Robotic Mechanochemical Synthesis of HKUST-1 with Process Monitoring

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1. Introduction

Mechanochemical synthesis refers to chemical reactions initiated by mechanical factors such as shearing, compression and grinding. Since these reactions are carried out without solvents or with small amounts of solvents, they reduce solvent consumption and environmental impact [1,2]. Understanding mechanochemical reaction processes can reveal intermediates and reaction pathways that cannot be observed in solution-phase reactions. However, conventional studies using ball mills, which employ sealed containers, have limited reaction observation capabilities. Recent works have demonstrated that robotic systems can improve the reproducibility of such processes [3], although their application to materials beyond perovskites has not been explored.

In this study, we developed an open mechanochemical synthesis system using robotic arms to automate and quantify powder mixing and grinding. As a target compound, the synthesis of the metal-organic framework HKUST-1 was investigated (Figure 1a). The system employed two robotic arms: one for powder mixing and grinding and another equipped with an electronic pipette for methanol addition (Figure 1b).

2. Robotic Arms System for Powder Mixing

2.1. Hardware

We utilized two types of robotic arms. Powder mixing was performed by the UR3e (Universal Robots). The other (Cobotta, Denso Wave) was used for solvent addition with an electronic pipette (Pipetty, Icomes Lab). In this study, the methanol was used as the solvent. The methanol was added in several steps. It was first added onto the pestle to remove any adhered powder, and then added to the mortar several times to wash down powder on the mortar walls. Real-time monitoring of the reaction was achieved using a vibration sensor (Digiducer, TOYO Corporation) and a gas sensor (TP-401A, Bit Trade One).

2.2. Experiment

To prevent powder agglomeration, trimesic acid (0.60 mmol, 0.13 g) was first mixed for 5 min. Copper(II) acetate (0.90 mmol, 0.18 g) was then added, and the mixture was further mixed for 10 min to make the particle size more uniform. During mixing, the pestle motion was alternated between clockwise and counterclockwise directions. The powder was periodically gathered at the center of the mortar to maintain uniform mixing. This was performed by rotating the pestle while scraping the powder toward the center of the mortar. Mixing uniformity was evaluated using a camera mounted on the robotic arm. After inspection, insufficiently mixed regions were identified;

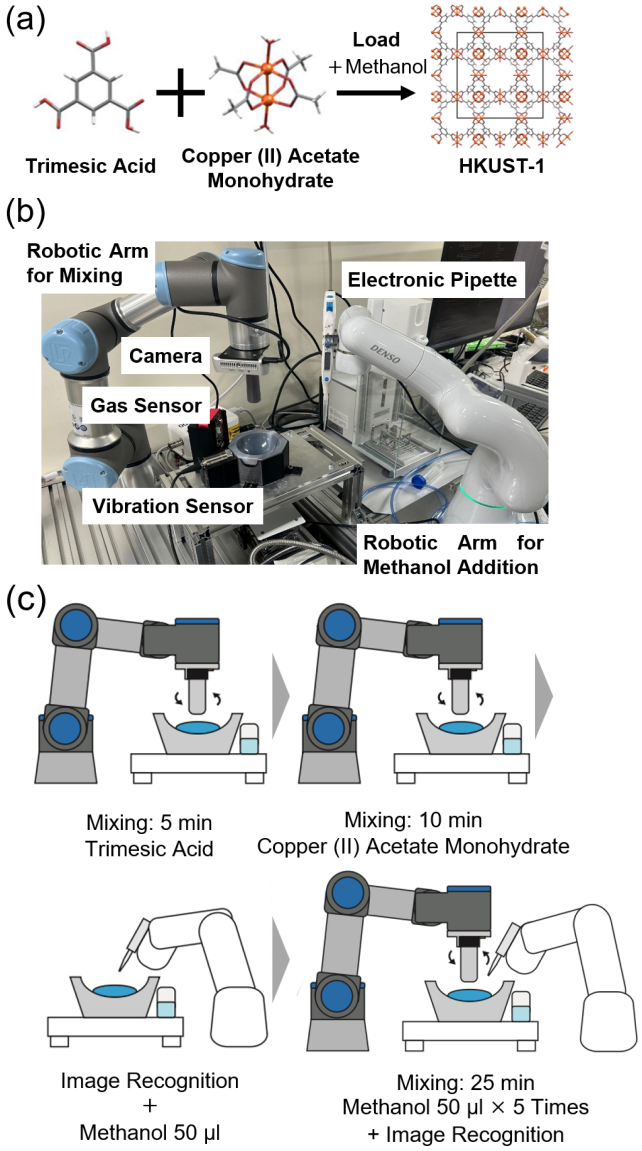

Figure 1: Mechanochemical synthesis of HKUST-1 using robotic arms. (a) Chemical reaction scheme of HKUST-1. (b) Schematic illustration of the robotic arms system. (c) Powder mixing workflow.

the powder was gathered from these areas, and the mixing step was repeated. After solvent addition, mixing/grinding was resumed for 25 min. Methanol was added six times (50 µl each). Finally, we confirmed that the powder was sufficiently mixed using image recognition (Figure 1c).

