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Hydrogen isotope separation in hydrophobic catalysts between hydrogen and liquid water

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ABSTRACT

Hydrogen isotope catalytic exchange between hydrogen and liquid water is a very effective process for deuterium-depleted potable water production and heavy water detritiation. To improve the characteristics of hydrophobic catalysts for this type of reaction, foamed and cellular structures of hydrophobic carbon-supported platinum catalysts were successfully prepared. Separation of deuterium or tritium from liquid water was carried out by liquid-phase catalytic exchange. At a gas–liquid ratio of 1.53 and exchange temperature of 70 °C, the theoretical plate height of the hydrophobic catalyst (HETP = 34.2 cm) was slightly lower than previously reported values. Changing the concentration of the exchange column outlet water yielded nonlinear changes in the height of the packing layer. Configurations of deuterium-depleted potable water and detritiation of heavy water provide references for practical applications.

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1. Introduction

Hydrogen isotope catalytic exchange between hydrogen and liquid water (LPCE) presents better operational safety and lower energy consumption for hydrogen isotope separation than conventional vapor-phase catalytic exchange [1,2]. As such, hydrogen isotope catalytic exchange has gained increased research interest for its applicability in deuterium-depleted potable water production and heavy water detritiation. This process was previously developed by Atomic Energy of Canada, Limited (AECL) for different hydrogen isotope applications [3]. A laboratory-scale LPCE system was built and operated at Chalk River Nuclear Laboratories (CRNL) and other countries [4–6]. Afterward, Romania and Korea also independently developed similar processes based on a trickle-bed reactor packed with a hydrophobic catalyst [7–10]. LPCE columns with various structures have been fabricated. However, the designs of these exchange columns have not been reported.

In an exchange column, the overall transfer of Q (deuterium or tritium) between streams of hydrogen and liquid water over hydrophobic catalysts occurs through two consecutive steps. The first reaction involves transfer from liquid water to vapor, while the second reaction involves catalytic transfer of Q from water vapor to hydrogen stream, as shown in Eqs. (1) and (2):

$$\mathrm{HQO_{(liquid)}} + \mathrm{H_2O_{(vapor)}} \rightleftarrows \mathrm{HQO_{(vapor)}} + \mathrm{H_2O_{(liquid)}} \qquad (1)$$

$$\mathrm{HQO_{(vapor)}} + \mathrm{H_{2(gas)}} \rightleftarrows \mathrm{HQ_{(gas)}} + \mathrm{H_2O_{(vapor)}} \qquad (2)$$

The catalytic reaction (2) occurs on active catalyst sites, whereas the vapor liquid transfer reaction (1) mainly occurs on a hydrophilic packing interface [11]. Thus, an advantage of trickle-bed-type reactors is that the structure of the column is quite simple: hydrophobic catalysts and hydrophilic packings are packed within the column. Two types of hydrophobic catalysts, namely, Pt/C/polytetrafluoroethene (Pt/C/PTFE) and Pt/styrene divinylbenzene copolymer (Pt/SDB), have been used to achieve isotopic exchange between hydrogen and liquid water [12–15,11]. PTFE, which exhibits a high contact angle with water, is a high-performance hydrophobic agent; Pt is a highly active and efficient catalytic metal used in isotope exchange reactions between hydrogen and water [16,17]. Because Pt/C/PTFE presents high strength, good chemical stability, and strong activity, the catalyst is extensively used in exchange reactions. To ensure that the second reaction does not become reaction-rate limiting, the catalyst bed is mixed with hydrophilic packing to increase the gas–liquid interfacial area.

In the present work, hydrogen and liquid water were countercurrently passed through a packed column. Different column heights resulted in changes in the concentrations of the exchange column outlet water or gas. Exchange reactions at the top or bottom of the exchange column can also achieve equilibrium at a certain column height. Therefore, high exchange columns do not have to

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be built. This study examines the hydrogen isotope exchange reaction in a modified hydrophobic catalyst with various designs of the catalytic column to achieve different LPCE processes. The configurations of deuterium-depleted potable water and heavy water detritiation discussed in this work provide useful references for practical applications.

2. Experiments

2.1. Catalyst preparation

To prepare the catalyst, Pt was deposited onto carbon substrates by impregnation and in situ liquid-phase reduction as described in a previous work [18]. Carbon black XC72R ($S_{BET} = 230\,m^2\,g^{-1}$, Cabot Corp.) was used as an active metal dispersant, and hexahydrated chloroplatinic acid ($H_2PtCl_6{\cdot}6H_2O$) was used as the catalyst precursor. Carbon powder (1000 mg of XC72R) was ultrasonically dispersed in 180 mL of a mixture of ethylene glycol and deionized water. A water solution of the Pt precursor was then added to the suspension under constant stirring, and the solution pH was adjusted to 9 using 1 mol L^{-1} aqueous NaOH solution. The synthesis reaction was performed at 80 °C for 4 h with formaldehyde as the reducing agent. After cooling to ambient temperature, the catalyst powder was filtered, washed, and freeze-dried, thereby yielding a Pt/C catalyst with 10 wt.% Pt. The Pt nanoparticles were homogeneously dispersed in carbon black and showed a narrow particle size distribution.

