

Development of catalysts for hydrogen production and application to fuel cells

Koichi Eguchi

Department of Energy and Hydrocarbon Chemistry,
Graduate School of Engineering, Kyoto University

1. Introduction

Hydrogen has been attracting great interest as a future clean fuel for combustion engine and fuel cells. The efficient and compact production process of hydrogen should be developed for such application purpose. Multi-step processing of hydrocarbon-based fuel is the most practical approach in deriving hydrogen efficiently (Fig.1). Steam reforming of hydrocarbon has been operated popularly in chemical industries for production of hydrogen. The recent development of fuel cell research activity, however, triggered the processing of fuels for compact and portable systems. Partial oxidation of hydrocarbon or steam reforming of hydrocarbons is located at the first process. The decomposition of hydrocarbon structure is followed by a water gas shift reaction for conversion of fuel component from CO-rich to H₂-rich fuel. This process should be carried out at significantly lower temperature than steam reforming, since the exothermic nature of the reaction. For the fuel cell application, final step of fuel processing should be CO removal by preferential oxidation.

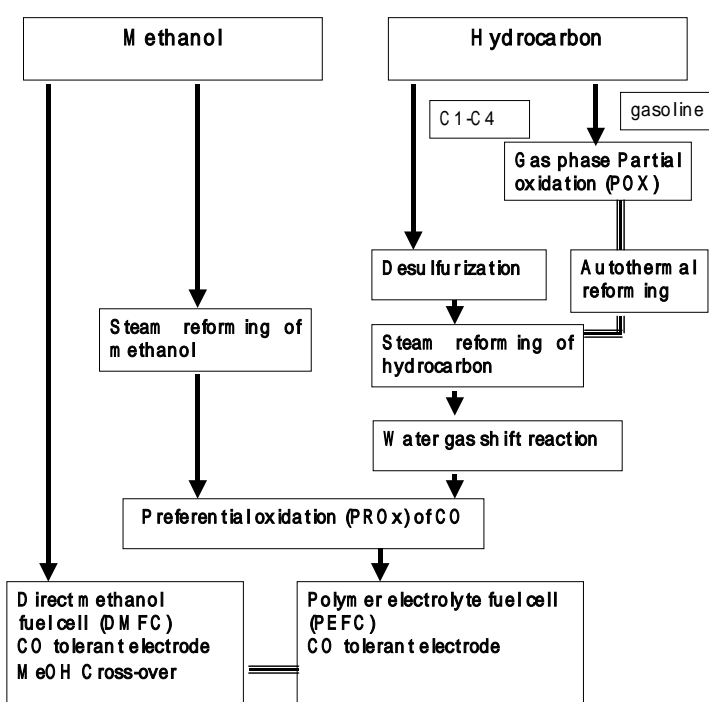
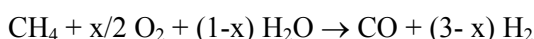


Fig. 1 Block diagram of hydrogen production for PEFC

2. Autothermal reforming of methane and propane

The partial oxidation is the reaction with large exothermic heat, whereas the steam reforming is a large endothermic reaction. The partial oxidation is therefore could be easily startup even

without an aid of catalyst. However, conversion efficiency is lowered as a released heat and dilution of product with nitrogen when air is used as an oxidant. On the other hand, the efficiency could be gained when steam reforming of hydrocarbons has been employed since the reaction adsorbs thermal energy. The disadvantage of steam reforming should be extra heating for the reactor and steam generator. The mixture of these two reactions is autothermal reforming where steam reforming of hydrocarbons has been carried out in the presence of oxygen. Exothermic, endothermic, and thermo-neutral condition can be selected by controlling appropriate mixing ratio of oxygen and steam, x .



Carbon deposition may cause a serious damage for the stable operation and high conversion for these reactions. Although the reaction condition for carbon deposition can be estimated from thermodynamic equilibrium, the real deposition condition is very complicated. The catalytic action in the steam reforming of hydrocarbon has been extensively investigated, whereas the catalytic partial oxidation and autothermal reforming has not been investigated well. The purpose of the present study is to obtain general behavior of the autothermal reforming using supported metal catalysts using methane and propane as fuel. The difference in reactivities of these two hydrocarbons is also the interest of the present study.

