

Preparation of Fe₂O₃/Al₂O₃ and Fe₂O₃/TiO₂ 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 Al₂O₃ and TiO₂ 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 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; TiO₂; Al₂O₃; Iron cations diffusion.

INTRODUCTION

In order to combat global warming and mitigate the CO₂ 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 CO₂ 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,

* Corresponding author.

Tel.: +886-2-2378-5535; Fax: +886-2-2737-6644 *E-mail address:* ku508@mail.ntust.edu.tw and lower tendency to carbon formation. Nevertheless, Febased oxygen carriers have exhibited relatively low oxygen carrying capacities, as well as low reactivity toward fuels (Takeuchi et al., 2007). Various supporting materials, especially Al₂O₃ and TiO₂, were investigated to improve the thermal and mechanical stability of oxygen carriers for CLC operation. Johansson et al. (2004) found that the MgAl₂O₄supported Fe₂O₃ oxygen carriers prepared through freezegranulation and sintered at 1100°C demonstrated high reactivity and no tendency to agglomerate or break apart during consecutive redox-cycle for methane combustion in bed reactor. Insignificant deactivation, а fluidized agglomeration, carbon deposition, and attrition were observed by Abad et al. (2007) using the Al₂O₃-supported Fe₂O₃ oxygen-carriers for natural gas or syngas combustion in a thermogravimetric analyzer. Chiu et al. (2014) reported that Fe₂O₃/Al₂O₃ oxygen carriers demonstrated reasonable oxygen conversion and delivered high CO₂ yields for chemical looping combustion of methane and syngas (CO/H₂) in a fixed bed reactor. Ku et al. (2014) revealed that the completely methane combustion was achieved for experiments carrier out with Fe₂O₃/Al₂O₃ in a moving bed fuel reactor, and carbon deposition was significantly reduced. Kuo et al. (2015) reported that the high H₂ generation for chemical looping hydrogen generation process (CLHG) with NiFeAlO₄ oxygen carriers was contributed to the spinel structure of NiFeAlO₄.

In this study, the reduction and oxidation conversions of prepared alumina- and titanium-supported Fe_2O_3 oxygen carriers (Fe_2O_3/Al_2O_3 and Fe_2O_3/TiO_2) 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 Fe_2O_3/Al_2O_3 and Fe_2O_3/TiO_2 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 Fe_2O_3/Al_2O_3 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 by a texture machine (TA.XT plus) following 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 Febased 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 800–950°C under air atmosphere to confirm the oxygen carrier is in fully oxidation state. 200 mL min⁻¹ syngas was introduced into the TGA chamber to reduce the oxygen carriers; and then 200 mL min⁻¹ nitrogen was 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:

$$X_{red} = \frac{m_{oxi} - m(t)}{m_{oxi} - m_{red}}$$
(1)

$$X_{oxi} = \frac{m(t) - m_{red}}{m_{oxi} - m_{red}}$$
(2)

where X_{red} and X_{oxi} are the reduction and oxidation conversions of Fe-based oxygen carriers, respectively; m_{oxi} is the weight of fully oxidized oxygen carriers; m_{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 Fe_2O_3 dispersion of in Al₂O₃ and TiO₂ was suggested beginning at 1100°C, which was slightly higher than 2/3 of melting point of Fe_2O_3 (1560°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



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.

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_2O_3/Al_2O_3 particles is possibly greater than that of pure Fe_2O_3 particles because of the different crystallite sizes of Fe_2O_3 and Al_2O_3 . The comparatively



Sintering temperature (°C)

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

		Crush str	ength (N)		
Oxygen carriers	Sintering temperature (°C)				
	1000	1100	1200	1300	
FeA1320-S0	218.42	466.68	> 550	> 550	
FeA1320-S1	209.86	457.87	> 550	> 550	
FeA1320-S5	99.80	168.48	293.69	500.70	
FeA1320-S10	70.43	73.61	113.02	363.44	
FeA1320-S20	12.68	27.39	45.44	294.12	

