Durability and Sulfur Tolerance of Li-Ru/Al_2O_3 Dual Function Material for the Integrated CO2 Capture and Methanation

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Highlights

- Aging study during the Chemical Looping CO_2 Capture and Methanation
- Highly stable performance of Li-Ru DFM at moderate temperatures
- High tolerance to Sulfur poisoning due to the formation of stable Li-sulfates

1. Introduction

Reversing climate change and global temperature rise requires mitigating greenhouse gas emissions from industry and energy sectors (decarbonization) and reducing atmospheric CO_2 levels with CO_2 removal technologies (including Direct Air Capture, DAC) [1-2]. Carbon Capture and Utilization (CCU) is especially promising because it enables a net CO_2 consumption and at the same time the recycling of the carbon content of CO_2. The challenge is to sustainably convert CO_2 from industrial processes or from air into synthetic fuels using renewable energy-driven processes approaching a circular carbon economy [1-2]. This is also a valuable and efficient solution to store excess energy that is generally seasonal and fluctuating. A possible innovative solution to reduce the costs and increase the efficiency of the current multi-step CO_2 Capture and Utilization (CCU) processes is represented by the integration of the CO_2 capture and hydrogenation into a single chemical looping process performed with Dual Function Materials [1-4]. 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 [1-4]. 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. As for any emerging chemical looping processes, the key to success relies on the development of advanced materials (sorbents/catalysts/dual function) strictly coupled to optimized process design and reaction engineering.

In this work we set out to investigate performance and durability of a Li-Ru/Al_2O_3 DFM during the integrated CO_2 capture and methanation, assessing the individual and mutual effects of the main species (O_2 and H_2O) found in real flue gas as well as the impact of SO_2 impurities (up to 100ppm).

2. Methods

Ru (1% wt) and then Li (3% wt)were sequentially and uniformly dispersed inside γ-Al_2O_3 spherical particles (1mm, Sasol) by impregnation with nitrate precursors followed by reduction under 20%H_2 at 450 °C. ICCM tests were performed in a fixed bed quartz reactor operated at atmospheric pressure and at a fixed temperature in the range from 260 °C to 320 °C. First, a feed gas stream consisting of 5% vol. CO_2 in N_2 with the possible additional presence of 0.25% O_2 and/or 1.5% H_2O as well as 10-100 ppmv SO_2 was stepwise admitted and flowed over the DFM for 18 min. Then, after an intermediate purge step (2 min, under N_2), the methanation phase was started by switching the feed to 15% vol. H_2 in N_2 for 14 min. The main physicochemical properties of the fresh and sulfated DFM were correlated with the results from catalytic CO_2 hydrogenation tests.

3. Results and discussion

The DFM showed very repeatable performances across several cycles of alternated CO_2 capture and methanation in the temperature range 260 – 320 °C with high CO_2 conversion (>90 %) and no CO formation (Figure 1). When both oxygen and water were present in the simulated flue gas a maximum CH_4 production of 250 μmol/g was achieved at ca 260-280 °C (Figure 1), i.e. only 5% below the results obtained under ideal capture conditions (CO_2 in dry N_2). While further improvements of the specific

CH_4 productivity are possible by increasing the Li loading, the Li-RuA outperformed by ca. 35% a similar state-of-the-art Na-RuA DFM with identical metals loading [4].

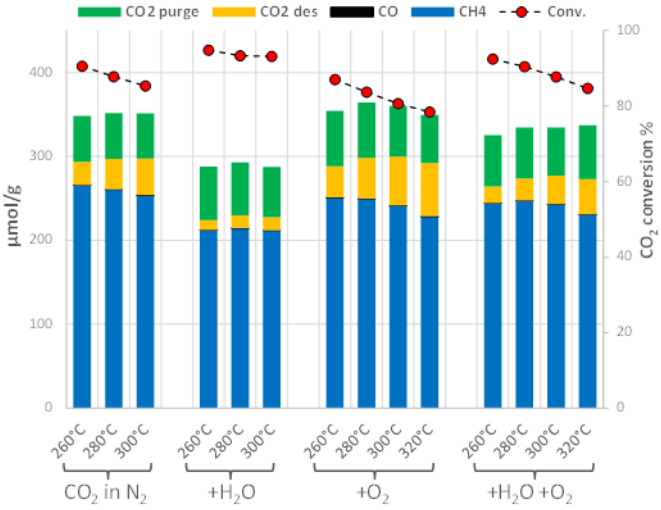

Figure 1. Effect of the feed gas composition and the reaction temperature on the average values of CH_4 and CO produced, CO_2 desorbed and purged (bars), CO_2 conversion (dots) during 3 consecutive cycles of ICCM with Li-RuA DFM

Eventually, we performed a prolonged ageing study of the DFM under challenging feed conditions with a simulated flue gas containing 10-100 ppmv SO_2 in addition to H_2O and O_2. The Li-RuA DFM showed a remarkable sulfur tolerance during the cyclic operation at 280 °C preserving constant CO_2 conversion and CO selectivity. The DFM completely removed SO_2 storing it as lithium sulfate, which was stable during the subsequent hydrogenation stage, thus avoiding any severe poisoning of the catalytic Ru sites. However, the accumulation of sulfates progressively lowered the CO_2 capture capacity, and, in turn, the CH_4 production, due to the saturation of the Li adsorption sites, which were not regenerated. The removal efficiency for SO_2 approached a breakthrough condition at ca 800 $\mu mol_{SO2}/g_{DFM}$: up to that point no H_2S was detected during the methanation stage.

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 limited increase of the average size of Ru nanoparticles due to sintering. Accordingly, the residual intrinsic methanation activity of the S-aged Li-Ru/A was comparable to the fresh unpromoted Ru catalyst. Notably, the high intrinsic catalytic activity of the Li-RuA DFM allows to optimally operate the process at temperatures as low as 260 – 280 °C, thus minimizing the potential poisoning effect of sulfur by preventing the formation of any RuS_x, because the catalytic assisted decomposition of Li-sulfates on the DFM is generally negligible below 280-290 °C.

4. Conclusions

The ageing study of a Li-Ru/Al_2O_3 DFM during the ICCM process optimally operated at 280 °C with challenging and representative flue-gas compositions including up to 100ppmv SO_2 demonstrated its high stability of catalytic performance and remarkable tolerance to sulfur poisoning.

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