Reduction Kinetics of YBaCo$_4$O$_{7+\delta}$ Oxygen Carrier for Chemical Looping Air Separation

Limin Hou, Qingbo Yu*, Kun Wang, Shuo Zhang and Qin Qin
School of Metallurgy, Northeastern University, Shenyang, Liaoning, 110819, China
*Corresponding author’s e-mail: yuqb@smm.neu.edu.cn

Abstract. The kinetics of YBaCo$_4$O$_{7+\delta}$ and Y$_{0.5}$Dy$_{0.5}$BaCo$_4$O$_{7+\delta}$ oxygen carriers is determined using the experimental data obtained by fixed-bed apparatus. The results show that rate of oxygen release increases with the increase of reaction temperature. The mechanism function of reduction reaction is not affected Dy substituting. The Avrami-Eroféev mechanism function describes solid phase change of oxygen desorption adequately. The results show that the distributed activation energy of reduction process obtained by A model is about 29.72 kJ/mol and 23.30 kJ/mol for YBaCo$_4$O$_{7+\delta}$ and Y$_{0.5}$Dy$_{0.5}$BaCo$_4$O$_{7+\delta}$ oxygen carrier, respectively. The pre-exponential factor obtained is about 29.727 mol/(Lꞏmin) and 12.826 mol/(Lꞏmin) for YBaCo$_4$O$_{7+\delta}$ and Y$_{0.5}$Dy$_{0.5}$BaCo$_4$O$_{7+\delta}$ oxygen carrier, respectively.

1. Introduction
A huge amount of CO$_2$ emissions, has captured attention of people in recent years. Oxyfuel combustion, one of the most promising technologis for reducing CO$_2$ emissions, has met bottleneck in industrial application as costly production of oxygen. Chemical looping air separation (CLAS), developed by B Moghtaderi in 2010, is characterized with low-cost, low-energy consumption, easy-operation[1-2]. Oxygen carrier, circulated between oxygen absorption reactor and oxygen desorption reactor, is recognized the core in CLAS technology. The metal oxide oxygen carriers such as Cu-based, Co-based, and Mn-based have been studied intensely[3-9]. As low melting point of Cu-based oxygen carrier, it is easy to aggregate[10]. Adding binder, such as ZrO$_2$, TiO$_2$, or SiO$_2$, can enhance the anti-sintering capability[11]. The research found that A2 and R2 model are fitted well with reduction and oxidation of CuO/SiO$_2$ experimental data, respectively[12]. The research showed that the distributed activation energy of the oxidation of CuO/ZrO$_2$ and reduction of CuO is 202 kJ/mol and 313 kJ/mol, respectively[13-14]. The research showed that A model can properly describe the reduction process of CoO-NiO/α-Al$_2$O$_3$ oxygen carrier[15]. Unfortunately, the high reaction temperatures of metallic oxides consume large amount of energy. Thus, oxygen carriers, reacted at low temperatures, are urgently needed. What’s more, waste heat resources of low temperature have not been utilized effectively. It is perfect if the waste heat of low temperatures can be utilized as heat resources. YBaCo$_4$O$_{7+\delta}$, donated Y114 phase, absorbing and desorbing oxygen at 200°C-400°C[16-17], is a potential candidate as oxygen carriers worked at low temperatures. As decomposition of Y114 phase at temperatures above 600°C, works mainly concerned the exploration of improving instability[18]. The rosy attempt is substituting. Ca, Tb-Lu, and Zr can partially or completely substitute Y[15, 19-20]. Fe, Al, Ga, Mn, Ni, Cu, and Zn can partially substitute Co[20-22]. The results showed that substituted with rare earth Dy-Yb completely in Y site for YBaCo$_4$O$_{7+\delta}$, the oxygen desorption temperature decreased and the decomposition temperature increased with decrease of substituting ionic size[18]. The research indicated that the phase-decomposition temperature decreased with increasing the
substituting ionic size. And amount of oxygen absorption and desorption at low temperatures increased with increasing the substituting ionic size[22].

