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Hydrogen Isotope Separation via Liquid Phase Catalytic Exchange using Composite with Platinum Modified Mesoporous Silica and Hydrophobic Polymer

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1. Introduction

Tritium is a radioactive isotope of hydrogen with a half-life of 12.3 years and emits beta ray. In heavy-water reactors, neutron capture results in the formation of tritiated water (HTO, DTO, and T_2O). Since they have physicochemical properties similar to natural water, the separation is extremely difficult. In South Korea, the Wolsong Nuclear Power Plant manages tritiated water through the Wolsong Tritium Removal Facility, which utilizes combination of liquid phase catalytic exchange (LPCE) and cryogenic distillation. While cryogenic distillation is effective for final purification, LPCE serves as the primary separation process, transferring tritium in liquid to gas phase. Also, it plays a crucial role in overall efficiency. Thus, optimizing LPCE performance is necessary for improving overall separation efficiency, reducing operational costs, and ensuring a more reliable tritium removal system [1].

In this study, a composite catalyst was developed by incorporating platinum (Pt) into mesoporous silica, which provides a high surface area and well-structured pores that facilitate catalytic reactions. On the other hand, polydimethylsiloxane (PDMS) was introduced to form supportive framework and tailor hydrophobicity, thereby building a composite for continuous operation. The synthesized catalyst was tested under various operational conditions to evaluate its potential application in tritium separation.

2. Methods and Results

2.1. Materials

The following chemicals and gases were used as received without further purification. Tetraethyl orthosilicate (TEOS, 98 %), cetyltrimethylammonium bromide (CTAB, > 98 %), ethanol (EtOH, 99.99 %) and ammonium hydroxide solution (NH_4OH, 28.0~30.0 wt%), were purchased from Sigma-Aldrich. Tetraammineplatinum(II) nitrate ($Pt(NH_3)_4(NO_3)_2$) was purchased from Alfa Aesar. PDMS (Sylgard® 184), including a silicone elastomer base and a curing agent, was purchased from Dow Corning. Deionized (DI) water was supplied from Direct-Q® 3 water purification system with resistivity of 18.2 MΩ cm at 298 K. The stainless steel Dixon ring (KT-DR, KAITE) with 3 mm of diameter and 3 mm of height for distillation column packing was also purchased. Hydrogen (H_2, 99.999 %) and nitrogen gas (N_2, 99.999 %) were purchased from Daesung Industrial Gases Co., Ltd. Air (78 % of N_2, 21 % of O_2 and ~0.9 % of trace amounts of other gases) was purchased from Joongang Industrial Gases Co., Ltd., and argon gas (Ar, 99.999 %) was obtained from Sejong Industrial Gases Co., Ltd.

2.2. Catalyst preparation

Mesoporous silica was prepared according to a previously reported method [2]. CTAB (2.4 g) was dissolved in the equivolume mixture of DI water (50 mL) and ethanol (50 mL). After 10 min of fierce stirring, NH_4OH (12 mL) was added. Subsequently, TEOS (3.4 g) was drop-wisely dispersed into the solution mixture. The mixed solution was additionally stirred for another 2 h until it converted as gel. The molar composition of the final gel is TEOS: 0.43 CTAB: 12.5 NH_3: 54.3 EtOH: 416 H_2O. The resulting gel was washed with DI water for 5 times, and solid/liquid was separated by centrifugation at each cycle. Then, the resulting solid was dried in the oven at 65 ˚C overnight. The CTAB template, pore directing agent, was removed by calcination at 550 ˚C with a heating rate of 1˚C min^{-1} for 6 h under stagnant air conditions in the furnace.

