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Hydrogen production from partial oxidation and reforming of DME

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Hydrogen production from partial oxidation and reforming of dimethyl ether (DME) was investigated with a fixed bed continuous-flow reactor. H_2 yield of over 90% was obtained with 100% DME conversion at 700 °C over Pt/Al_2O_3 + Ni–MgO dual catalyst bed, while keeping CH_4 yield at low level. Such results indicated that partial oxidation and reforming of DME to produce hydrogen at high temperature is possible and effective.

KEY WORDS: hydrogen production; partial oxidation; reforming; DME.

1. Introduction

The quick development of the global economy requires more and more energy supply, while the deteriorating environment requires more and more stringent restriction for the emissions. Both of the energy requirement and the emission restriction stimulate research on clean and high energy efficient power generating technology. Fuel cell is known as a clean and efficient electrical generator for both mobile and stationary applications, and it is considered as the next generation of energy supply. Fuel cell usually uses hydrogen (or hydrogen-rich gas) as fuel. Currently, the application of pure hydrogen suffers from low energy density, high safety risk and extreme difficulty in storage and transportation. It is necessary to find some hydrogen carriers as a substitute of pure hydrogen so as to overcome the above disadvantages. Dimethyl ether (DME) is one of the most promising candidates, because of its high H/C ratio, high energy volumetric density, and it can be stored, transported and handled conveniently, just like LPG due to the similar physical properties. Comparing to methanol, another potential candidate, DME is non-corrosive, non-carcinogenic and virtually non-toxic. In addition, DME can also be synthesized directly from syngas, just as methanol, and the direct synthesis process is more economically profitable and more thermodynamically favorable than methanol synthesis. DME, therefore, is believed to play an important role in future's energy supply system.

Literature survey showed that there were only a few articles concerning with H_2 production from DME by steam reforming via the hydration of DME to methanol at 200–350 °C [1,2]. H_2 so produced may be suitable for fuel cells operated at low temperature, such as polymer electrolyte membrane fuel cell (PEMFC). But for PEMFC, CO must be eliminated from the reformate, because it will poison the Pt catalyst of the fuel cell and cause sharp decrease of its performance. On the contrary, it is not necessary to worry about the effect of CO concentration in high temperature fuel cells, such as solid oxide fuel cell (SOFC), in which CO can even act as a fuel. Additionally, in high temperature fuel cell, internal reforming is possible and the energy efficiency can be further improved. It is, therefore, interesting to investigate the possibility of hydrogen production from partial oxidation and reforming of DME at high temperature. Unfortunately, there was no literature concerned with this.

In this work, the possibility and efficiency of hydrogen production from partial oxidation and reforming of DME was investigated. Noble metals are well-known oxidation catalysts with high activity, and Ni catalyst is considered the most promising industrial catalyst for the reforming reaction, especially Ni–MgO solid solution was found to be an ultra stable catalyst for CO_2 reforming of CH_4 [3,4]. $Pt/\gamma\text{-}Al_2O_3$ and Ni–MgO were, therefore, selected as the oxidation/reforming catalysts.

2. Experimental

The 0.25 wt% $Pt/\gamma\text{-}Al_2O_3$ catalyst was prepared by impregnation with $PtCl_4$ solution on $\gamma\text{-}Al_2O_3$ (AKP-GO15, supplied by SUMITOMO Chemical CO., LTD). $Ni_{0.03}Mg_{0.97}O$ was prepared by co-precipitating nickel nitrate and magnesium nitrate aqueous solutions using potassium carbonate according to the literature [5]. After being filtered and washed with hot water, the precipitate was dried at 120 °C over night and then calcinated at 850 °C for 20 h.

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Activity measurements were carried out with a fixed-bed continuous-flow quartz tube reactor, where 0.3 g of each catalyst with 1.0 g silica sand was loaded, under ambient pressure. Prior to each run, catalysts were reduced in a flow of hydrogen ($H_2/Ar = 1/1$) at 500 °C for 30 min, followed by purging with Ar for 10 min. A thermocouple was located in the catalyst bed to monitor the temperature profiles under reaction conditions. DME and O_2/Ar were fed into the reactor separately with the standard composition of DME:O_2: Ar = 32:30:128 ml/min (STD). The reactor structure and catalysts loading manner were shown in figure 1.

