Integrated direct air capture and activation of CO_2 on metal-free covalent triazine frameworks

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Significance and Relevance

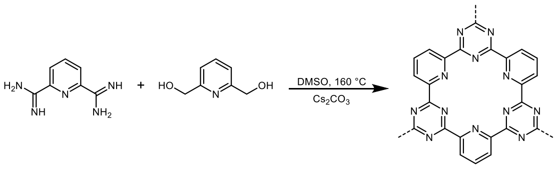
We present a novel process, that couples carbon dioxide capture from ambient air (direct air capture: DAC) with subsequent thermocatalytic CO_2-activation to carbon monoxide over a dual-functional, metal-free covalent triazine framework (CTF). The herein presented integrated approach combining CO_2- capture & -utilization is, to the best of our knowledge, the first system of its kind to achieve DAC and metal-free, thermocatalytic CO_2 conversion over one dual-functional material.

Introduction and Motivations

Mitigating the impact of CO_2-emissions on our planet's environment constitutes one major challenge in the 21st century. Within the diverse field of mitigating measures, carbon capture constitutes one key technology. Established carbon capture technologies are predominantly solution-based, entailing high energy-demand for solvent regeneration.[1] In addition, solvent-based systems are not optimized for DAC conditions and are difficult to couple within an integrated carbon capture and utilization process (ICCU).[1] Accordingly, research focus shifted towards solid sorbent materials, for example, covalent triazine frameworks (CTFs).[2, 3] The application of solid sorbents enables the possibility to elegantly circumvent the inherent uncertainty of underground CO_2-storage by valorizing the inexpensive C_1-building block carbon dioxide *via* CO_2-conversion. Hereby, the innovative ICCU approach not only mitigates the impact of CO_2-emissions, but enables the flexible, decentralized and cost-efficient production of platform chemicals.

Materials and Methods

The used CTF in this work, 2,6-pyridine-CTF (2,6-py), was synthesized *via* polycondensation of 2,6-pyridinediamidine and 2,6-pyridinedimethanol (Scheme 1). After workup, the CTF was calcined at 300 °C for 4 h. Structural integrity was confirmed *via* ^{13}C solid-state NMR spectroscopy, infrared spectroscopy, x-ray diffraction and N_2-physisorption. Framework stability until 300 °C was confirmed by TGA-MS and TPR under H_2-atmosphere. ICP-OES analysis confirmed the elemental composition and the absence of metals in the system.



Scheme 1: Polycondensation of 2,6-pyridinediamidine and 2,6-pyridinedimethanol to 2,6-pyridine-CTF.

ICCU-experiments consisted of two phases, CO_2 adsorption and CO_2 conversion. The former was conducted statically under a standard laboratory atmosphere for 12 h to recreate realistic DAC conditions. The adsorbent was subsequently transferred to a fixed-bed continuous gas-phase reactor. After loading, the reactor was flushed with Ar (100 mL min^{-1}, 3 h) to flush out loosely adsorbed species before it was pressurized to 20 bars (50/50 v/v H_2/Ar). Under the same gas composition, the temperature was ramped in 50 °C-steps between 100 °C and 300 °C while the reactor outlet was monitored by mass spectrometry for increased time resolution.

Results and Discussion

Preliminary gas adsorption studies on five different CTF structures revealed superior CO_2-uptake at low CO_2 partial pressures on 2,6-py (1.43 mmol CO_2 g^{-1} at $p/p_o = 0.1$) while N_2-physisorption confirmed a well-developed pore structure with a BET-surface area of 476 m^2 g^{-1}. As high CO_2 affinity at low CO_2-concentrations is desirable for DAC-applications, 2,6-py was ICCU experiments (Figure 1).

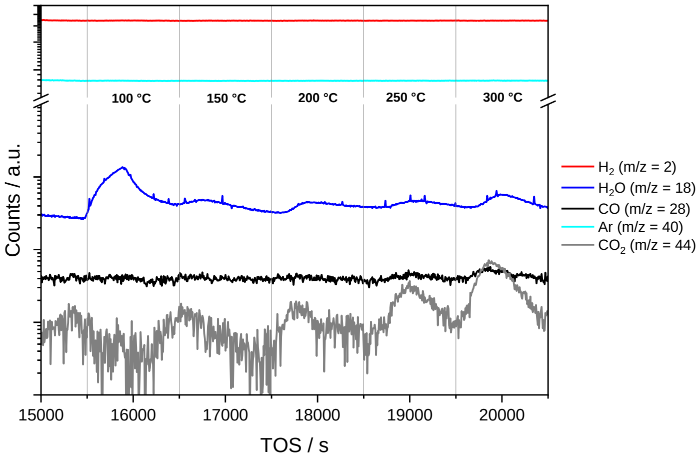


Figure 1: Mass spectra for mass-to-charge ratios (m/z) 2, 16, 18, 28, 40, and 44 for an ICCU experiment on 400 mg 2,6-py. T = 100-300 °C, 20 bar, total flow = 100 mL min^{-1} (50/50 v/v H_2/Ar).

ICCU-experiments consist of an adsorption, a flushing and a conversion phase. For clarity, figure 1 only displays the CO_2-conversion phase. At 100 °C, the desorption of water (m/z = 18) and physisorbed CO_2 (m/z = 44) is observed. A temperature increase to 150 °C triggers another minor water desorption. Starting from 200 °C, chemisorbed CO_2 is desorbed increasingly with increased temperature. Simultaneously, m/z = 18 (H_2O) and 28 (CO) were increased. High-temperature water desorption and decomposition of the framework or synthesis artefacts were excluded through thorough preliminary tests. Hence, CO_2, CO and H_2O between 200 and 300 °C indicate an intrinsic activation of CO_2 to CO according to water-gas shift equilibrium (Scheme 2).[4] This behavior was qualitatively reproducible over 5 cycles with the same catalyst batch as well as with different batches of the 2,6-py-CTF.

$$CO_{2\ (g)} + H_{2\ (g)} \rightleftharpoons CO_{\ (g)} + H_2O_{\ (g)}$$

Scheme 2: Water-gas shift equilibrium.[4]

To confirm the intrinsic activation of adsorbed CO_2 to CO, the reactor outlet gas stream at 250 °C was sampled and analyzed *via* gas chromatography. Besides H_2, Ar and CO_2, carbon monoxide could be confirmed in the outlet gas stream. In addition, 2,6-py was tested under CO_2 hydrogenation conditions (250 °C, 20 bars, H_2/CO_2 3:1) and displayed consistent CO_2 conversion (< 0.5 %) to CO for 24 h.

In conclusion, a metal-free 2,6-py-CTF was employed in a novel ICCU-process. This system combines true DAC with coupled conversion of the adsorbed CO_2 to CO in a solvent-free system, thereby enabling a cost-efficient and highly flexible solution to simultaneously combat CO_2-emissions while valorizing CO_2 as C_1-building block for platform chemicals.

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