SYNTHESIS AND CHARACTERIZATION OF Cu-X/γ-Al₂O₃ CATALYST BY INTERVAL MICROWAVE IRRADIATION FOR HYDROGEN GENERATION FROM DIMETHYL ETHER STEAM REFORMING

Article Highlights
- 2Cu-Fe/72γ-Al₂O₃ performs excellent for DME steam reforming
- The intermittent microwave irradiation provides a rapid method for Cu-Fe/γ-Al₂O₃ synthesis
- Adjusting micro-irradiation on and off time can effectively control the crystallite size of CuO
- Ferric oxide particles are active in water-gas shift reaction, which lower CO concentration

Abstract
A series of Cu-X/γ-Al₂O₃ (X = Fe, Co, Ni) catalysts were synthesized by a rapid intermittent microwave irradiation method for hydrogen generation from dimethyl ether steam reforming. Different parameters, such as the promoters of X (X = Fe, Co, Ni), microwave irradiation procedure and the ratio of metal to γ-Al₂O₃, were investigated. The results show that 2Cu-Fe/72γ-Al₂O₃ has the best performance, for which the agglomeration is prevented, CuO is well dispersed and the catalytic activity is improved. Promoter iron oxide in 2Cu-Fe/9γ-Al₂O₃ facilitates the water-gas shift reaction, which lead to an increase in the conversion of CO to CO₂ and hydrogen yield. Particularly, the 2Cu-Fe/72γ-Al₂O₃ catalyst, with the best molar ratio of metal to γ-Al₂O₃, shows a dimethyl ether conversion of >99% and a hydrogen yield of >98% and produces the lowest CO content of 1.4%, indicating that the synergism between dimethyl ether hydrolysis and methanol reforming requires an appropriate balance between the metallic Cu-Fe and the acid γ-Al₂O₃. The intermittent microwave irradiation technique provides a simple but effective method of the Cu-Fe/γ-Al₂O₃ synthesis with a good catalyst performance for the dimethyl ether steam reforming.

Keywords: hydrogen generation; dimethyl ether; intermittent microwave; catalytic steam reforming.
DME is an excellent process to produce hydrogen and an attractive route to provide hydrogen as fuel cells on a small or medium scale. An integrated system of DME steam reforming (Eq. (1)) for hydrogen generation usually involves two consecutive processes: the DME hydrolysis (Eq. (2)) and the MeOH steam reforming (Eq. (3)). Besides, the reverse water-gas shift reaction (Eq. (4)) takes place. Generally, a solid acid catalyst such as γ-Al2O3, HZSM-5, zeolites, Ga2O3 or ZrO2 is needed to catalyze the hydrolysis of DME, whereas Cu-, Pt-, Ru-, Pd-, and Ni-based catalysts are used for MeOH steam reforming [4-9]. Consequently, suitable metallic and acid components are required to synthesize the bi-functional catalyst for high DME conversion, high H2 selectivity and high stability.

DME steam reforming:

\[
\text{CH}_3\text{OCH}_3(g) + 3\text{H}_2\text{O}(g) = 2\text{CO}_2 + 6\text{H}_2; \quad \Delta H_{298K}^\circ = 122 \text{ kJ mol}^{-1}
\]  

DME hydrolysis:

\[
\text{CH}_3\text{OCH}_3(g) + \text{H}_2\text{O}(g) = 2\text{CH}_3\text{OH}(g); \quad \Delta H_{298K}^\circ = 24 \text{ kJ mol}^{-1}
\]  

MeOH steam reforming:

\[
\text{CH}_3\text{OH}(g) + \text{H}_2\text{O}(g) = \text{CO}_2 + 3\text{H}_2; \quad \frac{\Delta H_{298K}^\circ}{\Delta H_{298K}^\circ} = 49 \text{ kJ mol}^{-1}
\]  

Reverse water-gas shift reaction:

\[
\text{CO}_2 + \text{H}_2 = \text{H}_2\text{O}(g) + \text{CO}; \quad \Delta H_{298K}^\circ = 41 \text{ kJ mol}^{-1}
\]  

