

研究快报

KINETICS OF HYDROGEN PRODUCTION BY
PARTIAL OXIDATION AND STEAM
REFORMING OF METHANOL

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1 INTRODUCTION

With decreasing oil reserves and deteriorating environment, the problem of energy and environment has become the main obstacle to the sustainable development of economy and the progress of mankind. In many developed countries fuel cells are extensively researched. In all kinds of fuel cells, the proton exchange membrane fuel cell (PEMFC) has lots of advantages^[1,2], such as high specific power, quick to initiate, no corrosion, adjustable dimensions. Pt or carbon carried Pt serves as catalyst and hydrogen as fuel. Whereas the storage and carriage of hydrogen have many difficulties, generation of hydrogen from methanol or other hydrogen-rich materials is an attractive technology. Generation of hydrogen by steam reforming of methanol is widely studied. However, it is a strong endothermic reaction and needs external heat supply, which causes low response and secondary pollution. Especially the by-product CO is the poison of anode catalyst. The coupled generation of hydrogen on Cu/Zn catalyst by steam reforming of methanol and partial oxidation was developed by Ahmed *et al.*^[3]. However, the stability and selectivity of catalysts leave room for improvement. Moreover the catalytic kinetics of this process has not been reported yet.

2 EXPERIMENTAL

Based on prior researches, a Cu/Zn/Al₂O₃/ZrO₂

composite catalyst was prepared by co-deposition. Measured with Mecromeritics ASAP2400 specific surface aperture analyzer, the specific surface area of the catalyst was 56.5 m² · g⁻¹, the average aperture was 14.9 nm and the total pore volume was 0.04 cm³ · g⁻¹. 154.29 mg of the composite catalyst whose average grain size was 427 μm was loaded into a homemade reactor. The hydrogen generation experiments were carried out with a feed flow rate of 5000 mol · h⁻¹ · kg⁻¹ in a normal pressure flow system at 380 °C. The percentage conversion of methanol was 100%. There was no carbon monoxide detected in outgrowths. After two weeks running, the activity of the catalyst showed no obvious decline. Then the 4 mm ID stainless steel micro-reactor was put into an electric heating chamber in which the temperature fluctuation can be controlled to within ±0.5 °C. 252 mg of the catalyst was loaded in the micro-reactor. In the front of the micro-reactor a vaporizing-preheating mixer with static hybrid component was fitted. Methanol and water were introduced into the vaporizing-preheating mixer pro rata by a ZJT037 precision high-pressure metering pump. Oxygen was added to the mixer after passing a Model 8209 mass flow meter. The mixtures were preheated up to reaction temperature and charged into the reactor. Some electric heating bands were wrapped around the pipeline to prevent some products from freezing. The products were on-line analyzed with a refitted GC9800 gas chromatograph. The fixed phase of the chromatographic column was 601 carbon molecular sieve (Shanghai Reagent Plant) concatenating modified PEG 20M.

The inner and external diffusions of the catalyst bed were eliminated by some prior experiments. Then the

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continuous flow reaction kinetics experiments were carried out at normal pressure and within 200—340 °C. The mole ratios of methanol, water and oxygen are 0.45 : 0.45 : 0.10, 1.5 : 1.0 : 0.20 and 1.0 : 2.0 : 0.20 respectively. 96 group of experimental data in 12 set of experiments were measured. When each experiment condition was changed, the system was kept steady for 1 h before sampling. Each experimental point was repeated three times. Some experimental results are shown in Fig. 1.

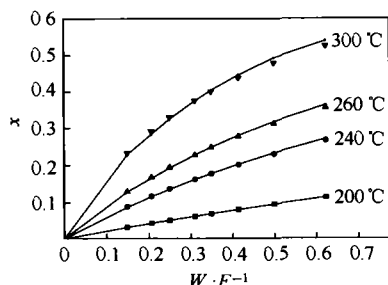


Fig. 1 Contrast curves of prediction of kinetics model and experimental data when $\text{CH}_3\text{OH} : \text{H}_2\text{O} : \text{O}_2 = 1.0 : 2.0 : 0.2$ (mole ratio)
— prediction curve; ▲, ● experimental data

3 RESULTS

The kinetics experimental data are the changes of methanol percentage conversion x with feed flow rate F under set reaction temperature and mixing ratio. Because the ratio of the catalyst particle diameter and the inner diameter of the reactor is very little, one dimensional piston model can be met approximately. By use of least-squares procedure, the $x \sim W/F$ experimental data in different mixing ratios and different temperatures can be presented as the following quantitative equation

$$x = \frac{a \times (W/F)}{b + (W/F)} \quad (1)$$

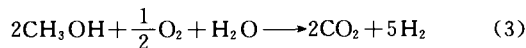
where W represents the mass of catalyst.

By use of numerical differentiation, the reaction rate r can be calculated as follows

$$r = \frac{dx}{d(W/F)} = \frac{a}{b + W/F} \left[1 - \frac{W/F}{b + W/F} \right] \quad (2)$$

where a , b are the fitting parameters of the $x \sim W/F$ experimental data at different mixing ratios and different temperatures.

Hydrogen generation by partial oxidation and steam reforming of methanol is a complex reaction system which includes a series of reactions. According to the thermodynamic analysis for this system, the total reaction is^[4]



Considering the complexity of this reaction process, the kinetics equation can be expressed

$$r = k p_{\text{CH}_3\text{OH}}^m p_{\text{H}_2\text{O}}^n p_{\text{O}_2}^c \quad (4)$$

The partial pressure p_i of each component can be calculated by material balance and the results are shown as follows

$$p_{\text{CH}_3\text{OH}} = \frac{n_1(1-x)}{\sum n} \quad (5)$$

$$p_{\text{H}_2\text{O}} = \frac{n_2 - n_1 x/2}{\sum n} \quad (6)$$

$$p_{\text{O}_2} = \frac{n_3 - n_1 x/4}{\sum n} \quad (7)$$

$$\sum n = n_1 + n_2 + n_3 + 1.75n_1 x \quad (8)$$

where n_1 , n_2 and n_3 are the initial input quantity (mol) of methanol, water and oxygen respectively.

According to Eqs (4) — (8), m , n , c and k in different mixing ratios and reaction temperatures could be fitted by least-squares procedure. m , n and c are approximate constants in different mixing ratios and reaction temperatures and their average value were 0.934, 0.710 and 0.832 respectively. The change of k at three mixing ratios and five reaction temperatures with temperature could be fitted to Arrhenius equation

$$k = Z \exp\left(-\frac{E}{RT}\right) \quad (9)$$

where R is the gas constant, T is the reaction temperature. Using least-squares procedure, the results could be computed as $Z = 9.56 \times 10^7$, reaction activation energy $E = 63.7 \text{ kJ} \cdot \text{mol}^{-1}$. The correlation coefficient $R > 0.99$.

For evaluating the developed reaction kinetics model, Jackknife interactive verification is used, *i. e.* every time one sample is charged off and the rest $N-1$ samples are modeled to predict this weeded sample. Contrasting 96 prediction values of interactive verification with the experimental data, the total average relative error is 2.19%. Some comparison data are demonstrated in Fig. 1. Apparently the results are satisfactory.

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