

Copper Modified Mesoporous Silica for H₂ and D₂ Separation via Chemical Affinity Quantum Sieving

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1. Introduction

Tritium is radioactive isotope, emitting beta ray, released as tritiated water from nuclear power plants. Due to the danger of radioactive isotope, the appropriate separation of tritium is necessary for environment and safety of living organisms. The tritiated water can be treated by diverse techniques such as water distillation, cryogenic distillation, catalytic exchange and electrolysis [1,2]. After treatment, it is more desirable to convert as gas phase for storage, comparing to liquid phase. However, achieving complete separation of hydrogen isotope gases with very similar physical and chemical properties is significantly challenging. Thus, it is necessary to develop materials with effective separation properties in gas separation.

Kinetic quantum sieving (KQS) and chemical affinity quantum sieving (CAQS) are the main mechanisms for separation of hydrogen isotopes using porous materials [3,4]. KQS occurs when the de Broglie wavelength of molecules is similar to the pore size of porous materials. An optimal pore size of 3.0 to 3.4 Å is suggested for the separation of H₂/D₂ gas mixtures. This effect only appears at extremely low temperature below 77 K. CAQS arises from the mass differences between hydrogen isotopes. This mass difference affects the zero-point energy of each isotope, resulting in variations in enthalpy of adsorption (ΔH). Consequently, heavier isotopes are preferentially adsorbed, achieving substantial separation factors even above 77 K. CAQS utilizes these thermodynamic properties to enable efficient isotope separation.

Mesoporous silica is one of the commonly used porous materials for a wide range of applications due to tunable pore structure, large surface area and stability under aggressive conditions. It is a form of silica that is characterized by its mesoporous structure possessing pore size that ranges from 2 to 50 nm. This material can be modified to selectively capture and separate molecules having specific size and affinity.

In this study, we investigate hydrogen isotope separation in the gas phase using modified mesoporous silica. The copper (Cu) incorporated mesoporous silica was synthesized via co-condensation method to tailor a CAQS effect, thereby providing separation performance in D₂/H₂.

2. Methods and Results

2.1. Materials

Tetraethyl orthosilicate (TEOS, 98 %), cetyltrimethylammonium bromide (CTAB, > 98 %), ethanol (EtOH, 99.99 %), ammonium hydroxide solution (NH₄OH, 28.0~30.0 wt%) and copper (II) nitrate trihydrate (CuN₂O₆·3H₂O, 99~104 %) were purchased from Sigma-Aldrich. Deionized water was supplied from Direct-Q[®] 3 with 18.2 MΩ. Hydrogen (H₂, 99.999 %) and nitrogen gas (N₂, 99.999 %) were purchased from DIG airgas CO., LTD. Deuterium gas (D₂, 99.999 %) and Neon gas (Ne, 99.999%) were purchased from NOBLE gas CO., LTD.

2.2. Preparation of bare-mesoporous silica

CTAB (2.4 g) was dissolved in the mixture of deionized water (50 mL) and ethanol (50 mL). After 10 min of stirring, NH₄OH (12 mL) was added and TEOS (3.4 g) was drop-wisely dispersed into the solution mixture. The mixed solution was additionally stirred for another 2 h. The molar composition of the final gel was TEOS: 0.43 CTAB: 12.5 NH₃: 54.3 EtOH: 416 H₂O. The resulting mixture was separated by centrifugation and washed with deionized water for 5 times. Then, the resulting solid was dried in the oven at 338 K overnight. The CTAB template was removed by calcination at 823 K with a heating rate of 274 K min⁻¹ for 6 h under stagnant air in furnace.

2.3. Preparation of Cu-mesoporous silica

CTAB (5.1 g) was dissolved in the mixture of deionized water (200 g) and ethanol (79 g). Then, ammonia solution (6.1 g) was added. After 10 min of stirring, TEOS (6.7 g) was drop-wisely dispersed into the solution mixture. After that, the CuN₂O₆·3H₂O (0.156 g) was doped into the solution. The mixed solution was stirred for another 4 h. The molar composition of the gel was TEOS: 0.02 CuN₂O₆·3H₂O: 0.41 CTAB: 12 NH₄OH: 54 EtOH: 173 H₂O. Following the centrifugation, the product was subjected to identical washing and drying as described in section 2.2. The CTAB template was removed by calcination at 823 K with a heating rate of 276 K min⁻¹ for 6 h under stagnant air in furnace.

