Plasma-Driven Modulation of Metal-Organic Frameworks for CO2 hydrogenation

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Significance and Relevance

Achieving controllable pore structure design while preserving the original topology of metal-organic framework (MOF) materials remains a formidable challenge. In this study, we introduce a novel plasma-assisted radical etching (PRE) strategy to modulate the pore structure of HKUST-1 under ambient conditions. Utilizing OH* and CO* radicals as etchants, the PRE strategy enables tailored pore structure modulation through ligand substitution and the reduction of metal ion oxidation states, respectively. CO demonstrates the best reduction result. 80% Cu(II) was converted to Cu(I) within only 3 hours, and the MOF crystal structure is well preserved. The obtained Cu(I)-HKUST catalyst exhibited good selectivity of alcohols in the plasma-assisted CO_2 hydrogenation.

Preferred presentation: (Oral only)

Introduction and Motivations

Metal-organic frameworks (MOFs) are constructed via the self-assembly of metal ions (or clusters) and organic ligands, have attracted attention owing to their predictable and designable pore structures, excellent porosity, and diverse functionalities[1-3]. These characteristics make MOFs highly potential in various applications, such as gas storage, gas separation, catalysis, etc.[4-7]. However, most MOFs exhibit microporous structures with pore sizes less than 2 nm, which limits the entry of large molecules into the internal pores and therefore limits MOFs application in some cases[8-10]. Hence, there is a high expectation for the fabrication of MOFs with larger pore sizes.

Until now, various methods have been reported to modify the pore structures of MOFs, such as the extended ligand method[11, 12], templating method[13-15], acid/base etching method[16, 17], etc. The first two methods are performed during the MOF synthesis, which may lead to sacrifices in the stability of the MOF structure. The acid/base etching method allows larger pores to be generated while maintaining the original topological structure of MOFs, but it challenges the acid/base resistance of MOFs. Therefore, despite considerable efforts, the development of a facile method to fabricate hierarchical porous MOFs (HP-MOFs) remains a pronounced challenge.

This work proposes a systematic plasma-assisted active radicals etching (PRE) strategy capable of modulating the pore structure of HKUST-1 at room temperature and ambient pressure. The results demonstrate that hierarchical porous of HKUST was obtained with maintaining the original topological structure of HKUST-1. The reduced catalysts become effective in hydrogenating CO2 into ethanol.

Materials and Methods

Chemicals: Copper nitrate trihydrate, anhydrous ethanol 1,3,5-benzene tricarboxylic acid, N, N-dimethylformamide, were purchased from Sigma-Aldrich and used as they were.

Methods: HKUST-1 was synthesized according to the reported method[18]. The PRE strategy was operated at ~35°C and ambient pressure in a DBD reactor. 0.5 g HKUST-1 samples are filled in the inner tube while cooling water is circulated in the outer tube to maintain the temperature. Water vapor and CO are fed into the reactor and excited by plasma to OH^* and CO^* etchants. Operating conditions: 35°C, ambient pressure, 25 mL/min of etchants. The catalysts were evaluated in the same DBD reactor right after the catalyst reduction at is set at 30 mL/min with H_2: CO_2 = 3:1, maintained at 35 W for 2 hours.

Results and Discussion

XRD analysis (Fig. 1a) demonstrated the influence of the PRE strategy using OH^* as the etchant on the crystal structure of HKUST-1. Characteristic peaks corresponding to the {200}, {220}, and {222} crystal planes are observed at 2θ = 6.5°, 9.5°, and 11.5°, respectively, indicating the successful synthesis of HKUST-1. After PRE treatment, the XRD patterns are in perfect agreement with those of the original HKUST-1, suggesting the maintenance of the characteristic topology structure of HKUST-1. The decreased peak intensity observed on the catalyst with prolong treatment time, 12 hours.

The pore size distribution curve (Fig. 1b) showed the pore structure of original and modulated catalysts. The untreated HKUST-1 has microporous structures with 7 Å and 8 Å pore sizes. With the increasing duration of PRE treatment, mesoporous structures began to appear on the HP-HKUST-n(OH^*) samples, with a gradually increasing trend in mesopore sizes, thus confirming the effective modulation of the HKUST-1 pore structure using the PRE strategy. Unlike the PRE-OH^* strategy, the PRE-CO^* strategy does not achieve pore modulation by ligand substitution in the HKUST-1 coordination structure. Instead, it induces the spontaneous dissociation of ligands by reducing the oxidation state of copper ions to prepare HP-HKUST-n. As shown in Fig. 2c, the capacity of the PRE-CO^* strategy to reduce the valence state of Cu^{2+} ions to Cu^+.

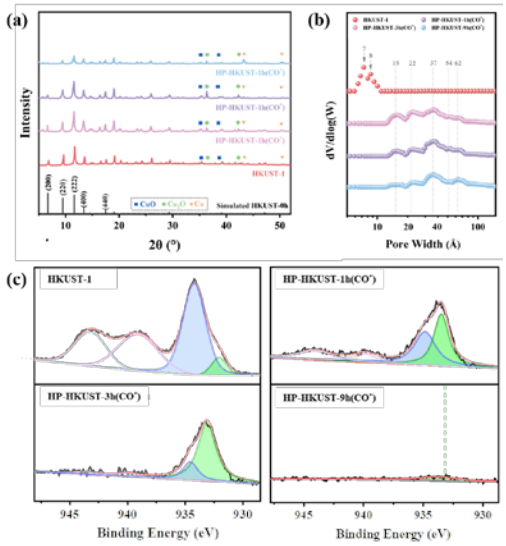

Figure 1. (a) XRD patterns, (b) Pore size distribution and (c)XPS spectra of HP-HKUST-n(CO).*

The PRE-CO^* strategy demonstrates surprisingly high efficiency in reduction. 80% Cu(II) was converted to Cu(I) within only 3 hours, and the MOF crystal structure is well preserved. This reduced catalyst is continued to undergo CO2 hydrogenation reaction. About 33% CO_2 was converted in one throughput. The selectivity of ethanol reach 64.3% of the liquid products.

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