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

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

		Cr	ush strength (N)		
Oxygen carriers Sintering temperature (°C)					
	1000	1100	1200	1300	
FeTi320-S0	250.99	340.58	> 550	> 550	
FeTi320-S1	215.50	310.98	> 550	> 550	
FeTi320-S5	213.15	299.81	> 550	> 550	
FeTi320-S10	204.53	289.60	> 550	> 550	
FeTi320-S20	173.73	236.49	527.37	> 550	

loose-packed Fe₂O₃/Al₂O₃ particles might result in inferior crush strength than that of Fe₂O₃ particles. In our previous research, crush strengths of Fe₂O₃ 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 Fe₂O₃ and Al₂O₃, while Fe₂TiO₅ was observed to be the major crystalline phase of fresh FeTi320 pellets. The crystal systems of Fe₂O₃ and Al₂O₃ contained in the FeAl320 pellets are rhombohedral, while the crystal systems of Fe₂TiO₅ 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



Fig. 4. XRD patterns of fresh FeAl320 pellet sintered in various sintering temperatures.



Fig. 5. XRD patterns of fresh FeTi320 pellet sintered in various sintering temperatures.

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.



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

Storah	FeAl320 pellet			FeTi320 pellet				
Starch	Fresh		After 20 redox cycles		Fresh		After 10 redox cycles	
$(xyt^{0/2})$	Bulk density	Porosity	Bulk density	Porosity	Bulk density	Porosity	Bulk density	Porosity
(wt/0)	$(g \text{ cm}^{-3})$	(%)	$(g \text{ cm}^{-3})$	(%)	$(g \text{ cm}^{-3})$	(%)	$(g \text{ cm}^{-3})$	(%)
0	3.67	19.57	3.17	21.26	3.31	23.97	2.12	51.60
1	3.66	19.63	3.13	23.97	3.27	24.90	2.10	51.94
5	3.39	25.59	2.84	29.48	3.01	27.29	2.07	52.38
10	3.25	29.95	2.70	34.82	2.84	30.94	2.05	53.47
20	2.62	39.61	2.59	41.18	2.47	35.51	2.03	54.55

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

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. Fe₂O₃ 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 Fe₂O₃. 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 Fe₂O₃ was considerably improved with Al₂O₃ support. Chiu *et al.* (2014) indicated that the conversion of Fe₂O₃ pellet was decayed rapidly after the second redox cycle. However, the conversion of Fe₂O₃/Al₂O₃ 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



Fig. 7. SEM-EDS analysis of FeAl320-S10 pellet.



Fig. 8. SEM-EDS analysis of FeTi320-S0 pellet.

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.



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.

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. 11. Reduction conversions of Fe-based oxygen carriers operated at 900°C for syngas combustion in TGA.

Rhygical properties	FeA	1320-S10 pellet ^d	FeTi320-S0 pellet ^e		
Filysical properties	Fresh	After 20 redox cycles	Fresh	After 20 redox cycles	
Porosity (%) ^a	29.95	34.82	23.97	51.60	
Bulk density $(g \text{ cm}^{-3})^a$	3.25	2.70	3.31	2.12	
Crush strength (N) ^b	363.44	328.27	340.58	126.59	
Attrition (%) ^c	4.61	_	10.67	_	

Table 4. Physical properties of prepared FeAl320-S10 and FeTi320-S0 pellets.

^a Tested by ASTM C373-88 (2006).

^b Tested by ASTM D4179-01 (2006), the value is over the instrument limited and maximum value of the instrument is 550 N. ^c Tested by ASTM D4058-96 (2006).

^d FeA1320-S10 pellet contained 10% starch and sintered at 1300°C for 2 hours and pelletized as 3 mm pellet.

^e FeTi320-S0 pellet contained 0% starch and sintered at 1100°C for 2 hours and pelletized as 3 mm pellet.

