

# Enabling continuous capture and catalytic conversion of flue gas CO<sub>2</sub> to syngas in one process

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## ABSTRACT

Albeit a variety of available strategies for CO<sub>2</sub> conversion to useful chemicals and fuels, most technologies require relatively pure CO<sub>2</sub>, especially without oxygen and water. This requires additional steps of CO<sub>2</sub> 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<sub>2</sub> conversion processes. We have developed an effective technology which combines CO<sub>2</sub> capture and conversion processes using isothermal unsteady-state operation and a catalyst consisting of earth-abundant chemical elements (FeCrCu/K/MgO-Al<sub>2</sub>O<sub>3</sub>). Diluted CO<sub>2</sub> 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<sub>2</sub>) and hydrogen mixture, can be produced. A possible scheme of

reactor integration for continuous CO<sub>2</sub> 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<sub>2</sub>) accumulation largely relies on advances in chemical sciences and technological innovations [1]. One of the most promising strategies for the mitigation of anthropogenic CO<sub>2</sub> emission is its utilization by converting CO<sub>2</sub> into chemical fuels and value-added chemicals such as methanol and polymers [2]. Prior to the chemical transformation, however, CO<sub>2</sub> must be first captured from emission sources such as power, refinery, chemical, steel, and ceramic plants. This stage represents an increase from 40 to 80% of the total capital cost for a conventional post-combustion carbon capture and storage (CCS) process [3]. These steps drastically increase capital costs and investments for CO<sub>2</sub> 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<sub>x</sub> 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. Without transiently switching between NO<sub>x</sub> storage phase and reduction phase (as a short pulse of increased fuel for the latter), efficient NO<sub>x</sub> reduction is not possible.

Among possible strategies proposed in the literature, *chemical looping* process represents an attractive technology that offers means to effectively purify CO<sub>2</sub> for subsequent conversion by changing the environment of catalyst within the reactor system [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<sub>2</sub> 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<sub>2</sub> transformation unless the two conversion steps of CO<sub>2</sub> to CO and H<sub>2</sub> oxidation to H<sub>2</sub>O 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<sub>2</sub> to CO efficiently. Very recently, Farrauto has reported dual-functional materials based on ruthenium and calcium oxide which capture CO<sub>2</sub> from a model flue gas stream and subsequently

reduce the captured CO<sub>2</sub> 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<sub>2</sub> 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<sub>2</sub> conversion strategy through CO<sub>2</sub> capture and subsequent reduction combined in one process, utilizing unsteady-state operation denoted here as CO<sub>2</sub> capture-reduction (CCR). In CCR, two distinct regimes, (i) capture of CO<sub>2</sub> on a storage component of a catalyst and (ii) release of CO<sub>2</sub> or direct catalytic reduction of stored CO<sub>2</sub> 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<sub>2</sub> reduction to CO, and the same duration for the CO<sub>2</sub> capture and reduction phases. The last point is crucial for an advanced process integration concept, enabling continuous and complete CO<sub>2</sub> capture and reduction of captured CO<sub>2</sub> 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<sub>2</sub> 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<sub>2</sub>O<sub>3</sub>. 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 system (IR/MS). In (i) there are two gas lines which allows preparing a gas mixture, one containing CO<sub>2</sub>, synthetic air, and nitrogen (capture phase gas), and another one containing H<sub>2</sub> (reduction phase gas) at desired concentrations and flow rates. In order to investigate the effect of water, the nitrogen flow can be passed through the water saturator maintained at 30 °C. These two lines enter the (ii) switching valve and only one of the two gas lines enters the (iii) catalytic reactor and the other line goes to a gas exhaust. There is a by-pass line at the reactor to measure ‘blank’ response of the gas flow under the same conditions for the flow controllers and detectors so that the results can be precisely calibrated and

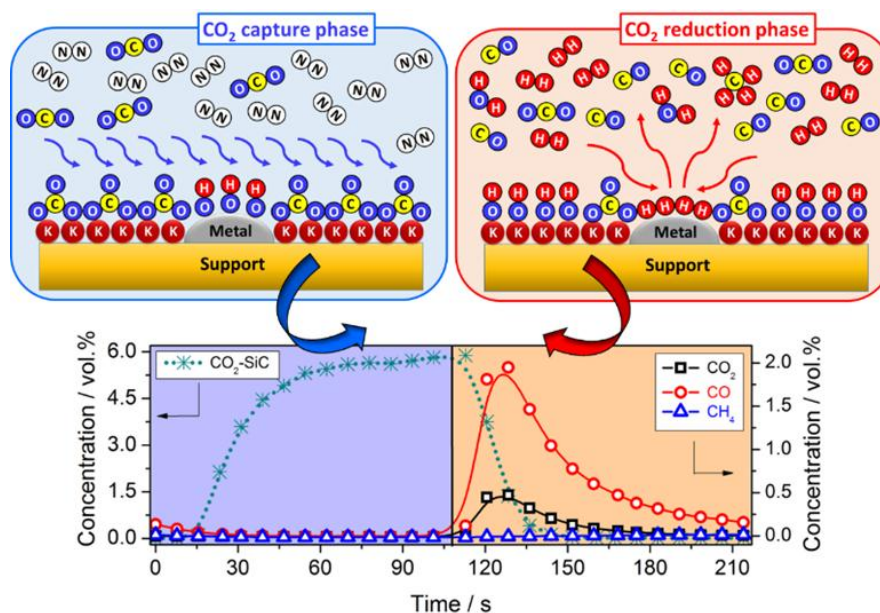
quantified. The effluent gas stream was passed into the transmission gas cell of an IR spectrometer (Bruker ALPHA) for quantitative product analysis. All valve switching and spectrum acquisition were synchronized by means of dedicated LabVIEW program in order to facilitate the data analysis and also precisely average over a number of CCR cycles to increase the S/N of the data.