Catalyst preparation

\[
2\text{Cu}-\text{X}/\gamma\text{Al}_2\text{O}_3 \quad (X = \text{Fe, Co, Ni}) \text{ with Cu: X: } \gamma\text{Al}_2\text{O}_3, \text{ mole ratio of 2:1:9, was prepared by the impregnation method: an aqueous precursor containing Cu(NO}_3)_2, X(NO)_n (X = \text{Fe, Co, Ni}) \text{ and } \gamma\text{Al}_2\text{O}_3 \text{ powder was made at room temperature and then was processed in the microwave (FT-2KW, Guangzhou Futao microwave equipment co. ltd at 2 kW). IMI was in the pulse form of 5 s-on and 5 s-off for 20 times (2Cu-Fe/9γAl}_2\text{O}_3, 5 s). The catalyst was dried at 110 °C for 12 h and calcined at 400 °C for 5 h.}
\]

Effects of the microwave irradiation procedure were investigated by the different irradiation times with a total irradiation time of 100 s, irradiation and relaxation time remain the same ratio of 1:1. 2Cu-Fe/9γAl}_2\text{O}_3 (0 s) meant that no microwave irradiation was applied. 2Cu-Fe/9γAl}_2\text{O}_3 (20 s) was heated by intermittent microwave in the pulse form of 20 s-on and 20 s-off for 5 times. 2Cu-Fe/9γAl}_2\text{O}_3 (50 s) was heated in the pulse form of 50 s-on and 50 s-off for 2 times.

Catalyst characterization

X-ray diffraction (XRD) analysis was performed in the PANalitical X’Pert diffractometer (X’Pert PRO MPD, PW3040/60) within the 2-θ ranged from 20 to 80° by a speed of 2° per min with Cu-Kα (λ = 0.154060 nm) radiation (40 kV, 40 mA). The crystallite size of CuO and Fe2O3 was calculated by the Sherrer equation on the basis of the data of the line broadening at half the maximum intensity (full width at half-maximum, FWHM) and the Bragg angle (θ). The Brunauer-Emmett-Teller (BET) specific surface was determined from the adsorption and desorption isotherms of nitrogen at -196 °C after outgassing procedure under vacuum at 250 °C for 20 h, using a Quantachrome SI-8PoreMaster 33. The catalyst was characterized by the Scanning electron microscope (SEM) with a S-4800 instrument at 2.0 kW. The hydrogen temperature-programmed reduction (H2-TPR) was carried out to estimate the reduction performance of the catalyst by Quantachrome ASIQACIV200-2. H2-TPR was conducted in the following method: 100 mg of a powder sample was
heated at a rate of 10 °C/min up to 120 °C in helium atmosphere and kept for 1 h. The sample was cooled down to 40 °C in the He atmosphere, and then followed by a pure hydrogen flow for 1 h. Subsequently, H2-TPR was initiated by a heating rate of 10 °C/min up to 750 °C. The consumption of hydrogen was determined by a Thermal conductivity detector (TCD) and recorded by an online computer.

Catalytic reaction and analyses of the products

DME steam reforming was executed in a bench-scale fixed-bed reactor (a quartz tube with inner diameter of 20 mm) under ambient pressure. The fixed-bed reactor consists of a gas supplier, a catalyst reaction part, an analyzer, and a controller, as shown in Figure 1. The catalyst was placed in the quartz tube and was heated by an electric furnace equipped with a temperature controller. The catalyst (m = 2 g) was reduced in 5 vol.% H2 in N2, heating rate of 10 °C min⁻¹ from room temperature up to 400 °C for 4 h, then the system was balance with N2 for 1 h at the same temperature. Standard reaction conditions for DME steam reforming were steam to DME molar ratio of 5 to 1 at a space velocity of 3600 ml/(g cat h). The system was run for 1 h then the product gas was cooled and dried before analyzing by the chromatograph (WUFENG GC522) equipped with a TCD detector and a Flame ionization detector (FID) detector. The steam reforming reaction performance over Cu-X/γ-Al2O3 catalysts was evaluated by conversion of the CO2 and selectivity CO, CH4. The representative values are given as follows:

\[ X_{\text{DME}} = \frac{100F_{\text{DME,in}} - F_{\text{DME,out}}}{F_{\text{DME,in}}} \]  