2.4. Characterization

The X-ray diffraction (XRD) patterns of the samples were measured using a D2 PHASER (Bruker) with Cu-K-alpha radiation source. Diffractograms were assessed within 0 to 10° and 20 to 80° of 2θ. Both samples exhibited the characteristic of mesoporous silica based on (211) peak centered at 3.3° of 2θ (Fig. 1a). On the other hand, Cu-mesoporous silica exhibited diffraction peaks at 35.5 and 38.7° of 2θ, indicating the copper oxide crystals (Fig. 1b).

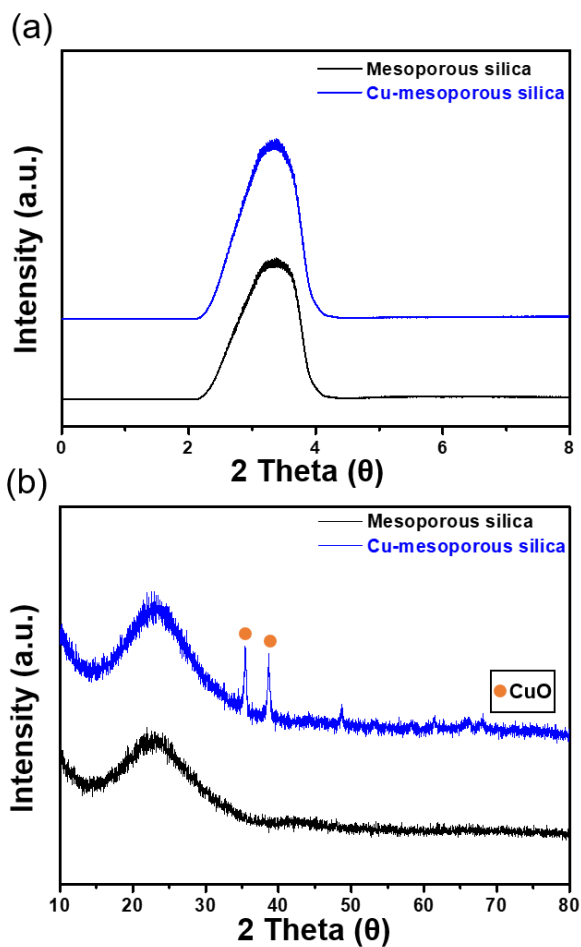


Fig. 1. The (a) low- and (b) high-angle XRD patterns of bare and Cu-mesoporous silica.

The scanning electron microscope (SEM) images were obtained SU-8020 (Hitachi). Fig. 2 shows both samples have spherical shape, and particle sizes were varied between 330 and 860 nm.

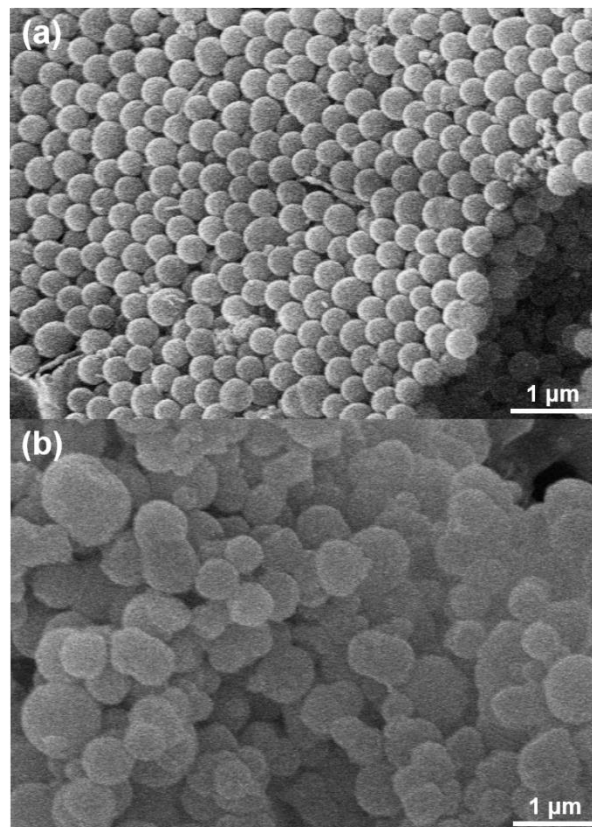


Fig. 2. SEM images of (a) bare and (b) Cu-mesoporous silica.

2.5. Gas physisorption isotherm measurements

The N₂, H₂, and D₂ physisorption isotherms were measured at 77 K using an Autosorb iQ-XR Viton (Quantachrome). Before measurement, the both samples were degassed overnight at 423 K under vacuum to remove the pre-adsorbed gases, moisture, and any other impurities.

The N₂ physisorption isotherms were analyzed to specify the pore-volume (V_p), multipoint surface area and pore size distribution (PSD) of the samples. The V_p was determined by the Barrett-Joyner-Halenda method using desorption isotherm. The multipoint surface area was determined by the Brunauer-Emmett-Teller (BET) method and the pore size distribution was determined by Brokhoff-de Boer/Frenkel-Halsey-Hile method.

