SULFUR TOLERANT DUAL FUNCTION MATERIALS FOR THE INTEGRATED CO_2 CAPTURE AND METHANATION

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Abstract

The combined CO_2 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, we set out to investigate for the first time the impact of sulfur poisoning over a Na-Ru/Al_2O_3 DFM operated in a fixed bed reactor with alternate feeds under realistic conditions including the presence of SO_2, H_2O and O_2 in the process gas stream. The results of the extensive characterization of the fresh and sulfated (reaction-aged) DFM evidenced a remarkable intrinsic tolerance of the combined CO_2 capture and methanation process to high concentrations of SO_2 in the feed due to a self-regeneration mechanism of the Ru catalytic sites.

Introduction

Converting CO_2 captured from flue/process gases or even from air using green hydrogen made from renewable energy is a way to contribute to reaching the ambitious decarbonization goals set for 2050 and also a valuable solution to store excess electrical energy in fuels/chemicals solving the intrinsic variability of renewable sources. The integrated CO_2 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 [1-2]. DFMs contain both a CO_2 adsorbent and a hydrogenation catalyst, which are intimately coupled and generally nanodispersed on a high surface area oxide support [1-2]. Therefore, the DFM can work as the chemical looping mediator, being exposed to alternate steps of CO_2 capture and reduction with H_2 (regeneration) in cyclic operations. Previous works focusing on the screening of several DFM formulations for methane production at intermediate temperatures (200–400 °C) treated simplified flue gas compositions containing various concentrations of CO_2 in N_2: best performances were reported with DFMs containing Li, Na, or Ca (hydro)oxides/carbonates (5-15 %wt.) as the regenerable sorbent phase, and Ru (0.5-5 %wt.) or Ni (5-15 %wt.) as the active phase both dispersed on γ-Al_2O_3 [1-4]. However, when capturing CO_2 from either flue gas or air, the DFM has to be exposed to O_2, H_2O, and other common impurities such as NO_x and SO_x, which cause

pronounced effects on the catalyst and challenge the stability of performance over multiple cycles. In particular, sulfur species can induce strong adverse effects by completely and irreversibly deactivating both the sorption and the catalytic sites in the DFM [5]. This is a common issue affecting other CO_2 capture techniques [1], and catalyst poisoning by sulfur compounds is one of the main factors to be considered when designing and operating methanation plants [5], which must be equipped with an appropriate sulfur removal system. Therefore, testing the S-tolerance and durability of DFMs during prolonged cyclic operation with feeds containing sulfur impurities is an area requiring detailed investigation before the integrated process is to be scaled up to applications [1]. In this work, we set out to investigate for the first time the effect of sulfur poisoning during the cyclic CO_2 capture and methanation performed over a Na-Ru on γ-Al_2O_3 DFM, which is reported among the best performing formulations at mid-low temperatures [1-4].

Experimental
Ru and Na were dispersed sequentially inside 1mm Al_2O_3 spheres by impregnation with water solutions of nitrate precursors. Their loadings in the final DFM were deliberately kept low (ca. 1 % and 2.8 % wt., respectively) to better highlight the possible sulfur-poisoning effects on both the sorption and catalytic functionalities.
Combined CO_2 capture and methanation tests were performed in a fixed bed quartz reactor with an annular section (d_{in}=4mm, d_{out} =10 mm) that was loaded with ca 2.3 cm^3 (packed-volume) of Na-Ru/A DFM. The reactor was operated at atmospheric pressure and at a fixed temperature of 300 °C and total inlet flowrate (20 Sl/h) by switching alternatively the feed between the CO_2 capture and methanation phases. During the first step a feed gas stream containing 5% vol. CO_2 in N_2 with the possible additional presence of 0.25% O_2 and/or 1% H_2O as well as 10-100 ppmv SO_2 was stepwise admitted to the reactor and flowed over the DFM. After an intermediate purge (2 min, pure N_2), the methanation phase was started by switching the feed to 15% vol. H_2 in N_2. Continuous gas analyzers (ABB Optima Advance) were used to measure the molar fractions of CO_2, CH_4, CO, and SO_2, H_2S.