To impregnate Pt onto the silica framework, 0.5223 g of $Pt(NH_3)_4(NO_3)_2$ was thoroughly mixed with 5.0 g of prepared mesoporous silica, resulting a 5 wt% Pt loading. Subsequently, 9.6 mL of DI water, corresponding to 1.2 times the pore volume of mesoporous silica (measured by N_2 physisorption), was slowly and drop wisely added to the mixture while continuous mixing with spatula to ensure homogeneous dispersion. Then, $Pt(NH_3)_4(NO_3)_2$ infiltrated into the surface and pores of mesoporous silica while drying. The dried sample was calcined under an air flow at 400 ˚C with a heating rate of 2 ˚C min^{-1} for 6 h, decomposing the Pt precursor ligands and forming Pt oxide, which was stably incorporated onto the silica surface and pores. Following calcination, the sample was purged with an Ar gas for 30 min to remove residual air and volatile impurities. Afterward, it was reduced by H_2 at the same heating rate and temperature, which converted Pt oxide into metallic Pt and integrated it uniformly into the mesoporous silica. The final powder was denoted as Pt@SiO_2.

Silicone elastomer base and curing agent were mixed with a weight ratio of 5:2 until a uniform mixture was obtained. Then, 1.0 g of Pt@SiO_2 was added in the 4 g of PDMS mixture and mixed for 10 min to ensure evenly distributed mixture. The mixture was degassed under 1.3 kPa at room temperature for 10 min to eliminate air bubbles causing cracks and pinholes of final catalyst. After degassing, the mixture was poured into a lattice mold without overflow, composed of multiple trapezoidal prisms with dimensions of 2.1 mm of top base, 3.6 mm of bottom base, and 1.2 mm of height. After curing at 60 ˚C for 4 h, the composite was carefully recovered from the mold. The resulting composite, denoted as Pt@SiO_2-PDMS composite, was composed of 1 wt% Pt. Additionally, pristine PDMS and Pt free mesoporous silica incorporated PDMS were also fabricated respectively for comparison. Each product is denoted as PDMS and SiO_2-PDMS composites.

2.3. Characterization of Pt@SiO₂

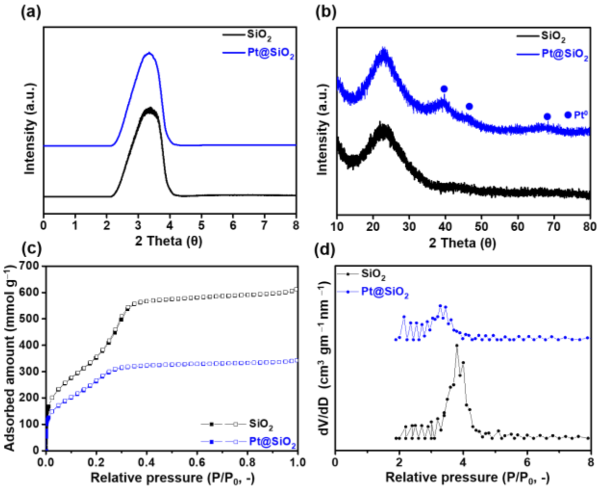

Fig. 1. The (a) low- and (b) high-angle XRD patterns of SiO_2 and Pt@SiO_2, (c) N_2 physisorption isotherms for SiO_2 and Pt@SiO_2 at 77 K (filled square: adsorption; open square: desorption), and (d) pore size distributions for SiO_2 and Pt@SiO_2.

Table I: Textural property of SiO_2 and Pt@SiO_2.

	Pore volume (cm^3 g^{-1})	**BET surface area (m^2 g^{-1})**
SiO_2	0.80	1800
Pt@SiO_2	0.53	710

The X-ray diffraction (XRD) patterns of the samples were measured using a D2 PHASER (Bruker) from 0 to 10 ˚ (low angle) and 20 to 80 ˚ (high angle) using a Cu-K-alpha radiation source. Fig. 1a shows both samples exhibit a low-angle diffraction peak at $2\theta = 3.3$ ˚ (211), indicating the retention of an ordered mesoporous structure after Pt incorporation. In Fig. 1b, a broad diffraction peak at $2\theta = 21–23$ ˚ confirms the amorphous phase of silica, while Pt@SiO_2 shows additional peaks at $2\theta = 39.8$ (111), 46.3 (200) and 67.8 ˚ (220), corresponding to metallic Pt.

