

Synergistic Carbon Dioxide Capture and Conversion in Porous Materials

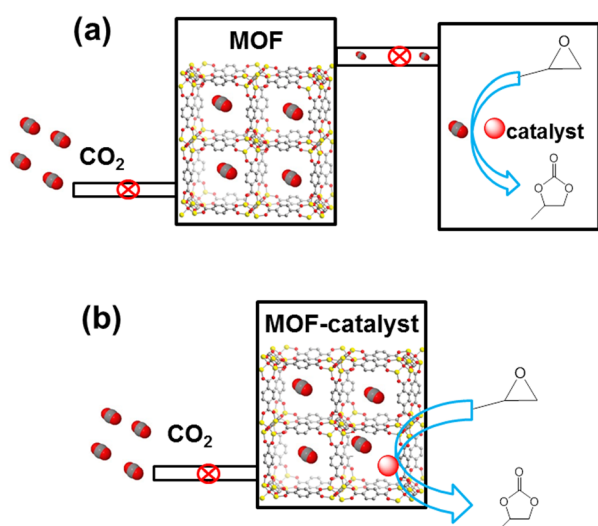
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Global climate change and excessive CO₂ emissions have caused widespread public concern in recent years. Tremendous efforts have been made towards CO₂ capture and conversion. This has led to the development of numerous porous materials as CO₂ capture sorbents. Concurrently, the conversion of CO₂

into value-added products by chemical methods has also been well-documented recently. However, realizing the attractive prospect of direct, in situ chemical conversion of captured CO₂ into other chemicals remains a challenge.

Global climate change and excessive CO₂ emissions have caused widespread public concern in recent years. Tremendous efforts have been made towards CO₂ capture and conversion.^[1,2] This has led to the development of numerous porous materials as CO₂ capture sorbents.^[1] Concurrently, the conversion of CO₂ into value-added products by chemical methods has also been well-documented recently.^[2] However, realizing the attractive prospect of direct, in situ chemical conversion of captured CO₂ into other chemicals remains a challenge.

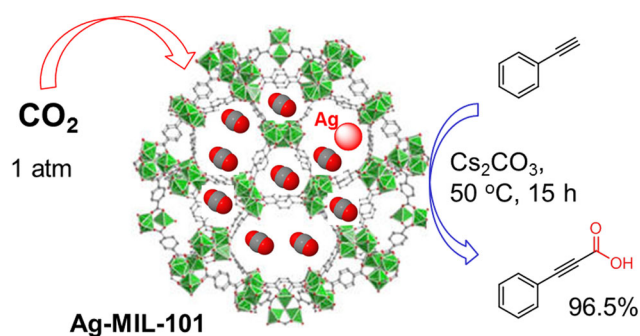
Darensbourg et al. recently demonstrated that metal-organic frameworks (MOFs) can capture and store CO₂, and subsequently release it (via heating) for chemical fixation (polymerization with epoxides to form polycarbonate; Scheme 1a).^[3]



Scheme 1. (a) MOF materials perform as CO₂ capture and storage containers, providing CO₂ for catalytic transformations. (b) MOF-supported catalyst systems capture and concurrently convert CO₂.

Typically, porous materials can capture and store up to 10–40 wt% of CO₂ in their pore structure. The CO₂ density in the pore may be tens to hundreds of times higher than that of gaseous CO₂ in ambient atmosphere. This makes catalytic CO₂ conversion within pores, where the CO₂ concentration could be comparable to CO₂ gas under pressure, very interesting. Thus, a synergistic effect for CO₂ capture and transformation can be expected of well-designed functionalized porous materials that incorporate both porous characteristics and active catalytic sites (Scheme 1 b).

