

Hydrophobic Catalyst Mixture for the Isotopic Exchange Reaction between Hydrogen and Water

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SUMMARY

Pt/SDBC catalyst, which is used for the hydrogen-water isotopic exchange reaction, was prepared. The various properties of the catalyst, such as the thermal stability, pore structure and the platinum dispersion, were investigated. A hydrophobic Pt/SDBC catalyst which has been developed for the LPCE column of the WTRF (Wolsong Tritium Removal Facility) was tested in a trickle bed reactor. An experimental apparatus was built for the test of the catalyst at various temperatures and gas velocities.

INTRODUCTION

The isotopic exchange reaction between hydrogen and water on platinum supported catalysts provides a useful step for separating the hydrogen isotopes such as deuterium and tritium[1,2]. Although platinum supported catalysts on various oxides are well known as active catalysts for this process, they come to lose their activity gradually, presumably owing to the condensed water in the capillary[3]. Therefore, the development of suitable wet-proofing catalysts is essential for a satisfactory reaction process. SDBC (Styrene Divinyl Benzene Copolymer) was of particular interest since it has a negligible water adsorptivity and practically no capability for activating the water molecule and a platinum catalyst supported on SDBC presents a high activity even with a gas saturated with water vapor[4]. Pt/ SDBC catalyst has been developed in Korea for the LPCE(Liquid Phase Catalytic Exchange) column of the WTRF (Wolsong Tritium Removal Facility). The WTRF project is now on-going at KHNP with the completion

date of June, 2006. This facility is designed to use the liquid-phase separated-bed catalytic exchange process for the removal of tritium from heavy water. However, the authors have selected the CECE (Combined Electrolysis Catalytic Exchange) process for a small type tritium removal plant from different sources of tritiated water. The CECE process with a hydrophobic catalyst is ideally suited for extracting tritium from water because of its high separation factor and mild operating conditions. The CECE column is composed of an electrolysis cell and a liquid phase catalytic exchange column. Liquid phase catalytic exchange columns with various structures were developed. The multistage type provided better results than the trickle-bed type. However, the structure of the column is complicated. The trickle-bed type has a significant advantage in that the structure of the column is quite simple: the hydrophobic catalysts or the catalysts and packings are packed within the column. This structure would lead to a smaller column height than the multistage type [5].

This study shows how to prepare the Pt/SDBC catalysts and the various properties of the catalyst. Furthermore, this paper deals with an experiment for the hydrogen isotope exchange reaction in a trickle-bed reactor packed with the mixture of a hydrophobic catalyst and hydrophilic packing.

EXPERIMENTAL

Several types of macroporous styrene-divinyl-benzene copolymer (SDBC) were synthesized and selected as support materials. These materials were prepared by the general procedures published papers [6,7]. SDBC was synthesized to obtain a porous structure. Toluene was used as a good solvent, and 2-ethyl-1-hexanol as a poor solvent. The specific surface area and the pore volume could be controlled by the ratio of the monomer to the solvent[8]. This polymer support has a form of a cylindrical pellet (4 mm dia. ; 4mm height)

The platinum precursor solution was made by dissolving hexachloroplatinic acid (H_2PtCl_6) in ethanol. The Pt/SDBC catalysts were prepared by pouring an appropriate volume of the platinum solution to make a slurry, and then evaporating the stirred slurry to a near-dryness in a rotary evaporator at 80°C. After the platinum was impregnated over the SDBC support, the sample was directly reduced. The standard reduction

procedure was to maintain the sample at 230°C for 15 hours in flowing hydrogen after purging it with pure nitrogen at room temperature for 30 minutes.

The physical properties of the polymer supports and the Pt/SDBC catalysts, such as the BET surface area, pore volume and pore size distribution, etc., were measured by a physical adsorption of the nitrogen gas at the liquid nitrogen temperature of 77K by using Autosorb-6. The surface area of the supported platinum particles was determined by a hydrogen chemisorption on the catalysts by using a conventional volumetric apparatus at 298K. Thermal stability of the samples was investigated by TGA analysis. The sample powder was heated in an argon or a oxygen flow of 100ml/min. The heating rate was 1.0°C/min. 20mg of the sample and an equal amount of the reference alumina powder were used in the platinum crucibles.