\[ S_X = \frac{100F_{X,\text{in}}}{2(F_{\text{DME,in}} - F_{\text{DME,out}})} \]  

where \( X_{\text{DME}} \) is DME conversion, \( S_X (X = \text{CH}_4, \text{CO}) \) are CH4 selective and CO selectivity, \( F_{\text{DME,in}} \) and \( F_{\text{DME,out}} \) are the inlet and outlet molar flow rates of DME, respectively. \( F_{\text{H}_2} \) are the molar flow rate of H2 in the gas out reactant, \( F_{X,\text{in}} (X = \text{CH}_4, \text{CO}) \) are the molar flow rate of CH4 or CO in the gas out reactant.

RESULTS

Effect of promoter on steam reforming of DME

Figure 2a shows the XRD patterns of 2Cu-X/γ-Al2O3 (X = Fe, Co, Ni) and γ-Al2O3. The peaks of γ-Al2O3 and CuO can be seen for all the 2Cu-X/γ-Al2O3 catalysts. The strong peaks assigned to CuO appears at 2θ 35.6 and 38.5 °. The X-ray phase analysis results for the 2Cu-Fe/γ-Al2O3 (Figure 2a, e) shows the composition of the sample includes the phase CuO, Fe2O3 and γ-Al2O3. A broadened low-intensity peak in the range of 2θ 33° indicate the presence of a hematite phase Fe2O3 (2θ = 33.18°). The low-intensity of reflection from crystallized ferric oxide phase allows us to assume that in 2Cu-Fe/γ-Al2O3, ferric compounds are found in an X-ray amorphous or highly dispersed state [17]. The peaks of Co3O4 crystals can be found in 2Cu-Co/γ-Al2O3 (Figure 2a, d)). There is no peak of NiO, which may be existed in amorphous or microcrystal state.

Figure 2b shows the results of the H2-TPR of the catalysts. Cu species are the main center of the activity for methanol steam reforming. It was reported that usually there are two CuO species in copper based catalysts, the highly dispersed CuO reacts at lower reduction temperature (peak α) and the bulk CuO species reacts at higher temperature (peak β) [18]. This 2Cu-X/γ-Al2O3 (X = Fe, Co, Ni) series show that introducing a second metal into the copper

![Figure 1. Schematic diagram of DME catalytic reaction apparatus. (MFC: mass flow controller, GC: gas chromatograph).](image-url)
Figure 2. a) XRD patterns and b) H₂-TPR profiles of the Cu-based catalysts (a: γ-Al₂O₃, b: 2Cu/9γ-Al₂O₃, c: 2Cu-Ni/9γ-Al₂O₃, d: 2Cu-Co/9γ-Al₂O₃, e: 2Cu-Fe/9γ-Al₂O₃); c) XRD patterns and d) H₂-TPR profiles of 2Cu-Fe/9γ-Al₂O₃ catalysts by different microwave irradiation time. a: 2Cu-Fe/9γ-Al₂O₃ (0 s), b: 2Cu-Fe/9γ-Al₂O₃ (5 s), c: 2Cu-Fe/9γ-Al₂O₃ (20 s), d: 2Cu-Fe/9γ-Al₂O₃ (50 s); e) XRD patterns and f) H₂-TPR profiles of the catalysts derived from the Cu-Fe/γ-Al₂O₃ by different loading of 2Cu-Fe and γ-Al₂O₃ (a: γ-Al₂O₃, b: 2Cu-Fe/72γ-Al₂O₃, c: 2Cu-Fe/36γ-Al₂O₃, d: 2Cu-Fe/18γ-Al₂O₃, e: 2Cu-Fe/9γ-Al₂O₃, f) SEM images of 2Cu-Fe/9γ-Al₂O₃ (5 s) and h) 2Cu-Fe/9γ-Al₂O₃ (20 s).
based catalyst change the copper reduction property. The change of the reduction temperature for bicomponent catalysts can be explained by the several possible factors: the dispersity of the copper oxide in the presence of the second metal, formation of mixed oxides (leading to changing the metal-oxygen bonds). In the presence of the promoter Fe, Co and Ni, the reduction of dispersed CuO species all shifts to higher temperature (Table 1).

