

## Preparation of a Water-based Al/Fe/Mo Catalyst Using a Microfluidic System

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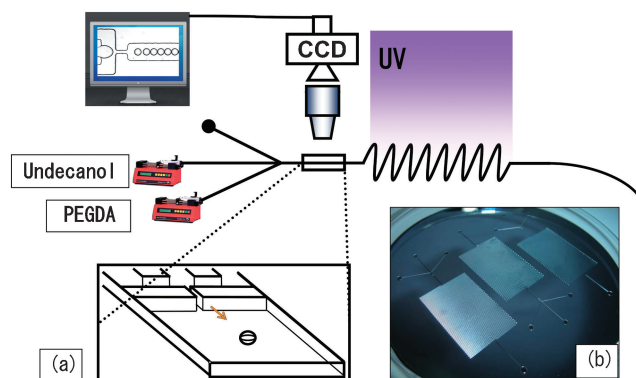
We adapted a microfluidic system using water drops in an oil phase to make an Al/Fe/Mo catalyst with a well-defined shape, with the assistance of UV polymerization on the microfluidic channel.

Microfluidic (MF) system-based synthesis has become widespread in many applications, including production of organic, inorganic, polymer, electronic, and biomaterials, as well as analytical chemistry.<sup>1–3</sup> These composite microsystems, also known as lab-on-a-chip, provide a number of advantages over conventional laboratory systems. They take up less space and automate repetitive lab tasks by replacing huge experimental equipment with miniaturized and integrated systems. Such systems also make it possible to handle very small amounts of fluid, e.g., micro- to sub-micrometers, allowing them to offer high detection sensitivity with much lower cost per unit and less chemical use than traditional laboratory systems. Recently, remarkable development has been achieved in MF synthesis of polymer particles with sizes ranging from a few micrometers to several micrometers. Polymer particles on the micrometer scale can be used in chromatography and ion-exchange columns in various medicinal and biological applications, including calibration standards, coatings, catalysts, and supports for catalysts.<sup>4</sup> For many of these applications, particle size and size distribution are the most important factors. The production of monodisperse nanosized polymer particles with predetermined surface and bulk properties has already been well described.<sup>5</sup> In contrast, the synthesis of sub-millimeter particles with a narrow size distribution exhibits a number of challenges and is often material-specific or time-consuming. When polymer beads are manufactured, the resulting particles do not provide reasonable monodispersity.

Wet processing is the most frequently used method in the synthesis of catalysts, because of its simplicity and use of a solution that contains the desired metals. Mo-containing organometallic compounds such as Al/Fe/Mo are used to catalyze the growth of carbon nanotubes. These catalysts are typically provided as a thin film or multilayer structure, but there are many applications that use spherical particles that contain Al/Fe/Mo.<sup>6</sup>

We describe here the use of microfluidic reactors for the production of water-based particles in the micrometer size range. Most research on the production of polymer particles<sup>7</sup> has been oil based. We tried to make water-based particles to use as catalysts in order to overcome the unstable condition of water drops in oil.

The microfluidic devices were fabricated using a photolithography technique for the master. The masters were prepared by selective photopolymerization of SU-8, which was the

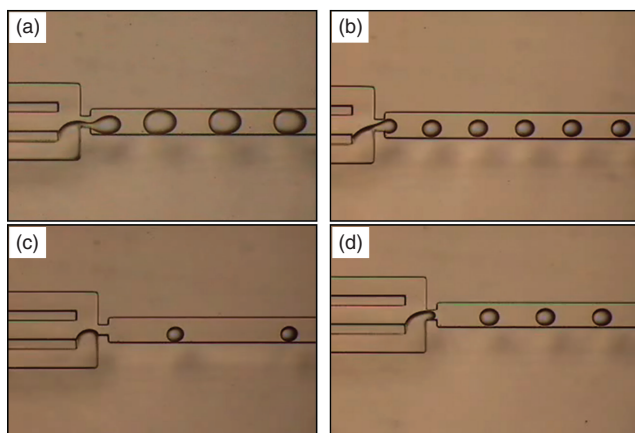


**Figure 1.** (a) Experimental setup for the formation of micro-particles through the microfluidic channel. (b) Real system of the PDMS MF channel.

negative photoresist. The process involved spin coating of photoresist, soft baking, UV exposure, post baking, developing, and washing. Catalyst particles were prepared by the photopolymerization of monomer drops mixed with an aqueous solution of Al, Fe, and Mo ions in microfluidic devices. Droplet formation was captured by a CCD camera (Figure 1). We tried to fabricate monodispersed water-based polymer particles of various sizes, to determine whether the flow rate, surface energy, device morphology, and interfacial tensions were important factors in microfluidic systems. The final catalysts were made after calcination with the mixture of polymer matrix and metal compounds.

