Joint adsorption of light hydrogen by CuO and 5A molecular sieves

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Abstract. H₂ is the primary cause of the deteriorating vacuum degree of high-vacuum multilayer insulation tank (HVMLIT). At present, the precious metal PdO is used to adsorb H₂ and maintain the high vacuum of HVMLIT. In this study, CA, a compound hydrogen adsorbent integrated with the cheap metal CuO and 5A molecular sieves, is adopted to jointly adsorb light hydrogen in HVMLIT. This work also investigates the adsorption characteristics and mechanisms of CA.

1. Introduction

With developments in science, technology, and industry, the demands for cryogenic liquid have increased for high-vacuum multilayer insulation tank (HVMLIT) [1]. The cold state vacuum degree of HVMLIT should exceed 10⁻² Pa to ensure excellent heat insulation [2]. According to domestic and foreign research, the inevitable leakage and outgassing decrease the vacuum degree of HVMLIT; the content of H₂ gas in the tank is as high as 60%–75%, which cannot be adsorbed by a conventional adsorbent at liquid nitrogen temperature and above [3, 4]. Therefore, the high vacuum in HVMLIT must be maintained by adding PdO to adsorb H₂. However, PdO exhibits small absorption quantity of unit mass and unfavorable economic efficiency because its price is influenced by the international market of precious metals [5-7]. In this regard, scholars have focused on searching materials that can replace PdO.

To our knowledge, CuO is widely used as catalyst and catalyst carrier in chemical reactions with H₂ as reactant or product [8-11]. However, no report has been presented on the adsorption of light hydrogen by CuO. CA, a compound hydrogen adsorbent integrated with the cheap metal CuO and 5A molecular sieves, is adopted to jointly adsorb light hydrogen in HVMLIT. The absorption property and laws of CA are investigated.

2. Experiment

2.1. Experimental setup

As shown in figure. 1, the experimental setup is mainly composed of the following parts.

1) Vacuum system: Buffer pipe, buffer tank, and test tank were evacuated by vacuum pumps.

2) Measurement and collection system: ZDF-5227 compound vacuum gauges equipped with resistance and ionization gauges were used to measure the pressure of buffer pipe, buffer tank, and test tank. The temperature was measured by Omega type T thermocouple, which extended into a chamber
through an aviation plug and was collected with Keithley2700. The pressure and temperature data were recorded via a computer.

3) Air supply system: He and H2 tanks supplied high-purity gases for the experiments.

4) Tank system: The volumes of the getter container, buffer pipe, and buffer tank were 0.12, 1.28 and 48.63 L, respectively. The chamber volume was 64.37 L with a residual volume of 56.44 L (chamber volume minus the volume of 5A and multilayer insulation materials). The actual test volume was 56.56L (residual volume plus getter container volume). All the volumes were accurately calibrated with the inert gaseous He.

![Figure 1 Experimental apparatus of H2 adsorption](image)

1, 3, 5. Resistance gauges. 2, 4, 6. Ionization gauges. 7. Aviation plug. 8, 9, 10, 11, 12, 13, 14, 15, 16. High-vacuum flap valves. 17, 18. Vacuum pumps. 19. He tank. 20. H2 tank. 21. Buffer pipe. 22. Buffer tank. 23. Test tank. 24. Multilayer insulation material. 25. Molecular sieve 5A. 26. Getter container. 27. Getter temperature controller. 28. Vacuum gauge. 29. Data acquisition instrument. 30. Computer.

2.2. Experimental steps
First, 1.0 kg of 5A was fixed at the bottom of the outer surface of the inner tank, the multilayer insulation material was wrapped on the outside, and the getter container was inserted into the system. Second, liner heating was performed, and interlayer heat N2 displacement evacuation was used to evacuate the experimental tank until the interlayer vacuum degree was better than 1×10^{-2} Pa. Third, H2 displacement process was used to evacuate buffer pipe and buffer tank, until the vacuum degree was better than 1×10^{-5} Pa. Finally, the valve of the getter container was closed, and appropriate amount of H2 was charged into the interlayer of the experimental tank through two-level buffer (i.e., buffer pipe and buffer tank). The valve of the getter container was opened after 1 h of standing. The interlayer vacuum degree, interlayer temperature, and ambient temperature were recorded at about 1 h before adsorption equilibrium. After the equilibrium, appropriate amount of H2 was charged into the interlayer of the experimental tank, until the adsorption isotherm was obtained.

