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Marked enhancement of the methane dehydrocondensation toward benzene using effective Pd catalytic membrane reactor with Mo/ZSM-5

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Steady state product formation rates of benzene, hydrogen, naphthalene, toluene in methane dehydrocondensation reaction on 3 wt% Mo loaded ZSM-5 catalyst was enhanced 2–10 times by the removal of hydrogen using Pd membrane for 100 h at 883 K. The amount of permeated hydrogen through the Pd membrane was measured before and during the methane dehydrocondensation reaction. About 50–60% of hydrogen from the total hydrogen produced during the methane dehydrocondensation was selectively removed by the Pd membrane, owing to which the equilibrium of the methane dehydrocondensation was shifted toward the product side.

KEY WORDS: heterogeneous catalysis; hydrogen permeability; methane dehydrocondensation; Pd membrane reactor.

1. Introduction

Efforts have been made to convert methane into value-added products for the industrial utilization of natural gas. Among them, the methane dehydrocondensation reaction has been studied since the last decade for producing hydrogen and aromatics as the main products, which can be used for fuel cell application and as a source of raw materials for the chemical industry, respectively [1–5]. However, methane conversion in the methane dehydrocondensation stays at a low level due to the thermodynamic limit. Methane conversion could be increased by increasing the reaction temperature or by decreasing the reaction pressure, which may not be industrially favorable or suitable. Therefore, the question still remains as to how to increase methane conversion.

The equilibrium position in the methane dehydrocondensation reaction will be shifted toward the product side if hydrogen is selectively removed from the system. According to the thermodynamic calculation, the methane conversion in the methane dehydrocondensation reaction towards benzene and hydrogen would increase with the removal of hydrogen as shown by the open circles in figure 1. The hydrogen in the reaction product can be separated *in situ* by using catalytic membrane reactors. It has been known that Pd-based membranes can separate hydrogen with 100% permselectivity and was applied for the oxidative conversion of methane [6,7]. The Pd membrane reactor was also applied for hydrogen removal in the methane dehydrocondensation reaction [8,9]. These authors claimed that methane conversion increased above the thermodynamic limit by continuous removal of hydrogen. However, they evacuated the hydrogen from the reaction product by a vacuum pump. Therefore, there is no way to estimate how much hydrogen was removed and produced during the methane dehydrocondensation. Without quantitative analysis of hydrogen, the activity could not be correlated with that of the thermodynamically calculated value.

In this paper, therefore, the amount of hydrogen removed before and during the reaction is quantitatively analyzed. In addition, the detail and quantitative analysis of products including coke, during the methane dehydrocondensation reaction was carried out for a long period of time.

2. Experimental

2.1. Catalyst preparation and characterization

The 3 wt% Mo loaded ZSM-5 catalyst was prepared by adding 20-ml aqueous solution of ammonium heptamolybdate with the appropriate concentration to 5 g of commercial NH_4-ZSM-5. The solution was stirred for 4 h and the excess water was evaporated until dry at 328 K for 4 h in a rotary evaporator. The decomposition of the precursor was carried out in an oven at 773 K for 4 h. The catalyst was then applied to the reaction and characterized by XRD for its crystallinity.

2.2. Catalytic Pd membrane reactor

As shown in figure 2, the Pd membrane reactor consists of upper and lower parts, which are made from

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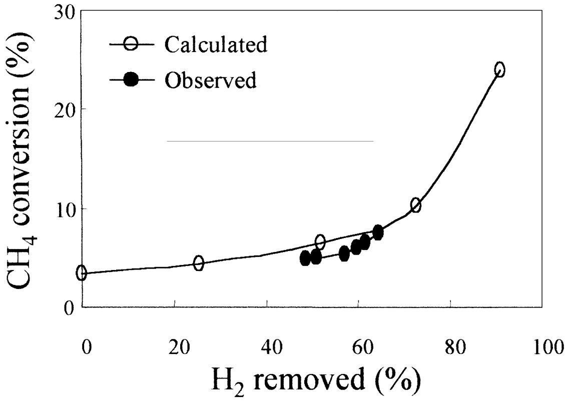