The N_2 physisorption isotherms were measured at 77 K using an Autosorb iQ-XR Viton (Quantachrome). Before measurement, the samples were degassed overnight at 423 K under vacuum to remove the pre-adsorbed gases, moisture and other impurities. The N_2 physisorption isotherms were analyzed to specify the pore volume, multipoint surface area and pore size distribution (PSD) of the samples. The multipoint surface area was determined by the Brunauer-Emmett-Teller (BET) method and the PSD was determined by Broekhoff-de Boer/Frenkel-Halsey-Hill (BdB-FHH) method. Fig. 1c shows that the adsorbed amount decreased from 612 to 342 mmol g^{-1} after Pt incorporation, while both samples followed Type IV isotherms indicating mesoporous material. Fig. 1d indicates that the average pore size slightly decreased from 4.0 to 3.8 nm. Table I shows that the BET surface area and pore volume decreased from 1800 to 710 m^2 g^{-1} and from 0.80 to 0.53 cm^3 g^{-1}, respectively. These results suggest that Pt incorporation partially blocked or reduced pore accessibility, leading to a decrease in quantity adsorbed, surface area, and pore volume, while the mesoporous structure maintains.

2.4. Characterization of fabricated Pt@SiO₂-PDMS composites

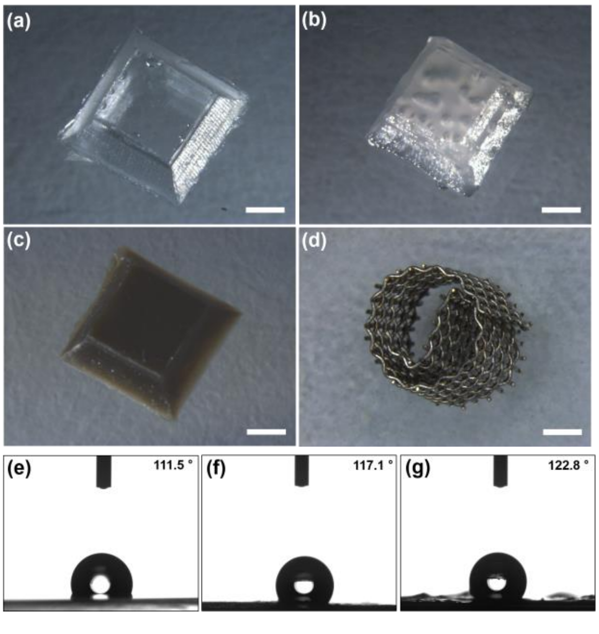

Fig. 2. The OM images of (a) PDMS, (b) SiO_2-PDMS, (c) Pt@SiO_2-PDMS composites and (d) Dixon ring (scale bar = 1 mm). The water contact angle of (e) PDMS, (f) SiO_2-PDMS, (g) Pt@SiO_2-PDMS composites.

The morphology of the fabricated PDMS, SiO_2-PDMS and Pt@SiO_2-PDMS composites and Dixon ring were observed using an optical microscope (OM, LEICA). Fig. 2a shows that PDMS exhibited a smooth surface with high transparency. In contrast, Fig. 2b shows that SiO_2-PDMS is opaque due to the uniform dispersion of white SiO_2 powder, while Fig. 2c shows that Pt@SiO_2-PDMS exhibited a dark brown color due to Pt incorporation. Fig. 2d shows the stainless steel mesh structure of the Dixon ring.

The wettability of the fabricated composites was evaluated by measuring the water contact angle using a Cam 200 (KV Instruments). Fig. 2e, Fig. 2f, and Fig. 2g show that PDMS, SiO_2-PDMS, and Pt@SiO_2-PDMS exhibited contact angles of 111.5 °, 117.1 °, and 122.8 °, respectively. Pt@SiO_2-PDMS exhibits the highest among the prepared composites which demonstrates enhanced hydrophobicity. This indicates that Pt@SiO_2-PDMS possessed stable hydrophobicity, which can prevent water adsorption, tailors deactivation of catalyst, on the surface.

