Triazole-based MOF for the efficient solvent-free CO2 fixation reaction via cyclic carbonates synthesis

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he increase of greenhouse gases such as carbon dioxide (CO2) in the atmosphere causes serious climate problems. The release of CO2 by anthropogenic activity may lead to a rise in global temperature over the past several hundred years. Hence, effective methods to capture CO2 and mitigate CO2 emissions are urgently demanded. Several strategies have been attempted to reduce CO2, including physical adsorption, and chemical sequestration of CO2. In situ conversion of the captured CO2 into useful product could be the most effective method for CO2 treatment. The CO2 cycloaddition reaction is an important reaction for producing cyclic carbonate, which has a wide range of applications in many fields. Various heterogeneous catalysts have been developed for CO2 cycloaddition reactions, including metal oxides, zeolites, metal-organic frameworks (MOFs) and supported catalyst. Among these catalysts, MOFs have attracted increasing interest due to their excellent properties such as many reactive sites, large surface area, high absorption capacity and well tunable pore structures. It has been reported that MOF-5, Co-MOF-74, Mg-MOF-74, MIL-125-NH2, UiO-66-NH2, Fe-MIL-101, Cr-MIL-101, PCN-224, PCN-700, Hf-Nu-1000, MMCF-2 and MMPF-18 as catalysts can well accelerate the CO2 coupling with epoxide. In this seminar, a highly new porous and stable metal-organic framework containing both metal sites (Zr clusters as Lewis acid sites) and nitrogen rich triazole group (as Lewis base sites) was successfully synthesized via solvothermal reaction. Triazole containing MOF exhibit superior catalytic activities in solvent free CO2 cycloaddition with epoxides. It was demonstrated that the highly performance of triazole containing catalyst is due to the presence of nitrogen groups of triazole moiety which can act as Lewis base. In addition the MOF catalyst showed excellent stability and easy recyclability in comparison with homogenous catalysts. The constructed MOF featuring CO2-adsorbing property and exposed Lewis-acid metal sites could serve as an excellent catalyst for CO2-based chemical fixation. Catalytic activity of the MOF was confirmed by remarkably high efficiency on CO2 cycloaddition with small epoxides. When extending the substrates to larger ones, its activity showed a sharp decrease. These observations reveal that MOF-catalyzed CO2 cycloaddition of small substrates was carried out within the framework, while large ones cannot easily enter into the porous framework for catalytic reactions. Thus, the synthesized MOF exhibits high catalytic selectivity to different substrates on account of the confinement of the pore diameter. The high efficiency and size-dependent selectivity toward small epoxides on catalytic CO2 cycloaddition make this MOF a promising heterogeneous catalyst for carbon fixation.