The obtained sample was washed with ethanol and pure water three times, respectively. Activation of the sample was performed by heating at 60 ℃ under dynamic vacuum for more than 24 h.

We conducted the X-ray Diffraction (XRD; Rigaku, MiniFlex 600) and the Fourier Transform Infrared Spectroscopy (FTIR; JASCO FT/IR-4100). By comparing the data with those of the precursors and the reference data, we confirmed the synthesis of HKUST-1.

3. Results and Discussion

After all mixing steps, the powder was observed to gather near the center of the mortar, suggesting that the mixing and gathering motions worked as designed (Figure 2a). Because the desired product is known to exhibit a characteristic blue in previous research, the synthesis of HKUST-1 was expected. Although a slight color gradation was observed, it can be attributed to incomplete evaporation of the added solvent.

After washing and activation, we conducted the XRD and the FTIR. The XRD pattern showed that the peak positions of our sample were broadly consistent with the reference pattern of HKUST-1 (Figure 2b). Meanwhile, the XRD patterns of the precursors and an obvious intermediate [4] were different, supporting the synthesis of the target compound. The FTIR spectrum also exhibited peak positions similar to those reported for HKUST-1 (Figure 2c). On the other hand, additional bands were observed around 1710, 1412, 1220 and 1185 cm^{-1}. According to DFT calculations of HKUST-1, these bands were mainly assigned to ν(COOH) and defect-related modes [5]. Therefore, these defect-specific bands suggested that two Cu atoms may be missing from paddlewheel sites.

In addition, we monitored the reaction process using the vibration sensor and the gas sensor. We systematically repeated the same procedure under different conditions by varying the load, mixing speed and motion mode. Subsequently, we analyzed these results to examine the relationship between experimental parameters and mechanisms of defect formation in HKUST-1.

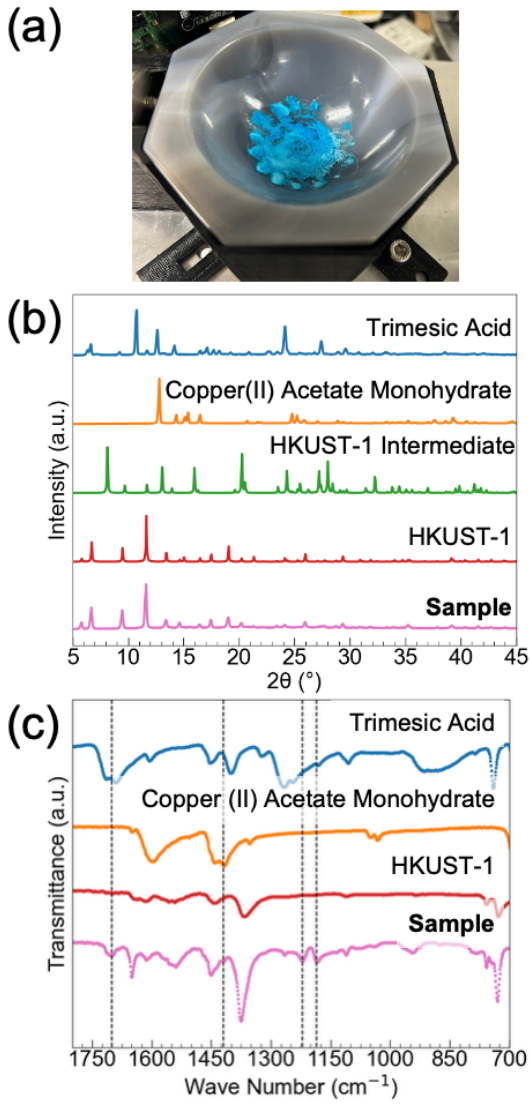

Figure 2: (a) Powder mixture after robotic mixing. (b) XRD pattern and (c) FTIR spectrum of the precursors, intermediate [4], and the obtained sample, compared with HKUST-1.

Acknowledgments

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