Results and Discussion
Temporal profiles of (CO_2, CH_4, and CO) concentrations and temperatures measured at the exit of the DFM fixed bed during representative tests of integrated CO2 capture and methanation are shown in Figure 1. Average results relevant to four sequential runs for each one of the four different feed compositions are presented in Figure 2, showing highly repeatable performances across cycles. In particular, the Na-Ru/A DFM was able to capture ca 300 μmol/g_{DFM} of CO_2 from a dry N_2 stream at 300 °C, producing 207 μmol/g_{DFM} of CH_4: those values fall within the range of data obtained in the literature with other Na-Ru/Al_2O_3 DFMs (CH_4 prod from 47 to 614 μmol/g [4]). Roughly, 20% of the CO_2 uptake was released during the purge of the reactor by N_2; thereafter, upon feeding H_2, methane was quickly formed with negligible CO production (CH_4 selectivity above 99.6%) and ca 90% CO_2

conversion. Due to the exothermal nature of both the CO_2 adsorption and methanation processes, a transient temperature increase was measured in the DFM bed at the beginning of each phase (Figure 1d): the maximum temperature gradients during each step were similar (5.3 and 6.0 °C, respectively).
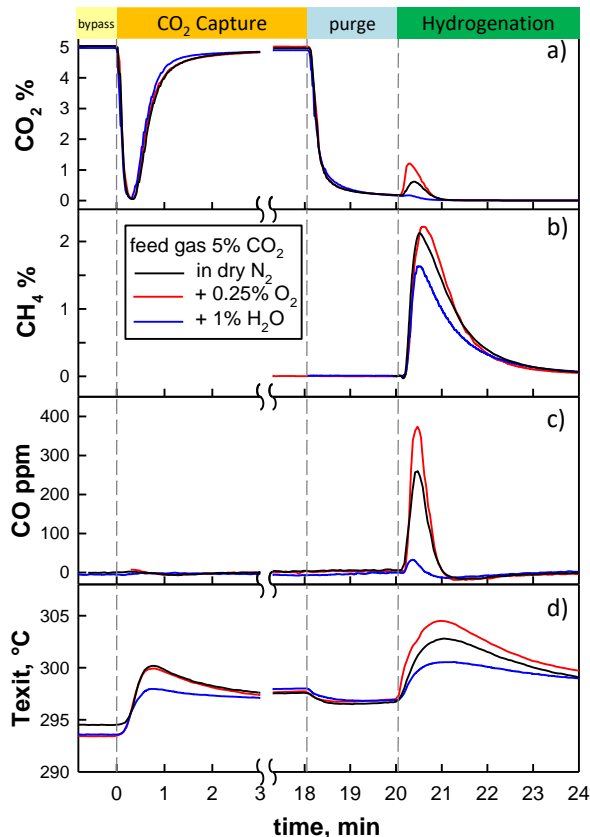

Figure 1. Integrated CO_2 capture and methanation cycles on Na-Ru/A DFM at 300 °C with 3 different feed gas compositions: 5% CO_2 in N_2, with the addition of +0.25% O_2 or +1% H_2O. Temporal profiles of CO_2 (a) CH_4 (b) and CO (c), and corresponding temperature at the exit of the catalytic bed (d). Step duration: 18 min CO_2 capture, 2 min N_2 purge, 14 min hydrogenation (15% H_2 in N_2).

