Bifunctional catalysts for sorption-enhanced reaction processes

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Significance and Relevance

Sorption-enhanced reaction processes integrate adsorption capacity with catalytic reactions to directly convert reactants such as CO_2, methanol, and dimethyl ether into value-added fuels and chemicals within a single reactor, operating under relatively mild conditions and achieving high conversion. Material approaches to fully integrate the sorption and reaction functionalities avoid the challenging (e.g. abrasion, mass transfer) physically mixing of sorbents and catalyst particles.

Introduction and Motivations

The conversion of carbon dioxide (CO_2) to transport fuels with hydrogen has the potential of the integration of CO_2 capture and energy storage and conversion[1]. In particular, synthetic aviation fuel (SAF) production with renewable H_2 and CO_2 is attractive. Where in other transport direct electrification is feasible, hydrocarbons will remain the dominant fuel for airplanes. This drop-in fuel can be synthesized via the well-known Fischer-Tropsch route and via the emerging methanol route. Both synthetic routes benefit from a syngas containing CO and H_2, produced via the selective CO_2 reduction process to CO. The traditional thermochemical conversion is achieved by an endothermic reverse water-gas-shift reaction limited by thermodynamic equilibrium with low single pass conversion of CO_2 that operates above 850°C, requiring high energy input, creating a risk of catalyst deactivation and the formation of undesired side-products. The key challenge is to design a low temperature process that combines a high conversion with a high selectivity. The conversion at lower temperatures, i.e. 300 - 400 °C can be greatly enhanced if reaction product water is selectively removed[2]. Recently, first proof-of-concept was presented of the successful design of a bifunctional catalyst (reactive sorbent) for sorption-enhanced reverse water-gas shift (SE-RWGS, here designated as 'COMAX'), which combines CO_2 activation and water adsorption functionalities in an integrated reactive sorbent[3,4]. Here, we present COMAX optimization with reactive sorbent with focus on productivity, selectivity and cyclic stability. This contribution also highlights our advances in the integration of functionalities with other sorption-enhanced reaction processes. An outlook to the utilization of these materials in pressure swing adsorption cycle design and process integration will also be presented. The successful integration of catalytic activity and adsorption capacity into a single particle opens opportunities in the further intensification of sorption-enhanced reactions.

Materials and Methods

Experimental runs up to 30 bar(a) pressure were conducted on two high-pressure test rigs. During adsorption, the reactor was operated between 250 and 1200 h^{-1} at temperatures up to 400 °C. The gas mixtures consisted of various CO_2:H_2 ratios and 5 mol% argon as tracer. Reactive sorbent regeneration consisted of periodic switching to dry nitrogen, feed or product gas followed by decreasing the pressure to 1 - 3 bar(a). Gas analysis was performed by a gas chromatograph (uGC, equipped with TCD and FID), non-dispersive IR analyzer (NDIR) and a mass spectrometer (MS). Molecular sieve beads 4A zeolite (2-3 mm) were used with incipient wetness impregnation with $H_2PtCL_6.6H_2O$ to obtain the reactive sorbent with Pt loading of 0.3wt%.

Results and Discussion

Figure 1 gives an example of the reactive adsorption step that typically convert over 90% of CO_2 to CO by the simultaneous RWGS reaction and adsorption of the product water. The selectivity of the process is governed by the time, i.e. the step time chosen for adsorption in the (pressure swing adsorption) cycle. Table 1 gives an example of the typical product distribution that can be obtained.

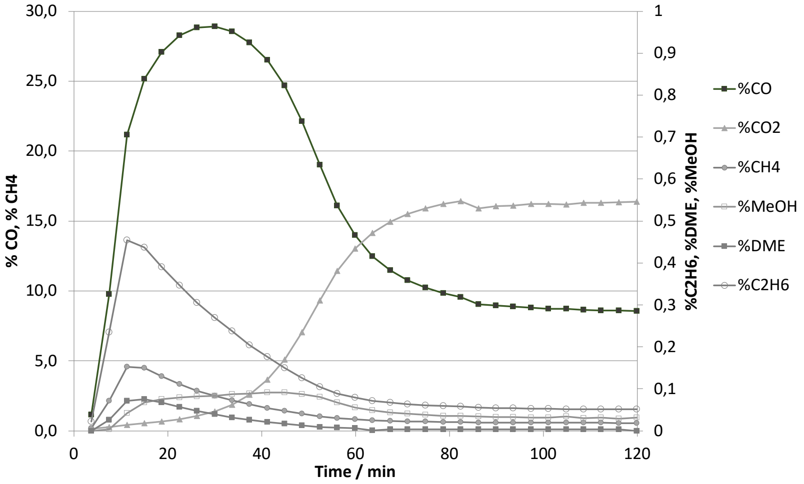

Figure 1. Example of the reactive adsorption step on 0.3wt%Pt_4A molecular sieve using 69,3% H_2, 25,7% CO_2, 5,0% Ar tracer at 390 °C, 25 bara, ±280 h^{-1}, 80 sccm.

Table 1. Product distribution based on 40 min. productivity using 71,3% H_2, 23,8% CO_2, 5,0% Ar tracer at 370 °C, 25 bara, ±280 h^{-1}, 80 sccm.

	CO (%)	**CO_2 (%)**	**CH_4(%)**	**DME(%)**	**MeOH(%)**	**C_2H_6(%)**
0.3wt%Pt_4A	87,5	6,7	4,6	0,4	0,4	0,4

0.3wt%Pt_4A was also tested in full pressure swing cyclic mode with (reactive) adsorption, blowdown, purge and repressurization steps and revealed very good cyclic stability provided that the temperature during the regeneration steps was high enough to ensure near-complete dehydration (>350 °C).

References

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