

Integrated CO₂ Capture and Methanation from a SO₂-bearing flue gas: S-tolerance and regeneration of the dual function material

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Abstract

The combined CO₂ capture and methanation with Dual Function Materials (DFM) is emerging as a vibrant field of research for its potential to increase the efficiency and reduce the cost of current multistage CCU processes.

In this work, a DFM containing Ru (1% wt) and Li (3% wt.) dispersed onto γ -Al₂O₃ was extensively tested in the integrated CO₂ capture and methanation process to assess the effects of the main species (O₂ and H₂O) as well as of poisonous impurities (SO₂) in realistic flue gases. The ageing study with up to 100ppmv SO₂ demonstrated a remarkable tolerance to sulfur poisoning coupled with a slow loss of CO₂ capacity due to long-term S-accumulation.

Introduction

Reversing global temperature rise requires mitigating greenhouse gas emissions from the industry and energy sectors. As the world will still rely on fossil fuels in the mid-term, and there are sectors which cannot be easily decarbonised or only partially so, carbon capture and utilization (CCU) technologies are required for the ambitious net zero carbon emission target to be met [1-2]. Recently, the integration of CO₂ capture and its direct conversion into valuable fuels or intermediates such as methane, CO or syn-gas is emerging as a vibrant field of research due to the potential to achieve a circular carbon economy while cutting the costs and increasing the efficiency of the energy-intensive multistep CCU technologies that are currently available [1-2]. In particular, many authors have recently demonstrated that the integrated CO₂ capture and in-situ methanation (ICCM) can be performed over Dual Function Materials (DFMs) [1-4], which combine at the nanoscale a CO₂ sorbent phase (e.g. alkali (hydro)oxides/carbonates) with a methanation catalytic active phase (e.g. Ni or Ru). The process is then operated in a chemical looping mode mediated by the DFM which is alternatively exposed to a CO₂-rich atmosphere (capture stage), and an H₂ stream (methanation stage) (Figure 1). Since both CO₂ adsorption and methanation are exothermic the ICCM process can be run isothermally in the 250-350 °C range by harvesting the sensible heat of typical flue gases and without any further energy input, utilizing either fixed bed reactors with alternate feeds or interconnected fluidized bed reactors with circulating DFM [2].

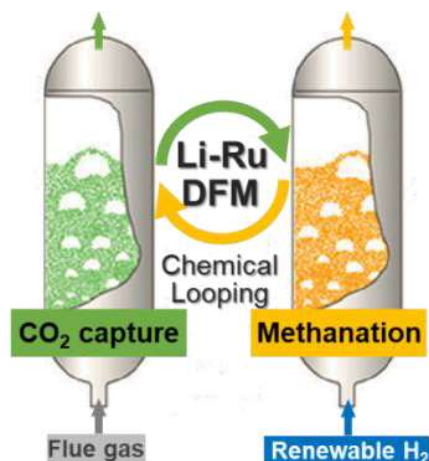


Figure 1. Schematic representation of the Integrated CO₂ Capture and Methanation process with a Li-Ru DFM circulating within interconnected fluidized bed reactors.

In this work we set out to investigate the performance of a DFM containing Li and Ru dispersed on γ -alumina during the ICCM with a more realistic flue gas including O₂, H₂O and SO₂ impurities (up to 100ppm), which can severely poison catalytic metal sites for hydrogenation. The ageing study involved more than 100 capture and methanation cycles in a fixed bed reactor operated in the temperature range 260 – 320 °C with alternate feed conditions.

Experimental

Ru and Li were dispersed sequentially within 1mm Al₂O₃ spheres by impregnation with water solutions of nitrate precursors. Their loadings in the final DFM were deliberately kept low (ca. 1 % and 3 % wt., respectively) to better highlight the possible sulfur-poisoning effects on both the sorption and catalytic functionalities. Combined CO₂ capture and methanation tests were performed in a fixed bed quartz reactor with an annular section ($d_{in}=4\text{mm}$, $d_{out}=10\text{ mm}$) that was loaded with ca 2.3 cm³ (packed-volume) of Li-RuA DFM. The reactor was operated at atmospheric pressure and at fixed temperature (260-320 °C) and total inlet flowrate (20 Sl/h) by switching alternatively the feed between the CO₂ capture and methanation phases. During the first step a feed gas stream containing 5% vol. CO₂ in N₂ with the possible additional presence of 0.25% O₂ and/or 1.5% H₂O as well as 10-100 ppmv SO₂ was stepwise admitted to the reactor and flowed over the DFM. After an intermediate purge (2 min, pure N₂), the methanation phase was started by switching the feed to 15% vol. H₂ in N₂. Continuous gas analyzers (ABB Optima Advance) were used to measure the molar fractions of CO₂, CH₄, CO, and SO₂, H₂S.

