Catalytic hydrogenation of CO_2 to fuel

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Introduction

Increase in global energy consumption leads to a significant rise in CO_2 concentration in the atmosphere due to the burning of fossil fuels (coal, oil and natural gas), affecting Earth's ecosystems and causing human and environmental health problems. The chemical conversion of carbon dioxide and green H_2 into value-added fuel provides a promising solution to mitigate CO_2 emission and generate renewable energy.

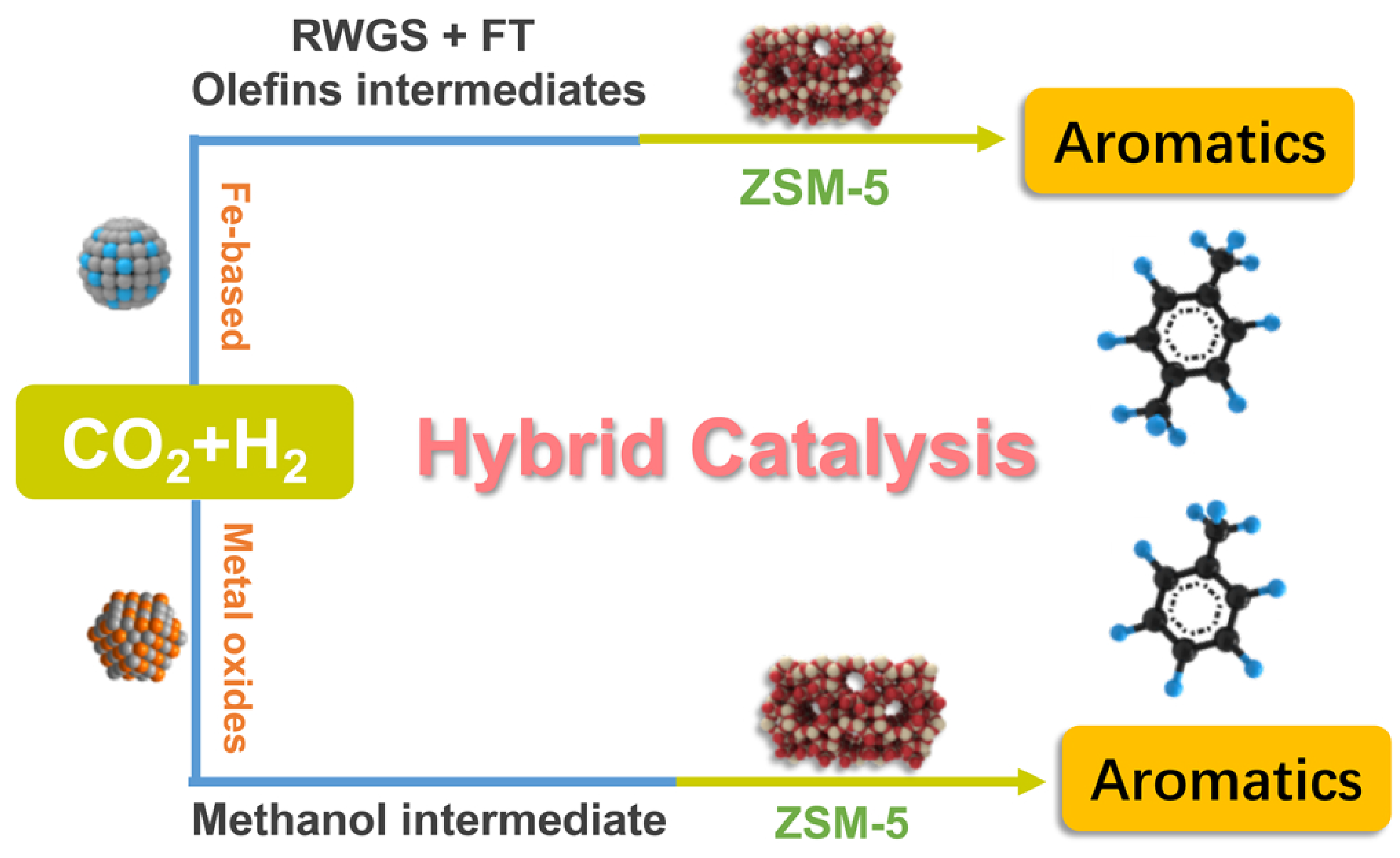

Fig. 1. Two reaction pathways to produce aromatics from $CO_2 + H_2$

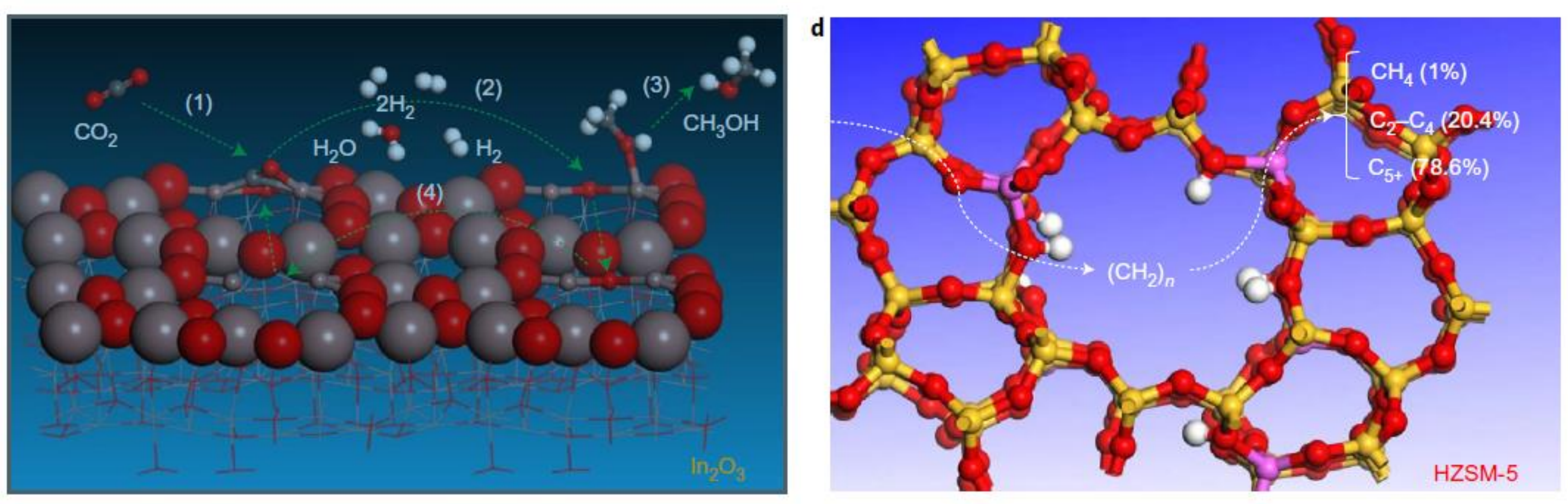

Fig. 2. The reaction pathway of CO_2+H_2→CH_3OH→C_{5+}

The challenges

- CO_2 is fully oxidized, thermodynamically and chemically inert molecule;
- Low heat of CO_2 adsorption on catalyst, low C/H ratio, fast hydrogenation of surface adsorbed intermediates, high CO and CH_4 selectivity;
