

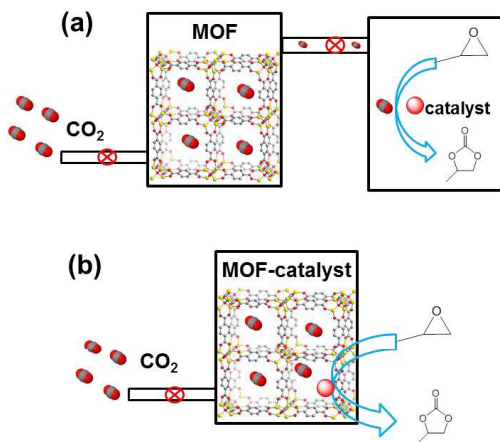
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Synergistic Effect of CO₂ Capture and Conversion in Porous Materials**

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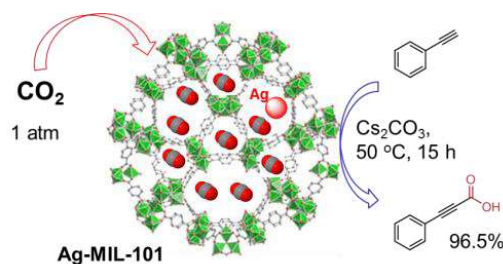
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Global climate change and excessive CO₂ emission have attracted widespread public concern in recent years. Tremendous efforts have been directed towards CO₂ capture and conversion.^[1-2] Leading to numerous porous materials having been developed as CO₂ capture sorbents.^[1] Concurrently, CO₂ conversion by chemical methods to value-added products has also been well documented recently.^[2] However, the attractive strategy for direct chemical conversion of *in situ* captured CO₂ to other chemicals still remains a challenge. Darensbourg has recently demonstrated that MOFs can capture and store CO₂ and subsequently release the gas for chemical fixation (polymerization with epoxides to form polycarbonate, Scheme 1(a)) *via* heating.^[3] Porous materials can capture and typically store up to 10-40 wt% of CO₂ in their pore structure. The CO₂ density in the pore could be tens to hundreds of times higher than gaseous CO₂ under ambient atmosphere. It would be interesting to have the catalytic CO₂ conversion occur within pores where the CO₂ concentration could be comparable to CO₂ gas under pressure. Thus, a synergistic effect for CO₂ capture and transformation could be expected for well-designed functionalized porous materials incorporating both porous characteristics and active catalytic sites (Scheme 1 (b)).



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.

One straightforward strategy is to load a CO₂ transformation catalyst into porous materials. Cheng *et al.* reported MOF (MIL-101) supported silver nanoparticles as an efficient heterogeneous catalyst for carboxylation of terminal alkynes with CO₂.^[4] Silver nanoparticles or salts have been proven as an efficient catalyst for this reaction.^[5] MIL-101 can take up over 6 wt% of CO₂ under ambient conditions (298 K, 1 atm). In this work, silver nanoparticles were combined with a porous material (MIL-101) for CO₂ transformation (Scheme 2). The novel nanoscale heterogeneous catalyst system Ag@MIL-101 was prepared by a simple liquid impregnation method. The Ag NPs with an average size of 1.4 nm, which is in good agreement with the size of the mesoporous cavities in MIL-101 (~3 nm), were homogeneously distributed into the 3D structure of MIL-101. The unique structure makes this porous material capable of simultaneously capturing and converting CO₂. This is a combination of CO₂ capture and transformation in one site. The Ag-MIL-101 gives excellent activity as compared to other silver catalysts and exhibits impressive reusability.^[5,6] The exceptional activity of this heterogeneous catalyst is due to good CO₂ adsorption properties which greatly increases CO₂ concentration in the pores where silver catalyst is located. Ag@MIL-101 can adsorb 60.37 mg/g of CO₂ at 1 atm while this material has total pore volume of 0.7944 cm³/g. The CO₂ density in the pore is >30 times higher than gaseous CO₂ (1 atm). It is well known that mass transfer is often 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 due to its gas adsorption property. In addition, MOF structures can also be designed as efficient catalysts by using their skeleton as catalytic sites for CO₂ transformations.^[7]