From the literature review, the works intensely focus on YBaCo₄O₇₊δ substitution. As oxygen carrier, kinetic knowledge provides the opportunity to grasp deep understanding of the oxygen desorption, which can’t get by direct observation of the experimental data. Kinetics of gas-solid reaction is complex. The reaction product is different from the reactant[23]. The knowledge got by kinetics is essential for designing CLAS system. The reduction kinetics of YBaCo₄O₇₊δ is critical as its characteristics of slower oxygen absorption rate and faster desorption rate[24-25]. In this study, the reduction kinetics of YBaCo₄O₇₊δ and Y₀.₅Dy₀.₅BaCo₄O₇₊δ monolithic oxygen carrier was performed with the experimental data in a fixed-bed reactor. The results got can be the vital reference data for practical design of CLAS process.

2. Materials Preparation and Reaction Mechanism Description

2.1. Preparation of Materials
YBaCo₄O₇₊δ and Y₀.₅Dy₀.₅BaCo₄O₇₊δ were synthesized by the solid-state reaction[15]. Cordierite honeycomb, with cell density of 400 channels per square inch (CPSI) and wall thickness of 0.15 mm, were washecoated by oxygen carrier slurry[16]. The slurry was prepared with appropriate stoichiometric amount of the active phase, Al₂O₃ sol and deionized water with ultrasonic vibration instrument[16]. To get the desired amount of loading, about 30 wt.% of the honeycomb, several times of impregnation were needed[26]. After impregnation, the monolithic samples were dried at room temperature and dried at 100 °C overnight, followed by calcined at 550°C for 3h.

2.2. Characterization of Materials
The fix-bed system, including a gas delivery subsystem, a mass flow rate measurement subsystem, a reactor subsystem, a cooling subsystem, and a data acquisition subsystem, was used to conduct the experiment. The monolithic samples with oxygen carrier mass about 10g, supported by distributor plate, were placed in the reactor (1200 mm height and 30mm i.d.). Before investigating the oxygen desorption behavior, sample absorbed oxygen at 350°C in air flow of 200 mL/min to get the oxygen saturated oxygen carrier. Then the sample was heated to target desorption temperature (390°C, 410°C, 430°C, and 450°C), followed by turning the reaction atmosphere to N₂ flow of 400 mL/min to investigate the oxygen desorption behavior. The effect of gas in the system has been eliminated[27]. Before the tests, phase composition of the sample was conducted by XRD (PANalytical, PW 3040/60; X’Pert Pro system with Cu Kα radiation) with 2θ between 10°-70° in a step of 0.02°. The microstructure of the samples got in a SUPERSCAN SSX-550 spectrometer system.

2.3. Reaction Mechanism Description
The reaction kinetics equation can be written as following[28].

\[ \frac{d\alpha}{dt} = k(T) f(\alpha) \]  

where, \( \alpha \) is extent of conversion, \( T \) is the reaction temperature, \( k(T) \) is reaction rate content, and \( f(\alpha) \) is kinetic model function. Changing Eq. (1), it can be modified as Eq. (2):

\[ \frac{d\alpha}{f(\alpha)} = k(T)dt \]  

Integrating both sides of Eq. (2), the Eq. (3) is got.

\[ \int_0^\alpha \frac{d\alpha}{f(\alpha)} = G(\alpha) = \int_0^t k(T)dt \] (3a)
The relationship of $G(\alpha)$ and $t$ should be straight line. The reaction rate $k(T)$ can be evaluated by the slope. And, the reaction model can be got by the linear correlation.

$k(T)$ can be described by the following equation:

$$k(T) = A \exp(-\frac{E}{RT})$$  \hspace{1cm} (4)

where, $R$ is the gas constant. Integrating both sides of Eq. (4), the Eq. (5) is got.

$$\ln k(T) = \ln A - \frac{E}{RT}$$  \hspace{1cm} (5)

Plotting $\ln k(T)$ versus $1/T$, $E$ and $A$ can be got by the slope and intercept, respectively.

