Enhancing CO_2 Hydrogenation Efficiency through *in situ* Formation of Active Species in Carbon Nitride Modified Catalysts

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Significance and Relevance

This research demonstrates a novel approach to enhance performance during CO_2 hydrogenation by using carbon nitride (CN) coated Al_2O_3 composites as a support material. Unlike conventional fine powdered CN, which has low surface area, the CN coating on Al_2O_3 enables tunable porosity and minimizes pressure drop in fixed-bed reactors. Co-based catalysts using CN@Al_2O_3 composites as support showed significantly increased CO_2 conversion with enhanced methane selectivity compared to the unmodified catalyst. The modification induced an activation phase with selectivity switch to CH_4 suggesting the formation of *in situ* active species.

Preferred and 2nd choice for the topic: CO2 utilization and recycling (2nd choice: Circular economy)
Preferred presentation: Oral only / Oral preferred or Short Oral

Introduction and Motivations

CO_2, the predominant greenhouse gas, requires innovative strategies to mitigate its environmental impact. Hydrogenation of CO_2 to methane and short-chain hydrocarbons offers a scalable solution compatible with existing natural gas infrastructure.[1] Earth-abundant metal catalysts (Ni, Fe, Co) on high-surface-area supports are common catalysts for this application. Herein, the support is modified by polymerized carbon nitride (CN), which has attracted considerable attention in catalysis due to its versatile photochemical properties as well as its chemical and physical characteristics, which make it an ideal photocatalyst or potential catalyst support for thermocatalysis.[2,3] CN may stabilize nanoparticles (NPs) by generating delocalized electron states that alter the electron density at the catalytically active metal centers, thereby increasing their reactivity. As an organic polymer semiconductor, CN interacts with the metal particles, causing the active phase and support to act as an integrated system rather than separate entities.[3]

Results and Discussion

This research focuses on enabling synergetic effects by using CN modified support in thermocatalytic CO_2 hydrogenation. While common fine powdered CN from melamine polymerization exhibits low surface area and minimal porosity,[3] we explore modifying Al_2O_3 with a CN coating (**Figure 1**) to create tunable porosity. These composites were created with various morphologies and structures to produce a support that can be customized in terms of its porosity. These CN@Al_2O_3 composites were investigated in terms of their structural characteristics using X-ray nano-tomographic measurements performed at NanoMAX beamline at MAX IV, Lund.[4] The aim of our project is to investigate the structural and reactive properties of CN@Al_2O_3 as a support material for the hydrogenation of CO_2 to CH_4 and short-chained hydrocarbons. Metal oxide NPs are synthesized separately[5] and immobilized on CN@Al_2O_3 composites and Al_2O_3 benchmarks.

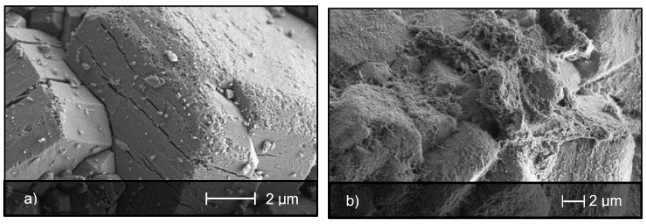

Figure 1. SEM micrographs of unmodified Al_2O_3 (a) and modified CN@Al_2O_3 support (b) with a scale of 2 µm.

Inductively coupled plasma optical emission spectroscopy (ICP-OES), N_2 physisorption, X-ray diffraction (XRD), temperature-programmed reduction (TPR), scanning electron microscopy (SEM), transmission electron microscopy (TEM), Fourier transform infrared spectroscopy (FT-IR), Raman spectroscopy and high-resolution solid-state ^{13}C and ^{1}H NMR spectroscopy were employed for the characterization of these materials.