An experimental apparatus was designed and built for the performance test of the Pt/SDBC catalyst at various temperatures and gas velocities(Fig.1).

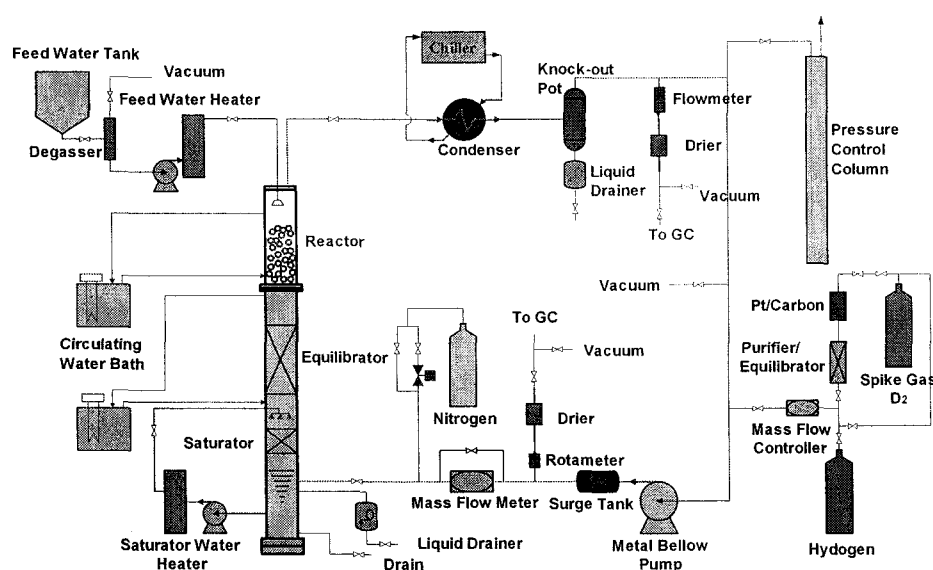


Fig.1 Experimental apparatus for the trickle bed reactor

The catalyst bed was a cylindrical column 3 cm in diameter by 40 cm in length. The trickle bed reactor was filled with the Pt/SDBC catalyst complex. A non-catalytic packed equilibrator was located below the catalyst bed to achieve an equilibration between the vapor in the hydrogen entering the bed and the liquid water leaving the bed. It operated on a recirculating gas once-through water principle. A metal bellows pump

was used for the hydrogen circulation in the system. The recycle flow rate of the hydrogen gas was measured with a rotameter. The water vapor in the circulation gas was removed with a condenser. The catalyst under study was packed wet into the bed and the water was injected at the top through a liquid distributor and allowed to flow by gravity through the packing. Hydrogen gas which had been passed through the bed and the gas samples was drawn off from the inlet and outlet of the bed. The concentration of the HD gas was analyzed with a gas chromatography. In order to maintain the column pressure, hydrogen was bled into the loop ahead of the gas circulator. HD gas was used as a spike gas for the catalyst performance. The temperature of the reactor was controlled by using water-jackets around the reactor and an equilibrator, a feed water heater, and a circulation water heater. After evacuating the system several times, the hydrogen gas was injected into the system and it began to circulate through the system with the use of the bellows pump, which provided a recycle flow rate of around 60 LPM.

RESULTS AND DISCUSSION

Fig.2 shows the TGA and DTA curves of the SDBC and Pt/SDBC which using argon gas. There is an endothermic peak at about 400°C and a drastic decrease of the weight is observed at the same temperature. The polymer support and the prepared catalyst show the same tendency of the TGA and DTA curves. It appears that the weight losses at about 400°C are caused by a pyrolysis of the SDBC.

