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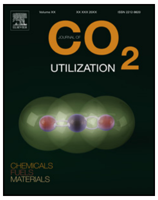

Enabling continuous capture and catalytic conversion of flue gas CO_2 to syngas in one process

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ABSTRACT

Albeit a variety of available strategies for CO_2 conversion to useful chemicals and fuels, most technologies require relatively pure CO_2, especially without oxygen and water. This requires additional steps of CO_2 capture and purification before its efficient conversion. This necessity increases energy requirement, leading to poorer carbon footprints and higher capital expenditures lowering the viability of overall CO_2 conversion processes. We have developed an effective technology which combines CO_2 capture and conversion processes using isothermal unsteady-state operation and a catalyst consisting of earth-abundant chemical elements (FeCrCu/K/MgO–Al_2O_3). Diluted CO_2 streams common in process flue gases, even containing oxygen and water, can be fed to the process and relatively pure product stream such as syngas, i.e. carbon oxides (CO and CO_2) and hydrogen mixture, can be produced. A possible scheme of reactor integration for continuous CO_2 abatement and conversion based on a two-reactors system is presented.

1. Introduction

Success in the quest for sustainable solutions to environmental threats induced by the atmospheric carbon dioxide (CO_2) accumulation largely relies on advances in chemical sciences and technological innovations [1]. One of the most promising strategies for the mitigation of anthropogenic CO_2 emission is its utilization by converting CO_2 into chemical fuels and value-added chemicals such as methanol and polymers [2]. Prior to the chemical transformation, however, CO_2 must be first captured from emission sources such as power, refinery, chemical, steel, and ceramic plants. This stage represents an increase of 40 to 80% of the total capital cost for a conventional post-combustion carbon capture and storage (CCS) process [3]. Thus, these steps drastically increase capital costs and investments for CO_2 transformation. Only the capture step is estimated to increase the energy requirements of a power plant by 25–40% [4].

Most chemical processes are designed to be operated under steady-state conditions. In case of heterogeneous catalytic processes, process performance is conventionally optimized under a given temperature, pressure, concentration, and flow conditions. Having this approach as the main stream, over the past 50 years intensive research and development work in academia and industry was devoted to improve the overall reaction performance using so-called *unsteady-state operation*. For a number of catalytic reactions, the advantages of unsteady-state operation and improvement in catalytic process performances were shown theoretically and also demonstrated in practice by forcing external parameter(s) such as concentration, temperature, pressure, and flow direction to change. Using such operations, the profiles of the catalyst states, coverage of active surface chemical species, concentrations, and temperatures in reactors can be influenced and controlled to a great extent, thus providing more favourable conditions for better process performance [5–7]. One of the catalytic technologies based on unsteady-state operation close to our daily life is NO_x storage-reduction (NSR) catalysis pioneered by TOYOTA and widely used in automotive industry [8,9]. The major advantage of NSR technology is to chemically reduce nitrogen oxides in fuel-lean and oxygen-rich conditions. By transiently switching between NO_x storage phase and reduction phase (as a short pulse of increased fuel for the latter), efficient NO_x reduction is made possible.

Among possible strategies proposed in the literature, *chemical looping* process represents an attractive technology that offers means to effectively purify CO_2 for subsequent conversion by changing the environment of catalyst within the reactor system

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[4]. Within the closed-system, the catalyst experiences unsteady-state reaction conditions. The fundamental concept of the process is based on the conversion of metal oxide sorbent to metal carbonate by *in situ* removal of flue gas CO_2 where calcium-based materials are typically used as the sorbent. The major general challenges of such processes are the required complex engineering, material resistance and drastic temperature changes for catalyst regeneration [4]. Generally this technology requires an additional reactor for CO_2 transformation unless the two conversion steps of CO_2 to CO and H_2 oxidation to H_2O are combined in one process (i.e. net reverse water-gas shift (RWGS) reaction operated under unsteady-state condition) as demonstrated by Kuhn using perovskite-type oxides [10,11]. The approach is promising although further material and process improvements are required to convert CO_2 to CO efficiently. Very recently, Farrauto has reported dual-functional materials based on ruthenium and calcium oxide which capture CO_2 from a model flue gas stream and subsequently reduce the captured CO_2 to methane at the same temperature in the same reactor [12]. Although the production of methane under the unsteady-state operation was demonstrated and even the catalyst functions in the presence of water vapour, the low CO_2 capture efficiency and high loading of previous ruthenium are the important points for further improvement.