3. Results and discussion

3.1. Characterization

Figure 1(a) displays the phase composition of YBaCo$_4$O$_{7+\delta}$ and Y$_{0.5}$Dy$_{0.5}$BaCo$_4$O$_{7+\delta}$ sample. The samples are single phase and indexed as 114 phase structure[29]. Figure 1(b) displays the phase composition of YBaCo$_4$O$_{7+\delta}$ monolith sample. The YBaCo$_4$O$_{7+\delta}$ ($P6_3 mc$), $\gamma$-Al$_2$O$_3$ ($F\bar{d}m$), and cordierite ($P6/mcc$) are identified, indicating that YBaCo$_4$O$_{7+\delta}$ and Al$_2$O$_3$/cordierite have not reaction in the process of calcination.

![Figure 1(a)](image)

![Figure 1(b)](image)

Figure 1. (a) The phase composition of YBaCo$_4$O$_{7+\delta}$ and Y$_{0.5}$Dy$_{0.5}$BaCo$_4$O$_{7+\delta}$ samples and (b) YBaCo$_4$O$_{7+\delta}$ monolith sample.

Figure 2(a) and 2(b) display the micromorphology of cordierite and Y$_{0.5}$Dy$_{0.5}$BaCo$_4$O$_{7+\delta}$ monolith sample at 40× magnification, respectively. Figure 2(c) and 2(d) display the micromorphology of cordierite and Y$_{0.5}$Dy$_{0.5}$BaCo$_4$O$_{7+\delta}$ monolith sample at 1000× magnification respectively. Figure 2(a) showed that the cordierite honeycomb was square and crude. Figure 2(b) showed that the cordierite honeycomb was coated by YBaCo$_4$O$_{7+\delta}$ sample uniformly. Figure 2(c) showed that the micromorphology of cordierite honeycomb was irregular polyhedron. Figure 2(d) showed that the micromorphology of oxygen carrier was sphere or sphere-like agglomerates.
The amount of maximum oxygen absorption per unit mass for YBaCo$_4$O$_{7+\delta}$ and Y$_{0.5}$Dy$_{0.5}$BaCo$_4$O$_{7+\delta}$ is 14.8 ml/g and 15.1 ml/g, respectively. The amount of oxygen absorption of Dy substituting sample is larger than that of the unsubstituted sample. The absorbed oxygen can be released at the target desorption temperature. Figure 3(a) and Figure 3(b) showed the conversions of YBaCo$_4$O$_{7+\delta}$ and Y$_{0.5}$Dy$_{0.5}$BaCo$_4$O$_{7+\delta}$ oxygen carriers at different desorption temperatures, respectively. As seen, the oxygen desorption rate of oxygen carriers increases with increasing of the desorption temperature.

**3.2. Kinetic Models**

Based on the reaction models shown in Table 1[30-31] and Eq. (3b), the most probable mechanism function, with the bigger linear correlation coefficient $R^2$ and smaller residual sum of squares RSS, can be got. By linear fitting the mechanism functions (under $\alpha$ ranges from 0.1 to 0.9), the $R^2$ and RSS of each function can be obtained, shown in Table 2 and Table 3, respectively. It can be found that the YBaCo$_4$O$_{7+\delta}$ and Y$_{0.5}$Dy$_{0.5}$BaCo$_4$O$_{7+\delta}$ sample under different temperatures is fitted well with A3 and A2, respectively. For reduction kinetics of YBaCo$_4$O$_{7+\delta}$ and Y$_{0.5}$Dy$_{0.5}$BaCo$_4$O$_{7+\delta}$, reaction rate was determined by nucleation and nuclei growth. For A model, several steps involved in the process of oxygen desorption reaction for YBaCo$_4$O$_{7+\delta}$ and Y$_{0.5}$Dy$_{0.5}$BaCo$_4$O$_{7+\delta}$: generating activation sites in YBaCo$_4$O$_{7+\delta}$ and Y$_{0.5}$Dy$_{0.5}$BaCo$_4$O$_{7+\delta}$ ($\delta\neq0$), formation of nuclei of YBaCo$_4$O$_{7+\delta}$ and
Y₀.₅Dy₀.₅BaCo₄O₇₋δ (δ=0), growth and further formation of nuclei, overlap of nuclei, and continued growth[15, 32]. Nucleation is a dynamic process, which practically initiates the reaction.