Though the SDBC samples have a similar chemical form, the physical properties are considerably different. Pore size distributions for the two selected SDBC samples are shown in Fig.3. It is also shown that BO has a considerable fraction of large pores at around 100Å. But AO mainly consists of micropores and the fraction of macropores in AO is smaller than that in BO. The platinum dispersions and the platinum surface areas for the 3wt% Pt/SDBC were measured by a hydrogen chemisorption experiment and the results are described in Table 1. For a calculation of the metal dispersion, the bonding of hydrogen to the platinum sites was assumed to be mono-atomic (single hydrogen atom per site, Pt:H=1:1). The platinum dispersions and the areas of the AO catalysts are larger than those of the BO catalyst. Higher metal dispersions were obtained when there was a greater surface area and a small pore size for the SDBC. This behavior is

undoubtedly related to the way in which the pore structure of the support controls the crystal growth of platinum, so that the behavior depends on the structure of the support. Therefore, it appears that the average platinum crystallite diameter on SDBC tends to decrease as the specific surface area increases, that is, as the average pore size decreases

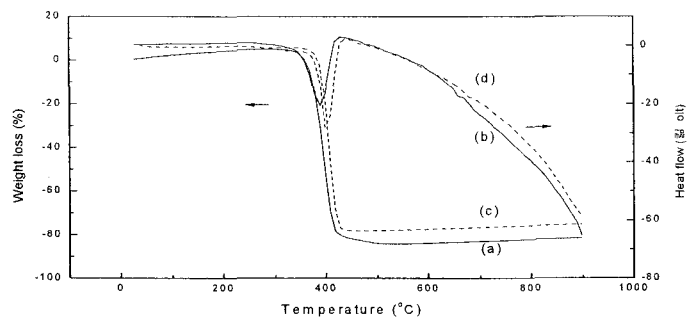


Fig.2 TGA and DTA curves for the SDBC support and Pt/SDBC catalyst using argon gas ; 1-TGA curve of SDBC ; 2-DTA curve of SDBC ; 3-TGA curve of Pt/SDBC ; 4-DTA curve of Pt/SDBC.

Table 1 Pt characteristics in 3wt% Pt/SDBC determined by hydrogen chemisorption at 25°C.

Catalysts	BET surface area, m ² /g	Dispersion, %	Pt surface area, m ² /g	D pt, Å
AO	417	67	4.9	17
BO	350	32	2.4	36

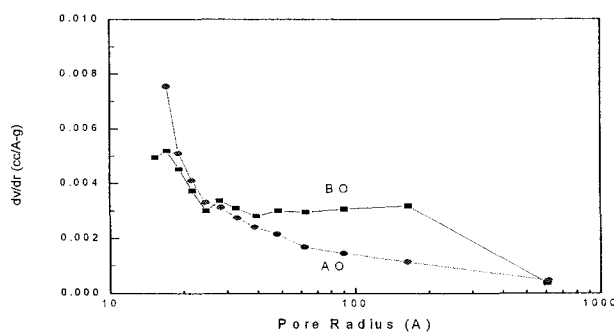


Fig.3 Pore size distribution for the SDBC supports.

Many tests have been carried out at KAERI for the activity of the catalyst, K_{ya} . In all the tests carried out, the liquid flow rate of the column was maintained as constant (120ml/min). The activities of the catalyst, K_{ya} , were measured for several days. Deuterium mol fractions of the inlet and outlet gas samples reached a steady state at about 100 minutes after an the injection. After 200 minutes from the injection, the gas samples were analyzed. Fig.4 shows the Deuterium mol fractions of the gas samples and the overall rate constants. The steady state Deuterium mol fractions from the inlet and outlet gas samples increased with time due to a deactivation of the catalyst. The decline in the catalysts performance could be a result of a catalyst poisoning by some foreign material or a slow condensation of the water in the pores of the catalyst particle. The effect of a water uptake is to slow down the pore diffusion of the reactants and the products and cause a reduction in the internal and direct transfer rates.