The sequence of the activities of the 2wt% metal on alumina support for autothermal reforming was $\text{Rh} > \text{Ni} > \text{Pd} > \text{Pt} > \text{Co}$ (Fig.2). The catalytic activity of 10wt% Ni/ Al_2O_3 was higher than the 2wt% Rh/ Al_2O_3 . The activity of Ni was significantly lowered by the preferential oxidation of the catalyst in the reactant gas at low temperatures. Although carbon deposition was scarcely observed for the autothermal reforming of methane in the deposition free region expected from the

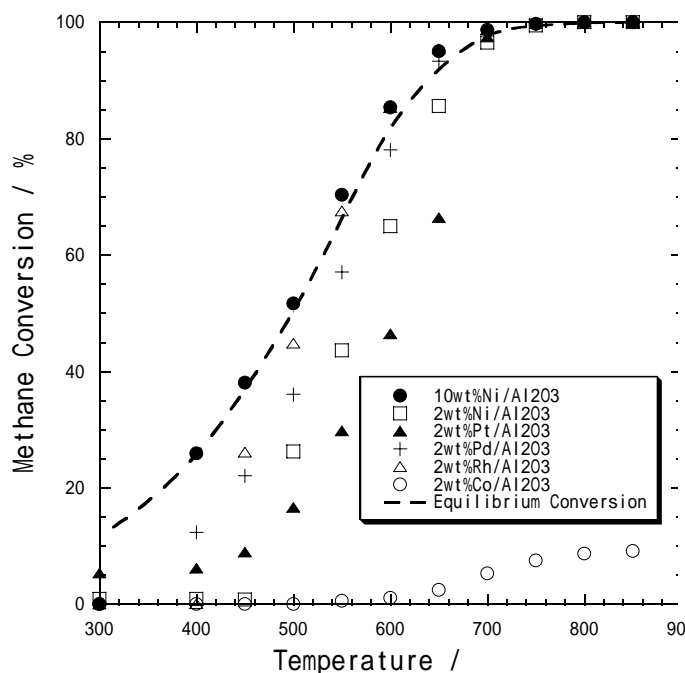
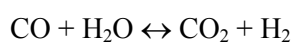


Fig. 2 Temperature dependence of conversion for autothermal reforming of methane over various metal catalysts. Reaction conditions: CH_4 , 16.7%; O_2 , 1.7%; H_2O , 41.6%; N_2 , balance; $\text{S/C} = 2.5$; $\text{S.V.} = 7200 \text{ h}^{-1}$. ----- equilibrium conversion.

equilibrium, a large amount of carbon deposition was observed for the propane autothermal reforming even in the steam rich conditions. The deposited carbon possessed fibrous morphology. The catalytic autothermal reforming appears to be initiated by decomposition of hydrocarbon then reforming.

3. Water gas shift reaction on base metal catalysts and precious metal catalysts

With a supply of hydrogen from reformed fuel to a polymer electrolyte fuel cells, electrode poisoning by strong adsorption of CO in reformed fuels becomes another issue, which leads to deterioration of the cell performance. The Pt electrode on PEFC is not tolerant to fuels containing CO more than 20 ppm. It is, therefore, necessary to develop electrodes to tolerate higher concentration of CO and to achieve low level of CO by removal from reformed fuels. In recent years, water gas shift reaction that produces hydrogen has been studied as one of CO removal technique.



Low-temperature shift reaction is more appropriate in achieving low CO concentration level since exothermic shift reaction leads to high equilibrium conversion of CO in low temperature region. We have reported that Cu-containing catalysts demonstrated high activity for CO removal from reformed methanol fuel by oxygen-added water gas shift reaction. Supported precious metal catalysts have been also studied for shift reaction by many researchers because of their potential stability in oxidizing atmosphere. However, the activities of precious metal catalysts for the shift reaction are generally lower than those of base metal catalysts.

