Multiple Steady States in Oxidative Steam Reforming of Methanol (OSRM)

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Fuel cell cars are operated on compressed hydrogen[1,2]. Although the storage pressure of the hydrogen is extremely high around 700 bar, the driving range between refueling is still short compared to conventional cars on liquid fuels. In addition, the new social infrastructure for hydrogen refueling needs to be established to make the use of fuel cell cars more attractive. An alternative to this is to produce hydrogen onboard by the oxidative steam reforming of methanol (OSRM):

$CH_3OH + 0.8\ H_2O + 0.10\ O_2 \rightarrow CO_2 + 2.8\ H_2$, $\Delta H = 0$ kJ/mol

Since OSRM does not require heat supply or removal, the reactor system becomes most compact and suitable for mobile applications. One liter of compressed hydrogen at 700 bar is 39 g while 1 liter of methanol can generate 139 g of hydrogen by OSRM and so methanol can be regarded as a hydrogen carrier.

OSRM has been considered as a combined reaction of steam reforming of methanol (SRM) and partial oxidation of methanol (POM)[3,4].

SRM: $CH_3OH + H_2O \rightarrow CO_2 + 3H_2$, $\Delta H = 49.5$ kJ/mol

POM: $CH_3OH + 0.5\ O_2 \rightarrow CO_2 + 2\ H_2$, $\Delta H = -192.5$ kJ/mol

A few studies on the other hand suggested the combustion of methanol (COM) as the exothermic reaction in OSRM[5].

COM: $CH_3OH + 1.5\ O_2 \rightarrow CO_2 + 2\ H_2O$, $\Delta H = -676$ kJ/mol

Resolving the reaction route of OSRM has been very difficult due to the very high heat of the exothermic reaction, POM or COM.

In the present study we carried out OSRM in an isothermal reactor and experimentally verified that COM is the exothermic part of the OSRM and POM is not an independent reaction and, like OSRM, is a combination of COM and SRM. We observed a hysteresis in the methanol conversion with respect to the reaction temperature as shown in Fig. 1.

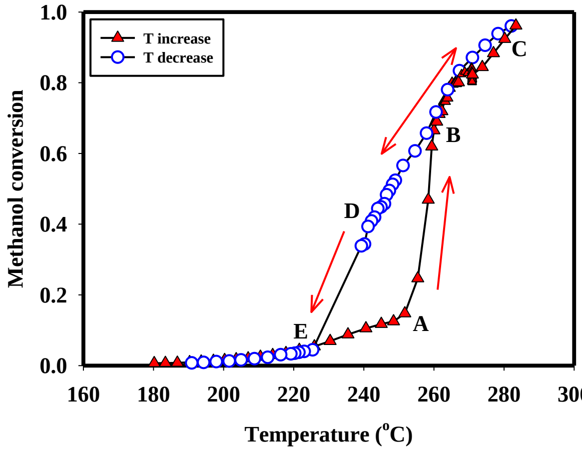

Fig.1. Multiple steady states in OSRM.

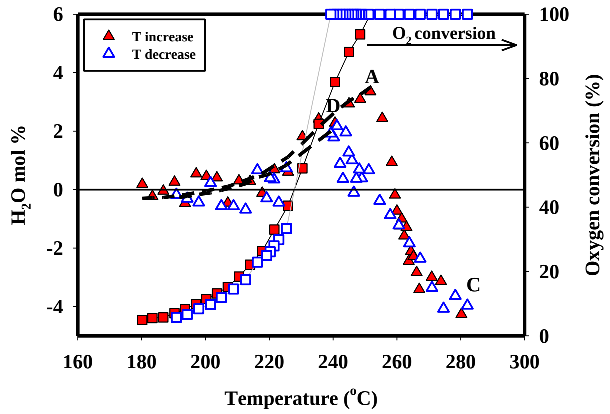

Fig. 2. Generated H_2O mol % in the product and O_2 conversion.

Only CO_2 and H_2O (shown in Fig. 2) was produced at the expense of O_2, showing that COM is the O_2 consuming reaction. Only after the complete O_2 conversion, H_2 was produced by SRM.

The multiple steady states are analyzed in terms of the mass and heat transfer between the flowing reaction mixture and a catalyst particle.

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