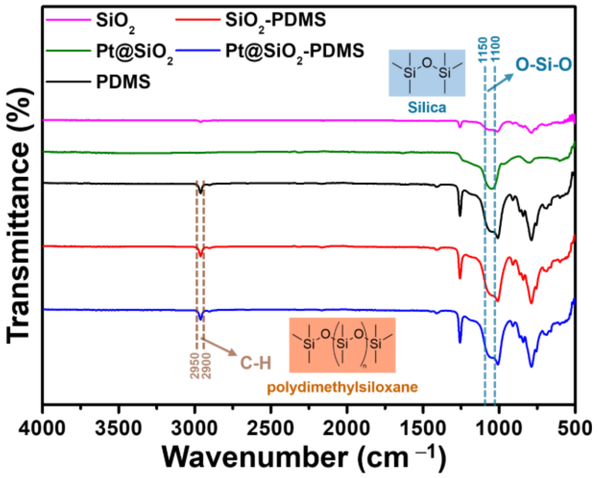

Fig. 3. FT-IR/ATR spectra of SiO_2 powder, Pt@SiO_2 powder, PDMS, SiO_2-PDMS and Pt@SiO_2-PDMS composites.

The Fourier transform-infrared/attenuated total reflectance (FT-IR/ATR) spectra of the samples were measured using a Nicolet iS5 (Thermo Fisher Scientific). The spectra were recorded in the range of 4000–400 cm^{-1} . Fig. 3 shows that the Si–O–Si stretching vibration appeared at 1100–1150 cm^{-1} in mesoporous silica and Pt@SiO_2, with increased intensity and a slight shift after Pt incorporation. PDMS exhibited C–H stretching vibrations at 2900–2960 cm^{-1}, which also appeared in SiO_2-PDMS and Pt@SiO_2-PDMS composites, confirming the retention of the organic chain structure. The spectra of Pt@SiO_2-PDMS shows distinct Si–O–Si and C–H stretching peaks, indicating that both SiO_2 and PDMS structures were preserved in the composite.

2.5. Liquid phase catalytic exchange performance

The LPCE performance of Pt@SiO_2-PDMS composite was evaluated in a catalytic reactor. The flow rates of H_2(g) and DI water are 0.365 SLPM and 0.3 mL min^{-1}, respectively, which stands for a gas-liquid molar ratio of 1:1. Column efficiency was calculated based on the mass balance of the measured liquid products [3]. The liquid sample is obtained for 180 min at every 15 min, and D concentration in the liquid samples was determined with a cavity ring-down spectroscopy using the L2140-i (PICARRO).

