Preparation of Fe$_2$O$_3$/Al$_2$O$_3$ and Fe$_2$O$_3$/TiO$_2$ Pellets as Oxygen Carrier for Chemical Looping Process

Young Ku*, Pao-Hsien Lin, Hsuan-Chih Wu, Yu-Cheng Liu, Yao-Hsuan Tseng, Hao-Yeh Lee

Department of Chemical Engineering, National Taiwan University of Science and Technology, Taipei 10607, Taiwan

ABSTRACT

Fe-based oxygen carriers supported by Al$_2$O$_3$ and TiO$_2$ were prepared as pellets for chemical looping combustion in this study. Over 90% conversions were obtained for most experiments operated in the TGA; however, experiments conducted with FeTi320 pellets exhibited higher conversions than those with FeAl320. The prepared pellets sintered at higher temperatures always exhibited higher crush strength. The crush strength of prepared FeAl320 and FeTi320 pellets were decreased for experiments conducted with greater starch content, because the more pore spaces are formed in the original places of the starch grains. For experiments conducted in the fixed bed reactor, the prepared pellets exhibited relatively high conversion. The conversions of FeTi320 were remained to be about 80% with increasing starch content because high porosity (approximately 50%) was formed for 0–20% starch contents of FeTi320 pellets after 10 redox cycles. Less porosity was formed after 20 redox cycles for experiments conducted with FeAl320 pellets prepared with higher starch contents. Therefore, the conversion of FeAl320 pellets was elevated with increasing starch content. Iron content for inner part of prepared pellets was significantly decreased after operated for 20 redox cycles, while iron content for outer part of pellets were increased. It is suggested that the iron ions may diffuse onto the surface of oxygen carriers to react with oxygen during the oxidation period.

Keywords: Chemical looping combustion; Iron-based oxygen carrier; TiO$_2$; Al$_2$O$_3$; Iron cations diffusion.

INTRODUCTION

In order to combat global warming and mitigate the CO$_2$ emissions, various carbon capture, storage and utilization technologies are recently developed. Chemical looping process (CLP) using metal oxides (also called oxygen carriers) is considered to be a novel alternative for fuel combustion to achieve efficient energy generation as well as inherent CO$_2$ separation. The oxygen carriers are functioned as oxygen source for fuel oxidation. The reduced oxygen carriers are subsequently regenerated by air for repetitive applications as well as heat generation to maintain heat balance of the process. A number of researches have aimed to investigate and improve the performance of various metal oxides used as oxygen carriers for chemical looping combustion. Amongst, the large natural reserves and cost effectiveness of Fe-based oxygen carriers also make it suitable for CLC implementation (Mattisson et al., 2004; Luo et al., 2014). In addition, most Fe-based oxygen carriers demonstrate higher melting point, better mechanical strength, and lower tendency to carbon formation. Nevertheless, Fe-based oxygen carriers have exhibited relatively low oxygen carrying capacities, as well as low reactivity toward fuels (Takeuchi et al., 2007). Various supporting materials, especially Al$_2$O$_3$ and TiO$_2$, were investigated to improve the thermal and mechanical stability of oxygen carriers for CLC operation. Johansson et al. (2004) found that the MgAl$_2$O$_4$-supported Fe$_2$O$_3$ oxygen carriers prepared through freeze-granulation and sintered at 1100°C demonstrated high reactivity and no tendency to agglomerate or break apart during consecutive redox-cycle for methane combustion in a fluidized bed reactor. Insignificant deactivation, agglomeration, carbon deposition, and attrition were observed by Abad et al. (2007) using the Al$_2$O$_3$-supported Fe$_2$O$_3$ oxygen-carriers for natural gas or syngas combustion in a thermogravimetric analyzer. Chiu et al. (2014) reported that Fe$_2$O$_3$/Al$_2$O$_3$ oxygen carriers demonstrated reasonable oxygen conversion and delivered high CO$_2$ yields for chemical looping combustion of methane and syngas (CO/H$_2$) in a fixed bed reactor. Ku et al. (2014) revealed that the completely methane combustion was achieved for experiments carrier out with Fe$_2$O$_3$/Al$_2$O$_3$ in a moving bed fuel reactor, and carbon deposition was significantly reduced. Kuo et al. (2015) reported that the high H$_2$ generation for chemical looping hydrogen generation process (CLHG) with NiFeAlO$_4$ oxygen carriers was contributed to the
spinel structure of NiFeAlO₄.

