

Editorial

Chemical Looping Technology for Energy Storage and Carbon Emissions Reductions

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Chemical looping (CL) technology, initially developed as an advanced combustion method, has been widely applied in various processes, including the selective oxidation of hydrocarbons (e.g., methane, ethane, and propane) and biomass, H₂O splitting, CO₂ splitting, air separation, and ammonia synthesis [1–6]. In most cases, metal oxides are introduced as oxygen carriers (OCs), which deliver the oxygen from oxidants (e.g., air, CO₂, and H₂O) to the reductants (e.g., hydrocarbons, biomass, H₂, and CO), avoiding the direct contact between these reactants [7–10]. Specially, metal nitrides or hydrides are applied as nitrogen carriers or hydrogen carriers, respectively, for the ammonia synthesis [11–13]. Such processes can decompose a reaction into multiple sub-reactions that are conducted in different reactors, which optimizes the reaction conditions independently and can inherently simplified subsequent separation processes [14,15]. In addition, the cyclic reaction mode is effective in restraining the catalyst deactivation induced by the coke deposition, which concurrently promotes the efficiency of the process.

Redox materials serve as both the catalyst and a medium for elemental (O, N, or H) transfer in the CL process [16–18]. Therefore, exploring suitable redox materials is one key issue for specific reactions. This Special Issue includes nine papers in total, of which eight are research articles and one is a review paper. The contributions of this collection are summarized below.

To address the problem of high reaction temperatures in methane conversion, Kang et al. (Contribution 1) proposed a plasma–catalyst hybrid system for the selective production of C₂₊ hydrocarbons, enabling C–H bond cleavage at ambient temperature. Detailed investigations show that the selection of dielectric materials is of crucial importance for the reaction and the performance of TiO₂ is superior to that of SiO₂ and Al₂O₃. When further decorated by MnO_x, the MnTi catalyst manifests the best C₂₊ yield of 27.29% and remains stable in 30 consecutive cyclic redox tests.

Wang et al. (Contribution 2) prepared a series of La_{1-x}Ce_xMnO_{3+δ} samples for the chemical looping oxidative dehydrogenation (CL-ODH) of ethane to ethylene. It was found that the substitution of La³⁺ by Ce⁴⁺ cations could significantly promote the Mn³⁺/Mn⁴⁺ and O_{lattice}/O_{adsorp} ratio at the catalyst surface. A possible mechanism is that the Mn³⁺-O_{lattice} redox couple is responsible for the selective production of ethylene from ethane. Therefore, La_{0.7}Ce_{0.3}MnO₃ shows the best performance of 22% ethane conversion, with 57% ethylene selectivity in the CL-ODH reaction.

Calcium looping is a promising technology for efficient CO₂ capture; however, measuring the kinetics in the fluidizing calcination of limestone remains challenging. Li et al. (Contribution 3) studied the effect of particle size (150–1250 μm), temperature (750–920 °C), and CO₂ concentration (0–30 vol.%) on the calcination characteristics of limestone. The results show that a higher temperature, lower CO₂ concentration, and smaller particles all contribute to the high calcination rate. The decomposition of limestone in particles is affected by both the chemical reaction and gas diffusion. It is inferred from the calculation results that the effects of chemical reaction and gas diffusion are overwhelming for particles with sizes below 80 μm and above 450 μm, respectively, while these two factors play a



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role in the same order of magnitude for particles between 80 and 450 μm . In addition, improving the CO_2 concentration can greatly weaken the influence of particle size for calcination process.

The efficient utilization of biomass resources has been widely accepted as a useful strategy to address the concerns regarding the scarcity of fossil fuels and the related environmental problems. Xia et al. (Contribution 4) screened various metal-modified ZSM-5 (metal = Zn, Mo, Fe, and Ga) catalysts for the fast catalytic pyrolysis of bio-derived furans (2-methylfuran, MF). It is found that all these metal promoters could improve the conversion of MF and corresponding yield of aromatic, wherein the 2%Fe-ZSM-5 showed the highest aromatic yield of 40.03% at a WHSV of 2 h^{-1} . Mechanism studies reveal that such promotion arises from the synergy between Brønsted and Lewis acid sites. Therefore, generating new Lewis acid sites without a notable reduction in the Brønsted acid sites in ZSM-5 is key for designing a prospective catalyst for the aromatization of MF.