In each run 1 g of the catalyst was used. Prior to the testing it was pressed, crushed, and sieved to the range of 200-300  $\mu\text{m}$ . The catalyst was heated up to 450  $^{\circ}\text{C}$  under 45  $\text{mL min}^{-1}$   $\text{N}_2$  flow and then activated at the temperature under unsteady-state conditions (30 cycles) with alternating flows of 45  $\text{mL min}^{-1}$  of  $\text{N}_2$  saturated with water and pure  $\text{H}_2$  for 90 s for each phase. This activation procedure was chosen to aim at avoiding over-reduction of the catalyst and partially reducing the hematite ( $\text{Fe}_2\text{O}_3$ ) to magnetite ( $\text{Fe}_3\text{O}_4$ ) as well as any  $\text{CrO}_3$  present in the catalyst to  $\text{Cr}_2\text{O}_3$  [13]. Moreover, we performed a blank test in each experiment using a fixed bed of an inert material (SiC) with the same particle size (200-300  $\mu\text{m}$ ) and passing the same feed gas compositions used in the catalytic tests.

### 3. Results and discussion

Figure 1 illustrates representative concentration profiles of  $\text{CO}_2$  and the product (CO in this case) in the CCR process based on switching between capture phase containing 5.8%  $\text{CO}_2$  in  $\text{N}_2$  (the first half period) at 27  $\text{mL min}^{-1}$  and pure  $\text{H}_2$  gas (the second half period) at 65  $\text{mL min}^{-1}$  passing through a reactor and the duration of each phase was 107.5 s. The reactor contained a CCR catalyst (1 g) consisting of Fe, Cr, Cu (reducing components) and K ( $\text{CO}_2$  capture component) supported on calcined Mg and Al-based hydrotalcites and it was maintained at 550  $^{\circ}\text{C}$ . The concentration profiles under the unsteady-state operation after a stabilization period are compared with that of  $\text{CO}_2$  in a blank test using a reactor packed with inert SiC pellets. It is evident that in the presence

of the CCR catalyst  $\text{CO}_2$  is efficiently trapped over the surface of alkali adsorption sites expectedly in the form of surface carbonates during the  $\text{CO}_2$  capture phase. Subsequently under the reducing condition by switching to  $\text{H}_2$  atmosphere, most of the captured  $\text{CO}_2$  reacts with  $\text{H}_2$  over the catalytically active sites, releasing the reduction product ( $\text{CO}$ ) accompanied by some release of unconverted  $\text{CO}_2$ .

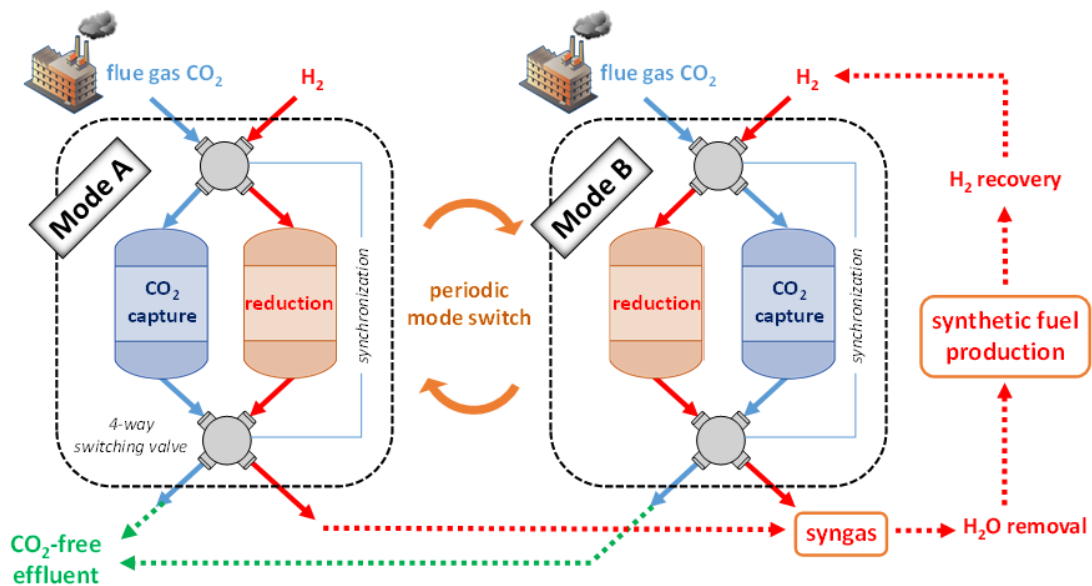


**Figure 1.** A pictorial representation of the function and a possible mechanism of CCR on the catalyst material and representative concentration profiles during the unsteady-state operation. In comparison, a  $\text{CO}_2$  concentration profile measured under the identical condition using an inert  $\text{SiC}$  material filled in the reactor is also shown.

The advantages of CCR process with the use of the specific catalyst are obvious. During the capture phase, no or very low concentration  $\text{CO}_2$  is detected in the effluent stream of the reactor. On the other hand, the effluent stream in the reduction phase contains mainly carbon oxides, mostly  $\text{CO}$  with some amount of  $\text{CO}_2$ , and unreacted  $\text{H}_2$ . The simplicity of the CCR process stems from the condition for  $\text{CO}_2$  capture and reduction; both are performed at the same temperature. This implies that identification of an excellent catalyst is of major importance for isothermal CCR. In addition, in the

presented case, both periods have the same duration and the process was operated at atmospheric pressure. These features are important in practice; the former for process integration (*vide infra*) and the latter to cope with most effluent stream released from various processes in industry.