Results and Discussion

Textural and morphological properties of the fresh Li-RuA material as well as its parent RuA catalyst are presented in Table 1. The dispersion of Li on RuA induced a 9.2% increase in the density of the resulting DFM spheres (stabilized in air after reduction). However, the specific surface area of Li-RuA was lowered from 180

down to $145 \text{ m}^2 \text{ g}^{-1}$, suggesting a deeper modification of the original textural properties. In particular, the Pore Size Distribution analysis indicates Li-addition caused an evident enlargement of the mesopores (Table 1) whose median size passed from 9.4 nm for RuA up to 10.9 nm for Li-RuA. XRD patterns indicate Li addition induced the formation of the mixed LiAl_5O_8 crystalline phase which shares the same spinel structure of γ -alumina. The characteristic dimensions of the Ru crystallites in RuA and Li-RuA, estimated by Scherrer's equation, were equal to 10.3 and 10.6, respectively (Table 1): therefore, Li addition and the subsequent reduction of the DFM at $450 \text{ }^\circ\text{C}$ did not alter the initial metal dispersion.

Temperature-programmed methanation tests performed by co-feeding CO_2 and H_2 over the DFM bed (not-shown) indicated that Li-addition significantly boosted the catalytic activity of Ru/A in the whole temperature range so that the temperature for 10% conversion decreased from $293 \text{ }^\circ\text{C}$ down to $265 \text{ }^\circ\text{C}$ while the activation energy was poorly unaffected (T_{10} , E_a in Table 1).

Table 1. Summary of the characterization results for (reduced) DFMs: Density of the spheres, Specific surface area (S_{BET}), pore size by N_2 physisorption; size of Ru (d_{Ru}) crystallites from XRD data; apparent activation energy (E_a) and temperatures for 10% conversion (T_{10}) for the catalytic hydrogenation of gaseous CO_2 .

	Density	S_{BET}	Pore size	d_{Ru}	S	E_a	T_{10}
	g cm^{-3}	$\text{m}^2 \text{ g}^{-1}$	nm	nm	% wt.	kJ/mol	$^\circ\text{C}$
RuA	1.40	180	9.4	10.3	-	71	293
Li-Ru/A	1.53	145	10.9	10.6	-	81	265
S-Li-Ru/A	1.59	133	11.3	16.5	2.1 ^a	71	303 ^b

^a estimated from TG analysis supposing the decomposition of Li_2SO_4 into Li_2O

^b S-aged DFM sample recovered to air and tested without any further pretreatment

Figure 2 presents the typical transient CO_2 , CH_4 , and CO concentration traces as well as the temperature profiles recorded at the exit of the DFM bed during standard cycles run at a fixed preheating ($280 \text{ }^\circ\text{C}$). As soon as admitted to the reactor, CO_2 was quickly captured by the DFM so that its concentration dropped to zero after ca. 25 seconds independently from the presence of O_2 or H_2O in the feed stream; thereafter, it started to raise progressively until the overall capacity was mostly saturated (within 4 min). The contribution from the reactor hold-up can be visualized by the dashed line in Fig. 2a. Some weakly bonded CO_2 was spontaneously desorbed from the DFM during the intermediate purge phase under N_2 flow (required to avoid gas mixing) before H_2 was admitted to the reactor. At that point, CH_4 formation occurred with an apparent initial rate that was not affected by the eventual presence of O_2 or H_2O during the previous stage. The peak production of CH_4 (up to 3.5% by volume) was achieved within 25s, being slightly lower when the simulated feed gas contained some H_2O , due to the lower amount of CO_2 stored on the DFM. Simultaneously, a very low amount of CO was formed ($\leq 40\text{ppm}$, Fig. 2c), and it

became almost undetectable for the humid flue gas case. Limited thermal desorption of CO₂ was observed at the beginning of the hydrogenation phase (Fig. 2a), driven by the heat released by the exotherm of the catalytic reaction, which indeed caused a temperature increase recorded at the exit of the DFM bed (Fig. 2d). The maximum and minimum values of ΔT_{exit} were measured when the flue gas contained O₂ or H₂O, respectively.