After removing water in the effluent gas with a cooling trap, the products were analyzed by two on-line gas chromatographs (SHIMADZU GC-8A) equipped with a thermal conductivity detector (TCD) and a flaming ionization detector (FID), separately. Active carbon column was used for the analysis of CO, CO_2, CH_4, and H_2, and Porapak N column was used to analyze DME, CH_4, and other hydrocarbons.

3. Results and discussion

DME conversion and H_2 yield as functions of time on stream with the dual bed catalysts at 700 °C are shown in figure 2. DME was always converted totally during the reaction period, and H_2 yield was kept higher than 90%. These results indicated that hydrogen production from partial oxidation and reforming of DME is possible and effective.

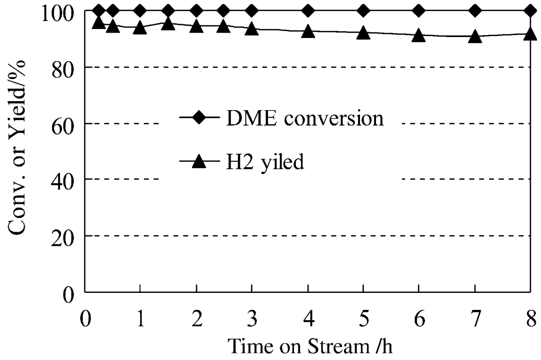

Figure 2. DME conversion and H_2 yield as functions of time on stream over Pt/Al_2O_3 + Ni–MgO dual bed catalysts T = 700 °C, DME/O_2/Ar = 30/32/128 (ml/min), Pt/Al_2O_3: 0.3 g, Ni–MgO: 0.3 g.

Distribution of carbon-containing products and H_2 yield with Pt/Al_2O_3 + Ni–MgO dual bed and individual Pt/Al_2O_3 or Ni–MgO catalysts are shown in table 1. CO and H_2 yield with the dual bed catalysts was much higher than that with individual Ni–MgO catalyst, either at 700 or 600 °C, indicating that Pt/Al_2O_3 was active in partial oxidation of DME, just as expected. In addition, CH_4 yield was decreased and CO/H_2 yield was improved significantly in the dual bed reaction by adding Ni–MgO bed under Pt/Al_2O_3 bed, which indicated that Ni–MgO was active for the reforming of CH_4. It is worth noticing that DME conversion over dual bed catalyst was higher than that over individual Pt/Al_2O_3 catalyst at 600 °C. At the same time, CH_4 yield did not show significant difference while H_2 and CO yields were much higher over

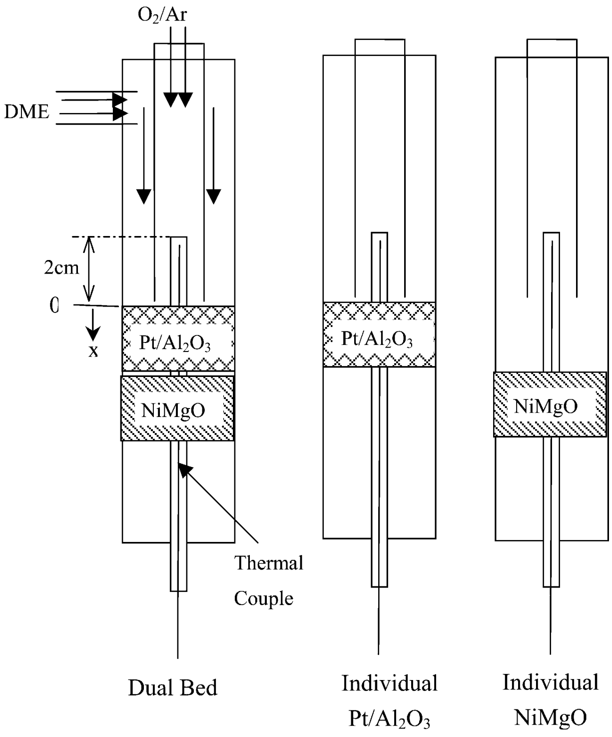

Figure 1. Reactor structure and catalysts loading manner.

