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# Enhancement of catalytic activity over TiO<sub>2</sub>-modified Al<sub>2</sub>O<sub>3</sub> and ZnO–Cr<sub>2</sub>O<sub>3</sub> composite catalyst for hydrogen production via dimethyl ether steam reforming

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#### ABSTRACT

The dimethyl ether steam reforming (DME SR) was carried out over the composite catalyst of ZnO–Cr<sub>2</sub>O<sub>3</sub> coupled with Al<sub>2</sub>O<sub>3</sub>, TiO<sub>2</sub> or TiO<sub>2</sub>–Al<sub>2</sub>O<sub>3</sub> in the microreactor. The results showed that the catalytic activities were greatly enhanced over the composite catalyst of ZnO–Cr<sub>2</sub>O<sub>3</sub> combined with TiO<sub>2</sub>–Al<sub>2</sub>O<sub>3</sub> (ZnCr–TiAl) in comparison to those combined with Al<sub>2</sub>O<sub>3</sub> or TiO<sub>2</sub> in DME SR. By evaluating the catalytic activity of solid acids in DME hydrolysis, it was proposed that the better performance of TiO<sub>2</sub>–Al<sub>2</sub>O<sub>3</sub> in DME hydrolysis contributed to the superior activity of ZnCr–TiAl in DME SR, indicating a higher DME hydrolysis activity favored DME SR. In view of the characterization of N<sub>2</sub> physisorption, scanning electron microscope, X-ray diffraction and NH<sub>3</sub> temperature-programmed desorption, the promotion effect of TiO<sub>2</sub> on the acid properties of Al<sub>2</sub>O<sub>3</sub> surface. The acid strength or total acid amount was enhanced by the addition of different TiO<sub>2</sub> content. In the 150 h medium stability test, there was no obvious deactivation for ZnCr–TiAl catalyst with the H<sub>2</sub> production rate of 345 mol h<sup>-1</sup> kg<sup>-1</sup><sub>cat</sub> and the CO selectivity in the dry reformate remained below 6%. The characterization results of the used catalyst revealed that no change in the crystalline phase and size occurred on the spent catalyst.

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### 1. Introduction

Proton exchange membrane fuel cells (PEMFCs) research and development has become a flourishing area in recent years, due to their stationary and mobile applications as clean and efficient power generators at a range of scales [1]. However, the commercialization of PEMFCs has been hindered by some difficulties, such as durability, cost and hydrogen storage and distribution. Thereinto, one of the most promising solutions to provide hydrogen is on site hydrogen generation from hydrocarbon fuels. Dimethyl ether (DME) has been considered as one of the potential fuels due to various advantages, such as high H/C ratio, high energy density, innocuous nature and easy storage and transportation due to the similar physical properties to those of LPG and LNG [2-4]. In addition, the direct synthesis of DME from syngas has been proved to be feasible by many literatures [5]. Among the reformation technologies, DME steam reforming (DME SR) has been regarded as the most suitable process to obtain H<sub>2</sub>-rich reformate for fuel cell application because of its higher hydrogen yield and lower selectivity to CO which is considered as the poison to Pt electrode of PEMFCs [6].

Generally, DME SR is a couple of two consecutive reactions: the hydrolysis of DME to methanol over a solid acid, and then

the steam reforming of methanol formed (MSR). Therefore, the overall process usually needs a hybrid catalyst consisting of dual sites of acid sites and MSR sites. So far, many catalysts have been developed for DME SR, which are usually in the form of the mechanical mixture of a solid acid and a MSR catalyst [7-10]. Various solid acids, such as zeolite, WO<sub>3</sub>-ZrO<sub>2</sub> and  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> are reported to be active for DME hydrolysis, while Cu-based catalysts are the common MSR catalysts. When zeolite and WO<sub>3</sub>-ZrO<sub>2</sub> are coupled with Cu-based catalysts, DME SR can proceed below 300 °C because of the existence of strong Brønsted acid. Nevertheless, these composite catalysts are prone to deactivation due to the coke deposition [11,12]. Kawabata et al. suggested that the formation of coke materials was originated from the polymethyl aromatics produced by polymerization on the solid acid catalyst, followed by the migration to the Cu-based catalyst [8]. Compared with zeolite and WO<sub>3</sub>–ZrO<sub>2</sub>,  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> with weaker acid sites has been reported to be more durable for DME hydrolysis, but a relatively higher temperature between 350 and 500 °C is required for efficient hydrolysis of DME. Many studies have employed  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> as the solid acid in the reforming process, such as Al<sub>2</sub>O<sub>3</sub> + Cu<sub>2</sub>Mn<sub>1</sub>Fe<sub>3</sub> [10], 2Cu-1Ni-17Al<sub>2</sub>O<sub>3</sub> [13], Cu 20%/γ-Al<sub>2</sub>O<sub>3</sub> [14] and particularly CuFe<sub>2</sub>O<sub>4</sub> + Al<sub>2</sub>O<sub>3</sub> [15]. Faungnawakij et al. found that CuFe<sub>2</sub>O<sub>4</sub> + Al<sub>2</sub>O<sub>3</sub> catalyst exhibited good activity and stability in DME SR at the temperature range of 350-450 °C. The high dispersion of metallic copper in the matrix of iron oxides reduced from spinel structure and their strong chemical interaction were

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