Fabrication of Microreactor Using Glass Capillary with Cu/SiO_2 Layer

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A catalytic reactor using a capillary column with Cu/SiO_2 layer on its inner surface was prepared by injecting a silica sol containing Cu ions in a fused silica capillary and by subsequent gelation under the conditions controlled in order to deposit silica gel uniformly on the inner wall of the capillary. Its catalytic activity was demonstrated in the hydrogenation of propene by constructing a pulse reactor using the catalyst capillary and a separation capillary with pure silica gel layer.

A microreactor attracts much attention in the synthesis of fine chemicals. A typical microreactor was constructed with stacked several glass plates on which various flow channels were drawn.[1] Application of microreactor to gas-phase reaction over a solid catalyst was also considered for constructing portable fuel cell, where steam-reforming of methanol was performed in the microreactor to produce pure hydrogen for fuel cell instead of direct methanol reaction.[2] In such microreactors, however, there are some disadvantages: requirement of special equipments for fabrication, difficulty in drawing long flow channel, and establishment of a method for supporting catalysts uniformly. On the other hand, complex channels are not always required in a gas-phase reaction. Construction of microreactor with a glass capillary would be a preferable approach to that purpose. Although several research groups have reported design of microreactor using glass capillary, application of glass capillary to catalysis using solid catalyst has rarely reported.[3] One of the reasons of less report on catalysis using capillary is the difficulty in the uniform formation of porous solid layer on the inner surface of the glass capillary. Incidentally, we have reported the formation of silica gel layer on inner surface of silica glass capillary and have applied the silica-gel-coated capillary to a separation column of light hydrocarbons.[4] In this work, we applied the technique to the formation of capillary column with Cu/SiO_2 layer for catalytic reaction and evaluated its efficiency in hydrogenation reaction.

A fused silica capillary with inner diameter of 0.1 mm coated with polyimide (GL Sciences, Inc.) was used for the fabrication of catalyst capillary column. Tetraethyl orthosilicate (TEOS, Shin-etsu Chemical Co., Ltd.) and copper nitrate trihydrate (Wako Pure Chemical Industries, Ltd.) were used as sources of catalyst. Polyethylene glycol with an average molecular weight of 20,000 (PEG, Wako Pure Chemical Industries, Ltd.) was used for deposition of silica on inner surface of the glass capillary. Copper nitrate and PEG were dissolved in $1\,\mathrm{mol\,dm^{-3}}$ aqueous nitric acid solution, and then TEOS was added with stirring. The mixture was injected into the capillary after the solution became homogeneous. The starting composition was TEOS:$Cu(NO_3)_2 3H_2O$:PEG:HNO_3 (60 wt % aqueous solution):H_2O = 14:x:1.2:1.6:16 in weight ratio, where x was varied by changing Cu content in the resultant Cu/SiO_2. Both ends of the capillary with the sol was sealed with silicone rubber and epoxy resin and the capillary was kept at 323 K for 1 day for gelation. Then, it was dried at 323 K and heated at 573 K for decomposition of PEG. A 2-m-length capillary with pure silica gel layer for gas separation was prepared as reported previously.[4] The residual solution was geled in a closed polystyrene container at 323 K for the use of characterization.

The morphology of cross section of the capillary was observed with scanning electron micrograph (SEM, SM200, Topcon). Temerature-programmed reduction (TPR) and thermal gravimetry-differential thermal analysis (TG-DTA) were carried out at heating rate of 5 K/min using a conventional apparatus and TG8120 (Rigaku), respectively. X-ray diffraction (XRD7000, Shimadzu) and nitrogen adsorption (AUTOSORB-1MP, Quantachrome) measurements were carried out to detect the structural features of the obtained material. The composition of resultant CuO/SiO_2 was confirmed with X-ray fluorescence analysis (EDX-900HS, Shimadzu) and TPR measurement.

A 1-m-length capillary column with CuO/SiO_2 layer was connected to the separation capillary with pure silica gel layer, and they were set in an FID-GC (GC14B, Shimadzu) to constructing a reacting system. The CuO/SiO_2 column was heated at appropriate reaction temperature whereas the pure silica gel column was held at ambient temperature. After CuO had been reduced to Cu with H_2 flow at 573 K to be Cu/SiO_2 column, the temperature was decreased at the prescribed temperatures. Propene pulse (0.5 µL by injecting 0.1 mL with split ratio of 1:200) was injected into the Cu/SiO_2 column with H_2 carrier gas ($0.02\,\mathrm{mL\,min^{-1}}$), and the mixed gas of propene and propane was separated in the pure silica separation column. Then, conversion of propene was calculated from the ratio of FID signals of both the gasses.

