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Tri-reforming of hydrocarbon mixtures for the production of syngas

Aim

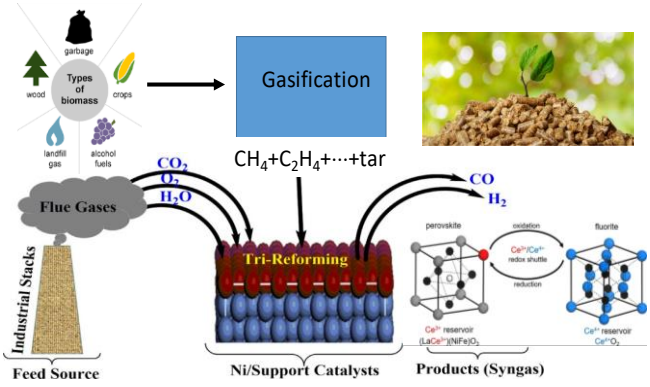
Tri-reforming of a hydrocarbons mixture utilizing CO_2, H_2O and O_2 is an emerging technique for the production of synthesis gas and CO_2 abatement. Nevertheless, formulation and design of a low-cost, active and stable catalyst is a major challenge due to the complex reaction network and rapid catalyst deactivation. The goal of this work is to establish the optimum conditions and optimum catalyst (Ni supported on perovskite) for the tri-reforming process.

Justification

Syngas ($CO+H_2$) plays an important role as an intermediate in the production of several industrial products, such as Fischer–Tropsch liquids, methanol and ammonia. Currently, syngas is produced from fossil fuels, mainly coal, natural gas and naphtha. Syngas from renewable resources, such as biomass, exhibits a promising prospective, because it is a CO_2 neutral resource, which is distributed extensively in the world. However, after the biomass gasification process, next to CO and H_2 there is a mixture of unreformed hydrocarbons (CH_4 + C_2H_4 + ⋯ +tar), which still contains 50% of the product energy potential. The most critical challenge is to reform these hydrocarbons to syngas. Steam reforming is one of the main technologies for hydrocarbon conversion to syngas. The endothermic reaction between C_xH_y and H_2O typically proceeds over a nickel-based catalyst at high temperature. Although nickel catalysts are effective for steam reforming of hydrocarbons mixtures, improvement is needed in terms of activity, stability, suppression of coke deposition, and regeneration.

The **tri-reforming process** is a synergetic combination of steam reforming, CO_2 reforming (carbon dioxide from power plants, …), and partial oxidation of hydrocarbons in a single reactor for more efficient production of syngas. The process has several potential advantages compared to steam and dry reforming: high hydrocarbon conversion can be achieved, CO_2 is utilized, the desired ratio H_2/CO can be controlled, and coke formation minimized. The main challenges in bringing this reforming technology to practice rest in novel catalysts development and the understanding of the reaction mechanisms for kinetic modeling and process optimization. **How can this be tackled?**

In recent studies, perovskite-type oxides have been used as catalyst precursor and support for tri-reforming. The general formula of perovskite is ABO_3, where the A site contains rare or alkaline earth metals, while the B site holds 3d transition metals. Moreover, perovskites allow easy modification of its oxidation states, oxygen mobility within the lattice, oxygen vacancies, and redox properties by partial substitution at the A or B sites, thereby improving catalytic activity, stability and suppressing carbon formation.



Program

- Energetic and exergetic analyses will be applied to the tri-reforming process in order to assess the suitability of this reaction for the production of syngas with a desired H_2/CO molar ratio for the Fischer–Tropsch process and methanol production;
- Synthesis of perovskite materials ($LaCeO_3$, $LaFeO_3$, $FeCeO_3$, $LaNi_{0.8}Fe_{0.2}O_3$, $La_{0.9}Ca_{0.1}Ni_{0.5}Fe_{0.5}O_3$, $La_{1-x}Ce_xNi_{0.5}Fe_{0.5}O_3$);
- Catalyst characterization by BET, H_2-TPR, O_2-TPO, CO_2-TPO, TEM, XRD, in situ XRD;
- Evaluation of the effect of the perovskite type and role (precursor vs. support) on the Ni catalyst's performance in the tri-reforming of a hydrocarbons mixture.

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