$2Cu$X/$\gamma$Al$_2$O$_3$ ($X$ = Fe, Co, Ni) was tested in steam reforming of DME at the condition of H$_2$O to DME of 5:1, temperature of 400 °C and space velocity of 3600 ml g$^{-1}$ h$^{-1}$ in Figure 3. All the catalysts show the DME conversions of >99%, while the hydrogen yield differ from each other. $2Cu$Ni/$\gamma$Al$_2$O$_3$ and $2Cu$Co/$\gamma$Al$_2$O$_3$ obtained 69 and 86%. The results obtained are in agreement with the H$_2$-TPR profiles, according to which for $2Cu$Ni/$\gamma$Al$_2$O$_3$, $2Cu$Co/$\gamma$Al$_2$O$_3$ and $2Cu$Fe/$\gamma$Al$_2$O$_3$, we observe an increase in the CuO reduction temperature. Usually the higher reduction temperature presents lower reducibility and catalytic activity [11], whereas the $2Cu$Fe/$\gamma$Al$_2$O$_3$ has the highest activity of H$_2$ yield 97% whose reduction temperature is slightly higher than $2Cu$Ni/$\gamma$Al$_2$O$_3$. It may be due to the presence of ferric oxides within the composition of the catalyst, which are active catalysts for the water-gas shift reaction. As a result, it leads to an increase in the conversion of CO to CO$_2$ and an increase in the hydrogen yield. The effect of ferric additives on the water-gas shift reaction has also been noted for Fe-Cu/ZrO$_2$ [17], Ni-Fe/La$_2$O$_2$CO$_3$ [19] and Fe/Ca-Al$_2$O$_3$ [20]. The addition of ferric promotes leading to the better catalytic performance and the lowest CO selectivity of 1.4% in the case of $2Cu$Fe/$\gamma$Al$_2$O$_3$. Therefore, the following study will focus on ferric as the promoter.

### Table 1. Specific surface area, pore structure and reduction peak temperature and ratio of dispersed CuO to bulk CuO of different catalysts prepared in this work. Chemical composition referred as mole ratio

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>BET (m$^2$ g$^{-1}$)</th>
<th>V / cm$^3$ g$^{-1}$</th>
<th>d / nm</th>
<th>Temperature, °C</th>
<th>Dispersed CuO</th>
<th>Bulk CuO</th>
<th>Dispersed CuO/Bulk CuO</th>
<th>Crystallite size, nm</th>
</tr>
</thead>
<tbody>
<tr>
<td>γ-Al$_2$O$_3$</td>
<td>256.7</td>
<td>0.50</td>
<td>7.86</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>$2Cu$Fe/γ-Al$_2$O$_3$</td>
<td>195.7</td>
<td>0.41</td>
<td>8.02</td>
<td>282</td>
<td>319</td>
<td>1.79</td>
<td>41.8</td>
<td>20.9</td>
</tr>
<tr>
<td>$2Cu$Co/γ-Al$_2$O$_3$</td>
<td>182.9</td>
<td>0.38</td>
<td>8.40</td>
<td>302</td>
<td>326</td>
<td>1.04</td>
<td>36.4</td>
<td>-</td>
</tr>
<tr>
<td>$2Cu$Ni/γ-Al$_2$O$_3$</td>
<td>181.9</td>
<td>0.39</td>
<td>8.47</td>
<td>286</td>
<td>322</td>
<td>0.79</td>
<td>51.1</td>
<td>-</td>
</tr>
<tr>
<td>$2Cu$Fe/γ-Al$_2$O$_3$ (5 s)</td>
<td>197.7</td>
<td>0.42</td>
<td>8.49</td>
<td>273</td>
<td>323</td>
<td>0.98</td>
<td>62.7</td>
<td>-</td>
</tr>
<tr>
<td>$2Cu$Fe/γ-Al$_2$O$_3$ (10 s)</td>
<td>195.6</td>
<td>0.40</td>
<td>8.21</td>
<td>257</td>
<td>319</td>
<td>0.73</td>
<td>42.8</td>
<td>31.5</td>
</tr>
<tr>
<td>$2Cu$Fe/γ-Al$_2$O$_3$ (20 s)</td>
<td>193.7</td>
<td>0.38</td>
<td>8.00</td>
<td>259</td>
<td>305</td>
<td>1.04</td>
<td>49</td>
<td>27.8</td>
</tr>
<tr>
<td>$2Cu$Fe/γ-Al$_2$O$_3$ (50 s)</td>
<td>192.1</td>
<td>0.39</td>
<td>8.20</td>
<td>258</td>
<td>305</td>
<td>1.04</td>
<td>52.4</td>
<td>31.2</td>
</tr>
<tr>
<td>$2Cu$Fe/18γ-Al$_2$O$_3$</td>
<td>206.0</td>
<td>0.42</td>
<td>8.00</td>
<td>283</td>
<td>319</td>
<td>2.30</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>$2Cu$Fe/36γ-Al$_2$O$_3$</td>
<td>233.2</td>
<td>0.46</td>
<td>7.96</td>
<td>287</td>
<td>320</td>
<td>2.61</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>$2Cu$Fe/72γ-Al$_2$O$_3$</td>
<td>237.6</td>
<td>0.48</td>
<td>7.95</td>
<td>317</td>
<td>343</td>
<td>4.03</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>
intermittent irradiation. The microwave irradiation of short on and off time results in lower reaction temperature of the synthesis reaction system, which limits the nucleation and the grain growth reaction of the CuO and Fe₂O₃ particles. Shorter irradiation time is required for the dispersion of CuO and Fe₂O₃ on the γ-Al₂O₃ supports [21-23]. The results indicate that regulating micro irradiation on and off-time can effectively control the crystallite size. From Table 1, 2Cu-Fe/9γ-Al₂O₃ (5 s) has the highest dispersed CuO/bulk CuO ratio of 1.79. Further increasing the irradiation time, the dispersed CuO concentration decreases, indicating that the shorter the irradiation time, the higher the ratio of CuO/bulk CuO.