Steam addition caused a 20% reduction of the CO_2 capture capacity of the DFM, possibly due to the competition of water for the same CO_2 adsorption sites. Moreover, the presence of H_2O mitigated the temperature rise during both the adsorption and methanation phases (Figure 1d): As a consequence, the CO_2 conversion increased up to ca. 94% and almost no CO was detected resulting in a process selectivity to CH_4 above 99.9%. At variance, the presence of O_2 during adsorption showed a marginal positive effect on the CO_2 uptake of the DFM. After purging (not affected), the DFM was able to produce roughly the same amount of

methane as in the reference ideal case, but with a slightly lower selectivity and conversion, due to a corresponding increase in the amount of thermally desorbed CO_2 and a marginally higher CO formation (Figure 1 a,c). This is consistent with the higher temperature increase observed in the DFM bed when O_2 was co-fed with CO_2.
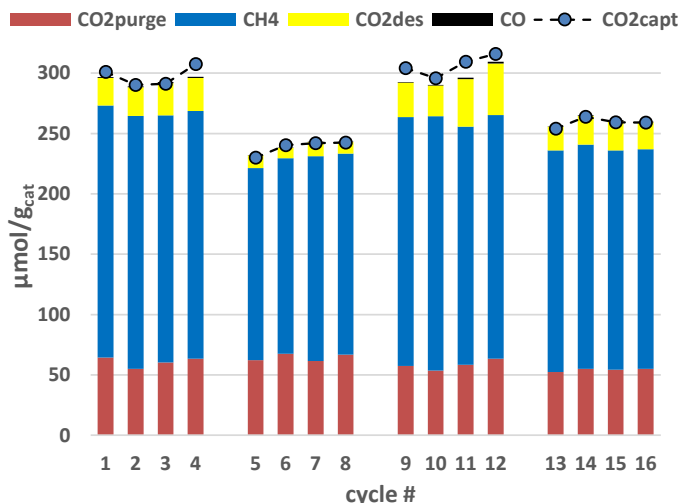

Figure 2. CO_2 adsorption (dots), CH_4 and CO production, and CO_2 desorption (bars) during 4 sets of 4 repeated cycles of CO_2 capture and methanation on Na-Ru/A DFM with variable feed gas compositions. All cycles were performed at 300 °C and 1 atm; adsorption conditions 5% CO_2 in N_2 (cycles # 1-4), +1% H_2O (# 5-8), +0.25% O_2 (# 9-12), +1% H_2O +0.25% O2 (# 9-12).

Reaction tests performed with the simultaneous presence of H_2O and O_2 with CO_2 in the feed gas showed the superimposition of the contrasting effects individually induced by single species. Specifically, the addition of O_2 partially mitigated the negative impact of H_2O on the CO_2 capture capacity of the DFM, which turned out to be only 13% lower than in the reference case (CO_2 in dry N_2). This circumstance directly translated into a similar recovery of methane production (up to 183 $\mu mol/g_{DFM}$), since CO_2 conversion was almost identical to the reference case, and the selectivity to CH_4 was even improved due to the effect of water.

The impact of the addition of 10 ppmv SO_2 to the inlet feed gas containing CO_2 and O_2 was investigated either under dry or humid conditions. Not surprisingly, during the capture step, the exit gas concentration of SO_2 quickly dropped to zero and the DFM retained all of the sulfur fed to the reactor due to the formation of stable sodium and/or aluminum sulfite/sulfates.

Therefore, the results are presented in Figure 3 in terms of SO_2 and CO_2 capture, CH_4 and H_2S production, CO_2 conversion during each cycle of CCM as a function of the cumulative amount of SO_2 retained by the DFM across cycles. It appears that the addition of SO_2 caused no adverse effect on the performance of the Na-Ru/A

