X-ray diffraction and TGA kinetic analyses for chemical looping combustion applications

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A B S T R A C T

Synthesis and characterization of supported metal-based oxygen carriers were carried out to provide information related to the use of oxygen carriers for chemical looping combustion processes. The Cu, Co, Fe, Ni metals supported with Al₂O₃, CeO₂, TiO₂, ZrO₂ were prepared using the wetness impregnation technique. Then, the X-ray Diffraction (XRD) characterization of oxidized and reduced samples was obtained and presented. The kinetic analysis using Thermogravimetric analyzer (TGA) of the synthesized samples was conducted. The kinetics of reduction reaction of all samples were estimated and explained.

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The data present the XRD analysis of metal-based oxygen carriers for CLC applications. The data are Supplementary materials for the study describing the “Synthesis and study of metal-based oxygen carriers (Cu, Co, Fe, Ni) and their interaction with supported metal oxides (Al₂O₃, CeO₂, TiO₂, ZrO₂) in a chemical looping combustion system” [1].

The XRD analysis of Co, Cu, Fe, Ni metals supported with Al₂O₃, CeO₂, TiO₂, ZrO₂ is shown in Figs. 1–4. It was reported a complete reduction of CuO supported with Al₂O₃, CeO₂, and ZrO₂ (Fig. 1). CuO supported with TiO₂ did not reduce to Cu under this experimental condition. The phases existed in the oxidized sample of Co supported with Al₂O₃ (Fig. 2) were Co₃O₄, Al₂O₃, and CoAl₂O₄, while only phases existed in the reduced sample were CoO, and Al₂O₃ phases. New phase of CoAl₂O₄ was observed in the oxidized sample of Co supported with Al₂O₃. A complete reduction of Co₃O₄ supported with CeO₂ was observed. No trace of Co was noticed in Co sample supported with TiO₂ and ZrO₂. The Fe sample supported with Al₂O₃ (Fig. 3) did not reduce under this experimental condition. A partial reduction of Fe₂O₃ sample supported with CeO₂ and TiO₂ was noticed, while a complete reduction of Fe₂O₃ to Fe occurred in the Fe sample supported with ZrO₂. No significant phase changes between the oxidized and reduced samples were observed in the NiO/Al₂O₃ (Fig. 4) sample; however, an intermediate phase (NiAl₂O₄) existed in both oxidized and reduced samples. A complete reduction of NiO supported with CeO₂ and ZrO₂ was observed. A partial reduction of NiO to Ni was found in the Ni sample supported with TiO₂.

The weight loss and gain during the CLC reaction in the TGA were recorded and analyzed to study the effect of temperature on the conversion of Cu, Co, Fe, and Ni samples. The conversion of the reduction reaction of all samples was calculated using the following equation:

\[ X = \frac{m-m_t}{m_0-m_c} \]  

1. Value of the data

- The data represent characterization of catalysts in term of different metal phases that existed during calcination and reduction experiments of metal-based oxygen carriers for CLC applications.
- The data show essential calculations used to estimate the kinetics of metal-based oxygen carriers for methane fueled CLC process.
- The data are useful for further studies on the development of kinetic models and determining the mechanism of reactions in the CLC process.
Fig. 1. Metal phases existed in Cu-based oxygen carriers using XRD analysis.
Fig. 2. Metal phases existed in Co-based oxygen carriers using XRD analysis.
Fig. 3. Metal phases existed in Fe-based oxygen carriers using XRD analysis.
Fig. 4. Metal phases existed in Ni-based oxygen carriers using XRD analysis.
where; \( m \) is the mass of sample at any time (g), \( m_r \) is mass of the reduced sample (g); and, \( m_o \) is the mass of the oxidized sample (g).

The conversion profiles during the reduction reaction showed no specific trend for all samples. However, a kinetic model that was developed by Gomez and Mahinpey [2] could be used to estimate the kinetic parameters of the reduction reaction. Considering that the surface reaction was the controlling step; hence, the equation used [2]:

\[
\frac{1}{t_X(T)} = k_o - G(X) + e^{-\frac{E_r}{R T}}
\]

where; \( t_X \) is residence time (min); \( X \) is conversion (-); \( T \) is absolute temperature (K); \( G(X) \) is conversion dependent function (-); \( k_o \) is the frequency factor (1/min); \( E_r \) is activation energy of reduction reaction (J/mol); and, \( R \) is the universal gas constant (J/mol K).