The N₂ isotherms for both samples demonstrated characteristics of Type IV isotherms as IUPAC classifications (Fig. 3a), indicating its properties of mesoporous materials. The textural property is summarized in Table I. The pore volume of bare and Cu-mesoporous silica was 0.8 and 0.87 cm³ g⁻¹, respectively, with a narrow pore size distribution centered at 4 nm (Fig. 3b). Bare mesoporous silica exhibited the high BET surface area of 1800 m² g⁻¹ while the Cu-mesoporous silica showed relatively lower surface area of 1410 m² g⁻¹, because Cu is modified in the framework of mesoporous silica during co-condensation.

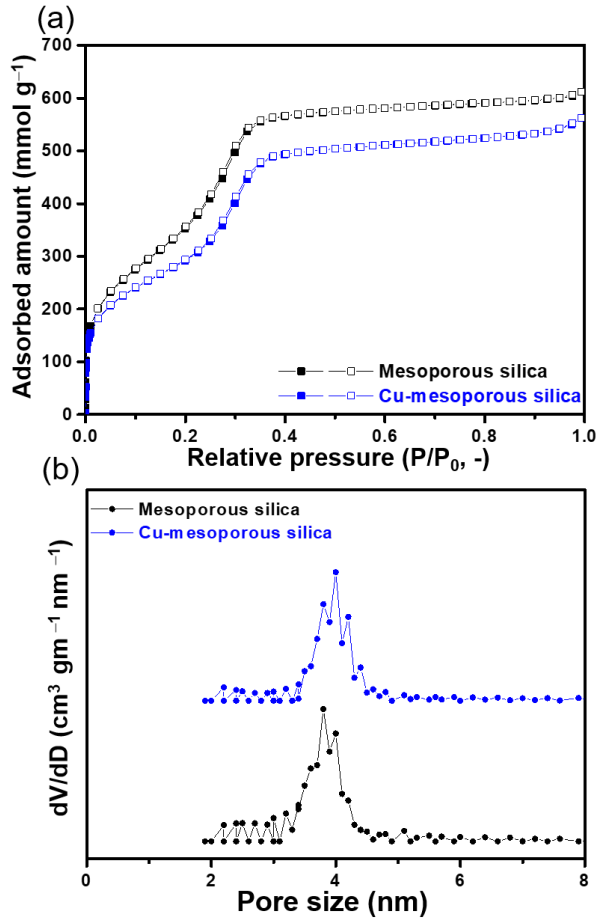


Fig. 3. (a) N₂ physisorption isotherms for bare and Cu-mesoporous silica at 77 K (filled symbols: adsorption; open symbols: desorption), (b) PSD for bare and Cu-mesoporous silica.

Table I: Textural property of bare and Cu-mesoporous silica.

	V _p (cm ³ g ⁻¹)	BET surface area (m ² g ⁻¹)	Pore size (nm)
Bare mesoporous silica	0.80	1800	4
Cu- mesoporous silica	0.86	1360	4

Fig. 4 shows the adsorbed amount of D₂ was higher than H₂ for both samples due to the quantum mass effect. The adsorption amount of D₂ was higher on Cu-mesoporous silica than that on bare mesoporous silica. Furthermore, difference in adsorbed amount between H₂ and D₂ was gradually increased as relative pressure increases for both samples. This indicates that Cu tailors the CAQS effect and preferentially adsorbs D₂ over H₂.