One possible scheme to implement CCR process at a diluted- $\text{CO}_2$  emission source is illustrated in Figure 2. It consists of two CCR reactors where one is capturing  $\text{CO}_2$  and the other is reducing captured  $\text{CO}_2$  and regenerating the catalyst for subsequent  $\text{CO}_2$  capture (Mode A). Upon saturation of catalyst with  $\text{CO}_2$  and/or at a defined time period, the functions of the two reactors are reversed; the first one for  $\text{CO}_2$  reduction and the second one for  $\text{CO}_2$  capture (Mode B). By synchronizing the switching of gas flow direction entering and exiting the two reactors with a possible time delay, it is possible to continuously clean  $\text{CO}_2$  from the effluent stream and produce valuable products (here syngas) also continuously.



**Figure 2.** Integrated two-reactor CCR process for continuous  $\text{CO}_2$  capture and reduction.



A successful CCR catalyst must satisfy the following requirements:

- High capacity to adsorb/absorb CO<sub>2</sub> at operation temperature
- Fast and complete reduction/release of stored CO<sub>2</sub> and thus fast regeneration for subsequent CO<sub>2</sub> capture at the same temperature
- High conversion of CO<sub>2</sub> stored on the catalyst, e.g. in the form of carbonates
- Selective hydrogenation to desired product(s)
- High levels of reversibility and durability of CO<sub>2</sub> capture and release/reduction processes
- Composed of abundant and economic chemical elements and materials

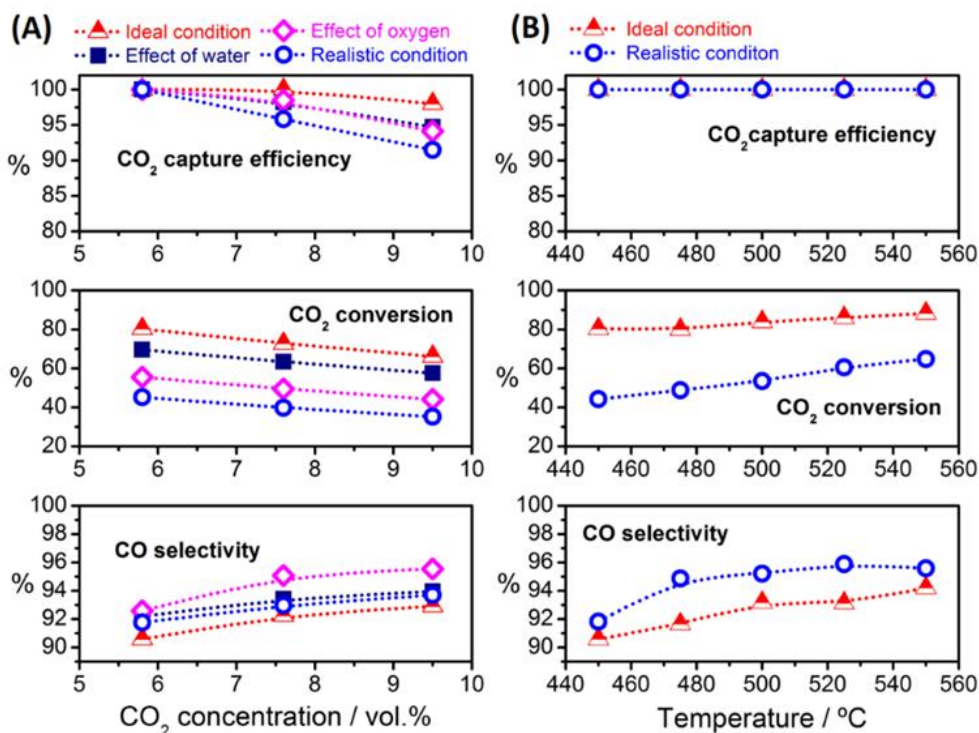
Very important properties of a successful catalyst are fast reducibility of captured CO<sub>2</sub> and catalyst regenerability within the time-scale of CO<sub>2</sub> capture, bearing the possible integrated implementation configuration (Figure 2) in mind. Achieving required high reactivity, fast regenerability, and high CO<sub>2</sub> absorption capacity at the same temperature are challenging. The degree of catalyst regeneration must be high and reproducible so that the function of catalyst as CO<sub>2</sub> absorber is retained over a long-term operation. Besides, product selectivity is of central importance to avoid further product separation steps. It is also worth mentioning that ideally hydrogen used in CCR process should be produced by a process powered by low carbon footprint energy sources, e.g. water electrolysis and photolysis powered by renewable energy or nuclear power.

Regarding the catalyst composition, promising catalyst materials for CCR process would consist of transition metal, alkali/alkali-earth metal carbonates supported over metal oxides according to our previous experience on comparable NO<sub>x</sub> storage-reduction catalytic processes [14-17]. The alkali/alkali-earth carbonates such as K<sub>2</sub>CO<sub>3</sub>

and  $\text{BaCO}_3$  can be reduced to respective oxides and hydroxides and they function as  $\text{CO}_2$  capture and storage material in a wide temperature range. Moreover, nanocrystalline carbonates such as nanosized  $\text{BaCO}_3$  and  $\text{K}_2\text{CO}_3$  can be an excellent reversible  $\text{CO}_2$  storage components because their decomposition temperatures drop from 1350 and 890 °C in the form of large bulk crystallites, respectively, to ca. 200-300 °C, likely due to enhanced surface carbonates composition (Supplementary Materials). The temperatures are expected to be even lower under reducing atmosphere of  $\text{H}_2$ . The type of metal oxides used as support will also alter the  $\text{CO}_2$  capture property drastically owing to their unique acidity, basicity, porosity, hydrophilicity, and reactivity, thus influencing the interaction strength and modes with  $\text{CO}_2$ . Support materials themselves can also participate in  $\text{CO}_2$  capture, forming surface carbonates and bicarbonates. On the other hand, depending on the active metal, there are several possible products synthesized from the reactions of the surface species like carbonates and formates formed by  $\text{CO}_2$  capture or released  $\text{CO}_2$  with a chemical reductant like hydrogen as used in this work. For example, Ni-based catalysts are selective in the production of methane while that Cu and FeCr-based catalysts are effective for CO production via RWGS reaction.