One straightforward strategy is to load CO₂ transformation catalysts into porous materials. Cheng et al. reported MOF (MIL-101)-supported silver nanoparticles (NPs) as an efficient heterogeneous catalyst for the carboxylation of terminal alkynes with CO₂ (Scheme 2).^[4] Silver nanoparticles or salts have



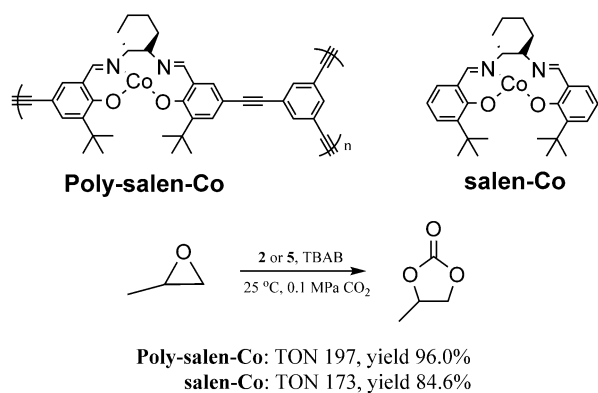
Scheme 2. Highly efficient Ag-MIL-101 catalyst for the carboxylation of terminal alkynes with CO₂.

proven an efficient catalyst for this reaction.^[5] MIL-101 can take up over 6 wt% of CO₂ under ambient conditions (298 K, 1 atm). The nanoscale heterogeneous catalyst system Ag@MIL-101 was prepared by a simple liquid impregnation method. The Ag NPs had an average size of 1.4 nm, in good agreement with the size of the mesoporous cavities in MIL-101 (ca. 3 nm). The NPs were homogeneously distributed within the 3D structure of MIL-101. The unique structure of this porous material allowed it to simultaneously capture and convert CO₂—a combination of CO₂ capture and transformation in one site.

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Ag@MIL-101 showed excellent activity compared to other silver catalysts, and impressive reusability.^[5,6] The exceptional activity is due to good CO₂ adsorption properties, greatly increasing the CO₂ concentration in the pores, where silver catalyst particles are located. Ag@MIL-101 can adsorb 60.37 mg g⁻¹ of CO₂ at 1 atm while this material has total pore volume of 0.7944 cm³ g⁻¹. The CO₂ density in the pore is >30 times higher than that of gaseous CO₂ (1 atm). Mass transfer is well-known to be a bottle-neck in porous-material-supported heterogeneous catalysis, especially for reactions involving both liquids and gases. Here, the pore structure provides a positive synergistic effect and advanced catalytic functionality owing to its gas adsorption properties. In addition, MOF structures can also be designed as efficient catalysts by using their skeleton as catalytic sites for CO₂ transformations.^[7]

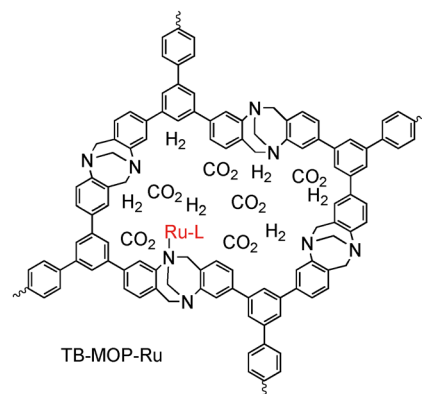
Porous organic polymers for gas adsorption and catalysis form another fast-growing area.^[1-2] Well-designed pore structures can produce positive synergistic effects in porous organic frameworks, and result in advanced catalytic functionality.^[8] Deng et al. reported conjugated microporous polymers (CMPs) with embedded Salen-Co/Al/Zn complexes (Scheme 2).^[9] These polymers showed high Brunauer–Emmett–Teller (BET) surface areas (>750 m² g⁻¹) and high pore volumes (1.81–2.81 cm³ g⁻¹). They demonstrated good CO₂ capture capacity owing to their microporosity. Al-CMP and Co-CMP achieved CO₂ uptakes of 76.5 mg g⁻¹ and 79.3 mg g⁻¹, respectively, at 298 K and 1 atm. Here, the CO₂ density in the pore is also more than 10 times that of gaseous CO₂ (1 atm). Salen-Co/Al/Zn-containing CMPs were also excellent catalysts for the conversion of propylene oxide into propylene carbonate with CO₂. These materials are capable of both CO₂ capture and conversion owing to their porous structure and metal–organic moieties. Co-CMP has a TON of 201 (yield=98.1%), which exceeds that of the homogeneous catalyst Salen-Co-OAc (TON=173, yield=84.6%) under the same reaction conditions (Scheme 3). Although the cobalt loading in Co-CMP approaches the theoretical limit, one important consideration is that cobalt centers deep within the material may be inaccessible to the reactants and therefore unable to catalyze the reaction, given that the



