Unravelling S Poisoning Effects on Ru/Al_2O_3 CO_2 Methanation Catalysts Through *in-situ* and *ex-situ* Approaches

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Significance and Relevance

Sulfur contaminants in CO_2 flows strongly hinder the methanation process. This study used *ex-situ* and *in-situ* poisoning to analyze sulfur's impact on the morphology and activity of a 4% Ru/Al_2O_3 catalyst. Additionally, a kinetic model was developed able to effectively describe the catalyst's deactivation.

Preferred choice for the topic: CO_2 utilization and recycling
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Introduction and Motivations

The constant increase of the average temperature on Earth due to greenhouse gases emissions is nowadays leading to a revolution in the energy sector. In this context, CO_2 hydrogenation to Synthetic Natural Gas (SNG) has already been proved to be a viable solution for both renewable energy storage and CO_2 emission reduction, two of the main challenges of energy transition [1]. However, when dealing with CO_2 streams, the presence of contaminants must be taken into account. Among these, sulfur-containing compounds are present in biogenic as well as in fossil-sourced CO_2, and their presence is detrimental to catalytic methanation processes [2,3]. In this study, various *ex-situ* and *in-situ* techniques are employed to elucidate the impact of sulfur on the characteristics and catalytic behavior during CO_2 hydrogenation to methane over a 4% Ru/Al_2O_3 catalyst. Additionally, the observed effects were rationalized with a suitable kinetic model as a function of the sulfur content.

Materials and Methods

The Ru-based catalyst is prepared by impregnating γ-Al_2O_3 pellets (d_p = 100 µm, Sasol Puralox) with an aqueous solution of $Ru(NO)(NO_3)_3$ salt (Alfa Aesar, Ru 31.5 wt.%). The precursor salt was then decomposed in H_2 flow at 400 °C. *Ex-situ* sulfur poisoning is performed by impregnating in inert environment a reduced 4% Ru/Al_2O_3 catalyst with a solution of $(NH_4)_2S$ diluted in ethanol. The preparation procedure was repeated to obtain samples with different sulfur loadings, ranging from 0.7 – 5.5 mg_S/g_{cat}. The *in-situ* deactivation was carried out over the same 4% Ru/Al_2O_3 catalyst by step feeding 10 ppm of H_2S or COS together with the reactant mixture (H_2/CO_2 = 4 mol/mol) at 310°C and constant GHSV.

The activity analysis was performed after reduction at 400°C under H_2 flow, in a temperature range of 230 - 410°C and at pressure values spanning from 0 to 20 barg. The S effect was studied via H_2 and CO pulse chemisorption, H_2-TPR, TEM and *in-situ* XPS analysis. Moreover, *in-situ* DRIFTS experiments were performed to follow the evolution of the surface species as the S loading was varied.

Results and Discussion

CO_2 reduction the tests on the *in-situ* poisoned catalysts showed a gradual decrease in CO_2 conversion and an increase in CO selectivity with increasing S content (Figure 1A). These results also revealed that the activity on the *ex-situ* and *in-situ* poisoned catalysts showed the same trends, regardless of whether H_2S or COS was fed into the system (Figure 1A).

The conversion values collected on *ex-situ* poisoned samples in the temperature range of 230-410°C and at 0-20 barg, were described with a kinetic model accounting for the S-deactivation. Figure 1B represents the parity plot of such model, demonstrating its capability to accurately describe the catalyst behavior in the presence of S in different amounts. *In-situ* XPS measurements indicated the presence of Ru sulfides in reducing environment, and as a result the H_2 chemisorption experiments showed a linearly decreasing trend of the amount of H_2 adsorbed as the sulfur content increased. However, the CO adsorption, performed in DRIFTS experiments at room temperature, showed no major differences between the spectra of the poisoned and the clean samples. Instead, the TPD analysis demonstrated that the presence of sulfur weakens the Ru-CO bond, leading to lowering of the desorption temperature of CO (Figure 2). The *operando* DRIFTS setup was also used to study the effect of S on the surface species under reaction conditions. The results pointed out that the formation of formates and bicarbonates were not significantly hindered by the presence of S. At variance, the carbonyls formation shifted to higher temperatures upon increasing the S content. This trend may be attributed to the reduced ability of the poisoned catalysts to activate hydrogen, therefore hampering the reduction of CO_2 to CO.