After reduction of the metal oxide NPs in H_2, we obtained the M/CN@Al_2O_3 (M = Co, Fe, Ni, Cu) catalysts for comparison in CO_2 hydrogenation. For the Co/CN@Al_2O_3 catalyst, our results (**Figure 2**) reveal a significant enhancement in CO_2 conversion under moderate conditions during an activation period, which also resulted in a notable increase in methane selectivity up to 97% at 325 °C. The activation phase of modified Co catalyst was not observed for the unmodified Co/Al_2O_3 and further studied under isothermal conditions. This suggests that the CN modification facilitates the formation of *in situ* active species. *Operando* XAS measurements at the CAT-ACT beamline at ANKA at KIT[6] suggest the formation of carbide species.

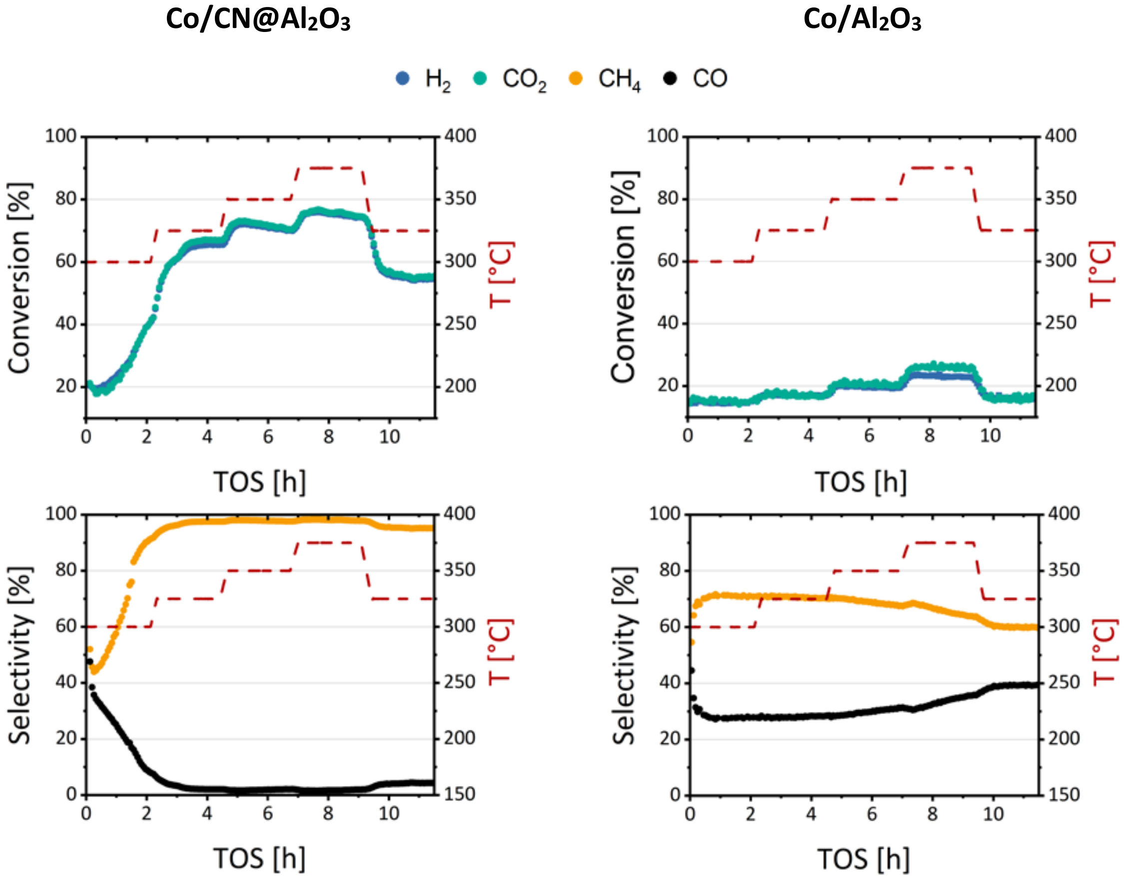

Figure 2. Conversion (top) and selectivity (bottom) in CO_2 methanation: Comparison of Co/CN@Al_2O_3 (left) and Co/Al_2O_3 (right) at 300 – 375 °C and 5 bar_g with H_2/CO_2 = 4.

References

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