2.3. Experimental samples and arrangements
Commercial CuO was obtained from Sinopharm Chemical Reagent Shanghai Co., Ltd. CuO has an average particle size of 200 μm and a purity of 99.9%. The inert gaseous He and active gaseous H2 were purchased from Wujiang Messer Industrial Gas Co., Ltd. (purity≥99.999%, which satisfies the standard of GB/T7445-1999). The experimental plan is shown in table 1.
Table 1 Information of the experiments

| Getter Code | Getters In Getter Containera | Adsorbent In Chamberb | Getter Temperature (°C) | Initial H₂ Pressure (Pa) |
|-------------|-------------------------------|-----------------------|-------------------------|-------------------------|
| CA          | 5g CuO 1000g 5A              | 60-260                | 50                      |
| CA          | 5g CuO 1000g 5A              | 220                   | 50-900                  |
| CA          | 5g CuO 1000g 5A              | 240                   | 50-900                  |
| CA          | 5g CuO 1000g 5A              | 260                   | 50–900                  |

a CA consists of 5 g of CuO located in the getter container, and 1.0 kg of 5A located at the bottom of the outer wall of the inner tank.

3. Results and discussion

3.1. Effect of AST on the H₂ getter

At adsorption temperature (AST) < 200 °C, CA does not adsorb hydrogen; the adsorption quantity is negative due to leakage and outgassing of HVMLIT. At ASTM= 200 °C, the CA adsorption quantity curve is horizontal, and H₂ is weakly adsorbed. At AST ≥ 220 °C, CA rapidly adsorbs H₂ (figure 2). Hence, the activation temperature of CA is 200 °C. With increasing AST, the CA adsorption rate is improved, the equilibrium adsorption ability is reduced, and the equilibrium pressure is increased by two orders of magnitudes (table 2). These findings indicate that AST affects the adsorption mechanism of CA.

Table 2 Adsorption characteristic values of different AST

| AST(°C) | 220  | 240  | 260  |
|---------|------|------|------|
| SA-1h(%)a | 56.65 | 78.34 | 86.11 |
| SA-E(%)b   | 99.92 | 92.20 | 88.37 |
| SEP(Pa)c   | 4.83×10⁻² | 3.96  | 5.84  |
| SEt(h)d    | 6     | 5     | 3     |
| SMr(mL(stp)/g/h)e | 0.383 | 0.497 | 0.533 |
| SMr(t)h    | 1     | 1     | 1     |
| SA Vr(mL(stp)/g/h)g | 0.113 | 0.125 | 0.197 |

a Sorption ratio of sorption amount at 1h to initial H₂ amount, %; b Sorption ratio of sorption amount at equilibrium to initial H₂ amount, %; c Sorption equilibrium pressure, Pa; d Sorption equilibrium time, h; e Maximum sorption rate, mL(stp)/g/h; f Time of maximum sorption rate; g Average sorption rate, mL(stp)/g/h

3.2. Adsorption performance of CA

The Langmuir [12], Freundlich [13], Temkin [14], and Redlich–Peterson [15] models are applied to calculate the adsorption isotherm of CA at 220 °C, 240 °C, and 260 °C. Experimental data are compared (figure 3(a)-(c)). CA chemically adsors H₂ and physically adsorbs H₂O. At 220 °C, CA mainly absorbs H₂ in a chemical way, as evident in the adsorption isotherm of Category I in accordance with
Langmuir adsorption mode (figure 3(a’)). At 240 °C and 260 °C, CA mainly adsorbs H₂O in a physical way with increasing adsorption difficulty, as shown in the adsorption isotherm of Category II in accordance with the Freundlich adsorption model (figure 3(b’)-3(c’)).

At 220 °C, in the CA adsorption isotherm (1), the Langmuir adsorption coefficient and the saturated adsorption quantity are $K_L = 9.678$ and $\alpha_m = 67.981 \text{ mL/(stp)g}$, respectively.

$$\alpha = \frac{657.895 Pe}{1 + 9.678 Pe} \quad (10^{-2} \text{ Pa} \leq Pe \leq 5.0 \text{ Pa})$$

At 240 °C, in the CA adsorption isotherm (2), the Freundlich adsorption coefficient and constant are $K_L = 4.781 \times 10^{-3}$ and $1/n = 3.535$, respectively.

$$\alpha = 4.781 \times 10^{-3} Pe^{3.535} \quad (3.0 \text{ Pa} \leq Pe \leq 15.0 \text{ Pa})$$

