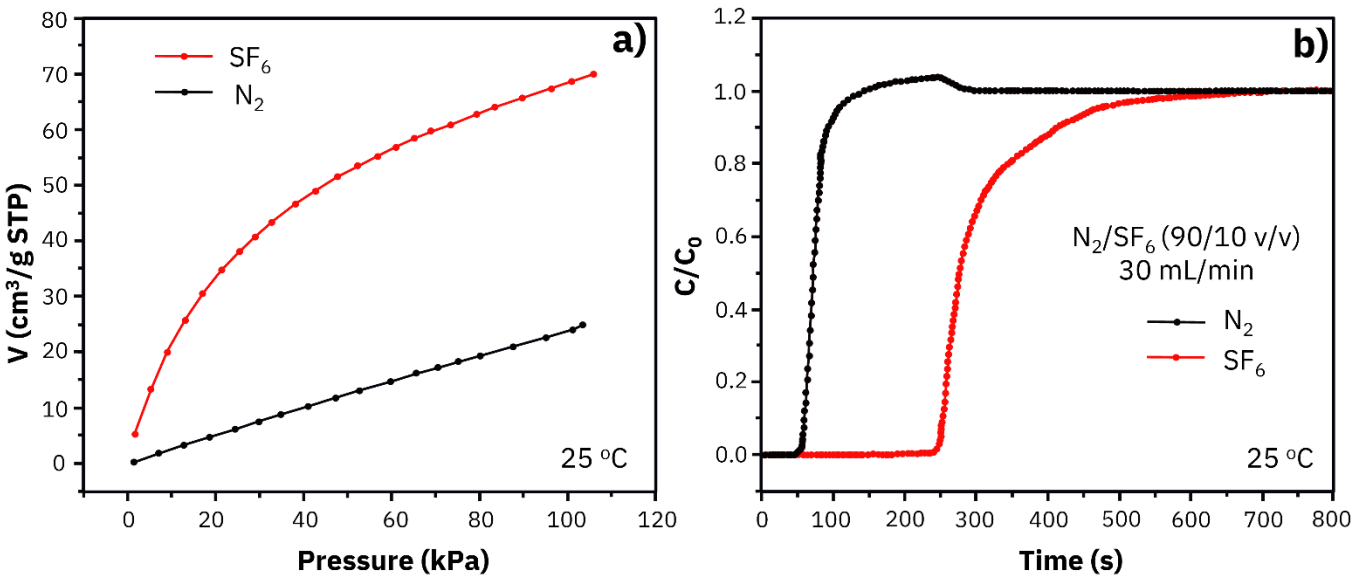


Figure 1: a) Static adsorption isotherms for SF_6 (red) and N_2 (black) on MOF-1, and b) dynamic breakthrough curves for a N_2/SF_6 mixture (30 mL/min, 90/10 v/v) through MOF-1.

The resulting separation window was approximately 200 seconds, representing the effective retention time of SF_6 on MOF-1 under these conditions.

Calculated dynamic adsorption capacities are shown in Table 1, which were consistent with the moles of gas adsorbed during static isotherm experiments. The close agreement between static and dynamic data confirms the reliability and practical relevance of the measured separation behavior. Taken together, these findings demonstrate that MOF-1 offers viable adsorption and separation performance for SF_6/N_2 systems and highlights the potential use in semiconductor exhaust gas purification processes.

As shown in Figure 2a, adsorption isotherms measured at 0 °C show that MOF-2 exhibits a significantly higher adsorption capacity for Xe compared to Kr. When the temperature increased to 25 °C, (Figure 2b) the adsorption capacities for both gases decreased, which was consistent with exothermic physisorption behavior. However, Xe remained more strongly adsorbed than Kr, suggesting favorable selectivity across a range of operating conditions.

Gas	Static (mmol/g)	Dynamic (mmol/g)
N_2	1.01 (95 kPa)	0.905
SF_6	0.896 (9.28 kPa)	0.857

Table 1: Uptakes of N_2 and SF_6 gas adsorbed in MOF-1 during static isotherm experiments at their respective pressures, compared to the calculated dynamic adsorption capacities of MOF-1 from dynamic breakthrough experiments.