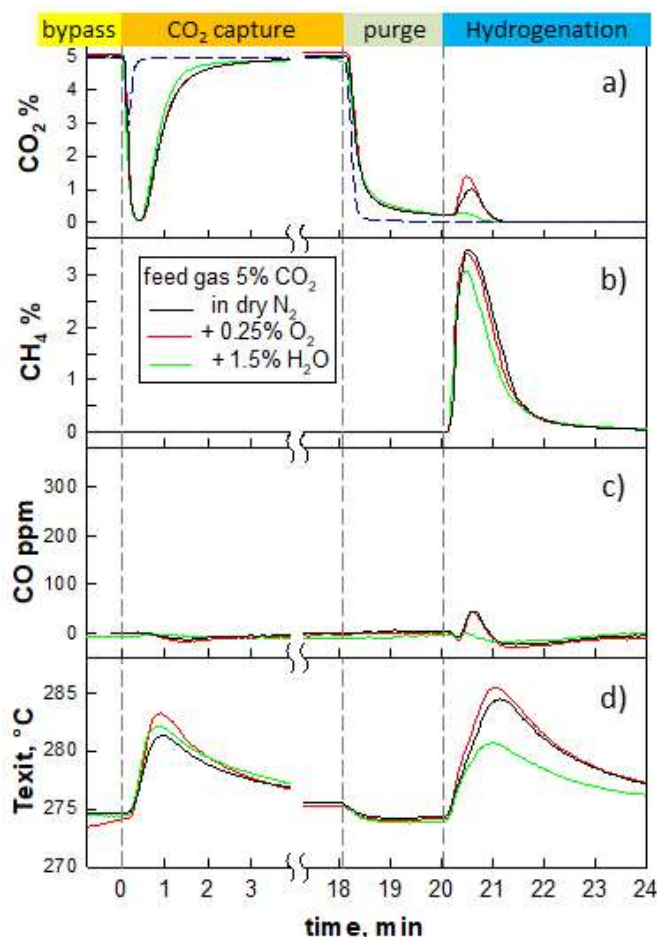


Figure 2. Integrated CO₂ capture and methanation cycles on Li-Ru/A DFM at 280 °C with 3 different feed gas compositions: 5% CO₂ in N₂, with the addition of +0.25% O₂ or +1.5% H₂O. Temporal profiles of CO₂ (a) CH₄ (b) and CO (c), and corresponding temperature at the exit of the catalytic bed (d).

Interestingly, also the CO₂ capture process caused similar temperature increases due to the exothermic nature of the surface reactions involved, which increased in the presence of O₂ in the flue gas (Fig. 2d). In particular, at temperatures exceeding 200 °C Ru can be easily oxidized during adsorption and then reduced back to its metal form during the methanation step: both the oxidation of Ru by O₂ and the reduction of RuO_x by H₂ are exothermic reactions which therefore contribute to enhancing the heat release during both half cycle (Fig. 2d).

Eventually, we set out to investigate the performance and stability of the Li-RuA DFM over time when SO₂ (10 or 100 ppm) was co-fed with CO₂ in the simulated flue gas also containing H₂O and O₂. During the capture step, the exit gas

concentration of SO_2 quickly dropped to zero while, during methanation, the Li-RuA DFM did not emit any measurable H_2S (nor SO_2) but retained all of the sulfur fed to the reactor. This is not surprising given the strong affinity of alkali-based sorbents for SO_2 leading to the formation of stable sulfite/sulfates [3]. Therefore, the general performances measured during the ageing study at 280 °C are presented in Figure 3 in terms of the CO_2 uptake, CH_4 production, CO_2 conversion, and CH_4 selectivity, as a function of the total amount of sulfur stored on the DFM. In particular, empty and close symbols refer to tests performed with either 10 or 100 ppm of SO_2 , respectively. For comparison purposes, the black dash-dotted lines report data relevant to our previous results obtained with a Na-RuA DFM [3].

Initially, the Li-RuA DFM showed remarkable tolerance to the presence of SO_2 in the flue gas so that all process outcomes were almost unaltered up to ca 70 $\mu\text{mol}/\text{g}_{\text{DFM}}$ of stored S. Thereafter, the CO_2 capture capacity and the corresponding CH_4 production started to decrease progressively following almost parallel trends, while the CO_2 conversion and CH_4 selectivity remained close to their original values or even increased slightly. This is a clear indication that SO_2 competed with CO_2 for the same basic adsorption sites of the DFM, which, once saturated with S-species, were not restored during the hydrogenation phase. Notably, the intrinsic catalytic methanation activity of Ru sites was substantially preserved even at high S-loadings. Furthermore, the performance enhancement measured over the Li-based DFM as compared to its Na-based counterpart (ca 35-40% larger capture capacity and methane production, Fig. 3 b,c) was steadily preserved along with the growing S-load over time on stream.