- High C-C coupling barrier;
- Thermodynamic equilibrium limitation;
- Catalyst deactivation by water.

The advantages of using zeolite X and LTA

- ✓ Zeolite X exhibits a **higher CO_2 adsorption activity**
- ✓ The source of synthetic zeolites (X, LTA) is derived from natural ore, making it environment friendly and **cost-effective**;
- ✓ The zeolite X has a low Si/Al ratio and small pore diameter, which can promote the formation of high value short-chain hydrocarbons ($\leq C_{12}$);
- ✓ LTA is a **hydrophilic zeolite**, breaking the thermodynamic equilibrium limitation, increasing CO_2 conversion and methanol selectivity.

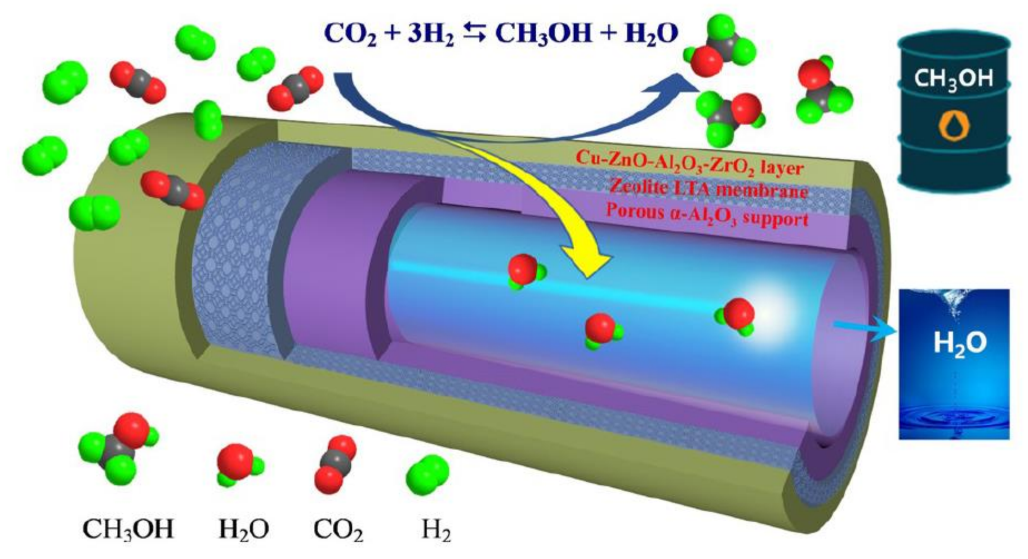

Fig. 3. Scheme of CO_2 hydrogenation to methanol through in situ and continuous removal of water in a reaction–separation bifunctional LTA@Cu-ZnO-Al_2O_3-ZrO_2 catalytic membrane reactor (CMR).