| Symbol | Reaction model | f(α) | g(α) |
|--------|----------------|------|------|
| R1     | Phase-boundary controlled reaction | (1-α)²/³ | [1-(1-α)²/³] |
| R2     | Avrami-Eroféev (n=1/2) | (1/2)(1-α)²/³ | [-ln(1-α)]²/³ |
| R3     | Avrami-Eroféev (n=1/4) | (1/4)(1-α)²/³ | [-ln(1-α)]²/³ |
| R4     | Avrami-Eroféev (n=1/3) | (1/3)(1-α)²/³ | [-ln(1-α)]²/³ |
| A1/2   | Avrami-Eroféev (n=1/2) | (1/2)(1-α)²/³ | [-ln(1-α)]²/³ |
| A2     | Avrami-Eroféev (n=2) | (1-α)²/³ | [-ln(1-α)]²/³ |
| A3     | Avrami-Eroféev (n=3) | (1-α)²/³ | [-ln(1-α)]²/³ |
| A4     | Avrami-Eroféev (n=4) | (1-α)²/³ | [-ln(1-α)]²/³ |
| D1     | One-dimensional diffusion | (1/2)² | α² |
| D2     | Two-dimensional diffusion | (1/2)(1-α)² | [-ln(1-α)]² |
| D3     | Three-dimensional diffusion (cylinder) | (3/2)[(1-α)⁻¹/³⁻¹]² | [1-(1-α)⁻¹/³⁻¹]² |
| D4     | Three-dimensional diffusion (sphere) | (3/2)[(1-α)⁻¹/³⁻¹]² | [1-(1-α)⁻¹/³⁻¹]² |

Table 2. The linear correlation coefficient of mechanism models fitted data

| Model | YBaCo₄O₇⁻δ | Y₀.₅Dy₀.₅BaCo₄O₇₋δ | Y₀.₅Dy₀.₅BaCo₄O₇₋δ | Y₀.₅Dy₀.₅BaCo₄O₇₋δ |
|-------|-----------|---------------------|---------------------|---------------------|
|       | 390°C     | 410°C               | 430°C               | 450°C               |
|       | 390°C     | 410°C               | 430°C               | 450°C               |
| R1    | 0.9730    | 0.9868              | 0.9928              | 0.9928              |
| R2    | 0.9517    | 0.9857              | 0.9761              | 0.9761              |
| R3    | 0.9352    | 0.9747              | 0.9596              | 0.9596              |
| A1/2  | 0.4409    | 0.4741              | 0.4704              | 0.4704              |
| A2    | 0.5308    | 0.5756              | 0.5702              | 0.5702              |
| A3    | 0.6767    | 0.7334              | 0.7275              | 0.7275              |
| A4    | 0.7767    | 0.8343              | 0.7960              | 0.7960              |
| D1    | 0.9512    | 0.9816              | 0.9689              | 0.9689              |
| D2    | 0.9746    | 0.9929              | 0.9874              | 0.9874              |
| D3    | 0.9907    | 0.9926              | 0.9943              | 0.9943              |
| D4    | 0.9976    | 0.9875              | 0.9900              | 0.9900              |
| R1    | 0.9066    | 0.9575              | 0.9553              | 0.9553              |
| R2    | 0.9028    | 0.9610              | 0.9117              | 0.9117              |
| R3    | 0.7790    | 0.8338              | 0.8281              | 0.8281              |
| A1/2  | 0.9956    | 0.9868              | 0.9891              | 0.9891              |