The removal efficiency for SO_2 approached a breakthrough condition (90%) at ca 800 $\mu\text{mol}_{\text{SO}_2}/\text{g}_{\text{DFM}}$: at that point, the residual CO_2 uptake and CH_4 production were reduced to ca 25% of their original values. Some H_2S started to be detected during the hydrogenation phase once the S-loading on the DFM approached the saturation level and the feed SO_2 concentration was raised to 100 ppm.

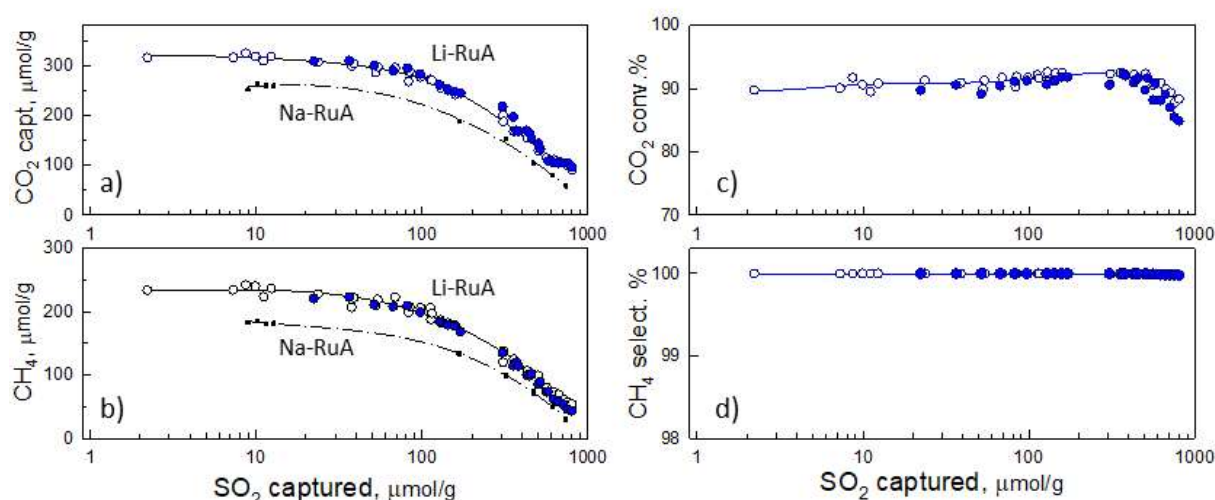


Figure 3. ICCM performance data with Li-RuA DFM operating at 280 °C with a simulated flue gas containing 5% CO_2 , 1.5% H_2O , 0.25% O_2 , and 10 or 100 ppmv SO_2 (open or closed symbols, respectively).

While S-species captured on the strong basic sites of the Li-RuA DFM appear too stable to be hydrogenated at 280 °C, it is suggested that more weakly bonded SO_x ad-species on a mostly saturated DFM surface can spill-over onto adjacent catalytic sites to form H₂S, provided that Ru sites are not covered by CO_x species involved in the formation of methane [3].

It should be mentioned that Ru-based catalysts are generally prone to severe poisoning effects by sulfur-bearing compounds under reducing atmospheres due to the easy formation of inactive metal sulfide species [5]: at variance, we only observed a marginal loss of activity (as measured by the CO₂ conversion and CH₄ selectivity), even in those last experiments run with a highly sulfated DFM when H₂S was detected in the product stream (Figure 3 c,d) and RuS_x species were likely formed during the methanation phase.

Post-ageing characterization of the sulfurized DFM, after more than 100 cycles during 50 days at reaction temperatures, indicated a high stability of its textural properties and a relatively limited increase of the average size of Ru nanoparticles due sintering (Table 1). Accordingly, the residual intrinsic methanation activity of the S-aged Li-Ru/A was comparable to the reference RuA catalyst, suggesting it only lost the initial promoting effect of Lithium due to the extensive formation of the corresponding sulfates (Tab. 1). A clear self-poisoning effect was observed during gas phase methanation tests for temperatures above 290 °C (not shown): this is attributed to the formation of RuS_x species by reaction (temperature activated) of Li-sulfates with nearby Ru nanoparticles [5]. Notably, exposure of the sulfurized (poisoned) DFM to oxidizing conditions such as those encountered during the CO₂ capture stage can easily decompose inactive RuS_x species, by this way self-regenerating the original catalytic activity for the following methanation stage.

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