The hydrophobic catalyst was composed of Pt/C/PTFE in the form of small rings (approximately 2 mm × 2 mm). A fiber blanket made of stainless steel was used as an inert carrier for the hydrophobic catalyst. PTFE was used to bind the carbon-supported catalyst and carrier, thereby generating a hydrophobic Pt/C catalyst. Polymethyl methacrylate (PMMA) was used to modify the hydrophobic membrane microstructure. Details of this preparation process are reported elsewhere [18]. The Pt contents of all of the hydrophobic catalysts were similar value.

2.2. Liquid-phase catalyst exchange

The experimental apparatus for hydrogen isotope exchange included a deuterated water source, a hydrogen gas source, and an exchange column (Fig. 1). The catalyst exchange column was a Pyrex glass tube with an internal diameter of 25 mm and length of 1200 mm and equipped with a water jacket. Thermostatically controlled water (70 °C) was passed through the jacket. Hydrophobic catalysts and hydrophilic packing of Dixon stainless steel gauze rings (approximately 2 mm × 2 mm) were mixed homogeneously in the exchange column. The filling volume ratio of catalyst to packing was approximately 1:3. The experiment filling heights were 200 mm, 450 mm, 700 mm, and 1000 mm, respectively. Deuterated water [D/(D + H) = 0.5%, at.%] and high-purity natural hydrogen were passed through the column counter-currently. The feed flow values of hydrogen and liquid water were 2 L(STP) min^{-1} (G) and 1.05 mL min^{-1} (L), respectively.

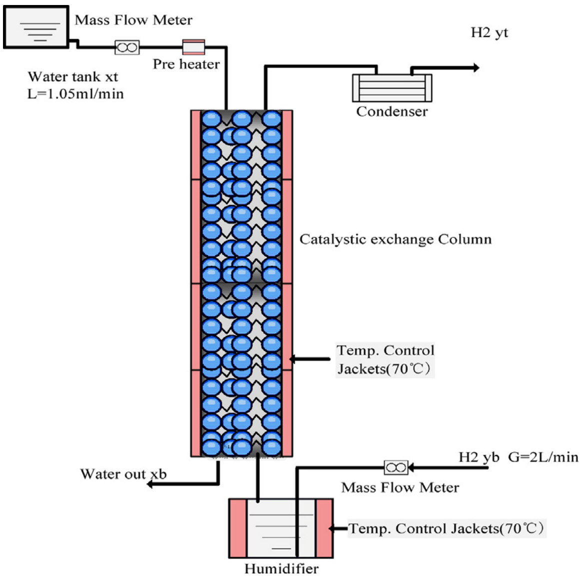

Fig. 1. Schematic of the experimental setup.

3. Results and discussion

3.1. Calculation of the exchange column height

At small packing heights dZ (m), the deuterium or tritium exchange rate per unit column area can be expressed as follows:

$$-Vdy = K_y a(y - y^*)SdZ \tag{3}$$

where V is the hydrogen gas flow rate ($m^3\,s^{-1}$), S is the cross-sectional area of the column (m^2), $K_y a$ is the overall exchange rate constant ($m^3\,s^{-1}\,m^{-3}$), y is the fraction of hydrogen isotope in the hydrogen gas, and y^* is the isotope equilibrium concentration in the hydrogen gas.

To integrate Eq. (3) over the exchange column, the height of the catalytic column, Z, can be written as:

$$Z = \frac{V/S}{K_y a}\int_b^t \frac{dy}{y - y^*} \tag{4}$$

The number of transfer units (NTUs) and height of a transfer unit (HTU) are defined as

$$NTU = \int_b^t \frac{dy}{y - y^*} = \frac{y_b - y_t}{(y_b - y_b^*) - (y_t - y_t^*)} \cdot \ln\frac{(y_b - y_b^*)}{(y_t - y_t^*)} \tag{5}$$

$$HTU = \frac{V/S}{K_y a} \tag{6}$$

Therefore, Eq. (4) is simplified to:

$$Z = NTU \cdot HTU \tag{7}$$

HTU can be estimated using Eqs. (5) and (7) from the experimental data obtained under specific working conditions in the exchange column with a given height of catalyst packing Z. Therefore, when the exchange result obtained under the same parameters is used to determine the required separation efficiency, the height of the exchange column, Z, can be calculated using the same equations.

3.2. Performance of the hydrophobic catalyst

Both the equilibrium and operating lines are linear over a range of low hydrogen isotope concentrations. The properties of hydrogen isotope catalytic exchange between hydrogen and liquid water are characterized in Table 1.

The foamed and cellular structures of the hydrophobic catalyst resulting from PMMA addition decreased internal diffusion and improved active site utilization [18]. Under similar operating conditions, the HETP value obtained in the present work was slightly lower than previously reported values in different countries [19]. Thus, the experimental results indicate that the catalysts exhibit excellent hydrogen isotope separation performance.

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