Microreactor utilizing a vertically-aligned carbon nanotube array grown inside the channels

Naoki Ishigami,[a] Hiroki Ago,*[ab] Yukihiro Motoyama,[ab] Mikihiro Takasaki,[a] Masashi Shinagawa,[a] Kohji Takahashi,[c] Tatsuya Ikuta[c] and Masaharu Tsuji[ab]

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We have fabricated a microreactor incorporating vertically-aligned carbon nanotubes supporting Pt nanoparticles and found that the presence of aligned nanotubes significantly enhances the catalytic reaction and extends the catalyst lifetime as compared with conventional microreactors using a Pt metal film or Pt nanoparticles directly deposited on the channel walls.

Carbon nanotubes, one-dimensional cylindrical graphene sheets with a nanoscale diameter, have attracted a great deal of interest, because they show excellent electron and thermal conduction as well as high mechanical flexibility.[1] Nanotubes are a promising catalyst support material, because of their high surface area, ease of chemical modification and high mechanical stability.[2] Several studies on catalysis using metal-supporting carbon nanotubes have shown high catalytic activity in hydrogenation,[3] dehydrogenation,[4] hydroformylation[5] and electrooxidation for fuel cells.[6] However, there are severe limitations in the use for catalyst supports due to their poor solubility in organic solvents and high cost of nanotubes which cannot be used in a large scale.

Recently, microreactors which consist of micro-scale flow channels, reaction zones, mixers and so on, have been recognized as an efficient means for chemical synthesis.[7] This is because microreactors have many advantages, such as high controllability of the reaction conditions, laminar flow, uniformity of reaction temperature and parallel-processibility. Catalytic reactions have been widely studied in microreactors and, in most cases, metal catalyst is deposited on the walls of the microchannel by evaporating thin metal films[8] or by attaching metal nanoparticles.[9] Therefore, catalytic reactions occur only at the periphery of the channel walls.

Here, we have fabricated a new type of microreactor which possesses Pt-supported aligned carbon nanotubes in the reaction zone and studied the efficiency of a catalytic reaction. Incorporating nanotubes in a microreactor has many advantages; (i) nanotubes are fixed inside the channel so that the difficulty in dispersing nanotubes in solvent is avoided, (ii) large contact area between reactants and the catalyst is expected as the nanotubes cover the whole channel and (iii) collection of nanotubes after a chemical reaction, such as filtration, is not required. Fig. 1 illustrates the comparison of a conventional microreactor and the nanotube-based microreactor. In the latter, the high contact area formed by the aligned nanotubes is expected to realize high catalytic conversion. Here, we have studied the hydrosilylation of an olefin using the nanotube-incorporated microreactor and observed a significant increase in the yield and extension of the catalyst lifetime.

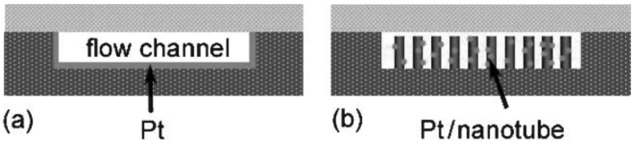

Fig. 1 Schematic illustration of (a) a conventional microreactor using Pt film deposited on the walls of the flow channel and (b) a microreactor with Pt-modified aligned nanotubes in the flow channel.

The nanotube-incorporated microreactor was fabricated by growing multi-walled carbon nanotubes inside the channels made on a Si substrate. The reaction zone (width: 2.5 mm, depth: 170 μm, length: 20 mm) was first covered with an evaporated Al film (20 nm), followed by growing carbon nanotubes by thermal chemical vapour deposition (CVD) using ferrocene and xylene.[10] We found that the Al buffer layer is important to strengthen the interface between the nanotubes and the Si substrate, as the absence of the Al film resulted in peeling off of the nanotubes when the reactant solution flows in. Fig. 2(a) shows a photograph of the nanotube-incorporated microreactor before sealing; the black part corresponds to the aligned nanotube array. Scanning electron microscope (SEM) images of the cross-section of the nanotube-based microreactor are shown in Fig. 2(b) and (c). The nanotubes were aligned normal to the Si substrate, and their length and diameter were around 100 μm and 30 nm, respectively.