In this study, the reduction and oxidation conversions of prepared alumina- and titanium-supported Fe₂O₃ oxygen carriers (Fe₂O₃/Al₂O₃ and Fe₂O₃/TiO₂) with syngas (CO/H₂) were investigated through consecutive redox-cycle operations in a thermogravimetric analyzer (TGA). The crystalline phases, surface morphology, and metal distribution of these oxygen carriers during the redox cycling were identified by X-ray diffraction (XRD), field-emission scanning electron microscope (FESEM), and field-emission scanning electron microscope (FESEM) with energy dispersive X-ray (EDX), respectively.

MATERIAL AND METHODS

Fe₂O₃ (99%, China steel Co.), Al₂O₃ (99%, Chin Jung Trading Co.), TiO₂ (99.5%, Unique Enterprise Co) and starch (99%, Acros) powder were used for preparation of oxygen carriers. The mass ratio of Fe₂O₃ to inert support (Al₂O₃ or TiO₂) was fixed at 60:40 for preparing different oxygen carriers. Water-based slurry with predetermined amounts of Fe₂O₃, starch and inert support powder was prepared, then dried at 80°C in a vacuum oven, was ground in a mortar, and was sieved to obtain the desired particle size of 0.3–0.5 mm. The well-mixed powder was pressed into cylindrical pellets of 3 mm in both diameter and height using a rotary tablet press, and later sintered at 1000 to 1300°C in a muffle oven (Linderg BLUE/M UP550) for 2 hours.

The nomenclature used to identify the prepared pellets includes information about the material and mass fraction of active metal oxide, inert support and starch of specified oxygen carriers. The weight ratio for both Fe₂O₃/Al₂O₃ and Fe₂O₃/TiO₂ pellets were determined to be 60:40; and the oxygen carriers are denoted as FeAl320 and FeTi320 in this study. For prepared pellets containing starch, for example, FeAl320-S10 denotes Fe₂O₃/Al₂O₃ oxygen carriers with extra 10 wt% starch.

Surface morphology and crystal structure of prepared Fe-based oxygen carriers were analyzed by field-emission scanning electron microscope spectra (FESEM, JOEL JSM-6500F) and X-ray diffraction (Bruker D2 Phaser), respectively. The crush strength of these prepared pellets was determined following ASTM methods ASTM method D4179-01, and the porosity and attrition of prepared pellets were determined following ASTM methods C373-88 and D4058-96, respectively. Furthermore, the metal distribution in the cross sectional surface of the fresh and used (after 20th redox cycles) oxygen carriers were observed using a field-emission scanning electron microscope (FESEM) with energy dispersive X-ray (EDX, Horiba EX-210).

A thermogravimetric analyzer (TGA, STA449 F3) was used for investigated the reactivity and recyclability of Fe-based oxygen carriers prepared as pellets. Sample of prepared pellets, approximately 45 ± 2 mg, was loaded in Al₂O₃ crucible and the temperature of TGA chamber was raised to 1,300°C, which was slightly higher than 2/3 of melting point of Fe₂O₃ (1,560°C). As depicted in Fig. 3, experiments conducted with FeAl320 pellets sintered at temperatures between 1,000°C and 1,300°C exhibited relatively invariable conversion of 95%, comparable to the results reported previously (Mattisson et al., 2004). Nearly complete conversion were achieved with FeTi320 pellets sintered at 1,000°C; however, the conversion was rapidly decreased to 67% for experiments carried out with FeTi320 pellets sintered at 1,300°C, the results were corresponded to preceding studies (Adánez et al., 2010), as shown in Table 3.

