Steam reforming of dimethyl ether by surface protonics in an electric field

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Abstract: Effects of surface proton conduction induced by an electric field on catalytic steam reforming of dimethyl ether (DME) were investigated. Results of activity tests revealed that the surface protonics promoted the hydrolysis of DME and inhibited the direct decomposition of DME. Kinetic analyses revealed that the partial pressure dependences on reactants were drastically different with or without the application of the electric field. These results strongly suggest that the proton conduction on the catalyst surface contributed to the steam reforming of DME.

Keywords: Steam reforming, Electric field, Surface protonics.

1. Introduction

Dimethyl ether is a good candidate for the hydrogen source of fuel cells since the steam reforming of DME can proceed much lower temperatures compared to those of methane and other hydrocarbons.[1] Steam reforming of DME proceeds via two consecutive reactions: DME hydrolysis and steam reforming of methanol (MeOH).[2] It is reported that DME hydrolysis is the rate limiting step and it actively proceeds over solid acid catalysts.[3] Recently, we have reported that the proton conduction induced by an electric field on the surface of Pd/CeO_2 catalyst promoted the steam reforming of methane.[4, 5] In this work, the effect of the surface proton conduction on the steam reforming of DME was investigated.

2. Experimental

1.0wt%Pd/CeO_2 was used as a catalyst for this study. Pd was loaded on CeO_2 (JRC-CEO-01) by an impregnation method using $Pd(CH_3COOH)_2$ as a metal precursor. The catalyst was calcined at 973 K for 12 h and the resulted powder was sieved into particles of 355-500 μm.

Catalytic activity tests were conducted using a fixed-bed flow-type reactor with a quartz tube (6.0 mm i.d.). 80 mg of catalyst was set into the reactor and two stainless steel electrodes (2.0 mm o.d.) were inserted into the top and bottom sides of the catalyst bed. The electric field was imposed by applying 3 mA of DC current. The furnace temperature was set at 473 K for the reaction in the electric field and 573 K for the reaction without the electric field. The reactant gas was a mixture of DME / H_2O / Ar = 5 / 15 / 80 SCCM unless otherwise stated. The product gases were analyzed using a GC-FID and a GC-TCD after passing a cold trap.

3. Results and discussion

The conversion of DME and the selectivity to methane under various contact times are depicted in Figures 1 and 2. Total flow rate was changed (20, 40, 60, 100 SCCM). As shown in Figure 1, the conversions of DME under the condition with/without the electric field are similar whereas the reaction temperature is different. Moreover, the selectivity of methane under the condition with the electric field is much lower than that without the electric field. Methane can be produced from methanation of the products i.e. CO and CO_2 or direct decomposition of DME. If the methanation reaction was the main pass of the methane formation, the selectivity to methane would increase as the contact time become longer. However, Figure 2 shows that the selectivity to methane is nearly constant regardless of the value of W/F. Therefore, methane is formed via the direct decomposition of DME. These results indicate that the direct decomposition of DME is suppressed and the hydrolysis of DME is promoted by the application of the electric field thanks to the surface proton conduction.

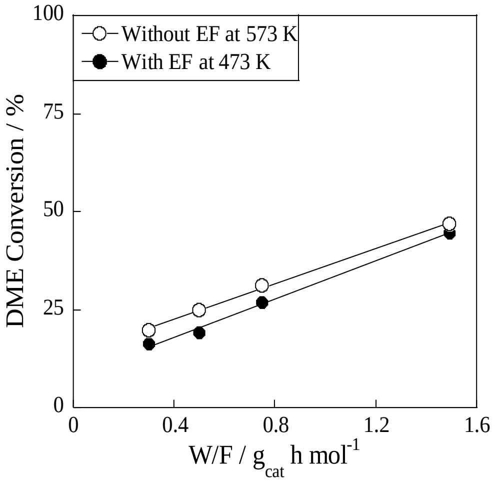

Figure 1. DME conversion under various constant times.

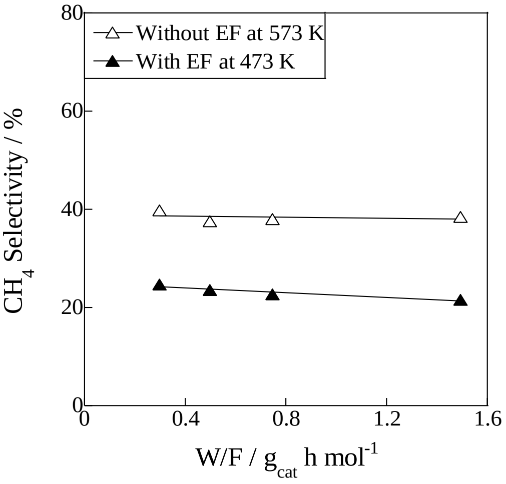

Figure 2. Methane selectivity under various constant times.

Next, we investigated the influence of partial pressure of reactants on the steam reforming of DME. Results revealed that the partial pressure dependences were drastically different in the conditions with/without the electric filed. Under the condition without the electric field, the reaction order for water partial pressure is constant value of 0.19, however, with the electric field, the reaction order for water partial pressure is not constant as shown in Figure 3. The value is 0.18 in the range above P_{H2O} = 0.08 atm and is 0.94 in the range below P_{H2O} = 0.05 atm. The strong dependence on the water partial pressure indicates that the concentration of proton and the reaction rate are limited by the water partial pressure. These results also suggest that the steam reforming of DME is promoted by the surface protonics in the electric field.

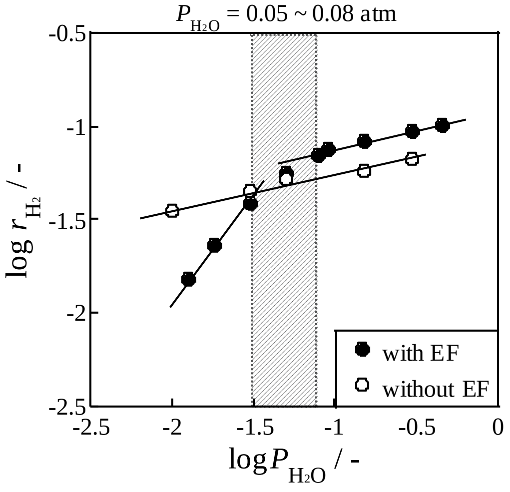

Figure 3. Effects of water partial pressure on the reaction rate.

4. Conclusions

Steam reforming of DME was conducted using Pd/CeO$_2$ as a catalyst with/without the application of the electric field and the effects of surface proton conduction were investigated. Although direct decomposition of DME was dominant without the electric field, it was suppressed and steam reforming of DME was promoted by imposing the electric field. The strong dependence on the water partial pressure in the electric field indicated that the reaction rate was limited by the concentration of proton in the lower water partial pressure range. These results strongly suggested that the surface protonics induced by the electric field promoted the steam reforming of DME.

References

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