DFM since all process outcomes obtained under either dry or humid conditions fell within the corresponding range of data previously measured with the S-free feeds.
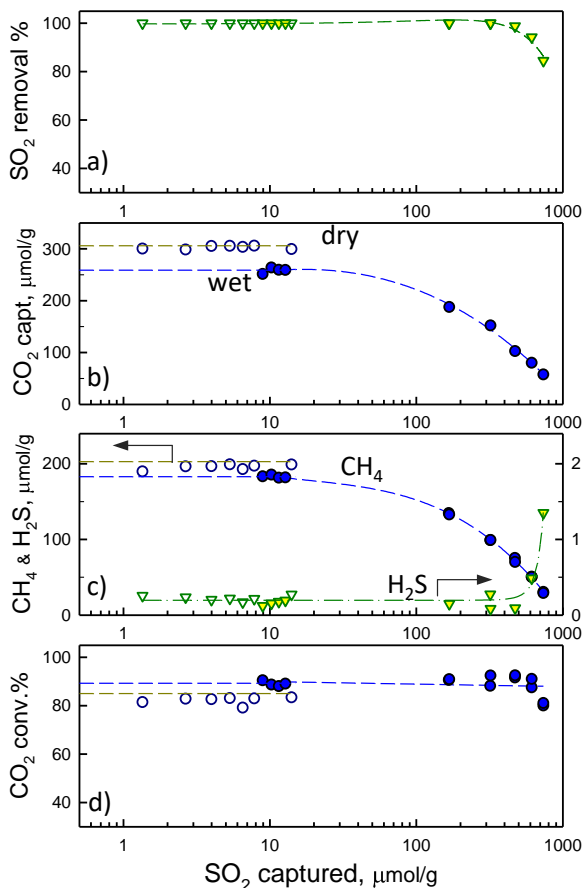

Figure 3 CO_2 capture and methanation cycles on Na-Ru/A DFM operating at 300 °C with a simulated flue gas containing 5% CO_2, 0.25% O_2, and 10ppmv SO_2 in dry N_2 (open symbols) or with the addition of 1% H_2O (closed symbols). SO_2 and CO_2 adsorption (a, b), CH_4 and H_2S production (c), CO_2 conversion (d) as a function of the cumulative amount of SO_2 retained on the DFM across cycles.

A close inspection of the temporal gas-phase concentration profiles at low sulfation levels of the DFM indicated a barely detectable emission of H_2S during methanation (≤ 1 ppmv), confirming that the stored sulfur species were rather refractory to react with hydrogen at 300 °C: H_2S production remained low across cycles (Figure 3c) corresponding to less than 10 % conversion of the previously captured SO_2. Generally, H_2S is a strong poison for supported Ru methanation catalysts, even at low concentrations, due to the rapid formation of inactive and stable superficial RuS_x

species [5]. Nevertheless, the Na-Ru/A DFM showed an uncommon/unexpected tolerance to S-poisoning, apparently preserving its catalytic activity unaltered under those conditions. The accumulation of sulfur on the DFM above ca 100 $\mu mol/g_{DFM}$ caused a slow and progressive decrease in the CO_2 capture capacity (Figure 3b), due to the corresponding saturation of the basic adsorption sites. However, the SO_2 removal efficiency of the DFM remained at 100 % up to roughly 600 $\mu mol/g_{DFM}$ (corresponding to S : Na atomic ratio close to 1 : 2) and the amount of H_2S formed during the methanation steps was constantly low (Figure 3a,c). The CH_4 production decreased following the same trend of the CO_2 uptake (Figure 3c) since the efficiency of the catalytic process was not altered even at the highest sulfation levels. In particular, the formation of methane was not delayed by the increasing sulfur content on the DFM, while the conversion of CO_2 was steady (around 90 %, Figure 3d) and the selectivity to CH_4 even increased approaching 100 %.

Those results demonstrate for the first time the high sulfur tolerance of Na-Ru DFM, and suggest the existence of a peculiar and favorable self-regeneration mechanism for the catalytic Ru sites, preserving them from any significant sulfur poisoning effect. Specifically, it can be argued that Ru nanoparticles, which are partially covered by inactive RuS_x species at the end of the CO_2 hydrogenation step, can be periodically restored by the oxidation/reduction cycle naturally occurring during operation in the combined CO_2 capture and methanation process with alternate feeds.

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