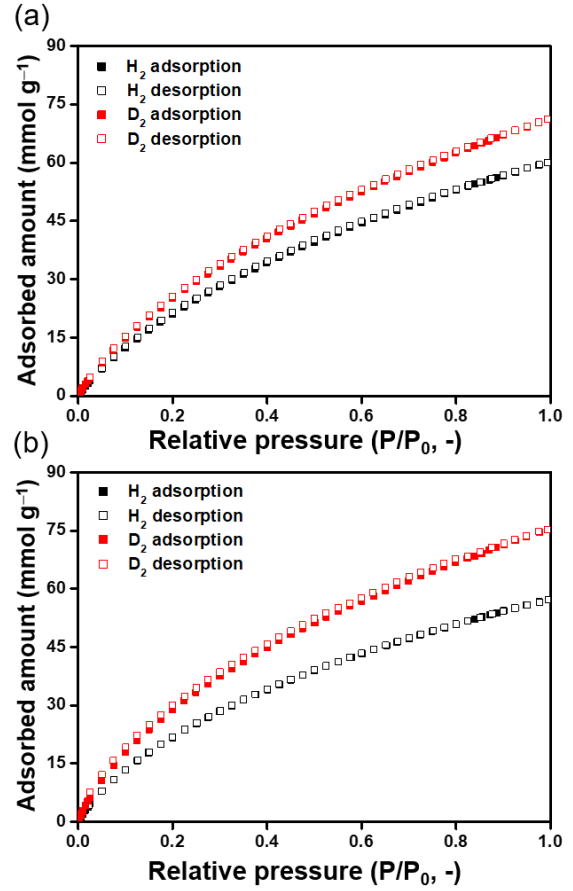


Fig. 4. H₂ and D₂ physisorption isotherms of (a) bare and (b) Cu-mesoporous silica at 77 K.

2.6. Breakthrough analysis

The dynamic breakthrough analysis was performed with lab-made instrument for evaluating hydrogen isotope separation performance under realistic mixed-gas conditions. Then, the gas composition was measured with a multi-purpose gas analysis system (EL) equipped with a quadrupole mass spectrometer (QMS, PrismaPro[®] QMG 250, Pfeiffer Vacuum). Initially, the both samples were mounted in the column (inner diameter of 4 mm and a length of 120 mm) and degassed under vacuum at 423 K for 12 h to clear adsorption sites, respectively. The degassed column was immersed in liquid N₂ to maintain 77 K. Before the gas flow, the breakthrough system was purged with Ne with 20 standard cubic centimeter per minute (sccm) for 5 min to remove residual gases. After that, the 1:1 mixture of H₂ and D₂ flowed to the column with the flow rate of 2 sccm under vacuum. Fig. 5a shows H₂ and D₂ passed almost simultaneously through the column packed with bare mesoporous silica. In contrast, H₂ firstly passed the column while D₂ was still trapped in the Cu-mesoporous silica (Fig. 5b). This indicates that the separation of H₂ and D₂ occurred under realistic mixed-gas conditions after Cu modification.

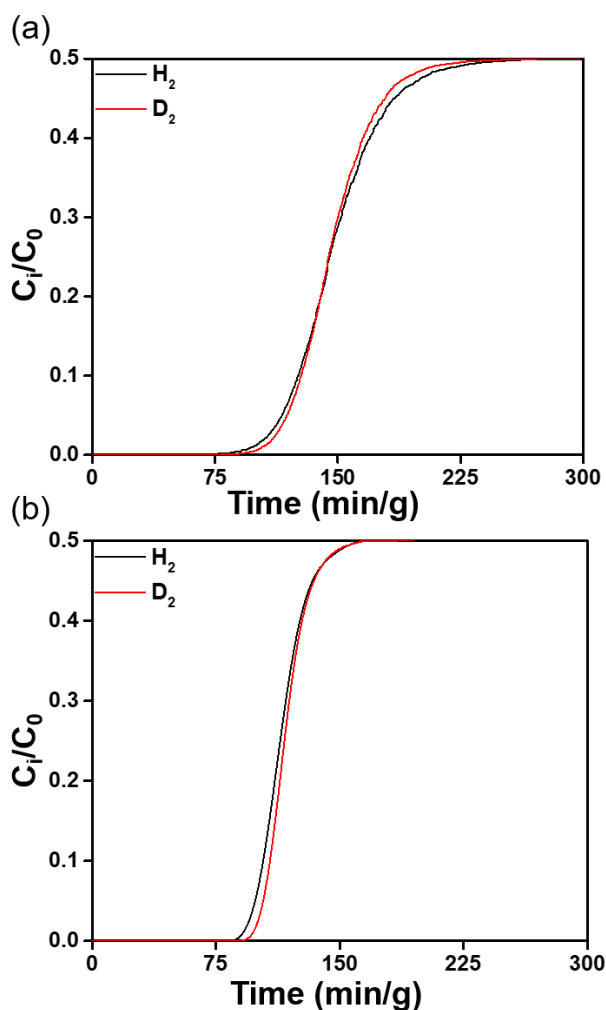


Fig. 5. The breakthrough curves of (a) bare and (b) Cu-mesoporous silica under 1:1 mixture of D_2 and H_2 at 77 K.

3. Conclusions

We have successfully synthesized Cu incorporated mesoporous silica and characterized physicochemical properties by multiple techniques. Cu-mesoporous silica possessed higher adsorption amount of D_2 than bare mesoporous silica under single gas isotherms. More importantly, the difference in adsorbed amount of H_2 and D_2 is higher for Cu-mesoporous silica. Further, mixed gas separation of H_2 and D_2 occurred when applying Cu-mesoporous silica. Thus, the modification of mesoporous silica with Cu tailors the CAQS effect.

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