Figure 1 shows a SEM image of cross section of a capillary with CuO/SiO_2. It is confirmed that porous layer with thickness of 25 µm was formed on the inner surface of capillary as has

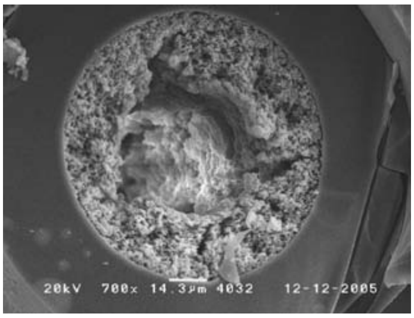

Figure 1. Cross section of silica glass capillary with CuO/SiO_2 layer.

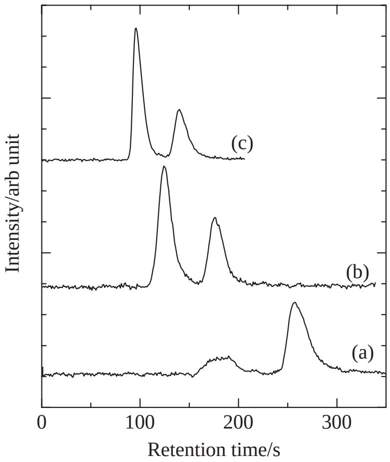

Figure 2. Reaction chromatograms of hydrogenation of propene to propane on a pulse reactor constructed with 1.0 m Cu/SiO_2 (5 wt% CuO) and 2.0-m silica gel columns. Reaction temperatures are (a) 333, (b) 353, and (c) 373 K. Pulse size of propene: 0.5 µL.

been done for pure silica gel without Cu.[4] This layer structure is formed through wetting transition of transitional structure of spinodal decomposition,[5] and the thickness of the layer was controlled from 20 to 30 µm by changing composition in the starting solution. In the measurement of pressure loss in gas flow, we assured that the center hole diameter estimated from the SEM photo in Figure 1 (50 µm) well agrees with that calculated from pressure loss using Hargen–Poiseuille's equation.[4] This result suggests that the thick silica gel layer is formed uniformly all through the capillary tube. In TG–DTA analysis, PEG added for deposition of silica gel layer was decomposed at around 473 K, whereas the polyimide coated on the outer surface of the capillary for strengthening was gradually decomposed over 773 K. Nitrogen adsorption measurement indicated the presence of mesopores and micropores smaller than 4 nm in the layers of silica gel and CuO. It was confirmed with TPR and XRD measurements that CuO in the silica gel was reduced at around 473 K to be Cu nanoparticles. Then, we adopted 573 K heating in air flow for the preparation of CuO/SiO_2-layer column and 573 K reduction in H_2 flow for obtaining Cu/SiO_2. The CuO content analyzed with XRF and TPR roughly coincided with that in the starting composition.

Figure 2 shows typical chromatograms when propene pulse was injected into the reaction system held at different temperatures. Propene was hydrogenated into propane over Cu nanometals in the Cu/SiO_2 column, then the mixture of propane and propene was separated in the subsequent pure silica gel column. The former peak is assigned to propane, and the latter one is assigned to propene. The ratio of propane to propene increased with increasing reaction temperature. This result clearly shows that the capillary reactor works well in the hydrogenation of propene.

Figure 3 shows the change in conversion of propene with reaction temperature for some Cu/SiO_2 columns with different Cu contents. All the columns showed no decay in activity for multiple pulses. The conversion depends on both reaction temperature and Cu content. At 20 wt% loading of Cu, conversion steeply increased with the reaction temperature at <373 K, and reached 100% over 373 K. The activity of columns with low Cu content was low. The results elucidate that the silica gel layer on the inner surface of capillary can be a support for metal nanoparticles. Its activity will be designed by simply extending the length of the reaction column, which is favorable for a reaction where high selectivity is only achieved at low reaction temperature with low reaction rate. The capillary reactor is expected to be applied not only for portable use but also for highly designed reaction systems.

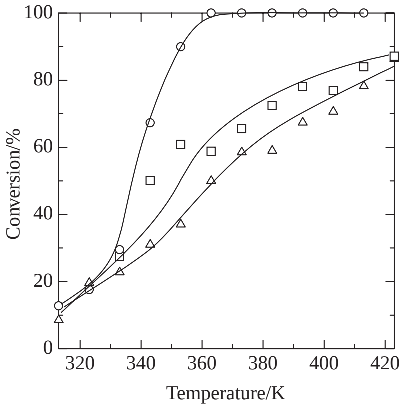

Figure 3. Dependence of conversion of propene on reaction temperature. (○) 20 wt% CuO, (□) 10 wt% CuO, and (△) 5 wt% CuO. The lengths of reaction and separation columns are 1.0 and 2.0 m, respectively. Pulse size of propene: 0.5 µL.

In conclusion, we prepared a capillary column with Cu/SiO_2 layer for catalytic reaction and proved its efficiency by constructing pulse reaction system using the catalyst column jointed to a column with pure silica gel layer for gas separation.

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