Figure 1. Calculated methane conversion at thermodynamic equilibrium (open symbol) and observed methane conversion (filled symbol) versus hydrogen removed (%) by the Pd membrane during methane dehydrocondensation at 883 K and 0.5 MPa.

stainless steel pipes of 40 mm i.d. × 300 mm length. Pd membrane sheet (20-μm thickness) supplied by Tokyo Gas Co. is mounted on a mesh plate and is situated in-between the upper and lower parts. The catalyst was charged in contact with the Pd membrane at the upper side of the reactor. The reaction temperature was monitored by a thermocouple situated at the center of the reactor and was controlled by another thermocouple placed outside the reactor.

2.3. *Hydrogen permeability and catalytic reaction*

Before the methane dehydrocondensation reaction, the hydrogen permeability of a fresh Pd membrane was measured by flowing 9.3 ml min^{-1} of a mixture gas of 9.8% H_2 in Ar from the upper side of the reactor at 0.5 MPa of total pressure and at 883 K. The methane dehydrocondensation reaction was conducted by flowing 10.7 ml min^{-1} of a mixture gas of 90% methane + 10% Ar from the upper side of the reactor on 2 g of catalyst (methane space velocity = 290 ml h^{-1} g^{-1}) at 0.5 MPa of total pressure and at 883 K. In both cases, nitrogen gas was introduced from the lower side of the reactor to sweep the permeated gas from the Pd membrane at atmospheric pressure. The exit gases from the upper and the lower sides of the reactor were analyzed by two online GCs fitted with FID and TCD, which were used for analyzing hydrocarbon and nonhydrocarbon products, respectively. The flow rate or formation rate of each compound was calculated by using argon as the internal standard for mass balance calculation.

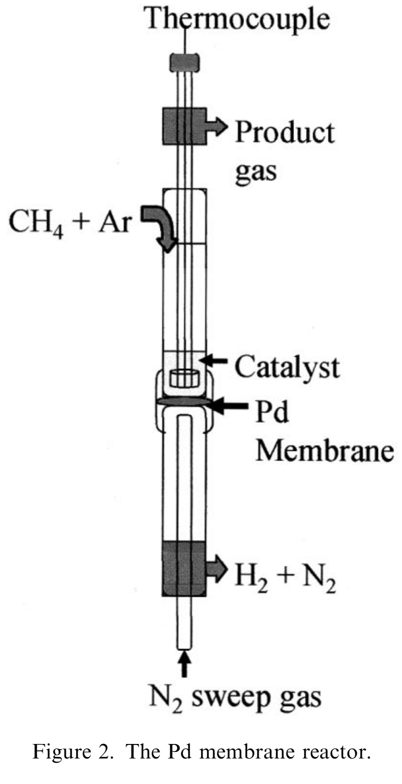

Figure 2. The Pd membrane reactor.

3. Results and discussion

3.1. *Hydrogen permeability*

As shown in figure 3, only hydrogen from a gas mixture of H_2 and Ar was permeated through the Pd membrane as expected and the amount of hydrogen removed was increased by increasing the flow rate of N_2 used as the sweep gas. This figure also shows that 95% hydrogen is permeated through the Pd membrane at more than 100 ml min^{-1} flow rate of N_2 sweep gas under experimental conditions. Therefore, 200 ml min^{-1} of N_2 sweep gas flow rate was selected to sweep the permeated hydrogen gas from the product stream during the methane dehydrocondensation reaction.