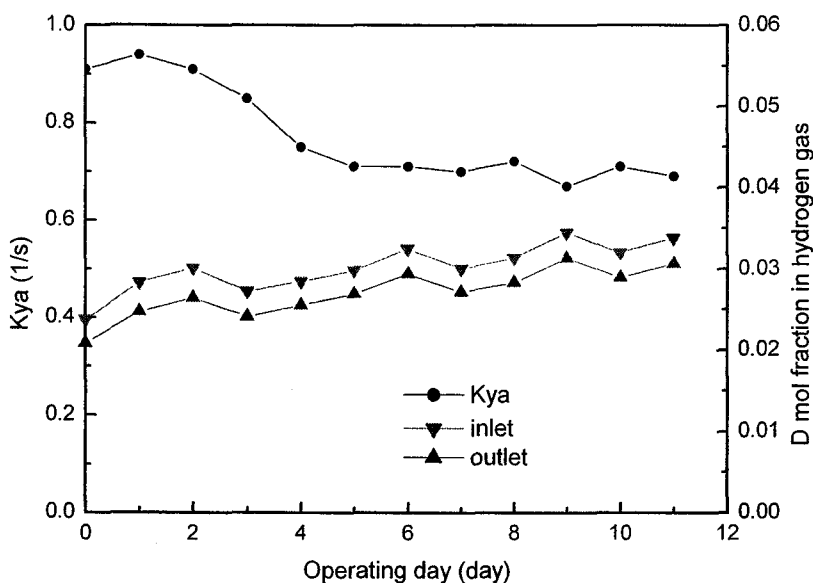


Fig. 4 Overall rate constants and deuterium fractions at the inlet and outlet of the catalyst bed.

Fig.5 shows the effect of the hydrogen gas flow on the overall rate constant for the Pt/SDBC complex. K_{ya} increases with the hydrogen flow rates in the range of 0.4 to 1.6 m/s at STP. This flow dependency indicates that an external resistance plays an important role in the exchange process. The variation in the flow dependency may be

due in part to an increase in the liquid holdup at the higher flows. As a result of the liquid holdup in the bed, the water distribution, and thereby K_{ya} will likely be improved.

CONCLUSION

It was shown by TGA analysis that macroporous SDBC can be used below 400°C under an inert gas. Nitrogen adsorption and hydrogen chemisorption results have shown that the average platinum crystallite diameter tends to decrease as the specific surface area of the SDBC increases, that is, as the pore size decreases. Catalyst performance of the trickle bed reactor is expressed as an overall rate constant of K_{ya} ($\text{m}^3(\text{STP})\text{s}^{-1}\text{m}^{-3}$). The overall rate constant of the Pt/SDBC catalyst was deactivated with the operating time because of a slow condensation of the water in the pores of the catalyst. K_{ya} increases with the hydrogen flow rates in the range of 0.4 to 1.6 m/s at STP. The overall rate constant may be high enough for less demanding applications such as the CECE process. Good liquid distribution is likely to enhance the overall rate constant, so the liquid distribution should be modified. To improve the liquid distribution, a modification of the catalyst bed design (changing the shape of the catalyst complex and diluting with inerts) will be investigated.

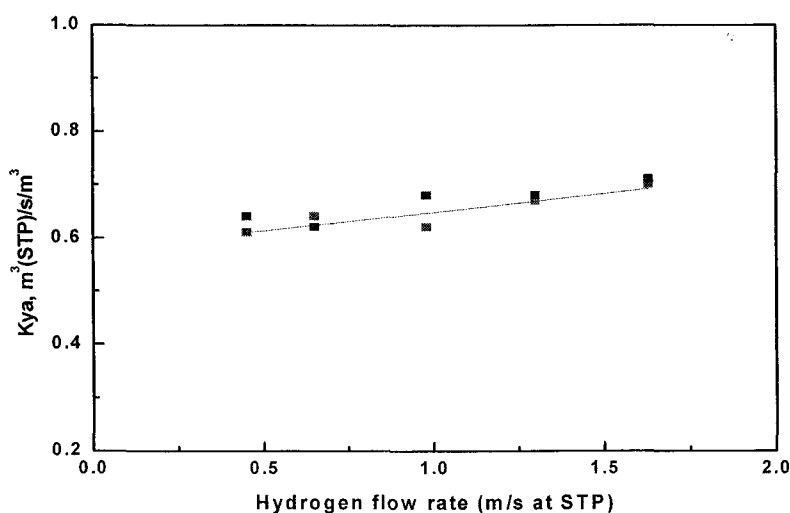


Fig. 5 Effects of the hydrogen gas flow rate on the overall rate constant of a Pt/SDBC catalyst.

Acknowledgement

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