After screening and optimizing various active catalyst components for  $\text{CO}_2$  capture and hydrogenation of stored  $\text{CO}_2$  (Supplementary Materials), we developed an active CCR catalyst consisting of Fe, Cr, Cu, and K supported over mixed Mg and Al oxides obtained by calcining a Mg- and Al-containing hydrotalcite material (SASOL, PURAL MG20, Mg/Al = 0.32) [18]. The non-precious, transition metal components and K-promoted Mg-Al oxides support are crucial for their RWGS activity and to achieve high capacity for  $\text{CO}_2$  capture, respectively. Potassium promotion has been reported to significantly improve  $\text{CO}_2$  reversible sorption capacity at the temperature we aimed at

(300–500 °C) [19, 20]. The details of the catalyst composition and synthesis are described in Supplementary Materials and key functions of Cu and K as efficient CO<sub>2</sub> reduction and capture, respectively, have been investigated by space- and time-resolved spectroscopy and reported elsewhere [21].

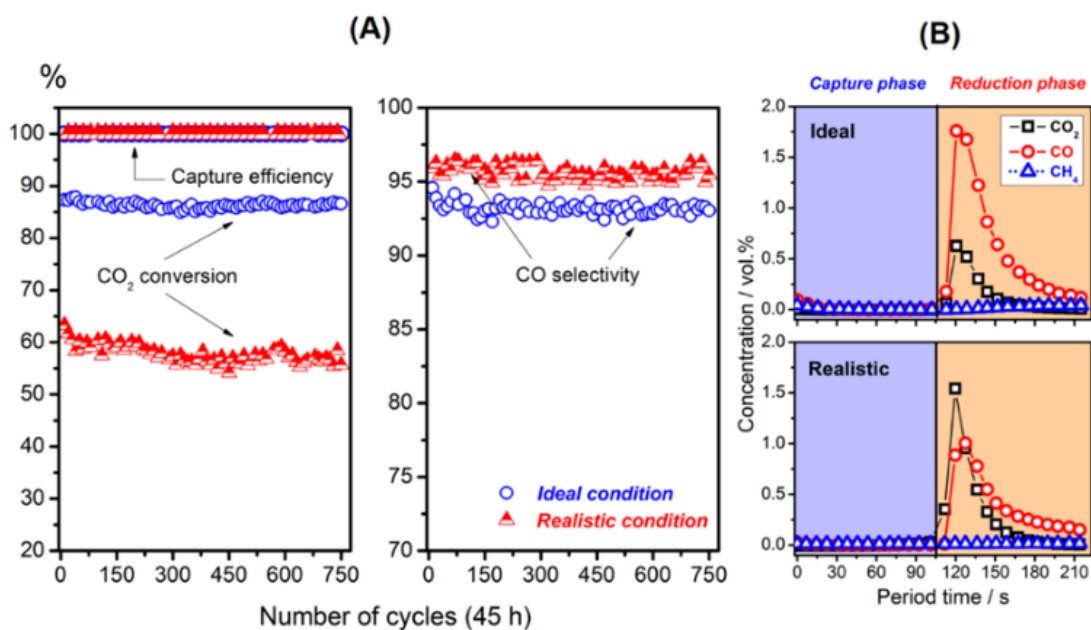


**Figure 3.** CO<sub>2</sub> capture efficiency, CO<sub>2</sub> conversion, and CO selectivity as a function of (A) CO<sub>2</sub> concentration (5.8-9.5%) at 450 °C and (B) reaction temperature with 5.8% CO<sub>2</sub>. Gas composition - Capture phase: CO<sub>2</sub> diluted in nitrogen (ideal condition), CO<sub>2</sub> diluted in nitrogen saturated with 4% of water vapour (effect of water), CO<sub>2</sub> diluted in nitrogen with 4 % of oxygen (effect of oxygen) and CO<sub>2</sub> diluted in nitrogen with 5% of oxygen and 4% of water (realistic condition). Gas hourly space velocity (GHSV) - 1620 mL g<sub>cat</sub><sup>-1</sup> h<sup>-1</sup>. Reduction phase: Pure hydrogen with GHSV of 3900 mL g<sub>cat</sub><sup>-1</sup> h<sup>-1</sup>. The CCR period length was 215 s, i.e. 107.5 s for CO<sub>2</sub> capture and reduction phase.

In a typical post-combustion capture process, which includes conventional process heaters and industrial utility boilers and represents most of today's fossil-fuel-based electricity generation, CO<sub>2</sub> is captured from flue gas that contains 4-8 vol% CO<sub>2</sub> for a natural-gas-fired power plant and 12-15 vol% for coal-fired power plants, at atmospheric pressures [3]. Other common major chemical components of flue gas are nitrogen, oxygen, and water. Therefore, we tested the FeCrCu/K/PMG-20 catalyst in the CCR process under model conditions with only CO<sub>2</sub> (in N<sub>2</sub>) in the capture phase and under more realistic conditions which additionally include O<sub>2</sub> and H<sub>2</sub>O vapor, mimicking post-combustion exhaust gas streams. The CCR performance was studied as a function of CO<sub>2</sub> concentration (Fig. 3A) and temperature (Fig. 3B) under the ideal and realistic conditions. In all cases, only carbon monoxide and methane were detected, with a dominant production of the former. One of the most important parameters assessing the CCR performance is CO<sub>2</sub> capture efficiency. This value was calculated based on the amount of CO<sub>2</sub> absorbed/adsorbed during the capture phase, indicating how much CO<sub>2</sub> is abated from the CO<sub>2</sub> containing gas stream using an integrated system as shown in Figure 2. There are some portion of unconverted CO<sub>2</sub> released mostly in the reduction phase (Figure 1). The other important parameters are product selectivity and CO<sub>2</sub> conversion. The latter value was calculated from the amount of CO<sub>2</sub> entered over one CCR cycle and converted to the products.