At 260 °C, in the CA adsorption isotherm (3), the Freundlich adsorption coefficient and constant are $K_L = 6.006 \times 10^{-4}$ and $1/n = 4.032$, respectively.

$$\alpha = 6.006 \times 10^{-4} Pe^{4.032} \quad (5.0 \text{ Pa} \leq Pe \leq 16.0 \text{ Pa})$$

The cold-state vacuum degree should exceed $10^{-2}$ Pa to maintain the heat insulation property of HVMLIT. The vacuum degree is increased by two to three orders of magnitudes due to the influences of the low temperature adsorbent and the temperature after the filling of cryogenic liquid into the hot-state HVMLIT [16]. Therefore, the hot-state equilibrium pressure in the HVMLIT should be lower than 5.0 Pa. At 220 °C, the Langmuir saturated extent of the adsorption of CA is 24.28% of the calculated chemical adsorption quantity. At 240 °C and 260 °C, the Freundlich constant of CA increases with increasing difficulty in the hydrogen adsorption of CA.

Favorable adsorption occurs when the equilibrium state does not deteriorate with increasing adsorption quantity (figure 4(a)-4(b)). At 220 °C, the favorable adsorption quantity at equilibrium time of CA is 10.0%, similar to those at 240 °C and 260 °C. At 220 °C, the favorable adsorption quantity at the equilibrium pressure is 15.0%, and the average equilibrium pressure is $4.52 \times 10^{-2}$ Pa. No favorable adsorption quantity at the equilibrium pressure is observed at 240 °C and 260 °C. With increasing AST, the equilibrium time decreases and the equilibrium pressure is improved by two to three orders of magnitude. CA is applicable to HVMLIT at 220 °C but not at 240 °C and 260 °C due to extremely high equilibrium pressure.
3.3. Adsorption mechanisms of CA

The hydrogen adsorption reaction of CA involves two steps, i.e., the translation of H₂ into H₂O and the adsorption of H₂O by 5A [Equations (4) and (5), respectively], to maintain the high vacuum in HVMLIT. At 220 °C, the adsorption rate of hydrogen by CA is equivalent to the generation rate of H₂O; the rate should not be higher than the total diffusion rate of H₂O to the interlayer of HVMLIT, the penetration rate of the multi-layer insulating materials, and the adsorption rate by 5A. CA exhibits a relatively high equilibrium vacuum degree at 220 °C. At 240 °C and 260 °C, H₂O leads to increased adsorption pressure by two orders of magnitudes. The obtained pressure is more than the required vacuum degree for HVMLIT.

\[
H_2(g) \xrightarrow{\text{Heat}} H_2O(g) \quad (4)
\]

\[
H_2O(g) + 5A \xrightarrow{\text{Physisorption}} 5A(H_2O) \quad (5)
\]

At 240 °C and 260 °C, CA exhibits the same adsorption mechanism. Therefore, the gas composition and content at the equilibrium state is analyzed only at 260 °C (figure 5(a)). The gas components are H₂O and H₂, which occupy 63.54% and 19.41% of the total quantity of gas, respectively; N₂ and O₂, which occupy 9.85% and 2.13%, respectively; and carbon gas and other gases, which occupy 3.16% and 2.92%, respectively. Therefore, H₂O is the main gas after CA adsorption equilibrium, and H₂O diffusion rate is the main factor that influences the equilibrium vacuum degree and the adsorption quantity. The existence of H₂O restrains the reaction of CuO and H₂, leading to the formation of excessive H₂ residual. Improving the resistance of H₂O diffusion is the major orientation for CA modification.

4. Conclusion
The adsorption of H\textsubscript{2} by CA is in accordance with pseudo-first-equation, and the activation energy of adsorption is 37.0 kJ/mol. The optimal AST for the adsorption of H\textsubscript{2} by CA is 220 °C, and the favorable adsorption quantity at equilibrium vacuum degree higher than 4.52×10\textsuperscript{-2} Pa is 42.0mL(spp)/g. The adsorption isotherm belongs to Category I and is in accordance with the Langmuir adsorption model. At 240 °C and 260 °C, no favorable adsorption quantity is obtained at the equilibrium pressure of CA. The adsorption isotherm belongs to Category II and is in accordance with the Freundlich adsorption model. H\textsubscript{2}O is the main gas after the adsorption equilibrium of CA. The diffusion rate of H\textsubscript{2}O is the main factor that influences the increment in the equilibrium vacuum degree and the adsorption quantity. Improvement in the resistance of H\textsubscript{2}O diffusion is the orientation for CA modification.

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