If the reaction rate at a constant conversion is only a function of temperature, the following assumption applies [2]:

\[
\ln G(X) \approx \ln [k_o]
\]

The following graphs (Figs. 5–8) were generated for each sample to estimate \( E_r \) and \( k_o \):

All supported oxygen carriers exhibited an increase in the residence time as temperature decreased to achieve 50% solid conversion. Fast reduction profiles compared to other supported samples were noticed in the reduction reaction of all Cu-based oxygen carriers. As the temperature increased, the reaction rate increased but reduction time decreased. Similar reduction behaviour of Cu-based oxygen carriers was observed in the supported Co-based (Fig. 6), Fe-based (Fig. 7), and Ni-based (Fig. 8) oxygen carriers. However, the reduction of Fe (Fig. 7) exhibited an additional resistant step that could be due to the deep reduction (i.e. phase transitions from FeO to Fe, Fe\(_2\)O\(_3\) to FeO and/or Fe\(_2\)O\(_3\) to Fe\(_3\)O\(_4\)). The Cu/Al\(_2\)O\(_3\) sample showed a complete reduction time between 1 to 1.5 min during the first cycle of CLC, while other supported Cu samples with CeO\(_2\), TiO\(_2\), and ZrO\(_2\) showed a complete reduction time of more than 5 min. The Co/Al\(_2\)O\(_3\) sample showed a complete reduction time of less
than 5 min during the first cycle of CLC. The other supported Co samples by CeO2, TiO2, and ZrO2 showed a fluctuated reduction time that ranged from 2.5 to 10 min. The Fe/ZrO2 and Fe/Al2O3 samples showed the fastest reduction rates (90% in only 1.5 min) compared to other Fe supported oxygen carriers. The Ni/ZrO2 sample reported a complete reduction time of 3 min.

Referring to Eq. (2), the slope in Figs. 5–8 represents the $E_r/R$ term in which the activation energy of the reduction reaction ($E_r$) was estimated by multiplying the slope with the universal gas constant. The intercept in Figs. 5–8 represents $\ln[k_o]$ term in which the frequency factor was estimated by taking the logarithmic inverse.

2. Experimental design, materials, and methods

The metal-based oxygen carriers were prepared using the incipient wetness impregnation method [3] at atmospheric pressure.

The following units were obtained beforehand and thoroughly cleaned:

- Digital scale
- Glass beaker (size: 250 ml)
- Magnetic stirrer
- Spatula
- Metal nitrates
- Support oxides
- Hotplate/stirrer
- DI water
- Ceramic mortar/bowl
Fig. 7. Residence time as a function of reciprocal of reaction temperature for (a) Fe/Al₂O₃ (b) Fe/CeO₂ (c) Fe/TiO₂ (d) Fe/ZrO₂.

Fig. 8. Residence time as a function of reciprocal of reaction temperature for (a) Ni/Al₂O₃ (b) Ni/CeO₂ (c) Ni/TiO₂ (d) Ni/ZrO₂.
The molar calculations performed based on the required percentage of both active metals and supports to determine the exact required mass. Then, in a beaker/magnetic stirrer, a 50 ml of DI water was added and the magnetic stirrer launched to a speed of 400-rpm. The appropriate amount of the metal nitrates obtained in a weighting paper and then carefully added to the beaker. The sample left to dissolve for 10 min. Next, a 100 ml of DI water was added to the beaker and the appropriate amount of the support oxides was weighted and carefully added to the beaker. The beaker was then covered and left stirred for 24 h at room temperature. Next, heating of the beaker started until the temperature of solution reached to 75 °C. Most of water evaporated and the muddy sample was then collected into a ceramic bowl using a spatula. The sample dried in a conventional oven for 12 h at 120 °C. Crushing of the dried samples using a ceramic mortar/bowl into a fine powder-like was accomplished. Finally, the dried sample calcined in air at 500 °C for 3 h and reduced with hydrogen gas (50 ml/min) through a stainless-steel tubular reactor at 350 °C for 3 h.

The X-ray diffraction (XRD) analysis was conducted using a Rigaku ULTIMA III X-ray diffractometer with Cu K-alpha radiation. The oxygen carriers scanned with 2-theta equal to 20–80, a 0.05° step, and a counting time of 2.0° per min, operating at 40 kV and 44 mA.

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Transparency document. Supporting information

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References

[1] Mansour Mohammedramadan Tijani, Aqsha Aqsha, Nader Mahinpey, Synthesis and study of metal-based oxygen carriers (Cu, Co, Fe, Ni) and their interaction with supported metal oxides (Al₂O₃, CeO₂, TiO₂, ZrO₂) in a chemical looping combustion system, Energy 138 (C) (2017) 873–882.
[2] A. Gomez, N. Mahinpey, A new method to calculate kinetic parameters independent of the kinetic model: insights on CO₂ and steam gasification, Chem. Eng. Res. Des. 95 (2014) 346–357.
[3] A. Aqsha, L. Katta, N. Mahinpey, Catalytic hydrodeoxygenation of guaiacol as lignin model component using Ni-Mo/TiO₂ and Ni-V/TiO₂ catalysts, Catal. Lett. 145 (6) (2015) 1351–1363 (Jun 1).