Table 3. The residual sum of squares of mechanism models fitted data

| Model | YBaCo₄O₇⁻δ | Y₀.₅Dy₀.₅BaCo₄O₇₋δ | Y₀.₅Dy₀.₅BaCo₄O₇₋δ | Y₀.₅Dy₀.₅BaCo₄O₇₋δ |
|-------|-----------|---------------------|---------------------|---------------------|
|       | 390°C     | 410°C               | 430°C               | 450°C               |
|       | 390°C     | 410°C               | 430°C               | 450°C               |
| R1    | 0.0142    | 0.0069              | 0.0057              | 0.0038              |
| R2    | 0.0152    | 0.0050              | 0.0047              | 0.0075              |
| R3    | 0.0126    | 0.0049              | 0.0052              | 0.0078              |
| A1/2  | 0.3327    | 0.3313              | 0.3159              | 0.3401              |
| A2    | 0.5264    | 0.4764              | 0.4824              | 0.5034              |
| A3    | 0.6853    | 0.5607              | 0.5776              | 0.6605              |
| A4    | 2.0241    | 1.5016              | 1.5486              | 1.8491              |
| A1    | 0.4100    | 0.2398              | 0.2493              | 0.3302              |
| A3/2  | 0.0834    | 0.0314              | 0.0330              | 0.0533              |
| A2    | 0.0265    | 0.0074              | 0.0070              | 0.0131              |
| A3    | 0.0035    | 0.0004              | 0.0030              | 0.0027              |
| A4    | 0.0006    | 0.0040              | 0.0032              | 0.0020              |
The slope of plot $G(\alpha)$ versus $t$ under different reaction temperatures can be used to evaluate the reaction rate constant $k(T)$. For YBaCo$_4$O$_{7+\delta}$ and Y$_{0.5}$Dy$_{0.5}$BaCo$_4$O$_{7+\delta}$ sample, the reaction rate constant of A3 and A2 mechanism function is evaluated. The reaction rate constant of YBaCo$_4$O$_{7+\delta}$ oxygen carrier is $0.013600$ mol/(L·min), $0.15871$ mol/(L·min), $0.18521$ mol/(L·min), and $0.21387$ mol/(L·min) under reaction temperature of $390^\circ$C, $410^\circ$C, $430^\circ$C, and $450^\circ$C, respectively. The reaction rate constant of Y$_{0.5}$Dy$_{0.5}$BaCo$_4$O$_{7+\delta}$ oxygen carrier is $0.18496$ mol/(L·min), $0.21674$ mol/(L·min), $0.23743$ mol/(L·min), and $0.26462$ mol/(L·min) under reaction temperature of $390^\circ$C, $410^\circ$C, $430^\circ$C, and $450^\circ$C, respectively. The results showed reaction rate constant increases with increasing the reaction temperature, indicating that improving temperature is propitious to oxygen release. And, the reaction rate constant of Y$_{0.5}$Dy$_{0.5}$BaCo$_4$O$_{7+\delta}$ is larger than that of YBaCo$_4$O$_{7+\delta}$ oxygen carrier. The reason behind this may be accounted by the value of cell volume. The larger the cell volume is, the faster the oxygen release is.