Conversions of reduction in syngas atmosphere for prepared FeAl320 and FeTi320 pellets in the TGA operated at 900°C are shown in Fig. 3. It was reported that solid state sintering for ceramic materials would occurred at temperature (in °C) higher than 2/3 of its melting point for uniform dispersion of multiple ceramic materials (De Jonghe and Rahaman, 2003). The solid state sintering for Fe₂O₃ dispersion of in Al₂O₃ and TiO₂ was suggested beginning at 1,100°C, which was slightly higher than 2/3 of melting point of Fe₂O₃ (1,560°C). As depicted in Fig. 3, experiments conducted with FeAl320 pellets sintered at temperatures between 1,000°C and 1,300°C exhibited relatively invariable conversion of 95%, comparable to the results reported previously (Mattisson et al., 2004). Nearly complete conversion were achieved with FeTi320 pellets sintered at 1,000°C; however, the conversion was rapidly decreased to 67% for experiments carried out with FeTi320 pellets sintered at 1,300°C, the results were corresponded to preceding studies (Adánez et al., 2004). It was indicated that the agglomeration was avoided for syngas combustion with FeAl320 pellets, whereas the occurrence of agglomeration introduced for 5 minutes to purge syngas from the TGA chamber. The reduced oxygen carriers were subsequently regenerated by 200 mL min⁻¹ air.

RESULTS AND DISCUSSION

The reactivity of prepared FeAl320 and FeTi320 pellets were investigated and conducted in the TGA operated at temperature between 800 and 950°C by feeding syngas at flow rate of 200 mL min⁻¹ for reduction and air at flow rate of 200 mL min⁻¹ for oxidation. The reduction and oxidation conversions for specific oxygen carriers are defined by following equations:

$$X_{\text{red}} = \frac{m_{\text{oxi}} - m(t)}{m_{\text{oxi}} - m_{\text{red}}}$$

$$X_{\text{oxi}} = \frac{m(t) - m_{\text{red}}}{m_{\text{oxi}} - m_{\text{red}}}$$

where $X_{\text{red}}$ and $X_{\text{oxi}}$ are the reduction and oxidation conversions of Fe-based oxygen carriers, respectively; $m_{\text{oxi}}$ is the weight of fully oxidized oxygen carriers; $m_{\text{red}}$ is the weight of fully reduced oxygen carrier; $m(t)$ is the weight of oxygen carriers at a specific operation time, $t$, which measured by TGA during oxygen carrier reduction and oxidation. As demonstrated in Figs. 1 and 2, reduction conversions of the FeAl320 and FeTi320 for syngas combustion were increased with increasing operation temperature, whereas oxidation conversion of the FeAl320 and FeTi320 were maintained at about 95% for experiments conducted at temperature higher than 850°C. Higher reduction conversion was observed for experiments conducted with FeTi320 than those with FeAl320, probably due to the greater porosity of FeTi320 (Adánez et al., 2010), as shown in Table 3.

Conversions of reduction in syngas atmosphere for prepared FeAl320 and FeTi320 pellets in the TGA operated at 900°C are shown in Fig. 3. It was reported that solid state sintering for ceramic materials would occurred at temperature (in °C) higher than 2/3 of its melting point for uniform dispersion of multiple ceramic materials (De Jonghe and Rahaman, 2003). The solid state sintering for Fe₂O₃ dispersion of in Al₂O₃ and TiO₂ was suggested beginning at 1,100°C, which was slightly higher than 2/3 of melting point of Fe₂O₃ (1,560°C). As depicted in Fig. 3, experiments conducted with FeAl320 pellets sintered at temperatures between 1,000°C and 1,300°C exhibited relatively invariable conversion of 95%, comparable to the results reported previously (Mattisson et al., 2004). Nearly complete conversion were achieved with FeTi320 pellets sintered at 1,000°C; however, the conversion was rapidly decreased to 67% for experiments carried out with FeTi320 pellets sintered at 1,300°C, the results were corresponded to preceding studies (Adánez et al., 2004). It was indicated that the agglomeration was avoided for syngas combustion with FeAl320 pellets, whereas the occurrence of agglomeration
was observed for syngas combustion with FeTi320 pellets, similar to the results reported by previous researchers (Johansson et al., 2004; Mattisson et al., 2004).