H_2O was removed by LTA zeolite, breaking the thermodynamic equilibrium and increasing the CH_3OH conversion

Recent advances in CO_2 conversion

Catalyst	CO_2 conversion (%)	Benchmarks	Reaction conditions
Na-Fe_3O_4/HZSM-5	22%	78% hydrocarbons (3% CH_4)	H_2/CO_2 = 3, 320°C, 3 MPa
In_2O_3/HZSM-5	13.1%	78.6% C_{5+} selectivity	H_2/CO_2 = 3, 340 °C, 3.0 MPa,
Co/$Si_{0.95}$	8.6 wt%	70.5% methanol	H_2/CO_2 = 3, 320 °C, 2.0 MPa;
Cu-ZnO-Al_2O_3-ZrO_2/LTA	36.1 wt%	100% methanol	H_2/CO=3, 260 °C, 3.0 MPa

Methods

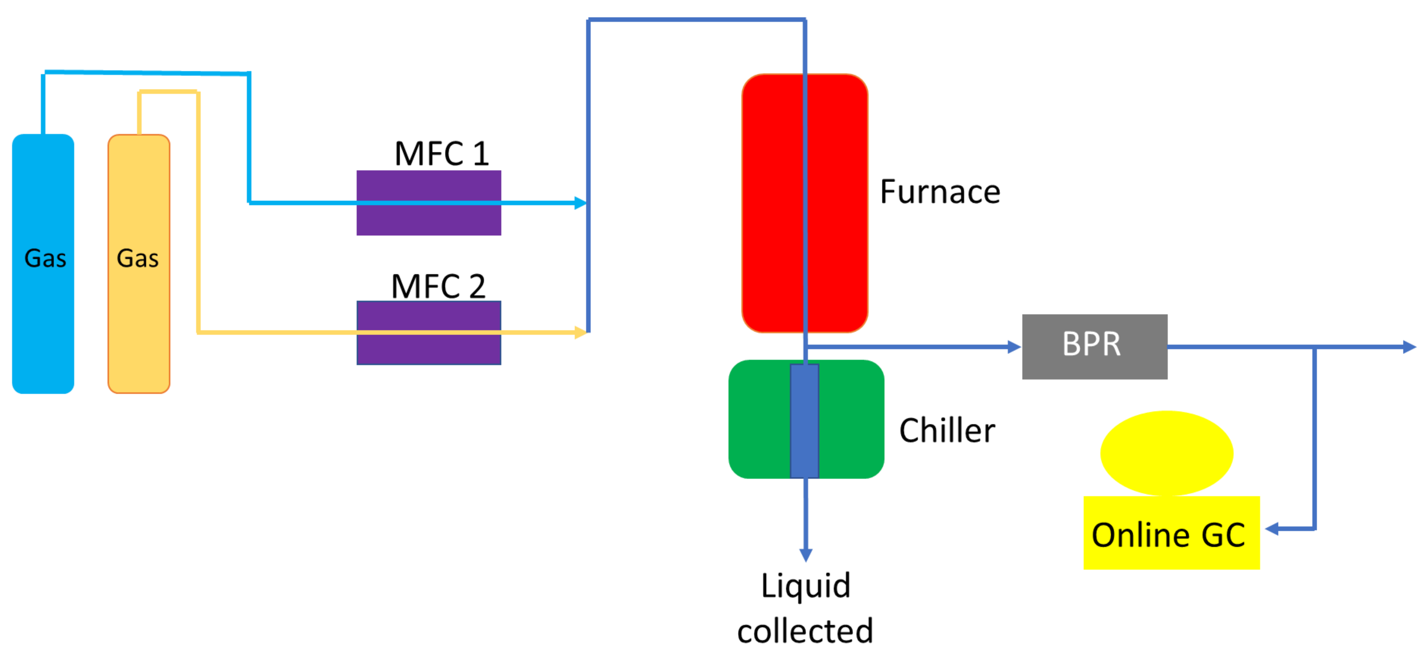

Fig. 4. Schematic diagram of flow reactor

Catalyst:

Preparation method: incipient wetness impregnation method; ion exchange-deposition-precipitation; deposition-precipitation,

Materials: LTA, X, SiO_2, Al_2O_3, ZrO_2, zeolites

Metals: Na, K, Fe, Ni, Cu, Zn, Mo, In

Characterisations:

HRTEM, SEM, XRD, XPS, Chemisorption, ICP, XRF

H_2-TPR, NH_3-TPD, H_2-TPD, NMR, *In situ* FTIR, XAS

Products analysis:

Liquid products: GC-MS and GC-FID

Gas products: online GC-FID

Conclusions

- The cheap materials (LTA and X) have the potential to be applied in hydrogenation of CO_2 to fuels;
- The product selectivity can be modified by using different metal species;
- Cu-based catalysts promote the formation of methanol from CO_2;
- Fe-based catalysts facilitate the conversion of CO_2 to long-chain hydrocarbons;
- The acid and pore properties of zeolites play an important role in the CH_3OH to C_{5+} hydrocarbons.

Reference:

[1] Gao, et.al. Nature Chem. 2017, 9, 1019-1024
[2] Nezam, et.al. J. CO_2 Utilization. 2021, 45, 101405
[3] Yue, et. al. Angew. Chem. Int. Ed. 60 (2021) 18289

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