Our experimental setup is shown in Figure 1. Instead of a three-inlet system, we used a two-inlet system (the channel had three-inlets, so we blocked one side channel and the flow focusing device was used as a T-junction). SU-8 2050, 2075, and 2100, and the SU-8 developer were purchased from MicroChem, USA for mold preparation. Poly(dimethylsiloxane) (PDMS, sylgard 184 A, B) was purchased from Dow Corning (USA) and poly(ethylene glycol) diacrylate (PEGDA,  $M_w = 575, 750$ ), acrylic acid (AA) and hexadecane were obtained from Sigma-Aldrich and used as received. Other chemicals, including sodium dodecyl sulfate (SDS) and undecanol, were purchased from Alfa Aesar. Photoinitiator benzophenone and Irgacure 2959 were obtained from Aldrich and Shinyoung Rad. Chem. Ltd. Korea, respectively. The microfluidic devices were fabricated using PDMS molds and PDMS substrates.

The aqueous solution was a mixture of  $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O} : (\text{NH}_4)_6\text{Mo}_7\text{O}_{24} \cdot 4\text{H}_2\text{O} : \text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O} = 5:120:450$ . To polymerize the water drops, we used the water-soluble polymer PEGDA ( $M_w = 575$ ). The water phase solution was a mixture of catalyst sample, PEGDA, and Irgacure 2959 (a photoinitiator).



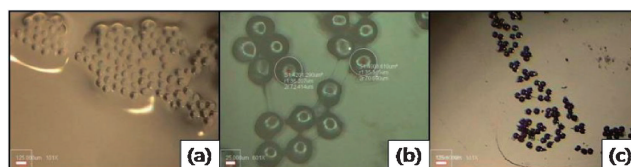
**Figure 2.** Formation of water drops in MF channel at different flow rate of continuous phase (undecanol) and dispersed phase (PEGDA) (a) 0.5, 0.25, (b) 0.5, 0.1, (c) 0.25, 0.001, and (d) 0.05, 0.001 mL h<sup>-1</sup>, respectively.

Undecanol was used as the oil phase (continuous phase). We prepared 10, 20, and 30% PEGDA solutions, and the 20% PEGDA solution yielded the best results. The mixed water phase with 10% PEGDA did not maintain a spherical shape during the polymerizing process because of the low percentage of PEGDA; the water phase had a high affinity for the PDMS surface, and so water drops stuck to the device. The device was hydrophobic and the high (30%) percentage of PEGDA made the water solution favor the hydrophobic surface.

We designed a microchannel that was a total of 120 cm long and a downstream channel of 300 μm to give sufficient time to polymerize. Because the channel was used like a T-junction, undecanol (continuous phase) was injected from the central channel and the catalyst sample (dispersed phase) was supplied through another channel. Undecanol adhered to the hydrophobic device, including orifices, and the water phase of the catalyst solution was sheared off at the corner of the junction to produce aqueous droplets. Generated droplets were polymerized in a wavy channel by a UV source (Double Bore Lamp, Jelight Co., USA). Figure 2 shows the formation of droplets at different flow rates of continuous phase (undecanol) and dispersed phase (PEGDA).

The velocity of the continuous phase was constant at 0.5 mL h<sup>-1</sup>. We varied the dispersed phase at 0.25 and 0.1 mL h<sup>-1</sup>. By reducing the flow rate of the dispersed phase, we were able to create droplets of decreasing size, from 200 to 150 and 130 μm, respectively. In droplet generation, the selection of appropriate device conditions is important. The continuous phase should wet the device, and the dispersed phase should have a lower affinity for the device than the continuous phase. Accordingly, only oil droplets could be generated in a hydrophilic device and only water droplets in hydrophobic devices, whether they were injected from a side or central channel.

When we fixed the dispersed phase at 0.001 mL h<sup>-1</sup> and varied the oil phase from 0.25 to 0.05 mL h<sup>-1</sup>, the change in continuous phase revealed an opposite trend. When we decreas-



**Figure 3.** Microscope images of the catalyst particles through the MF system (a) just after passing the MF channel, (b) after drying at room temperature, and (c) after calcination at 300 °C.

ed the oil speed, the system made a larger droplet, although the effect of the various concentrations of the oil phase was less dramatic than in the water phase. In addition to size change, the frequency of droplets changed according to the continuous phase. Because the velocity of the system depended on the continuous phase, the productivity of droplets also depended on the kind of continuous phase.

Figure 3 shows the product of the Al/Mo/Fe particles as they just emerged from the MF channel (a), dried at RT (b), and burned out at 300 °C (c). The particles were monodispersed and well defined when inside the channel but aggregated and changed their original shape as they came out. After calcination the particles shrunk, but the spherical shape was maintained. These separated particles could be used as a catalyst.

In this work, we demonstrated the fabrication of microfluidic devices by photo- and soft-lithography, and the synthesis of water-based polymer particles containing Al, Fe, and Mo ions that were used as catalysts. This microfluidic-based production of droplets allowed precise control of droplet size and facilitated monodispersed droplets. The speed change of the dispersed phase influenced droplet size directly, and the continuous phase controlled the velocity of the fluidic system, including the speed and frequency of droplet formation.

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