2Cu-Fe/9γ-Al₂O₃ (5 s) and 2Cu-Fe/9γ-Al₂O₃ (0 s) obtain over 99% DME conversion in Figure 4. The advantages of optimized IMI technique compared with the conventionally heated one can be seen in the following: 2Cu-Fe/9γ-Al₂O₃ (5 s) achieves a hydrogen yield of 97%, but the conventionally heated 2Cu-Fe/9γ-Al₂O₃ (0 s) achieves 86%. It is noted that the CO concentration of 2Cu-Fe/9γ-Al₂O₃ (5 s) is 2.3% while of 2Cu-Fe/9γ-Al₂O₃ (0 s) is 7.2%. Optimized microwave irradiation technique can decrease the CO selectivity of the 2Cu-Fe/9γ-Al₂O₃ catalyst. Further increasing the irradiation time leads to a lower DME conversion and hydrogen yield, and decreases the CO selectivity. Usually the micro structure such as BET, pore size distribution and high disperse CuO reduction property affect the catalyst activity. Since the microwave irradiation procedure has little influence on the BET and pore size distribution of the catalysts (Table 1), it is the reducibility of CuO that affects the activity of 2Cu-Fe/9γ-Al₂O₃. 2Cu-Fe/9γ-Al₂O₃ (5 s) achieve the >99% DME conversion, 97.5% hydrogen yield and 2.5% CO selectivity. The elevated catalytic property might be due to the highest ratio of dispersed CuO/bulk CuO of 1.79.

**Influence of reaction condition over 2Cu-Fe/9γ-Al₂O₃**

The effect of temperature, steam to DME ratio and space velocity were investigated for the 2Cu-Fe/9γ-Al₂O₃ (Figure 5). The runs were conducted in a fixed bed reactor in the 300-400 °C range, as shown in Fig. 5a, where the DME conversion increases with the increase of the reaction temperature. γ-Al₂O₃ typically shows an excellent DME hydrolysis activity at the temperature above 300 °C due to its moderate acid amount of weak acid strength [24]. The steam reforming reaction is a strong endothermic reaction. Increasing the reaction temperature will facilitate the reaction.