Generally, the inclusion of oxygen and water negatively impacted on CO<sub>2</sub> capture efficiency and CO<sub>2</sub> conversion. Nevertheless, the capture efficiency remained almost 100% when 5.8% CO<sub>2</sub> was employed under both ideal and realistic conditions between 450-550 °C (Figure 3B) and remained high (>90%) at all inlet CO<sub>2</sub> concentrations investigated (Figure 3A). The lower capture efficiency at higher CO<sub>2</sub> concentration is due to the earlier saturation of the catalyst with CO<sub>2</sub> using the CCR period investigated

(thus release of CO<sub>2</sub> towards the end of the capture phase) because of the higher amount of CO<sub>2</sub> passed through the CCR reactor per unit time and also a lower amount of CO<sub>2</sub> capture capacity under the realistic conditions likely due to competitive adsorption of oxygen and water over the catalyst. In other words, the CO<sub>2</sub> capture efficiency at higher CO<sub>2</sub> concentration can be improved by increasing the amount of catalyst or shortening the duration of the capture phase. This process flexibility is important to cope with effluent steams from different processes with varying concentrations of CO<sub>2</sub> and other gases. The remarkable effect of the realistic conditions was the lowered CO<sub>2</sub> conversion by 20-35% compared to the ideal conditions, resulting in larger release of unconverted CO<sub>2</sub> in the reduction phase. Possibly, the presence of water on the surface hindered the RWGS activity because presence of water is more favorable for the reverse reaction, i.e. WGS ( $\text{CO} + \text{H}_2\text{O} \rightleftharpoons \text{CO}_2 + \text{H}_2$ ), but this is unlikely because of the consistently higher selectivity to CO under the realistic condition. It is speculated that the presence of water and O<sub>2</sub> present in the capture phase influences the state of active sites (e.g. by surface oxidation or adsorption) in a way that hinder RWGS reaction. Besides, higher CO<sub>2</sub> concentration as well as higher temperature was found to be more favorable for CO selectivity. This is explained by the fact that the methanation reaction is an exothermic reaction which is favored thermodynamically at low temperatures, whereas RWGS is an endothermic reaction thus favored at high temperatures.



**Figure 4.** (A) Evolution of CO<sub>2</sub> conversion, capture efficiency and CO selectivity during 750 CCR cycles (45 h) under the ideal and realistic conditions at 550 °C with 5.8% CO<sub>2</sub> in capture phase. (B) Representation of the concentration profiles of the last CCR cycle.

Other important process factors in practice are stability and regenerability of the catalyst under unsteady-state operation in a long term. Catalytic tests over 750 CCR cycles (ca. 45 h) were performed at 550 °C (the temperature where the highest CO<sub>2</sub> conversion and CO selectivity were obtained) under the ideal and realistic conditions using the FeCrCu/K/PMG-20 catalyst. Figure 4 shows the CCR performance indicators as a function of CCR cycle number. The catalyst was found to be stable over the period of time under both conditions. This high stability as well as high carbon balance (100±5%) suggest that the captured CO<sub>2</sub> is totally reduced or released, and CO<sub>2</sub> is not accumulated over a long time cumulatively as carbonates, coke, formate or another surface carbonaceous species which can lead to catalyst deactivation. The only major difference between the CCR performances under the ideal and realistic conditions lies in the product selectivity. As discussed previously, under the realistic condition CO<sub>2</sub>

conversion is lowered significantly and CO<sub>2</sub> was released in the reduction phase. This lower CO<sub>2</sub> conversion is generally unfavored, but this may not be a problem depending on a targeted product to be synthesized from the syngas containing carbon oxides. The H<sub>2</sub>/CO<sub>x</sub> ratio of the gas stream in the reduction phase is ca. 40 and this value is higher than the stoichiometric ratio of methanol synthesis or Fischer-Tropsch (FT) reaction. Lower H<sub>2</sub>/CO<sub>x</sub> ratios will be targeted in our future work. Actually, such a high value can be considered beneficial as demonstrated for high-performance methanol synthesis due to thermodynamic and kinetic advantages [22] and unconverted H<sub>2</sub> can be recycled (Figure 2). Moreover, the direct employment of bio-syngas containing H<sub>2</sub>, CO, CO<sub>2</sub> and CH<sub>4</sub> has been developed for the production of Fischer-Tropsch (FT) hydrocarbons via one-pass through the reactor using unconverted syngas to generate electricity in a gas turbine combined cycle [23, 24].

#### **4. Conclusions**

We have demonstrated a strategy to combine CO<sub>2</sub> capture/purification (>99%) step and further conversion step in one process using unsteady-state operation under isothermal conditions to produce syngas. Depending on composition of catalysts and operation condition, the product selectivity and variety can be tuned and altered and thus the scope of the strategy is extremely broad. CCR offers a mean to simplify the CO<sub>2</sub> utilization strategy by potentially facilitating production of useful chemical directly at small and large CO<sub>2</sub>-emission sites.

#### **Acknowledgements**

We thank the financial support from Repsol. MINECO is acknowledged for support through CTQ2012-34153 and Severo Ochoa Excellence Accreditation 2014-2018 (SEV-2013-039).