When the reaction rate constant is obtained, the $A$ and $E$ can be evaluated with Eq. (5). Figure 4 shows the plots of ln$k(T)$ versus $1/T$. The obtained apparent activation energy for YBaCo$_4$O$_{7+\delta}$ and Y$_{0.5}$Dy$_{0.5}$BaCo$_4$O$_{7+\delta}$ sample is $29.72$ kJ/mol and $23.30$ kJ/mol, respectively. The obtained pre-exponential factor for YBaCo$_4$O$_{7+\delta}$ and Y$_{0.5}$Dy$_{0.5}$BaCo$_4$O$_{7+\delta}$ sample is $29.727$ mol/(L·min) and $12.826$ mol/(L·min), respectively. The apparent activation energy of YBaCo$_4$O$_{7+\delta}$ sample is larger than that of Y$_{0.5}$Dy$_{0.5}$BaCo$_4$O$_{7+\delta}$ sample, indicating that YBaCo$_4$O$_{7+\delta}$ sample is harder release oxygen than Y$_{0.5}$Dy$_{0.5}$BaCo$_4$O$_{7+\delta}$ sample. The reason accounted for this may be the value of cell volume. The larger the cell volume is, the easier the oxygen release is. The compensation effect between the $A$ and the $E$ indicates that they have a linear relationship[33]. The results also illustrate this point primly.

Based on the obtained mechanism functions $G(\alpha)$, the apparent activation energy $E$, and the pre-exponential factor $A$, the kinetic models of oxygen desorption for YBaCo$_4$O$_{7+\delta}$ and Y$_{0.5}$Dy$_{0.5}$BaCo$_4$O$_{7+\delta}$ oxygen carriers can be established. It is shown as

$$\frac{d\alpha}{dt} = 89.181\exp(-3574.693/T)(1-\alpha)^{-1/3} \ln(1-\alpha)$$

and

$$\frac{d\alpha}{dt} = 25.652\exp(-2802.502/T)(1-\alpha)^{-1/2} \ln(1-\alpha)$$

for YBaCo$_4$O$_{7+\delta}$ and Y$_{0.5}$Dy$_{0.5}$BaCo$_4$O$_{7+\delta}$ oxygen carrier, respectively.

4. Conclusions

In this work, kinetics on oxygen desorption of YBaCo$_4$O$_{7+\delta}$ and Y$_{0.5}$Dy$_{0.5}$BaCo$_4$O$_{7+\delta}$ oxygen carrier in the CLAS system was conducted. For YBaCo$_4$O$_{7+\delta}$ and Y$_{0.5}$Dy$_{0.5}$BaCo$_4$O$_{7+\delta}$ reduction kinetics, oxygen transfer materials were rate-determined by nucleation and nuclei growth. In mechanism, apparent activation energy $E$ and pre-exponential factor $A$ were obtained. The distributed activation energy of reduction process obtained by A model is about $29.72$ kJ/mol and $23.30$ kJ/mol for YBaCo$_4$O$_{7+\delta}$ and
Y₀.₅Dy₀.₅BaCo₄O₇+δ oxygen carrier, respectively. The pre-exponential factor of reduction process obtained by A model is about 29.727 mol/(Lꞏmin) and 12.826 mol/(Lꞏmin) for YBaCo₄O₇+δ and Y₀.₅Dy₀.₅BaCo₄O₇+δ oxygen carrier, respectively. And, the kinetic models of oxygen desorption for YBaCo₄O₇+δ and Y₀.₅Dy₀.₅BaCo₄O₇+δ oxygen carriers have been established. The obtained knowledge of kinetics can provide reference for designing the CLAS system configuration.

Acknowledgments
This study was financially supported by National Natural Science Foundation of China (Grant No. 51576035, 51604078) and Fundamental Research Funds for the Central Universities (Grant No. N162504012), and Post-Doctoral Science Foundation (Grant No. 2017M610185, 20170101).