Cu-Al₂O₃-ZnO and supported precious metal catalysts were investigated for CO removal from reformed fuels. Supported Ru catalysts readily converted CO in the reformed fuel via formation of CH₄. Supported Pt catalysts, especially Pt/Al₂O₃, at low temperatures demonstrated high CO conversion without formation of methane. The Cu-Al₂O₃-ZnO catalyst also had a high activity comparable to Pt/Al₂O₃

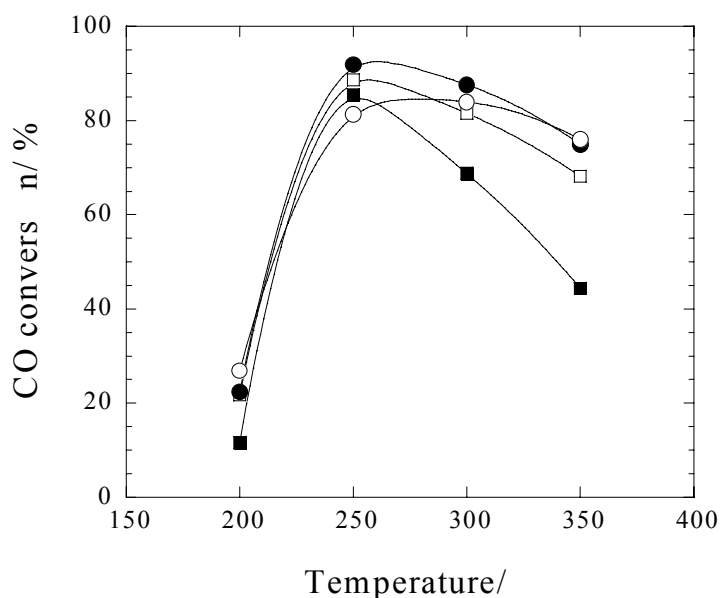


Fig. 3 Effect of initial CO concentration on CO conversion over Cu/MnO. Initial CO conc.: (■) 1.25%, (□) 2.50%, (●) 5.00%, (○) 10%. Reaction conditions: H₂, 37.5%; CO, 1.25-10.0%; H₂O, 25.0%; CO₂, 12.5%; space velocity, 6400 h⁻¹.

without methanation at low temperatures. An activity for CO removal by shift reaction was promoted for the catalysts with large adsorption H_2O . In concentrated CO conditions, the Cu- Al_2O_3 -ZnO catalyst was superior to Pt/ Al_2O_3 for CO removal due to high activity for the shift reaction. A small amount of oxygen added to reformed fuels accelerated shift reaction over the Cu- Al_2O_3 -ZnO catalyst. The additive effect is ascribed to thermal activation of shift reaction with heat supplied by CO and H_2 oxidation and facilitated dissociation of adsorbed H_2O with adsorbed oxygen.

Cu-based mixed oxides were investigated for WGSR in order to find catalysts with high activity and durability even under severe conditions including a large amount of H_2O in the reformed fuels. $CuAl_2O_4$ and $CuMn_2O_4$ showed much higher specific rate of CO conversion than Cu/ZnO/ Al_2O_3 . Although WGSR activity emerged from reduction of the mixed oxides, high temperature reduction gave rise to the sintering of Cu. $CuAl_2O_4$ showed moderate CO oxidation activity at lower temperatures and WGSR activity over $300^\circ C$. The $CuMn_2O_4$ catalyst exhibited high WGSR activity over $225^\circ C$ (Fig.3) comparable to that of Cu/ZnO/ Al_2O_3 and high durability for 20 h at 200 - $225^\circ C$.

Copper based catalysts showed higher activity for the shift reaction than precious metal catalysts. However, the metal catalysts are hardly suffered from the deterioration by oxidant gases, such as oxygen and water. With a supply of reformed fuel, methanation readily proceeded over Ru-based catalysts. The methanation can be suppressed by an appropriate selection of the support material for Ru. Platinum-based catalysts exhibited activity for waster gas shift reaction, though the methane conversion was lower than Cu-based or Ru-based catalysts.