Table 1
Reaction scheme over the dual bed catalysts

Temperature (°C)	Catalysts	Conv.(%) DME	Yield (%)				
			CO	CO_2	CH_4	C_2	H_2
700	Ni–MgO	98.5	45.4	29.4	22.9	0.8	55.5
	Pt/Al_2O_3	100	56.0	24.4	19.0	0.6	51.3
	Pt/Al_2O_3 + Ni–MgO	100	66.8	24.6	8.6	0.0	92.8
600	Ni–MgO	52.5	16.1	20.9	14.1	1.4	13.6
	Pt/Al_2O_3	48.5	14.6	27.0	6.6	0.4	7.5
	Pt/Al_2O_3 + Ni–MgO	66.9	30.5	31.3	4.9	0.1	58.2

$DME/O_2/Ar$ = 30/32/128 (ml/min); time on stream: 4 h; Pt/Al_2O_3: 0.3 g, Ni–MgO: 0.3 g.

the dual bed catalysts. These results indicated that Ni–MgO is active for the reforming of DME as well as for the reforming of CH_4.

Because neither the oxidation nor the reforming of DME would produce CH_4 or C_2H_6, the existence of CH_4 and C_2H_6 in the effluent implied that the homogeneous decomposition of DME took place at high temperature under the experimental conditions:

$$CH_3OCH_3 \rightarrow CH_3O\cdot + \cdot CH_3 \qquad (R\text{-}1)$$

$$CH_3O\cdot + \cdot CH_3 \rightarrow CH_4 + HCHO \qquad (R\text{-}2)$$

$$HCHO \rightarrow H_2 + CO \qquad (R\text{-}3)$$

$$2\cdot CH_3 \rightarrow CH_3CH_3 \qquad (R\text{-}4)$$

In the case of individual Ni–MgO catalyst, DME and O_2/Ar were mixed in a space before reaching the catalyst bed. There was enough time for the homogeneous decomposition to proceed. But in the case of dual bed catalysts, DME and O_2/Ar were mixed in the Pt/Al_2O_3 bed and Pt/Al_2O_3 can suppress the homogeneous decomposition of DME by controlling the propagation of free radicals. CH_4 and C_2H_6 yield with the dual bed catalysts were, therefore, much less than that with individual Ni–MgO catalyst.

Increasing O_2/DME ratio would further decrease CH_4 yield, but the catalyst system used here did not show preferential oxidation activity, more O_2 in the feed gas would also consume more H_2, the requiring product.

From the discussion above, a reaction scheme over the dual bed catalysts was summarized in figure 3. With Pt/Al_2O_3 catalyst, partial oxidation and complete oxidation takes place accompanying with homogeneous decomposition, producing CO, CO_2, H_2, CH_4 and C_2H_6. However, Pt/Al_2O_3 catalyst can suppress the homogeneous decomposition in a certain way. When the oxidation and decomposition products flow through Ni–MgO catalyst bed, reforming of DME and CH_4 with CO_2 or H_2O would takes place. The reforming reactions can further improve hydrogen yield. Since Ni–MgO is not a good oxidation catalyst and Pt/Al_2O_3 is not a good reforming catalyst, it is not suitable to configure catalysts with Ni–MgO first and Pt/Al_2O_3 second. Otherwise, DME conversion and H_2 yield would not reach the acceptable level.

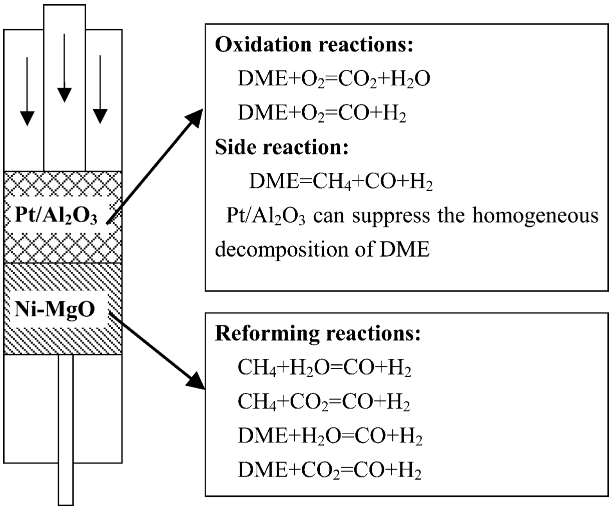

Figure 3. Reaction scheme over the dual bed catalysts.

4. Conclusion

Hydrogen production from partial oxidation and reforming of DME is possible and effective over dual Pt/Al_2O_3 + Ni–MgO bed. Higher than 90% H_2 yield was obtained at 700 °C with 100% DME conversion. Pt/Al_2O_3 not only catalyzed the partial oxidation of DME, but also suppressed the homogeneous decomposition of DME. Ni–MgO played the role of reforming of CH_4 and DME, producing more H_2.

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