The crush strength of oxygen carriers was generally reported to be enhanced for those sintered at higher temperatures, and to be decreased with the addition of pore-forming agent (Mattisson et al., 2004). It was observed that oxygen carriers sintered at elevated temperatures were less porous. Crush strength of FeAl320 and FeTi320 pellets prepared with the addition of various starch contents, and sintered at different temperatures were exhibited in Tables 1 and 2, respectively. The crush strength was enhanced for FeAl320 pellets sintered at higher sintering temperatures. The interspace for Fe$_2$O$_3$/Al$_2$O$_3$ particles is possibly greater than that of pure Fe$_2$O$_3$ particles because of the different crystallite sizes of Fe$_2$O$_3$ and Al$_2$O$_3$. The comparatively

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*Fig. 1.* Effect of reaction temperature on reduction conversion of Fe-based oxygen carriers for syngas combustion in TGA.

*Fig. 2.* Effect of reaction temperature on oxidation conversion of Fe-based oxygen carriers for syngas combustion in TGA.
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Fig. 3. Effect of sintering temperature on reduction conversion of Fe-based oxygen carriers for syngas combustion in TGA.

Table 1. Crush strength of FeAl320 pellets prepared with various starch contents.

<table>
<thead>
<tr>
<th>Oxygen carriers</th>
<th>Crush strength (N)</th>
<th>Sintering temperature (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>1000</td>
<td>1100</td>
</tr>
<tr>
<td>FeAl320-S0</td>
<td>218.42</td>
<td>466.68</td>
</tr>
<tr>
<td>FeAl320-S1</td>
<td>209.86</td>
<td>457.87</td>
</tr>
<tr>
<td>FeAl320-S5</td>
<td>99.80</td>
<td>168.48</td>
</tr>
<tr>
<td>FeAl320-S10</td>
<td>70.43</td>
<td>73.61</td>
</tr>
<tr>
<td>FeAl320-S20</td>
<td>12.68</td>
<td>27.39</td>
</tr>
</tbody>
</table>

Table 2. Crush strength of FeTi320 pellets prepared with various starch contents.

<table>
<thead>
<tr>
<th>Oxygen carriers</th>
<th>Crush strength (N)</th>
<th>Sintering temperature (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>1000</td>
<td>1100</td>
</tr>
<tr>
<td>FeTi320-S0</td>
<td>250.99</td>
<td>340.58</td>
</tr>
<tr>
<td>FeTi320-S1</td>
<td>215.50</td>
<td>310.98</td>
</tr>
<tr>
<td>FeTi320-S5</td>
<td>213.15</td>
<td>299.81</td>
</tr>
<tr>
<td>FeTi320-S10</td>
<td>204.53</td>
<td>289.60</td>
</tr>
<tr>
<td>FeTi320-S20</td>
<td>173.73</td>
<td>236.49</td>
</tr>
</tbody>
</table>

loose-packed Fe$_2$O$_3$/Al$_2$O$_3$ particles might result in inferior crush strength than that of Fe$_2$O$_3$ particles. In our previous research, crush strengths of Fe$_2$O$_3$ and FeAl320 pellets were reached about 251 N and 230 N (Chiu et al., 2014). Besides, the crush strength of prepared FeAl320 and FeTi320 pellets were decreased for experiments conducted with greater starch content, because the more pore spaces are formed in the original places of the starch grains (Ku et al., 2017). According to the XRD patterns illustrated in Figs. 4 and 5, the crystalline phases of freshly prepared FeAl320 pellets were mainly Fe$_2$O$_3$ and Al$_2$O$_3$, while Fe$_2$TiO$_5$ was observed to be the major crystalline phase of fresh FeTi320 pellets. The crystal systems of Fe$_2$O$_3$ and Al$_2$O$_3$ contained in the FeAl320 pellets are rhombohedral, while the crystal systems of Fe$_2$TiO$_5$ contained in the FeTi320 pellets is orthorhombic. Among, the crystal structure of orthorhombic is more compact than that of rhombohedral. Hence, the crush strength of FeTi320 pellets was generally higher than that of FeAl320 pellets, as presented in the Table 2.