Scheme 3. Microporous polymer coordinated cobalt catalyst demonstrated superb activity in CO₂ transformation as compared to homogeneous catalyst.

average pore size of the material is only 0.5 nm. The real TON, that is, of accessible active sites in Co-CMP, may be much higher because of the high CO₂ concentration achieved by the microporous structure by capturing CO₂ under the reaction conditions, and concentrating CO₂ around catalytic active sites. A similar enhancement of catalytic activity in the conversion of epoxides to carbonates was observed with other catalysts based on porous organic frameworks.^[10]

Generally, microporous organic polymers are able to capture CO₂. These materials are also suitable for supporting metal catalysts for CO₂ transformations.^[11] The synergistic effect of a pore structure to enhance catalytic functionality in porous organic frameworks is expected to be more pronounced when all substrates involved in the reaction are gases. This was demonstrated in a recently reported example, where Liu's group disclosed an interesting system of Tröger's base-derived ruthenium catalyst supported on a microporous organic polymer (TB-MOP-Ru).^[12] This material showed a good adsorption ca-



capacity for both CO₂ (9.6 wt% at 25 °C, 1 atm) and H₂ (0.95 wt% at -96 °C), and hence was used to catalyze the hydrogenation of CO₂ with H₂ to formic acid. Notably, TB-MOP-Ru demonstrated very good catalytic activity towards CO₂ hydrogenation and provided a TON up to 2254, which is about 100 times higher than when using a homogeneous ruthenium catalyst with or without polymer (TB-MOP) additives (Table 1). Herein, the CO₂/H₂-philic framework played a key role in the increased catalytic activity, amplifying the capture-to-transformation synergy in this gas/gas reaction system.

Mass transfer is one of the most critical issues in heterogeneous catalytic systems. However, the situation may differ for reactions involving gases. Because a microporous structure is particularly important for CO₂ adsorption, heterogeneous cata-

Table 1. Ruthenium-catalyzed CO₂ hydrogenation to formic acid.

Entry	Catalyst	TON
1	TB-MOP-Ru	2254
2	RuCl ₃ ·H ₂ O	0
3	RuCl ₃ ·H ₂ O/MeTB	0
4	RuCl ₃ ·H ₂ O/TB-MOP	25

lysts supported on microporous materials could have unique advantages in catalytic CO₂ conversions. The combination of CO₂ capture and transformation in the examples above show synergistic effects in CO₂ fixation process. This could increase the efficiency of catalytic reactions and allow for milder reaction conditions. In spite of the enhanced catalytic activity observed in these capture–conversion materials, more rigorous and direct methods for describing and quantifying such synergistic effects are needed. Experiments might include conducting the reaction under different pressures, as well as in the absence of an external supply of the gaseous reactant of interest, relying only on reactant that has been precaptured in the material. Furthermore, to have an impact on CO₂ emission, it would be critical for more efficient catalytic systems, especially those that convert CO₂ into large-scale bulk chemicals or energy materials, to be developed in the near future.

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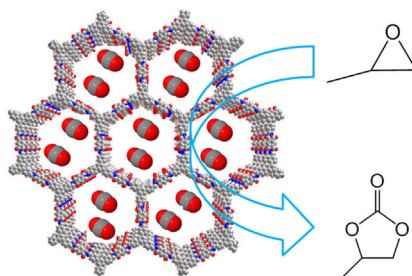
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HIGHLIGHTS

Y. Zhang,* D. S. W. Lim



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And when we are together: Global climate change and excessive CO₂ emissions have caused widespread public concern in recent years. Tremendous efforts have been made towards CO₂ capture and conversion. However, realizing the attractive prospect of direct, in situ chemical conversion of captured CO₂ into other chemicals remains a challenge. This Highlight showcases some recent successful, examples.