Core-Shell Chabazite Catalysts for the Tandem Catalysis of CO2 to Light Hydrocarbons:

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Introduction

In recent years increasingly more interest and research has been dedicated to the idea of "the circular carbon economy".[1] Devising catalytic processes, which can serve as alternatives to fossil fuels and their derivatives, is central to such an sustainable economy. As such, there is a need for the development of catalysts capable of converting carbon dioxide to specific products. CO_2 hydrogenation to light hydrocarbons has received much attention. Although substantial progress has been made in CO_2 hydrogenation catalysis to hydrocarbons, controlling the carbon chain length and type (paraffin, olefin, aromatic) remains largely elusive.

To achieve this control zeolites are used. Generally a metal(oxide) catalyst hydrogenates CO_2 to form some intermediate, which is then converted to the desired product by a zeolite catalyst. There are two routes: using a Fisher Tropsch or methanol synthesis (MS) catalyst .

The interplay between the two catalysts is crucial. Coupling two reactions can overcome the thermodynamic limits of the individual reactions [4]. In fact, the "proximity" of the two catalysts can have a large impact on catalytic behaviour. Both conversion and product selectivity can be influenced depending on the nature of the hydrogenation catalyst [5, 6]. In principle, a short distance between the two catalysts is favourable: A short diffusion path between two catalysts should increase pulling effect. However, a minimal distance is required to maintain bi-functionality of the two catalysts with In-based catalysts. In contrast, for Zr-based catalysts "the closer the better" applies.

The difference between In and Zr lies in their reducibility: while Zr is stable within its oxide lattice,[3] In is easily reduced. Hence, In can migrate to the zeolite, causing in-situ ion exchange. This reduces the zeolite acidity, leading to deactivation. As a result, C1 instead of C2+ products are formed. Importantly, the BAS sites on the zeolite facilitate this metal migration. Pacification of the surface can prevent metal migration. Protecting the zeolite from poisoning remains one of the most important challenges to achieve highly active and selective tandem CO_2 hydrogenation catalysis.

We combine a RhIn/MgO catalyst with SSZ-13, which is protected by an all silica shell (SSZ-13@Si-CHA) to inhibit poisoning. To the best of our knowledge, our research is the first to illustrate the effectiveness of SSZ-13@Si-CHA in tandem CO_2 hydrogenation.

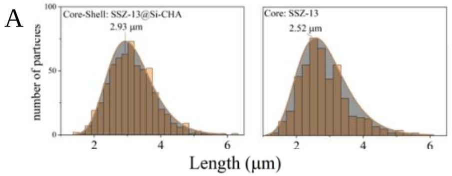
Materials and Methods

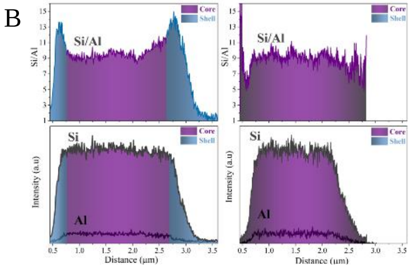
The SSZ-13@Si-CHA is synthesised by a hydrothermal secondary growth procedure according to the methods developed by Miyamoto et al.[3] Our RhIn/MgO catalyst was synthesized by coprecipitation using metal nitrates at a constant pH (~10) using NaOH to form an LDH precursor. The LDH is subsequently exfoliated, calcined and mixed with our SSZ-13@Si-CHA by grinding.

After reduction in 5%H_2 the CO_2 hydrogenation reaction was performed in a fixed-bed flow reactor at 45 bar at 320-380°C. Reaction products and conversion were quantified by GC by internal standard method.

Results and Discussion

The successful formation of the all silica CHA shell has been extensively studied using XPS, XRF, BET, pyridine and NH_3 IR adsorption experiments as well as SEM-EDX (see A &B).





Importantly, our results clearly show the benefit of surface pacification of SSZ-13. This is evidenced by the substantial suppression of the formation of CO under CO_2 hydrogenation conditions by the presence of the Si-CHA shell compared to the core alone. While the CO selectivity exceeds 60 % using the core SSZ-13, this can be significantly reduced to 20-30% when using a protected zeolite. The remainder of the products consist of light hydrocarbons up to C_4 including a small amount of methane (<10%).

Significance

The catalytic conversion of CO_2 to specific products is essential to establishing a circular carbon economy. To be able to establish such economy catalyst with a high degree of selectivity towards desired products are required. Considering the current challenges of tandem CO_2 conversion, new zeolite catalysts need to be investigated to insure the dual functionality of the catalytic system.

In order to achieve this we have, for the first time, employed RhIn/MgO with combined with a core-shell chabazite zeolite catalyst to prevent in-situ poisoning and control the hydrocarbon product to light hydrocarbons.

References

1. L. M., Alsarhan, A. S. Alayyar, N. B Alqahtani, N. H Khdary, *MPDI*. **2021**. *13(21),* 11625
2. Wang, Y.; Wang, G.; van der Wal, L. I.; Cheng, K.; Zhang, Q.; de Jong, K. P.; Wang, Y. *Angew Chem Int Ed Engl* **2021**, *60* (32), 17735-17743. DOI: 10.1002/anie.202107264 From NLM PubMed-not-MEDLINEX. Wang, P. J. Ramírez, W. Liao, J. A. Rodriguez, P. Liu, *J. Am. Chem. Soc.* **2021**, *143* (33), 13103–13112.
3. Miyamoto, M.; Iwatsuka, H.; Oumi, Y.; Uemiya, S.; Van den Perre, S.; Baron, G. V.; Denayer, J. F. M. *Chemical Engineering Journal* **2019**, *363*, 292-299. DOI: 10.1016/j.cej.2019.01.106.S. Li, H. Guo, C. Luo, H. Zhang, L. Xiong, X. Chen, L. Ma*, Catal. Lett*., **2013**, 143, 345–355