As shown in Fig. 6 and Table 3, the conversions of FeTi320 were remained to be about 80% with increasing
starch content because high porosity (approximately 50%) was formed for 0-20% starch contents of FeTi320 pellets after 10 redox cycles. Less porosity was formed after 20 redox cycles for experiments conducted with FeAl320 pellets prepared with higher starch contents. Therefore, the conversion of FeAl320 pellets was elevated with increasing starch content due to the increase of porosity, which was favorable for diffusion of syngas and oxygen molecules (Wang et al., 2010). Sun et al. (2012) reported that diffusion of iron cations, the lattice vacancies would form in the iron phase, which possibly resulted in agglomeration for the formed porous structure. According to the results of the Fig. 6, conversion of around 75% was achieved for the reduction of FeTi320 without starch content, while the conversion was significantly enhanced to 68.6% for the reduction of FeAl320 with starch content of 10%. Thus, the FeTi320-S0 and FeAl320-S10 pellets were employed as oxygen carriers for consequent iron migration study.
Reduction of Fe-based oxygen carriers
Sintering temperature of FeAl320 pellet: 1300°C
Sintering temperature of FeTi320 pellet: 1100°C
Reaction temperature: 900°C
Reduction time: 20 min
Oxidation time: 10 min
Flow rate of syngas: 200 mL/min
Flow rate of air: 200 mL/min

Fig. 6. Effect of starch content on reduction conversion of Fe-based oxygen carriers for syngas combustion in TGA.

Table 3. Physical properties of FeAl320-S10 and FeTi320 pellets prepared with different starch contents.

<table>
<thead>
<tr>
<th>Starch content (wt%)</th>
<th>FeAl320 pellet</th>
<th>FeTi320 pellet</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Fresh</td>
<td>After 20 redox cycles</td>
</tr>
<tr>
<td></td>
<td>Bulk density (g cm(^{-3}))</td>
<td>Porosity (%)</td>
</tr>
<tr>
<td>0</td>
<td>3.67</td>
<td>19.57</td>
</tr>
<tr>
<td>1</td>
<td>3.66</td>
<td>19.63</td>
</tr>
<tr>
<td>5</td>
<td>3.39</td>
<td>25.59</td>
</tr>
<tr>
<td>10</td>
<td>3.25</td>
<td>29.95</td>
</tr>
<tr>
<td>20</td>
<td>2.62</td>
<td>39.61</td>
</tr>
</tbody>
</table>

As shown in Fig. 7, the Fe content of FeAl320-S10 pellets were increased with increasing pellet radius based on the SEM-EDS analysis for these oxygen carriers, whereas the Al content were decreased. After operated for 20 redox cycles, the size of FeAl320-S10 pellets was observed to be unchanged while more Fe was observed on the surface of these pellets. For fresh FeTi320-S0 pellets, the Fe and Ti contents were not markedly varied along the pellet radius, as demonstrated in Fig. 8. However, the size of FeTi320-S0 pellets were observed to be notably increased after 20 redox cycles operation, and almost no Ti was observed on the surface of FeTi320-S0 pellets. Moreover, numerous vacancies and pores were found in the inner part of FeAl320-S10 and FeTi320-S0 pellets based on the SEM images, as exhibited in Fig. 9, probably due to the iron migration onto the surface of oxygen carriers. Qin et al. (2014) analyzed the core-shell structure formations of FeNi microparticles during the cyclic oxidation-reduction reaction, and reported that the outward iron ions diffusion was faster than the inward oxygen diffusion in iron oxide. Hence, the preliminarily simplified mechanism for iron cations diffusion of FeAl320-S10 and FeTi320-S0 pellets during reduction and oxidation operations are demonstrated as Fig. 10. Fe\(_2\)O\(_3\) of the oxygen carriers were reduced during the reduction period, and then while the air introduced during the oxidation period, and then iron ions on the surface of oxygen carriers were oxidized to be Fe\(_2\)O\(_3\). The iron ions in the core of oxygen carrier were not completely oxidized and were then diffused onto the surface of oxygen carriers to react with oxygen. Subsequently, vacancies and pores were generated within the oxygen carriers by iron ions diffusion.

