Synthesis of a Honeycomb-Type Carbon-Based Acid Catalyst for Flow Reaction Systems

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Introduction
Carbon-based acid catalysts have demonstrated prospective catalytic performances in various liquid-phase reactions relevant to conversions of renewable resources [1]. These catalysts are typically used in the form of fine particles in a batch reactor. If these catalysts are applied for a flow reaction system that provides several advantages such as easier separation of products and easier scale-up for mass production of chemicals, these catalysts meet the requirements of fast intraparticle mass transfer of substrates and low hydraulic resistance to a fluid flow [2]. Monolithic catalysts with a honeycomb structure are ideal for this goal. Here, we report the synthesis of a monolithic carbon-based acid catalyst with a honeycomb structure (Carbon MicroHoneycomb Catalyst, CMHC) by carbonization of a resorcinol-formaldehyde (RF) resin and subsequent surface functionalization with sulfonic acid groups. Uniqueness of the CMHC is the honeycomb structure consisting of nearly straight macropores of <100-µm diameters, which was formed using ice crystals as the template. These macropores are surrounded by thin walls (∼6 µm) of micro-mesoporous carbon, which facilitate mass transfer of substrates. We show that the CMHC exhibits significantly less pressure drops for liquid flow than those calculated for a bed of spherical particles of carbonized RF. We also report that the CMHC catalyzes esterification of acetic acid with ethanol stably at 333 K in a flow reaction system for the number of turnovers of 1400 before the reaction experiment was stopped.

Materials and Methods
RF resins with a honeycomb structure were synthesized by the reported procedure [3] with a slight modification. Carbonization of a RF resin was carried out in a nitrogen flow at 673 K. Sulfonation of the carbonized materials was performed using sulfuric acid at 353 K for 10 h and subsequently at 423 K for 5 h. Morphology and pore structure of the CMHC were characterized by scanning electron microscopy (SEM) and nitrogen gas adsorption at 77 K using a BELSORP-mini II (Belsorp Japan), respectively. Pressure-drop measurements were conducted by passing water through the CMHC at room temperature, and the data were analyzed by the Hagen-Poiseuille equation [4]. Pressure-drops for a bed of spherical particles were estimated by the Kozeny-Carman equation. Catalytic performance of the CMHC was tested in the liquid-phase esterification of acetic acid with ethanol at 333 K in a flow reaction system. The CMHC in a heat-shrinkable tube was held vertically in a thermostat bath at 333 K. An equimolar mixture of ethanol and acetic acid was fed upward from the bottom of the CMHC at a liquid hourly space velocity (LHSV) of 1.2 h⁻¹. The effluent from the catalyst was sampled from time to time and analyzed with a gas chromatography.

Results and Discussion
A CMHC typically prepared is a cylinder with ≈6-mm diameter and ≈18-mm length. A SEM image characterizing the cross-section of the CMHC (Figure 1) shows a honeycomb structure consisting of nearly straight macropores ranging from 47 to 78 µm in diameter, and these macropores are surrounded by walls of ∼6 µm in thickness. The CMHC has micropore and mesopore volumes of 0.22 and 0.26 cm³/g, respectively, and the BET surface area of 640 m²/g as determined by nitrogen gas adsorption experiment. These micro/mesopores are likely present in honeycomb walls and are easily accessible from the macropores.

When water was passed through the CMHC, pressure drops increased linearly with flow rates. Analysis of the data by the Hagen-Poiseuille equation shows a good fit with the tube diameter of 58 µm that is in the range of diameters observed by SEM. Thus, we infer that the CMHC is modeled as a bundle of tubes.

Calculation of pressure drops by the Kozeny-Carman equation for a bed of carbonized RF particles having the same diameter as the average thickness of the CMHC walls shows >1000-fold less pressure drops for the CMHC than particles, highlighting the advantage of the CMHC for applications in a flow system.

The CMHC has 1.1 mmol/g of acid sites as characterized by a standard back titration method. When the CMHC was tested for the liquid-phase esterification reaction in a flow reaction system, the conversion remained stable at approximately 27% during a time-on-stream up to 50 h (Figure 2). The number of turnovers was 1400 before the experiment was stopped. Because a control experiment without a CMHC shows conversions <1.0%, these results indicate that the CMHC functions as a catalyst stably for an extended period of time.

Significance
The CMHC exhibits prospective performances as a catalyst for flow reaction systems as demonstrated by the low hydraulic resistance to a liquid flow as well as the stable catalytic activity in the liquid-phase esterification of acetic acid with ethanol at 333 K in a flow system.

References