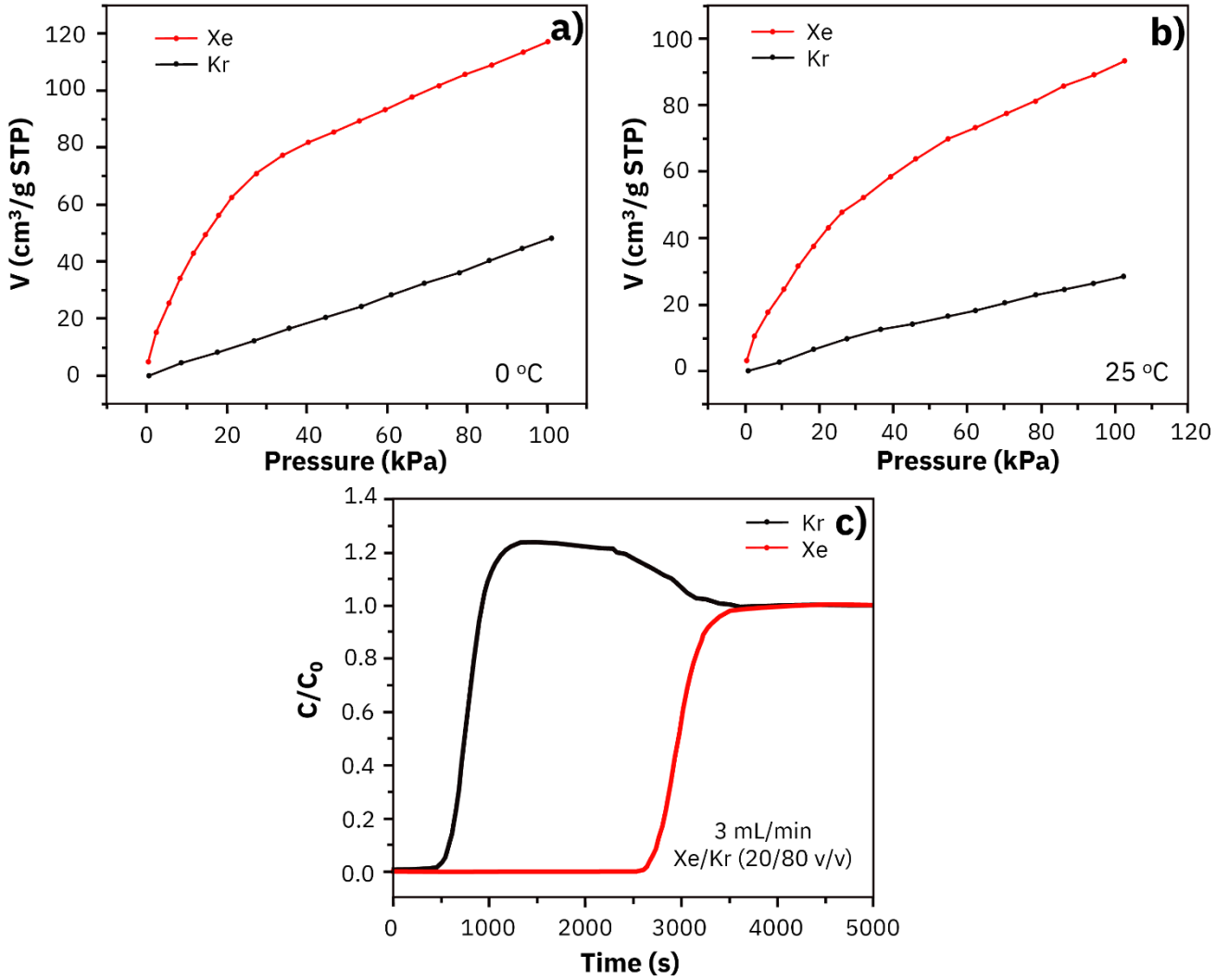


Figure 2: a) Static adsorption isotherms for Xe (red) and Kr (black) on MOF-2 at 0 °C and b) 25 °C, plus c) dynamic breakthrough curves for a Xe/Kr mixture (3 mL/min, 80/20 v/v) through MOF-2.

