

MOLECULAR VIBRATIONAL ENERGY DIFFERENCE INDUCED HIGH SELECTIVE SEPARATION OF $^{18}\text{O}_2$ FROM $^{16}\text{O}_2$ USING NANOPOROUS CARBONS

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Introduction

^{18}O , a stable isotope with natural abundance of 0.204 atomic % can exist with other stable isotopes of oxygen ^{17}O (0.037 %) and ^{16}O (99.759 %) as $^{18}\text{O}^{18}\text{O}$, $^{18}\text{O}^{17}\text{O}$, $^{18}\text{O}^{16}\text{O}$ etc¹. Recently, ^{18}O has been extensively utilized for medical imaging techniques such as Positron Emission Tomography (PET)² and several other applications involving reaction elucidating mechanisms in chemistry, environmental programs and basic sciences³. Consequently, obtaining a supply of pure ^{18}O is crucial in achieving improvements in health care and sustainable society. However, with its scant abundance, it is a major challenge to efficiently separate oxygen isotope molecules from the starting material, which is principally composed of $^{16}\text{O}^{16}\text{O}$ ($^{16}\text{O}_2$). A novel, cost-effective separation method is desired for efficient separation of oxygen isotopes. Currently used cryogenic distillation-based separation methods are plagued by very low separation factors < 1.05 and high energy consumption, leading to very high cost⁴.

In this report, we present a highly selective adsorption-based separation of $^{18}\text{O}^{18}\text{O}$ ($^{18}\text{O}_2$) having a separation factor of > 60 at a low temperature (112 K) utilizing cryogenic liquefied natural gas technology. The selective separation demonstrates high dependence on the nanoporous adsorbents pore geometry, temperature and dosing pressure.

Materials and Methods

Activated Carbon Fibers were Coal Pitch Based procured from Ad'all Co., Ltd. The CDC sample was derived from TiC^5 . Single-Walled Carbon Nanotubes(SWCNT) obtained from MEIJO NANO CARBON Co. Ltd were air oxidised before use. The zeolite BEA and zeolite MFI were synthesized as described previously by Matsukata et al. Molecular sieves MS5A and MS4A were purchased from Nacalai Tesque INC. $^{16}\text{O}_2$ (99.99995%; JAPAN FINE PRODUCTS-JPF) and $^{18}\text{O}_2$ ($>98\%$; TAIYO NIPPON SAN SO Corporation) gases were used for mixed gas $n^{18}\text{O}_2/n^{16}\text{O}_2 = 1:1$.

Results and Discussion

The adsorption based dynamic separation of $^{18}\text{O}_2$ from $^{18}\text{O}_2$ - $^{16}\text{O}_2$ mixed gases is measured using a custom designed flow-type adsorption equipment with a quadrupole mass spectrometer (QMS)⁶. Nanoporous adsorbents having different geometries namely slit-shape pores for ACFs and CDC,

uniform cylindrical pores for SWCNTs and interconnected cylindrical pores for zeolites MS4A, MS5A, MFI, and BEA are investigated to establish the relationship between $^{18}\text{O}_2$ and $^{16}\text{O}_2$ adsorption amount with the pore aperture and their effectiveness for cryo-sieving. The nanoporous parameters of the adsorbents calculated by N_2 isotherms at 77 K are presented in Table 1.

The nanoporous adsorbents possess different adsorption amount of $^{18}\text{O}_2$ and $^{16}\text{O}_2$ resulting in the difference in the selectivity at 112 K for different pore geometry. It is noteworthy that CDC having 0.65 nm slit pores preferentially adsorbs $^{18}\text{O}_2$, exhibiting large difference in the adsorption amount

Table 1. N_2 Adsorption Parameters of Nanoporous Adsorbents and Dynamic selectivity at 1% pore filling

Adsorbent	S_{SPE, α_s} ($\text{m}^2 \text{g}^{-1}$)	Pore width (nm)	Selectivity at 1%
ACF20	1520	1.1	1.02
ACF10	990	0.85	1.15
ACF5	830	0.65	1.4
CDC	1565	0.65	4.2
ox-SWCNT	645	1	1.5
ox-SWCNT	1150	1.5	1.02
MS4A	28	0.4	--
MS5A	710	0.5	1.2
MFI	437	0.55	1.2
BEA	406	0.66	1.12

$^{18}\text{O}_2$ and $^{16}\text{O}_2$ resulting in its high selectivity, $S(^{18}\text{O}_2/^{16}\text{O}_2) = 4.2$ at 1% pore filling. Other adsorbents also demonstrate similar trends as observed for CDC, exhibiting very high selectivity for adsorption of $^{18}\text{O}_2$ over $^{16}\text{O}_2$ initially, which decreases to attain equilibrium. The ox-SWCNT (1nm) and ox-SWCNT (1.5nm) having uniform cylindrical pores demonstrating $S(^{18}\text{O}_2/^{16}\text{O}_2) = 1.5$ and 1.02, respectively, while interconnected cylindrical pores of zeolites MS4A, MFI and BEA show intermediate selectivity

between slit porous carbons and cylindrical pores. The MS5A and MFI having pore width ~ 0.5 nm, exhibits highest $S(^{18}\text{O}_2/^{16}\text{O}_2) = 1.2$.

Conclusions

High selective separation of $^{18}\text{O}_2$ from $^{18}\text{O}_2$ - $^{16}\text{O}_2$ mixed gas is evidenced by the low temperature adsorption experiments using nanoporous carbons, ox-SWCNTs and zeolites adsorbents. The CDC adsorbent having slit pore width 0.65 nm and the ox-SWCNT having cylindrical pores of 1 nm are most promising pore geometry for the high $^{18}\text{O}_2$ selectivity. This remarkable adsorption selectivity is ascribed to the difference of molecular vibrational energy level of $^{18}\text{O}_2$ and $^{16}\text{O}_2$ by $\sim 0.57 \text{ kJ mol}^{-1}$, which provides the observed marked difference in adsorption. The selective separation results can act as proof-of-concept for industrial scale separation of oxygen isotopes.

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