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# **Supplementary Material**

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### **Catalyst optimization**

#### **Chemicals**

PURAL®MG hydrotalcites (Sasol Germany GmbH, Inorganic Specialty Chemicals) were employed as support. The following hydrotalcites were considered (their Mg/Al molar ratio is given in parentheses): PURAL®MG 5 (0.08), MG 20 (0.29), MG 30 (0.44), MG 63 (1.89) and MG 70 (2.59). Additionally, a sample consisting only of Al, PURAL®SB, was also included in this study. K<sub>2</sub>CO<sub>3</sub> from Panreac was used as precursor of potassium. All the metal precursors salts used in this study were in the form of nitrates purchased from Sigma-Aldrich.

## **Synthesis of hydrotalcites-based catalysts**

Cu was chosen as the active metal to find the best hydrotalcite-derived mixed oxide support. The calcined-hydrotalcite-supported Cu-K catalysts were prepared by sequential impregnation using the incipient wetness method. The catalysts were prepared in the following steps.

1) Thermal treatment of hydrotalcite support at 600 °C for 3 h in order to obtain the homogeneous mixed oxides.

2) Impregnation of first precursor: Cu solution was prepared by adding the necessary volume of deionized water to the metal precursor salts. After the impregnation the catalyst was dried overnight at 80 °C followed by calcination at 500 °C for 5 h.

3) Impregnation of second precursor: K<sub>2</sub>CO<sub>3</sub> solution was prepared by adding the necessary volume of deionized water. After the impregnation the catalyst was thermally treated in the same way as in step 2.

Furthermore, we have prepared two multimetallic catalysts containing Fe-Cr-Cu (Fe/Cr molar ratio = 10 and Fe/Cu molar ratio = 38) and Cu-Zn (Cu/Zn molar ratio = 2.6), respectively. The preparation of calcined-hydrotalcite-supported K-multimetallic catalysts was similar to that of the Cu catalysts described above. In step 2, the nitrate salts of both metals are dissolved in the same solution and they are co-impregnated.

## **Catalytic tests**

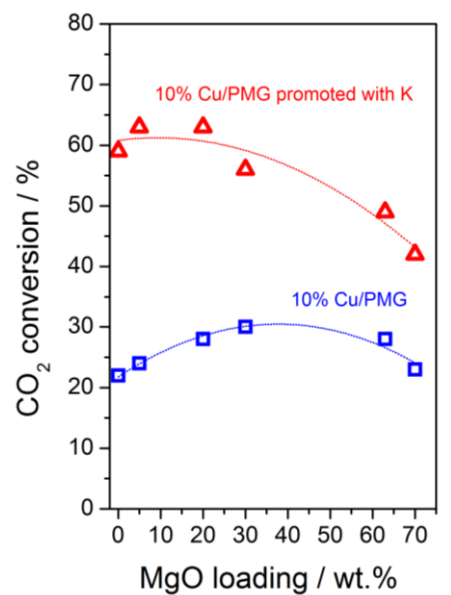
In each run 600 mg of the catalyst was used. Prior to the testing it was pressed, crushed, and sieved to the range of 200-300 µm. The catalysts are previously reduced at 450 °C for 1 h under 10% H<sub>2</sub>/He v/v at 40 mL min<sup>-1</sup>, except for the Fe-Cr based

catalysts. The pretreatment of the latter catalysts was carried out by partially reducing the hematite ( $\text{Fe}_2\text{O}_3$ ) to magnetite ( $\text{Fe}_3\text{O}_4$ ) using the addition of the process gas mixtures to activate the catalyst. This also converts any  $\text{CrO}_3$  present in the catalyst to  $\text{Cr}_2\text{O}_3$  [1]. Several  $\text{CO}_2$  capture/reduction cycles (typically 50) are examined to obtain reproducible catalytic performances (quasi steady-state). The selected conditions for the evaluation of the catalytic tests were:

- Capture phase:  $50 \text{ mL min}^{-1}$  of 10 % v/v of  $\text{CO}_2$  in helium with Gas hourly space velocity (GHSV) -  $500 \text{ mL g}_{\text{cat}}^{-1} \text{ h}^{-1}$
- Reduction phase: Pure hydrogen with GHSV of  $3900 \text{ mL g}_{\text{cat}}^{-1} \text{ h}^{-1}$ .
- Period time: 77 s (38.5 s in each phase)
- Temperature:  $450 \text{ }^\circ\text{C}$
- Pressure: 1 bar

### **Effect of Mg/Al molar ratio**

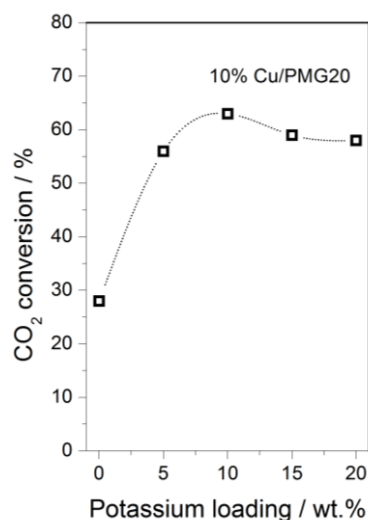
In order to evaluate the effect of the Mg/Al molar ratio on the catalyst performance, all hydrotalcites provided by SASOL and previously calcined were impregnated with 10 wt% of Cu and 10 wt% of K and compared with the series without potassium. Figure S1 shows the results of  $\text{CO}_2$  conversion of both series tested. It should be noted that the presence of potassium increased notably the conversion in all the range of Mg/Al molar ratio. Furthermore with an increase in Mg/Al molar ratio the conversion of  $\text{CO}_2$  gradually increased up to 10-20 wt% of MgO and above this loading the conversion decreased. The presence of excess of MgO likely resulted in the formation of highly stable  $\text{MgCO}_3$  species difficult to be reduced.