The static isotherms confirmed the potential of MOF-2 for selective Xe adsorption from a Xe/Kr mixture. To evaluate separation performance under flow conditions, a competitive dynamic breakthrough experiment was conducted using a 20:80 Xe/Kr gas mixture, as shown in Figure 2c.

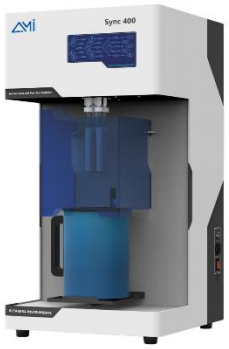
Gas	Static (mmol/g)	Dynamic (mmol/g)
Xe	1.5489 (20 kPa)	1.6749
Kr	1.025 (80 kPa)	0.9542

Table 2: Uptakes of Xe and Kr gas adsorbed in MOF-2 during static isotherm experiments at their respective pressures, compared to the calculated dynamic adsorption capacities of MOF-2 from dynamic breakthrough experiments.

- ✓ Kr broke through the adsorption column in under 500 seconds
- ✓ Xe did not appear in the effluent stream until ~2500 seconds

The breakthrough time difference exceeded 2000 seconds, indicating a long and effective separation window.

Calculated adsorption capacities and static gas uptake values are shown in Table 2. The close agreement between static and dynamic data, along with the large differential in breakthrough times, confirms that MOF-2 offers strong selectivity and capacity for Xe over Kr. These results demonstrate the practical utility of MOF-2 for Xe purification from Kr-containing gas mixtures, with potential applicability in industrial gas recovery and semiconductor process optimization.



AMI Sync 400

- ✓ High sensitivity and reproducibility
  - ✓ BET detection limit as low as 0.01 m^2/g SSA
  - ✓ RSD ≤ 1.0%
- ✓ Customizable for high-throughput analysis
  - ✓ Up to 4 stations for simultaneous experiments

- ✓ Comprehensive and versatile dynamic sorption analyzer
- ✓ Maintains temperature between -10 – 400 °C and pressures up to 100 bar
- ✓ Includes 2 evaporators for vapor studies

BTSorb 100

*Figure 3: Highlighted features of **AMI Sync 400** gas physisorption analyzer and **BTSorb 100** dynamic sorption analyzer.*

4. Conclusions

The results of this study confirm that advanced MOF materials offer strong potential for the selective adsorption and separation of high-value electronic specialty gases, including SF_6/N_2 and Xe/Kr mixtures.

Using the **AMI Sync 400** gas physisorption analyzer and the **BTSorb-100** breakthrough system, we were able to characterize adsorption behavior with high resolution and repeatability under realistic process conditions. These tools provided critical insights into both capacity and selectivity, enabling a comprehensive understanding of material performance.

5. References

(1) Juyal, V. *Global Electronic Specialty Gas Market Size, Share and Trends Analysis Report – Industry Overview and Forecast to 2032 ;* Data Bridge Market Research: 2024; https://www.databridgemarketresearch.com/reports/global-electronic-specialty-gas-market (accessed February 16, 2026).

(2) Kohl, A. L. ; Nielsen, R. B. *Gas Purification,* 5th ed.; Gulf Publishing Company, 1997.

(3) Wang, Q.; Ke, T.; Yang, L.; Zhang, Z.; Cui, X.; Bao, Z.; Ren, Q.; Yang, Q.; Xing, H. Separation of Xe from Kr with record selectivity and productivity in anion-pillared ultramicroporous materials by inverse-size sieving effect. *Angew. Chem., Int. Ed.* **2019**, *132*, 3451-3456.