3.2. *Time-on-stream of the methane dehydrocondensation reaction*

Figure 4 shows the catalytic performances with and without the removal of hydrogen by using a Pd

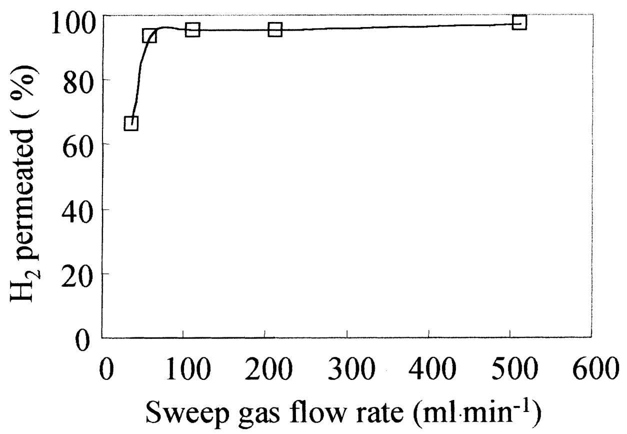

Figure 3. Effect of sweep gas flow rate on the amount of permeated gas through the Pd membrane in an Ar–H_2 mixture gas at 883 K.

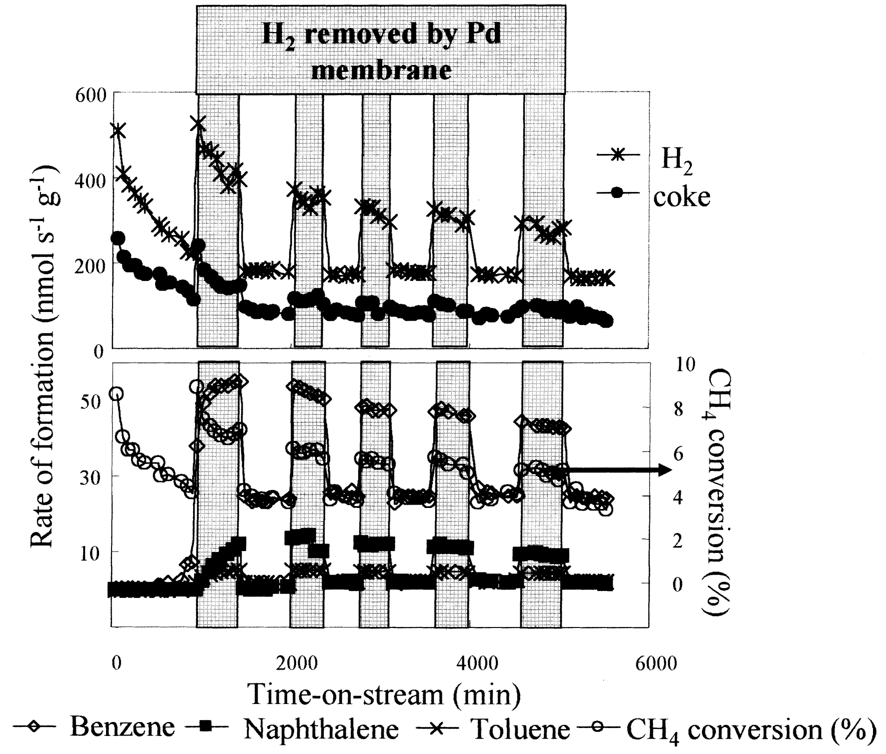

Figure 4. Enhanced methane activity and rate of product formation by removal of hydrogen from the product stream using Pd membrane in methane dehydrocondensation on Mo/ZSM-5 catalyst at 883 K, 0.5 MPa and 290 ml g^{-1} h^{-1} of methane space velocity.

membrane reactor at 883 K, 0.5 MPa of total pressure and 290 ml h^{-1} g^{-1} of methane space velocity on 3 wt% Mo loaded ZSM-5 catalyst. The formation rates of benzene, toluene, naphthalene and hydrogen were boosted to about 3, 4, 10 and 2.5 times, respectively, by the removal of hydrogen from the product stream in the methane dehydrocondensation reaction. As a result, the methane conversion increased two times by the removal of hydrogen from the product stream. Figure 4 also shows that hydrogen is formed at a rate range of 300 to 500 nmol g^{-1} s^{-1} during the reaction. Within the total hydrogen formed, 50–60% of hydrogen was permeated through the Pd membrane. The experimental increase in the methane conversion was plotted against the experimental percentage of hydrogen removal as shown in the filled circles of figure 1. The experimental points fall on a calculated line from the thermodynamic equilibrium as presented in the open circles of figure 1. These results suggest that methane primarily transforms to benzene in the methane dehydrocondensation reaction, which was really the case when the reaction was conducted in a plane reactor without having Pd membrane. The catalytic activity remains constant up to 90 h of time-on-stream without removal of hydrogen and it goes down slowly with time by removal of hydrogen.