Figure 5b shows the effect of steam to DME ratio on SRD over 2Cu-Fe/9γ-Al₂O₃. The DME conversion and hydrogen yield increases sharply from 51 and 45% to 95 and 92% as the stoichiometric ratio of steam to DME was 1 to 3. DME conversion and hyd-
Hydrogen yield flattens out as continued increasing the steam to DME ratio. The CO concentration clearly decreases when the steam to DME ratio was raised to 5. The hydrogen yield never reaches 100% for it is consumed by the reverse water-gas shift reaction [25].

Figure 5c shows the influence of space velocity on the catalytic activity. The DME conversion, hydrogen yield and CO decrease with the increase of space velocity. An over 99% DME conversion is seen in 3600 ml g⁻¹ h⁻¹ but only 46% in 18000 ml g⁻¹ h⁻¹. The increase of the space velocity leads to an insufficient residence time for the catalytic reaction, which decreases the DME conversion and hydrogen yield.

**Effect of weight ratio of γ-Al₂O₃ to 2Cu-Fe on Steam reforming of DME**

γ-Al₂O₃ and copper is used as the active component of the catalyst for DME hydrolysis and the steam reforming of methanol, respectively. The selection of appropriate ratio of γ-Al₂O₃ to 2Cu-Fe will significantly improve the performance of the catalyst in the DME reforming reaction.

From the XRD patterns in Figure 2e, 2Cu-Fe/9γ-Al₂O₃ (e) clearly shows the characteristic diffraction of the monoclinic phase CuO and Fe₂O₃. As the ratio of γ-Al₂O₃ increases, the diffraction from CuO and Fe₂O₃ becomes so weak, only γ-Al₂O₃ phase could be detected in 2Cu-Fe/36γ-Al₂O₃ (c) and 2Cu-Fe/72γ-Al₂O₃ (d), indicating that they exist as small crystals or in amorphous phase [12,26]. The results are also confirmed by the H₂-TPR. With the increase of γ-Al₂O₃ loading, the CuO reduction peak is weakening and shifted to higher temperature. The CuO reduction peak of 2Cu-Fe/72γ-Al₂O₃ is broader than that of 2Cu-Fe/36γ-Al₂O₃, indicating a higher dispersion of CuO in 2Cu-Fe/72γ-Al₂O₃. Meanwhile, as the Cu-Fe concentration decreases, CuO reduction peak shifts to higher temperature, which reveals that it enhances the interaction of CuO and γ-Al₂O₃. As discussed previously in part 3.2, the ratio of dispersed CuO and bulk CuO strongly affects the catalytic performance. 2Cu-Fe/72γ-Al₂O₃ has the highest ratio of 4.03 presenting the best activity and selectivity (Table 1).

The catalytic performance of different weight ratio of γ-Al₂O₃ to Cu-Fe starts with 2Cu-Fe/9γ-Al₂O₃ (Figure 6). High γ-Al₂O₃ content leads to high DME conversion and hydrogen yield at a temperature below 400 °C. When the reaction temperature reaches 400 °C, all the 2Cu-Fe/γγ-Al₂O₃ (γ = 9, 18, 36 or 72) catalysts achieve >99% DME conversion and >96% hydrogen yield. Moreover, the 2Cu-Fe/72γ-Al₂O₃ catalyst presented the least CO selectivity of 1.4%.

The CH₄ concentration in the outlet doesn’t change in the temperature range of 300-400 °C (Figure 6d), where usually methanation occurs in alumina-rich composite catalysts at above 350 °C [27].
The best performance of 2Cu-Fe/72γ-Al₂O₃ comes from: 1) its higher γ-Al₂O₃ content, which is the effective component for DME hydrolysis; 2) the highest ratio of dispersed CuO to Bulk CuO. γ-Al₂O₃ rich samples possess a large amount of acid sites, which result in high DME conversion; 3) the well dispersed CuO and Fe₂O₃ on the γ-Al₂O₃ phase. Hence, the weight balance between γ-Al₂O₃ and Cu-Fe should be regulated very carefully.