**Figure S1.** Effects of MgO percent in MgO-Al<sub>2</sub>O<sub>3</sub> mixed oxides on CO<sub>2</sub> conversion in CCR with and without K.

### Effect of potassium loading

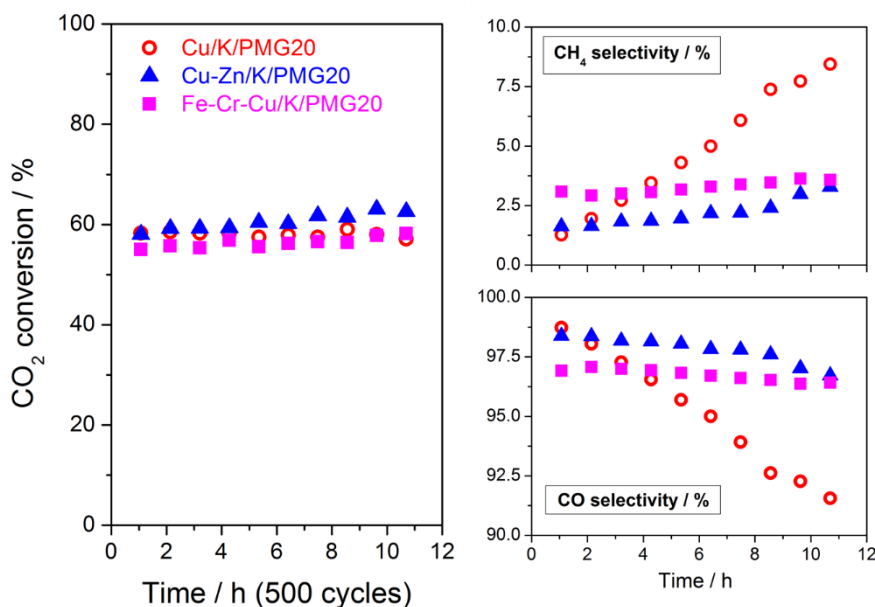
We have investigated the effect of potassium loading over the 10 wt% Cu/Pural MG20 catalyst in the range 0-20 wt% of K. Figure S2 shows the catalytic performance as a function of K loading under the CCR condition. The optimal K loading was found to be 10 wt%.



**Figure S2.** . Effect of K loading on the CO<sub>2</sub> conversion

### Multimetallic effect

Long test runs (500 cycles – 12h) using Cu/K/Pural MG20, Cu-Zn/K/Pural MG20 and Fe-Cr-Cu/K/Pural MG20 materials were performed in order to investigate the long-term stability and choose the optimal catalyst for the CCR process. Figure S3 compares the CO<sub>2</sub> conversion and the selectivity into CO and CH<sub>4</sub> as a function of the time for the three catalysts. We can observe that the CO<sub>2</sub> conversion of the three materials were similar and stable, while the CH<sub>4</sub> selectivity of Cu monometallic and Cu-Zn bimetallic catalysts increased with time possibly due to sintering of Cu. For this reason we have decided to focus on FeCrCu trimetallic catalyst in order to investigate the efficiency of the CCR process.



**Figure S3.** CO<sub>2</sub> conversion and selectivity to CO and CH<sub>4</sub> for Cu/K/PMG-20, Cu-Zn/K/PMG-20 and Fe-Cr-Cu/K/PMG-20 catalysts

## Catalyst characterization

### Characterization methods

The elemental composition was determined by ICP analysis.

Nitrogen isotherms at 77 K were measured on Quantochrome Autosorb 1-MP analyzer. Prior to analysis, the sample was degassed in vacuum at 573 K for 12 h.

The XRD pattern was recorded on Bruker AXS D8 Advance diffractometer equipped with a Cu tube, a Ge (1 1 1) incident beam monochromator ( $\lambda = 0.1541$  nm), and a Vantec-1 PSD operated in transmission mode. Data were recorded in the range of 5-70° 2 $\theta$  with a step size of 0.02° and a counting time of 4 s per step. For CO<sub>2</sub>-TPD, the sample (100 mg) were firstly reduced in 5% H<sub>2</sub> in N<sub>2</sub> at 20 mL min<sup>-1</sup> for 1 h at 450 °C, followed by exposure of 4% CO<sub>2</sub> in inert at 80 °C for 1 h at 20 mL min<sup>-1</sup>.

TPD was performed under 5% H<sub>2</sub> in N<sub>2</sub> flow at 20 mL min<sup>-1</sup> to investigate the stability of CO<sub>2</sub> adsorbed under a reducing environment as in CO<sub>2</sub> hydrogenation in CCR process. The temperature was increased from 50 up to 900 °C. The effluent gases were analyzed on a mass spectrometer (MS), Pfeifer Omnistar GSD 301 C, without any trap.

In order to estimate the CO<sub>2</sub> capture capacity we have calculated the amount of CO<sub>2</sub> captured in the equilibrium at 400 °C. The equilibrium CO<sub>2</sub> sorption uptake was measured by CO<sub>2</sub> chemisorption using Quantachrome Autosorb iQ system. Chemisorption is a strong specific interaction that affects only the surface parts occupied by atoms that can chemically interact with the gas. It allows determining the amount of surface active sites and possibly the amount of CO<sub>2</sub> chemisorbed and physisorbed. Before CO<sub>2</sub> sorption, moisture and CO<sub>2</sub> on samples was removed under hydrogen flow for 1 h at 450 °C. After the temperature was decreased to 400 °C under nitrogen flow, CO<sub>2</sub> was adsorbed at 400 °C until the system reaches the equilibrium pressure (800 Torr).