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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REFERENCES

- Abad, A., Adánez, J., García-Labiano, F., de Diego, L.F., Gayán, P. and Celaya, J. (2007). Mapping of the range of operational conditions for Cu-, Fe-, and Ni-based oxygen carriers in chemical-looping combustion. *Chem. Eng. Sci.* 62: 533–549.
- Adánez, J., Cuadrat, A., Abad, A., Gayán, P., de Diego, L.F. and García-Labiano, F. (2010). Ilmenite activation during consecutive redox cycles in chemical-looping combustion. *Energy Fuels* 24: 1402–1413.
- Adánez, J., de Diego, L.F., García-Labiano, F., Gayán, P. and Abad, A. (2004). Selection of oxygen carriers for chemcial-loopong combustion. *Energy Fuels* 18: 371– 377.
- Chiu, P.C., Ku, Y., Wu, Y.L., Wu, H.C., Kuo, Y.L. and Tseng, Y.H. (2014). Characterization and evaluation of

prepared Fe₂O₃/Al₂O₃ oxygen carriers for chemical looping process. *Aerosol Air Qual. Res.* 14: 981–990.

- De Jonghe, L.C. and Rahaman, M.N. (2003). In Handbook of Advanced Ceramics: Materials Science, Vol. 1, Sōmiya, S., Aldinger, F., Claussen, N., Spriggs, R.M., Uchino, K., Koumoto, K. and Kaneno, M. (Eds.), Elsevier, New York, pp. 187–264.
- Johansson, M., Mattisson, T. and Lyngfelt, A. (2004). Investigation of Fe₂O₃ with MgAl₂O₄ for chemicallooping combustion. *Ind. Eng. Chem. Res.* 43: 6978– 6987.
- Ku, Y., Liu, Y.C., Chiu, P.C., Kuo, Y.L. and Tseng, Y.H. (2014). Mechanism of Fe_2TiO_5 as oxygen carrier for chemical looping process and evaluation for hydrogen generation. *Ceram. Int.* 40: 4599–4605.
- Ku, Y., Shiu, S.H., Liu, Y.C., Wu, H.C., Kuo, Y.L. and Lee, H.Y. (2017). Liquid sintering behavior of cu-based oxygen carriers for chemical looping process. *Catal. Commun.* 92: 70–74.
- Kuo, Y.L., Huang, W.C., Hsu, W.M., Tseng, Y.H. and Ku, Y. (2015). Use of spinel nickel aluminium ferrite as selfsupported oxygen carrier for chemical looping hydrogen generation process. *Aerosol Air Qual. Res.* 15: 2700–2708.
- Luo, M., Wang, S., Wang, L. and Lv, M. (2014). Reduction kinetics of iron-based oxygen carriers using methane for chemical-looping combustion. J. Power Sources 270:

434-440.

- Mattisson, T., Johansson, M. and Lyngfelt, A. (2004). Multicycle reduction and oxidation of iron oxide particles-application to chemical-looping combustion. *Energy Fuels* 18: 628–637.
- Qin, L., Majumder, A., Fan, J. A., Kopechek, D. and Fan, L.S. (2014). Evolution of nanoscale morphology in single and binary metal oxide microparticles during reduction and oxidation processes. *J. Mater. Chem. A* 2: 17511–17520.
- Sun, Z., Zhou, Q. and Fan, L. S. (2012). Reactive solid surface morphology variation via ionic diffusion. *Langmuir* 28: 11827–11833.
- Takeuchi, N., Nomura, Y., Ohno, K. I., Maeda, T., Nishioka, K. and Shimizu, M. (2007). Kinetic analysis of spherical wüstite reduction transported with CH₄ gas. *ISIJ Int.* 47: 386–391.
- Wang, S., Wang, G. and Jiang, F., Luo, M. and Li, H. (2010). Chemical looping combustion of coke oven gas by using MgAl₂O₄ as oxygen carrier. *Energy Environ. Sci.* 3: 1353–1360.

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