As shown in the Fig. 11, the reduction conversion for experiments conducted with FeAl320-S10 pellets was decreased from about 90% to 70% after operated for 20 redox cycles, indicating that the recyclability of Fe\(_2\)O\(_3\) was considerably improved with Al\(_2\)O\(_3\) support. Chiu et al. (2014) indicated that the conversion of Fe\(_2\)O\(_3\) pellet was decayed rapidly after the second redox cycle. However, the conversion of Fe\(_2\)O\(_3$/Al\(_2\)O\(_3\)$ pellet was maintained at above 70% during continuous redox cycling. However, the reduction conversion was increased from 65% to nearly 90% after 40-cycle operation for experiments carried out...
with FeTi320-S0 pellets, probably due to the appearance of macropores or cracks on the FeTi320 pellets (Adánez et al., 2010). Characteristics of fresh and used FeAl320-S10 and FeTi320-S0 pellets were shown in Table 4. FeAl320-S10 pellets demonstrated excessive crush strength even after 20 redox cycles, whereas the crush strength of used FeTi320-S0 pellets was significantly decreased possibly because more interspace was generated within the expanded FeTi320-S0 pellets. Therefore, the attrition loss of FeTi320-S0 pellets was found to be roughly twice as much as that of FeAl320-S10 pellets.
CONCLUSIONS

For experiments conducted at temperature between 800 and 950°C in syngas atmosphere in a TGA, the conversion of FeAl320 and FeTi320 pellets during the reduction and oxidation stages were over 90% for most cases; nonetheless, higher conversions were achieved for experiments conducted with FeTi320 pellets. The crush strength was enhanced for prepared pellets sintered at higher sintering temperatures. The crush strength of FeTi320 pellets was mostly higher than those of FeAl320 pellets.

Nearly complete conversion were achieved for experiments conducted in the fixed bed reactor with FeTi320 pellets sintered at temperatures between 1,000 and 1,200°C. The conversions of FeTi320 were remained to be about 80% with increasing starch content because high porosity (approximately 50%) was formed for 0–20% starch contents of FeTi320 pellets after 10 redox cycles. Less porosity was formed after 20 redox cycles for experiments conducted with FeAl320 pellets prepared with higher starch contents.

Fig. 9. SEM images of cross-sectional Fe-based oxygen carriers; (a) fresh and (b) after 20 redox cycles of syngas combustion in TGA at 900°C.

Fig. 10. Scheme of iron-cation diffusion for Fe-based oxygen carriers during reduction and oxidation operations.
Therefore, the conversion of FeAl320 pellets was elevated with increasing starch content, which was favorable for diffusion of syngas and oxygen molecules. It is observed that iron content for inner part of pellets were significantly decreased after operated for 20 redox cycles, while iron content for outer part were increased. It is suggested that the iron ions may diffuse onto the surface of oxygen carriers to react with oxygen during the oxidation period; thus, vacancies and pores would be formed. Both FeAl320-S10 and FeTi320-S0 pellets demonstrated excellent crush strength even after 20 redox cycles. However, the attrition loss of FeTi320-S0 pellets was roughly twice as large as that of FeAl320-S10 pellets.

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