References
[1] Moghtaderi, B., Song, H. (2010) Reduction properties of physically mixed metallic oxide oxygen carriers in chemical looping combustion. Energ. Fuel., 24: 5359-5368.
[2] Song, H., Shah, K., Doroodchi, E., Moghtaderi, B. (2014) Development of a Cu-Mg-based oxygen carrier with SiO₂ as a support for chemical looping air separation. Energ. Fuel., 28: 163-172.
[3] Mattisson, T., Lyngfelt, A., Leion, H. (2009) Chemical-looping with oxygen uncoupling for combustion of solid fuels. Int. J. Greenh. Gas. Con., 3: 11-19.
[4] Song, H., Shah, K., Doroodchi, E., Wall, T., Moghtaderi, B. (2014) Reactivity of Al₂O₃ or SiO₂ supported Cu, Mn, and Co-oxygen carriers for chemical looping air separation. Energ. Fuel., 2014, 28: 1284-1294.
[5] Wang, K., Yu, Q.B., Qin, Q. (2013) The thermodynamic method for selecting oxygen carriers used for chemical looping air separation. J. Therm. Anal. Calorim., 112: 747-753.
[6] Shulman, A., Cleverstam, E., Mattisson, T., Lyngfelt, A. (2009) Manganese/iron, manganese/nickel, and manganese/silicon oxides used in chemical-looping with oxygen uncoupling for combustion methane. Energ. Fuel., 23: 5269-5275.
[7] Wang, K., Yu, Q.B., Xie, H.Q., Qin, Q. (2013) Performance and apparent redox kinetics of a Cu-based oxygen carrier for chemical looping oxygen production. Funct. Mater. Lett., 6: 1-5.
[8] Chuang, S.Y., Dennis, J.S., Hayhurst A.D., Scott, S.A. (2008) Development and performance of Cu-based oxygen carriers for chemical-looping combustion. Combust. Flame., 154: 109-121.
[9] Wang, K., Yu, Q.B., Qin, Q., Zuo, Z.L. (2015) Study of the sorption property of copper oxygen carrier used for chemical looping air separation. J. Therm. Anal. Calorim., 120:1627-1633.
[10] Adánez, J., de Diego, L.F, García-Labiano, F., Gayán, P., Abad, A. (2004) Selection of oxygen carriers for chemical-looping combustion. Energ. Fuel., 18: 371-377.
[11] Magnus, R., Henrik, L., Tobias, M., Anders, L. (2014) Combined oxides as oxygen-carrier material for chemical-looping with oxygen uncoupling. Appl. Energ., 113: 1924-1932.
[12] Song, H., Shah, K., Doroodchi, E., Wall, T., Moghtaderi, B. (2014) Analysis on chemical reaction kinetics of CuO/SiO₂ oxygen carriers for chemical looping air separation. Energ. Fuel., 28: 173-182.
[13] Whitty K, Clayton C. (2012) Measurement and modeling of kinetics for copper-based chemical looping with oxygen uncoupling. In: Proceedings of the 2nd International Conference on Chemical Looping; Darmstadt. pp. 1-10.
[14] Arjmand, M., Keller. M., Leion. H., Mattisson. T., Lyngfelt, A. (2012) Oxygen release and oxidation rates of MgAl₂O₄-supported CuO oxygen carrier for chemical-looping combustion with oxygen uncoupling (CLOU). Energ. Fuel., 26: 6528-6539.
[15] Hossain, M.M., de Lasa, H.I. (2010) Reduction and oxidation kinetics of Co-Ni/Al₂O₃ oxygen carrier involved in a chemical-looping combustion cycles. Chem. Eng. Sci., 65: 98-106.
[16] Motohashi, T., Kadita, S., Fjellvag, H., Karppinen, M., Yamauchi, H. (2008) Uncommon oxygen intake/release capability of layered cobalt oxides REBaCo₄O₇+δ: Noval oxygen-storage materials. Mater. Sci. Eng. B, 148: 196-198.
[17] Karppinen, M., Yanauchi, H., Otani, S., Fujita, T., Motohashi, T., Huang, Y.H., Valkeappää, M., Fjellvåg, H. (2006) Oxygen nonstoichiometry in \( \text{YBaCo}_4\text{O}_7 \): Large low-temperature oxygen absorption/desorption capability. Chem. Mater., 18: 490-494.

[18] Kadita, S., Karppinen, M., Motohashi, T., Yamauchi, H. (2008) R-site substitution effect on the oxygen-storage capability of \( \text{RBaCo}_4\text{O}_{7+\delta} \). Chem. Mater., 20: 6378-6381.