Taking benzene as a model compound of biomass tar, Huang et al. (Contribution 5) investigated the tar removal process using iron ore as an oxygen carrier. Compared with the blank experiment, the addition of hematite, functioning as both an oxygen donor and catalyst, can promote benzene conversion by 20%, which can be further enhanced to nearly 50% upon prolonging the residence time. In addition, the introduction of H_2O as a co-reactant is effective in reducing coke formation at the expense of lowering the benzene conversion, since the water vapor could reduce the residence time and weaken the catalytic activity by oxidizing the reduced iron species.

The migration of oxygen could exert great influence on the reactivity, selectivity, and stability of the oxygen carrier during redox cycles. In the study by Song et al. (Contribution 6), the oxygen migration mechanism of NiFe_2O_4 in chemical looping CO_2 splitting was investigated. It is suggested that the driving forces for diffusion of oxygen during the redox reaction are mainly attributed to the concentration gradient between the surface and the bulk. A highly reactive interface containing both lattice oxygen and metal atoms exists at the surface of OCs, which accounts for the outstanding redox performance of NiFe_2O_4 . The movement of Ni particles into and out of a spinel matrix can improve the oxygen migration during the reaction.

Chemical looping combustion holds the virtue of inherent CO_2 separation by avoiding direct contact between fuel and air. Ksepko et al. (Contribution 7) prepared a series of oxygen carriers by mixing and calcination of the Fe_2O_3 - MnO_2 - TiO_2 powder. Among these OCs, the F50M35 sample with 50 wt.% of Fe_2O_3 and 35 wt.% of MnO_2 displays the highest oxygen capacity of ca. 16–17 wt.%. It is found that the addition of TiO_2 could inhibit the formation of the negative manganese-rich spinel phase by reacting with Fe_2O_3 and MnO_2 to generate Fe_2TiO_5 and $\text{Fe}_{0.6}\text{Mn}_{0.4}\text{TiO}_3$, which contributes to a better cycling stability. In addition, it is suggested that a milder reaction temperature between 850 $^\circ\text{C}$ and 900 $^\circ\text{C}$ is useful to take full advantage of the OCs' potential.

CuO is a promising OC for the chemical looping with oxygen uncoupling (CLOU) process, which could release gaseous O_2 for the total combustion of fuel. To determine the oxygen release mechanisms of CuO , Wang et al. (Contribution 8) conducted detailed DFT calculations over the (110) and (111) surfaces. The results indicated that the CuO (110) surface is much more active than (111) for the oxygen release reaction. Barriers of 1.89 eV and 3.22 eV need to be conquered for the O_2 formation and desorption, respectively, over the (110) surface. Instead, the diffusion of subsurface oxygen to the surface oxygen vacancies only exhibits a low energy barrier of 0.24 eV, which indicates that the surface reactions (O_2 formation and desorption) are the rate-limiting steps.

Chemical looping water-splitting (CLWS) is an attractive method for hydrogen production. In this process, reducing gaseous (methane, syngas, or diluted hydrogen), thermal reduction, or photo-assisted thermal reduction methods could be utilized to abstract the lattice oxygen from OC, which is then recovered by water oxidation, giving hydrogen with high purity by simple condensation of the water vapor. In the review by Chang et al. (Contribution 9), the recent advances on oxygen carriers are summarized in detail. It is

suggested that the Fe- and Ce-based oxides are among the most studied redox materials. Composite oxides with perovskite structures (ABO_3) normally display outstanding performance by varying the A and B site cations.

Overall, chemical looping technology is effective in reducing the energy input for many reaction processes due to specific multi-step features. Although much progress has been achieved in these years, industrialized applications of this technology remain a great challenge. One main reason could be the lack of efficient redox materials. To tackle this issue, in situ characterizations, theoretical calculations, and thermodynamic analysis have been recommended for future studies; these are important for establishing clear structure–function relationships.

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