Herein, we report a highly efficient dual-function catalyst material and process concept of catalytic CO_2 conversion strategy through CO_2 capture and subsequent reduction combined in one process, utilizing unsteady-state operation denoted here as CO_2 capture-reduction (CCR). In CCR, two distinct regimes, (i) capture of CO_2 on a storage component of a catalyst and (ii) release of CO_2 or direct catalytic reduction of stored CO_2 by reducing gas (here hydrogen) and catalyst regeneration, are operated alternately and isothermally. The important differences from the current state-of-the-art are the very high capture efficiency enabled by potassium component of the catalyst, earth-abundant metal components (Fe, Cr, Cu) and high activity and selectivity for CO_2 reduction to CO, and the same duration for the CO_2 capture and reduction phases. The last point is crucial for an advanced process integration concept, enabling continuous and complete CO_2 capture and reduction of captured CO_2 in one process using multiple-reactors.

2. Experimental

2.1. Materials and chemicals

PURAL® MG 20 hydrotalcite (Mg/Al molar ratio is 0.29) provided by Sasol Germany GmbH, Inorganic Specialty Chemicals was employed as the pristine material of the support. Potassium carbonate from Panreac was used as precursor of potassium component. All the metal precursors salts used in this study were the nitrate form purchased from Sigma-Aldrich. Deionized water was used for catalyst synthesis. The gases were purchased from Linde at the quality of >99.9993% for CO_2 and >99.999% for the other gases.

2.2. Catalyst synthesis

The hydrotalcite supported FeCrCu-K catalyst was prepared by sequential impregnation using the incipient wetness method. Firstly, a thermal treatment of hydrotalcite support at 600 °C for 3 h was carried out in order to obtain the homogeneous mixed oxides of MgO and Al_2O_3. Afterwards, three metals (Fe, Cr and Cu) were impregnated using a solution prepared by adding the necessary volume of deionized water to the metal nitrates precursor salts. The resulting solid was dried overnight at 80 °C followed by calcination at 500 °C for 5 h. Finally, a solution of potassium carbonate was impregnated over the solid obtained and it was dried and calcined under identical conditions. The elemental composition of the catalyst was determined by ICP analysis (Table S1-Supplementary material).

2.3. Reaction procedure

The experimental system mainly consists of four sections; (i) gas feed system, (ii) switching valve, (iii) reactor, (iv) gas detection

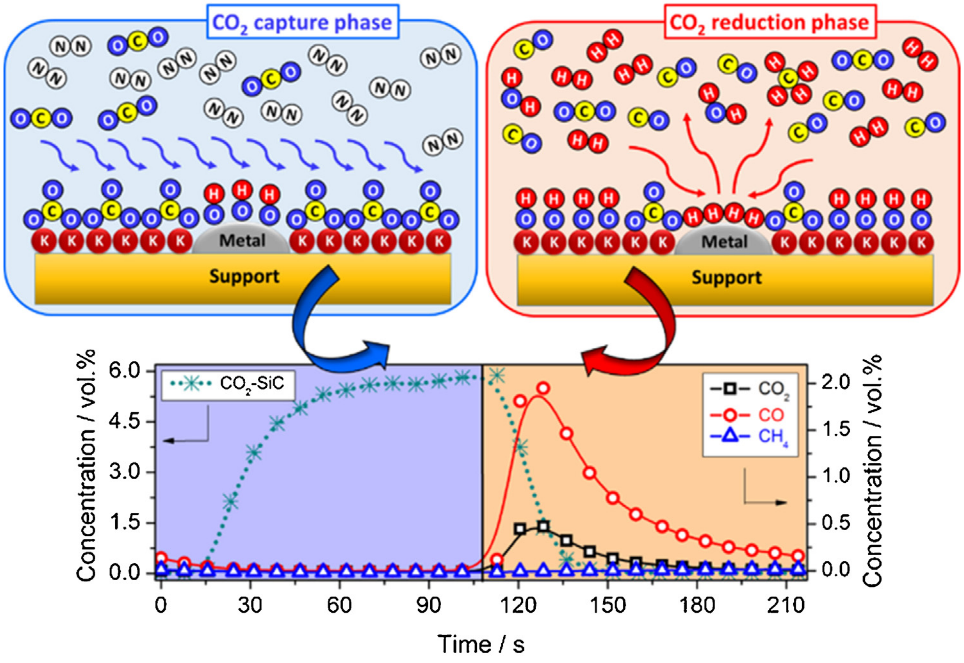

Fig. 1. A pictorial representation of the function and a possible mechanism of CCR on the catalyst material and representative concentration profiles during the unsteady-state operation. In comparison, a CO_2 concentration profile measured under the identical condition using an inert SiC material filled in the reactor is also shown.