[19] Kozeeva, L.P., Kameneva, M.Y., Lavrov, A.N., Podberezkaya, N.V. (2013) Synthesis and oxygen behavior of \( \text{RBaCo}_4\text{O}_{7+\delta} \) (\( \text{R}=\text{Y}, \text{Dy}-\text{Lu} \)). Inorg. Mater., 49: 626-631.

[20] Wang, S., Hao, H.S., Zhu, B.F., Jia, J.F., Hu, X. (2008) Modifying the oxygen adsorption properties of \( \text{YBaCo}_4\text{O}_7 \) by Ca, Al, and Fe doping. J. Mater. Sci., 43: 5385-5389.

[21] Zhang, S.M. (2011) Study on the oxygen adsorption/desorption properties of doped-\( \text{YBaCo}_4\text{O}_{7+\delta} \) and its oxygen permeation ability. MA Dissertation, Zhengzhou University.

[22] Parkkima, O., Yamauchi, H., Karppinen, M. (2013) Oxygen storage capacity and phase stability of variously substituted \( \text{YBaCo}_4\text{O}_{7+\delta} \). Chem. Mater., 25: 599-604.

[23] Sarshar, Z., Kaliaguine, S. (2013) Reduction kinetics of perovskite-based oxygen carriers for chemical looping combustion. Ind. Eng. Chem. Res., 52: 6946-6955.

[24] Hao, H.S., He, Q.L., Cheng, Y.G., Zhao, L.M. (2009) Oxygen adsorption/desorption behavior of \( \text{YBaCo}_4\text{O}_{7+\delta} \) and its application to oxygen removal from nitrogen. J. Rare Earth, 27: 815-818.

[25] Rui, Z.B., Ding, J.J., Li, F., Lin, Y.S., Li, Y.D. (2012) \( \text{YBaCo}_4\text{O}_{7+\delta} \) sorbent for oxygen-enriched carbon dioxide stream production at a low-temperature. Fuel, 94: 191-196.

[26] Li, F., Zeng, L., Velazquez-Vargas, L.G., Yoscovits, Z., Fan, L. (2010) Syngas chemical looping gasification process: Bench-scale studies and reactor simulations. Aiche J., 56: 2186-2199.

[27] Wang, K., Yu, Q.B., Qin, Q., Duan, W.J., Wu, T.W. (2016) Study of the sorption property of copper oxygen carrier used for chemical looping air separation. J. Therm. Anal. Calorim., 120: 1627-1633.

[28] Vyazovkin, S., Wight, C.A. (1999) Model-free and model-fitting approaches to kinetic analysis of isothermal and nonisothermal data. Thermachim. Acta, 340-341: 53-68.

[29] Valldor, M., Andersson, M. (2002) The structure of the new compound \( \text{YBaCo}_4\text{O}_7 \) with a magnetic feature. Solid State Sci., 4: 923-931.

[30] Jin, H., Okamoto, T., Ishida, M. (1998) Development of a novel chemical-looping combustion: synthesis of a looping material with a double metal oxide of CoO-NiO. Energ. Fuel., 12: 1272-1277.

[31] Jin, H., Okamoto, T., Ishida, M. (2005) Development of a novel chemical-looping combustion: Synthesis of a solid looping material of NiO/NiAl\(_2\)O\(_4\). Ind. Eng. Chem. Res., 38: 126-132.

[32] Hossain, M.M., Quddus M.R., de Lasa, H.I. (2010) Reduction kinetics of La modified NiO/La-\( \gamma\text{Al}_2\text{O}_3 \) oxygen carrier for chemical-looping combustion. Ind. Eng. Chem. Res., 49: 11009-11017.

[33] Janković, B., Adnadević, B., Jovanović, J. (2007) Application of model-fitting and model-free kinetics to the study of non-isothermal dehydration of equilibrium swollen poly (acrylic acid) hydrogel: Thermogravimetric analysis. Thermochem. Acta, 452: 106-115.