As shown in figure 3, over 95% of hydrogen was removed by flowing 9.3 ml min^{-1} of mixture gas containing 9.8% of H_2 in Ar or 0.9 ml min^{-1} of H_2 and under flowing 100 ml min^{-1} of N_2 sweep gas. Total formation rate of hydrogen was observed in the range of 300–500 nmol g^{-1} s^{-1} or 0.8–1.3 ml min^{-1} on 2 g catalyst, which is similar to the hydrogen flow rate used in the hydrogen permeability experiments. Therefore, over 95% of hydrogen should be permeated through Pd membrane, but only 50 to 60% of hydrogen was removed under the experimental conditions, suggesting the suppression of hydrogen permeation by some kind of blockage. To remove the blockage, the Pd membrane used for the reaction was treated with a mixture gas of 9.8% of H_2 in Ar at 883 K and 0.5 MPa and its hydrogen permeability was measured from time to time. The

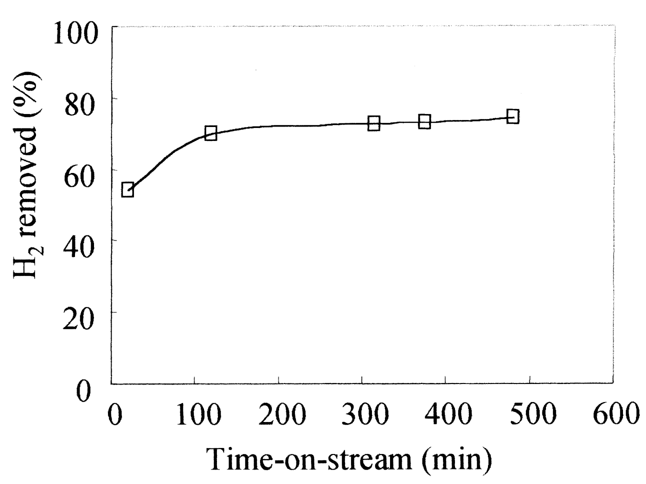

Figure 5. Change in hydrogen permeability during the reaction of H_2 with Pd membrane after the methane dehydrocondensation reaction.

results shown in figure 5 demonstrate that the initial 55% hydrogen removal by the Pd membrane was slowly recovered to 75% after 2 h of time-on-stream by the reaction of carbon on the Pd membrane with hydrogen. Therefore, it may be suggested that the carbon formed during the methane dehydrocondensation reaction lowers the hydrogen permeability to the level of 50–60%.

It should be noted that for the initial stage of the reaction up to 1000 min, only hydrogen and coke (plus CO, not shown) are formed from methane, and then the hydrocarbons start to form. During the induction period, the active phase of Mo-carbide was formed as reported previously [2].

4. Conclusions

The results are summarized as follows: (1) the methane conversion was increased and became two times above its thermodynamic equilibrium conversion by the removal of hydrogen from the product stream of the methane dehydrocondensation reaction, (2) the two times increase in methane conversion well agreed with the thermodynamic equilibrium calculation, when 50–60% hydrogen formed was permeated or removed by the membrane, (3) similar to the conversion, the formation rates of benzene, toluene, naphthalene and hydrogen were all boosted to more than two times by the removal of hydrogen from the product stream of methane dehydrocondensation, (4) the hydrogen permeability of the Pd membrane during the reaction was smaller than that of fresh Pd membrane, suggesting the hindrance of hydrogen permeation with deposited coke.

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