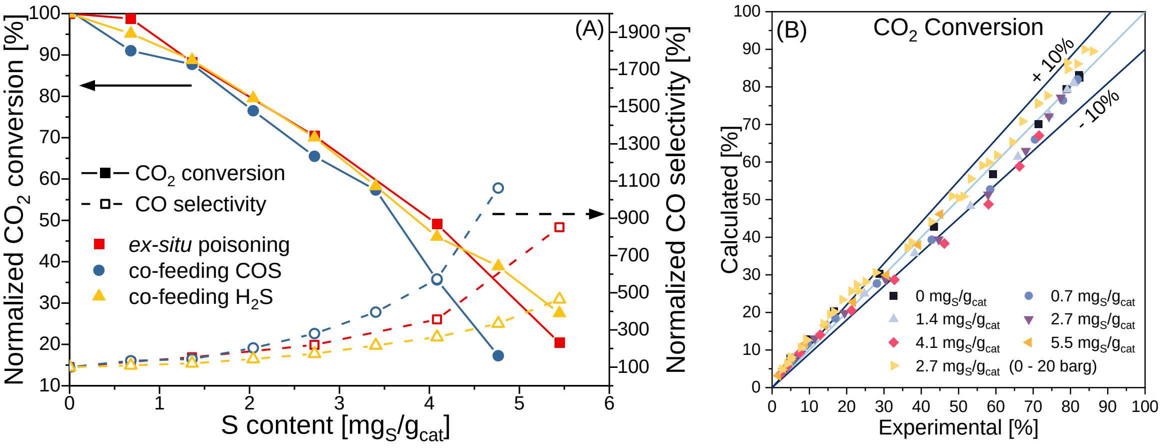

Figure 1. (A) Normalized CO_2 conversion and CO selectivity (100% at 0 mg_S/g_{cat}) trends in function of sulfur content deposited by *ex-situ* and *in-situ* (feeding COS and H_2S) poisoning. T = 310°C; P = 0 barg; H_2/CO_2 = 4 mol/mol. (B) Parity plot of CO_2 conversion kinetic modeling during catalyst deactivation.

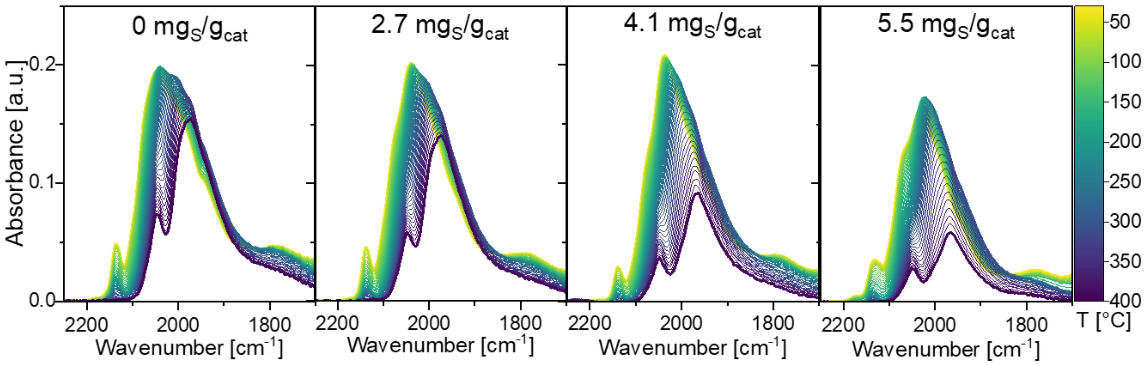

Figure 2. DRIFTS spectra collected during CO-TPD in He over the *ex-situ* poisoned Ru/Al_2O_3 samples.

References

1. C. Vogt, M. Monai, G.J. Kramer, B.M. Weckhuysen, Nat. Catal. **2**, 188–197 (2019).
2. S. Calbry-Muzyka and T. J. Schildhauer, Front. Energy Res. **8**, 570887 (2020).
3. M. Chen, L. Liu, X. Chen et al., Nat. Comm. **15**, 9478 (2024).