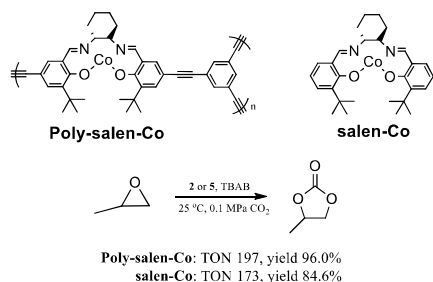


Scheme 2. Highly efficient Ag-MIL-101 catalyst for the carboxylation of terminal alkynes with CO₂.

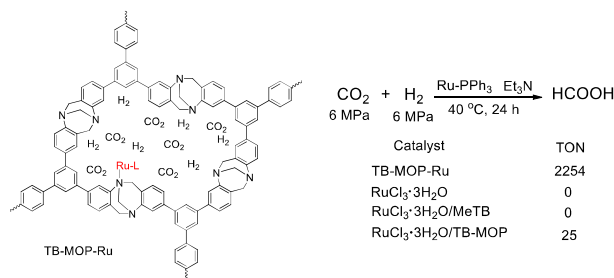
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surface areas (>750 m²/g) and high pore volumes (1.81–2.81 cm³/g). They demonstrated good CO₂ capture capacity due to their microporosity. Al-CMP and Co-CMP achieved CO₂ uptake of 76.5 mg/g and 79.3 mg/g, respectively at 298 K and 1 atm. Here, the CO₂ density in the pore is also more than 10 times higher than gaseous CO₂ (1 atm). Salen-Co/Al/Zn-containing CMPs were also excellent catalysts for the conversion of propylene oxide to propylene carbonate with CO₂. These materials were capable of both CO₂ capture and conversion due 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 the Co centers buried deep within the material may be inaccessible to the reactants and unable to catalyse the reaction, given the average pore size of the material is only 0.5 nm. The real TON of accessible active sites in Co-CMP may be much higher, due to the high CO₂ concentration. Its microporous structure captures CO₂ under the reaction conditions, concentrating CO₂ around catalytic active sites. Similar enhancement of catalytic activity in the conversion of epoxides to carbonates was also observed with other porous organic framework based catalysts.^[10]



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



Scheme 4. Microporous organic polymer supported Ru (TB-MOP-Ru) catalyses CO₂ hydrogenation to formic acid.

Microporous organic polymers are generally able to capture CO₂. Concurrently, these materials are also suitable for supporting metal catalysts for CO₂ transformations.^[11] The synergistic effect of the 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 is well demonstrated in one recently reported example. Liu's group disclosed an interesting

system of Tröger's base-derived microporous organic polymer supported Ru catalyst (TB-MOP-Ru).^[12] This material has good adsorption capacity for both CO₂ (9.6 wt% at 25 °C, 1 atm) and H₂ (0.95 wt% at -96 °C). Therefore, this material was used to catalyse CO₂ hydrogenation with H₂ to formic acid. Notably, TB-MOP-Ru demonstrated very good catalytic activity in CO₂ hydrogenation reaction and provided a TON up to 2254 which is about 100 times higher than homogeneous Ru catalyst with or without polymer (TB-MOP) additives. Herein, the CO₂/H₂-philic framework played a key role for the increased catalytic activity. The gas capture to transformation synergistic effect is amplified in this gas/gas reaction system.

Mass transfer is one of the most critical issues in heterogeneous catalytic system. However, the situation may differ for reactions involving gases. Since a microporous structure is particularly important for CO₂ adsorption, microporous material-supported heterogeneous catalysts could have unique advantages in catalytic CO₂ conversions. The combination of CO₂ capture and transformation provides positive synergistic effect in CO₂ fixation process. This synergistic effect 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 this synergistic effect are still needed. Such 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 pre-captured 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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