Figure 6e shows dimethyl ether conversion as a function of reaction time over the 2Cu-Fe/72γ-Al₂O₃ catalyst. 2Cu-Fe/72γ-Al₂O₃ had good stability over 50 h and dimethyl ether conversion stayed around 99%. The 2Cu-Fe/72γ-Al₂O₃ catalyst had been stable at 400 °C, while usually ordinary Cu-supported catalysts were gradually deactivated [27].

**CONCLUSIONS**

A series of 2Cu-X/γ-Al₂O₃ (X = Fe, Co, Ni) catalysts were synthesized by a rapid intermittent microwave irradiation (IMI) technique for hydrogen generation in dimethyl ether (DME) steam reforming. The promoter of ferric oxides within the composition of 2Cu-Fe/γ-Al₂O₃ are active catalysts for the water-gas shift reaction which leads to an increase in the conversion of CO to CO₂ and an increase in the hydrogen yield.

The preparation of 2Cu-Fe/γ-Al₂O₃ catalysts by IMI technique changes the average crystallite size of Cu and Fe. The optimized IMI procedure is in the pulse form of 5 s-on and 5 s-off for 20 times. The 2Cu-Fe/72γ-Al₂O₃ (5 s) catalyst provides >99% DME...
conversion, 97% hydrogen yield and 1.4% CO percent by volume. It may be due to the higher ratio of dispersed CuO to bulk CuO leads to better activity and selectivity. The optimal condition IMI technique gives great benefits to hydrogen yield and CO and CH₄ selectivity.

Acknowledgments

The authors are grateful for the financial support of CAS Renewable Energy Key Lab., Natural Science Foundation of China (51576201), Natural Science Foundation of Guangdong province (2015A030312007, 2015A030313716), Guangdong Science and Technology Project (2013B091300001, 2014A020216030) Guangzhou Science and Technology Project (2013J4500027).

REFERENCES

SHILIN HUANG
JUAN LI
CHANG-FENG YAN
ZHIDA WANG
CHANGQING GUO
YAN SHI

Key Laboratory of Renewable Energy, Chinese Academy of Sciences; Guangdong Key Laboratory of New and Renewable Energy Research and Development, Guangzhou Institute of Energy Conversion, Chinese Academy of Sciences, No.2, Wushan, Tianhe District, Guangzhou, China

SINTEZA I KARAKTERIZACIJA KATALIZATORA Cu-X/γ-Al₂O₃ INTERMITENTNIM MIKROTAŁASNIM ZRAČENJEM ZA PROIZVODNJU VODONIKA REFORMOVANJEM DIMETIL ETA VODENOM PAROM

Serija katalizatora Cu-X/γ-Al₂O₃ (X = Fe, Co, Ni) je sintetizovana metodom brzog intermitentnog mikrotałasnog zračenja za generisanje vodonika reformovanjem dimetil-etra vodnom parom. Ispitani su različiti parametri, kao što su: promotor X (X = Fe, Co, Ni), postupak mikrotałasnog zračenja i odnos metal/Cu-X/γ-Al₂O₃. Rezultati pokazuju da 2Cu-Fe/72γ-Al₂O₃ ima najbolje performanse, jer sprečava aglomeraciju, CuO je dobro dispergovan, a katalitička aktivnost je poboljšana. Promotor oksida gvožđa u 2Cu-Fe/9γ-Al₂O₃ olakšava reakciju vodene pare, što dovodi do povećanja konverzije CO u CO₂ i prinosa vodonika. Naročito, katalizator 2Cu-Fe/72γ-Al₂O₃ sa najboljim molskim odnosom metala i γ-Al₂O₃ omogućava konverziju dimetil etra veću od 99%, prinos vodonika veći od 98% i najniži sadržaj CO od 1,4%, što ukazuje da sinergizam između hidrolize dimetil-etra i reformovanja metanoza odgovara između metalnog dela CuFe i kisele γ-Al₂O₃. Tehnika intermitentnog mikrotałasnog zračenja obezbeđuje jednostavnu, ali efikasnu metodu sintheze Cu-X/γ-Al₂O₃ sa dobrim performansama katalizatora za reformiranje dimetil etra vodnom parom.

Ključne reči: generisanje vodonika; dimetil etar; intermitentno mikrotałasno zračenje; katalitička reformiranje vodnom parom.