### Characterization results

Table S1 shows the chemical compositions and textural properties (BET surface area, pore size and pore volume) of the FeCrCu/K/PMG20 catalyst.

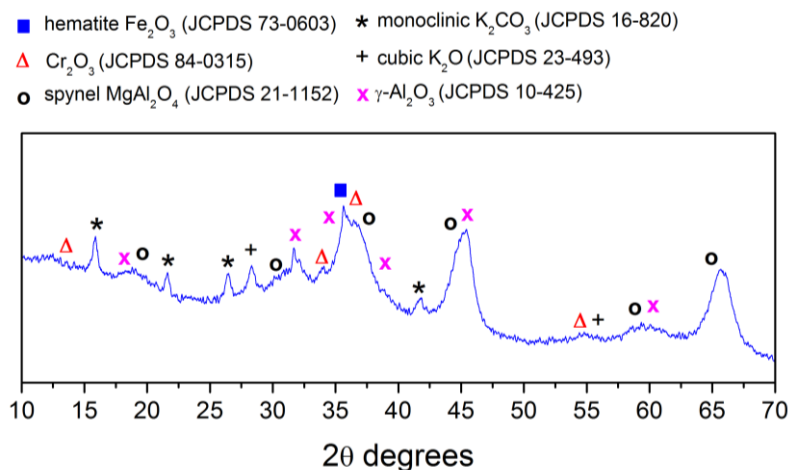
**Table S1.** Textural properties and elemental analysis

BET surface area m <sup>2</sup> g <sup>-1</sup>	Pore volume cm <sup>3</sup> g <sup>-1</sup>	Elemental analysis / wt. %					
		Al <sub>2</sub> O <sub>3</sub>	MgO	Fe	Cr	Cu	K
111	2.11	66.53	15.80	6.91	0.58	0.20	9.98

Figure S4 shows XRD patterns of FeCrCu/K/PMG20 catalyst. The diffraction peaks obtained can be assigned to the following phases: hematite Fe<sub>2</sub>O<sub>3</sub> (JCPDS 73-0603),



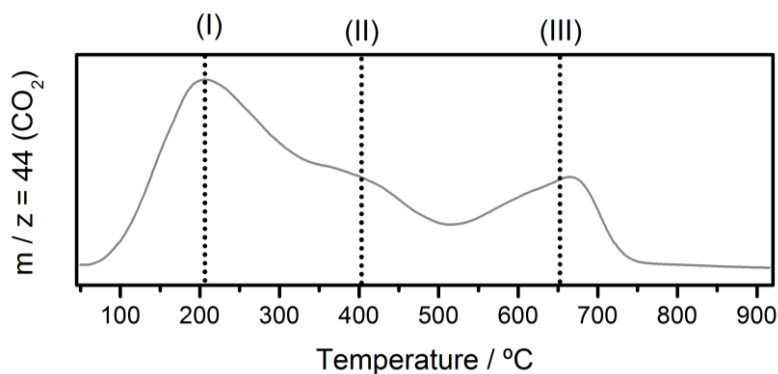
Cr<sub>2</sub>O<sub>3</sub> (JCPDS 84-0315), monoclinic K<sub>2</sub>CO<sub>3</sub> (JCPDS 16-820), cubic K<sub>2</sub>O (JCPDS 23-493), spinel MgAl<sub>2</sub>O<sub>4</sub> (JCPDS 21-1152) and  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> (JCPDS 10-425). Diffraction peaks associated to Cu phases were not observed likely due to its high dispersion and low concentration.



**Figure S4.** XRD pattern of FeCrCu/K/PMG20 catalyst

In order to investigate the stability of CO<sub>2</sub> adsorbed and stored as carbonates, CO<sub>2</sub>-TPD was performed after pre-reduction of the catalyst to render storage sites in their active oxide form prior to CO<sub>2</sub> adsorption (their decomposition was confirmed by MS) and subsequent CO<sub>2</sub> adsorption. CO<sub>2</sub> desorption was studied under a hydrogen atmosphere in order to study the stability of such adsorbed and carbonate species under a reductive environment as in CCR. Figure S5 shows the CO<sub>2</sub>-TPD profiles in the presence of hydrogen. CO<sub>2</sub> desorption shows three peaks (I), (II) and (III) at 200, 400 and 650 °C, respectively. These three peaks can be ascribed to three different surface carbonate species with different stability. Bansode et al. [2] assumed that peak (I) originates from the decomposition of surface formates and peaks (II) and (III) from that of surface carbonates. Importantly, the major desorption is characterized by peaks (I) and this suggests the high reactivity of CO<sub>2</sub> captured as carbonate/formate species and

that the desorption site corresponding to these peaks play crucial roles in determining the catalytic performance in the CCR process.



**Figure S5.** CO<sub>2</sub>-TPD profile of FeCrCu/K/PMG20 catalyst under hydrogen

The equilibrium CO<sub>2</sub> uptake was measured by CO<sub>2</sub> chemisorption. The amounts of chemisorbed and physisorbed CO<sub>2</sub> over the FeCrCu/K/PMG20 catalyst are shown in Table S2.

**Table S2.** CO<sub>2</sub> sorption capacity estimated by CO<sub>2</sub> equilibrium chemisorption at 400 °C

CO <sub>2</sub> chemisorbed mmol g <sup>-1</sup>	CO <sub>2</sub> physisorbed mmol g <sup>-1</sup>	CO <sub>2</sub> total mmol g <sup>-1</sup>
0.140	0.157	0.297

## References

- [1] Byron Smith R J, Muruganandam Loganathan, M.S. Shantha, *Int. J. Chem. React. Eng.*, 8 (2010) 1542-6580.
- [2] A. Bansode, B. Tidona, P.R. von Rohr, A. Urakawa, *Catal. Sci. Technol.*, 3 (2013) 767-778.