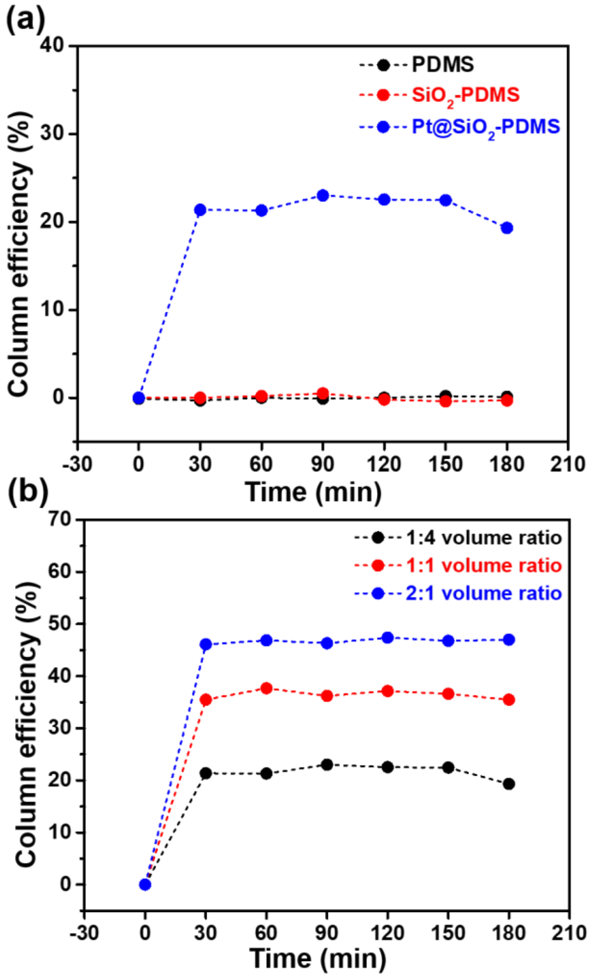

Fig. 4. (a) Column efficiency of PDMS, SiO_2-PDMS and Pt@SiO_2-PDMS composites, randomly packed in a 1:4 volume ratio with Dixon ring, and (b) column efficiency of the Pt@SiO_2-PDMS composite randomly packed at volume ratios of 1:4, 1:1, and 2:1 with Dixon ring.

Fig. 4a shows that PDMS and SiO_2-PDMS exhibited negligible column efficiency, whereas Pt@SiO_2-PDMS reached 23.0 % at 90 min and maintained over 20 % up to 180 min. Fig. 4b shows that increasing the Pt@SiO_2-PDMS over Dixon ring ratio improved efficiency. 2:1 ratio shows the highest value of

47.4 % at 120 min and stably maintains the value. These results indicate that a higher catalyst ratio enhances isotope exchange efficiency by increasing the available Pt surface participating in $H_2O(l)$ and $H_2(g)$ exchange reaction.

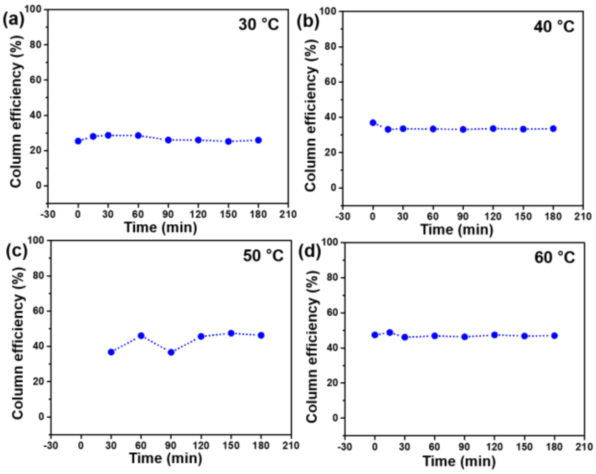

Fig. 5. Column efficiency of the Pt@SiO_2-PDMS composite randomly packed at a volume ratio of 2:1 with Dixon rings at temperatures of (a) 30, (b) 40, (c) 50 and (d) 60 ˚C.

Fig. 5 shows that column efficiency in diverse temperature. The efficiency reaches 28.7 % at 30 ˚C, 36.9 % at 40 ˚C, 46.0 % at 50 ˚C and 48.8 % at 60 ˚C, remaining stable for 180 min. This trend suggests that higher temperature further enhances isotope exchange efficiency, likely due to increased reaction kinetics.

3. Conclusions

We have successfully synthesized Pt-modified mesoporous silica and characterized its physicochemical properties using multiple techniques. The Pt@SiO_2 was then incorporated into PDMS to form a hydrophobic composite, thereby the hydrogen isotope separation performance was evaluated by LPCE. Column experiments confirmed its catalytic activity as well as the increased catalyst loading further enhances separation efficiency. In addition, column efficiency improved as the temperature increased, demonstrating that Pt@SiO_2-PDMS is promising for tritium separation applications.

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