The aligned nanotubes were modified with Pt nanoparticles for the catalytic reaction by the following two methods; impregnation of Pt salt and direct deposition of Pt nanoparticles. In the impregnation method, an acetone solution of $H_2PtCl_6·6H_2O$ (1.54 M) was dropped onto the nanotubes and reduced at 250 °C for 2 h in hydrogen atmosphere. In the direct deposition method, the micelle solution of Pt nanoparticles with 1.7 nm diameter[11] was dropped onto the nanotube array, followed by annealing in air at 350 °C for 2 h to remove the surfactant, dodecylamine. In both methods, the Pt amount was fixed to be *ca.* 15 wt% against nanotubes, which was estimated by thermogravimetry (TG) measurements. Finally, the Si substrate was sealed with Pyrex glass using a fluorine-based binder. For comparison, microreactors without nanotubes, *i.e.* a Pt salt or Pt nanoparticles were deposited directly on the channel wall, were prepared. A conventional

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[a] *Interdisciplinary Graduate School of Engineering Sciences, Kyushu University, Fukuoka, 816-8580, Japan. E-mail: ago@cm.kyushu-u.ac.jp; Fax: +81-583-7817*
[b] *Institute for Materials Chemistry and Engineering, Kyushu University and CREST-JST, Fukuoka, 816-8580, Japan*
[c] *Graduate School of Engineering, Kyushu University, Fukuoka, 819-0395, Japan*

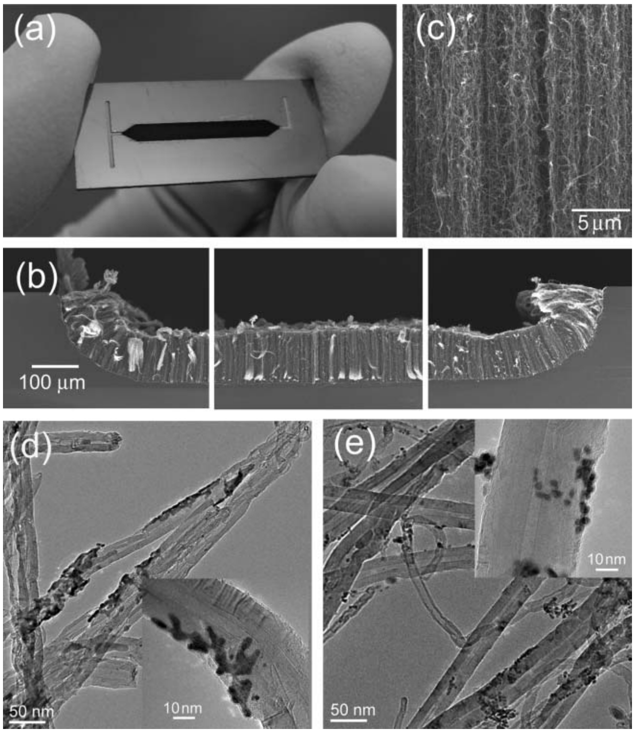
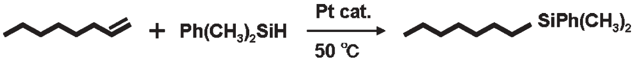


Fig. 2 Photograph of a nanotube-incorporated microreactor (a). SEM images of a cross section of the microreactor in which carbon nanotubes are aligned normal to the Si substrate (b). High-magnification SEM image of the aligned nanotubes (c). TEM images of Pt-modified nanotubes attached by the impregnation method (d) and the Pt nanoparticle deposition method (e).

microreactor with Pt/Ti film (Pt 20 nm on Ti 9 nm) was also fabricated by electron-beam evaporation.

Fig. 2(d) and (e) show transmission electron microscopy (TEM) images of Pt-modified nanotubes prepared by the two different methods. In the case of the impregnation method, Pt nanoparticles with diameters in the range of 1 to 10 nm were observed on the surface of nanotubes (Fig. 2(d)), while the diameter of the Pt nanoparticles was found to be uniform for the sample prepared by the Pt nanoparticle deposition method (Fig. 2(e)). Hydrosilylation of an olefin, which proceeds in the presence of Pt catalyst, was studied as a model system (Scheme 1).[12] Equal amounts of toluene solutions of 1-octene (1.15 M) and dimethylphenylsilane (0.96 M) were separately introduced to each inlet with a total flow rate of 1 μl min^{-1}. The reaction temperature was kept at 50 °C, and the yield was determined by a capillary gas chromatograph (GC) using *n*-decane as an internal standard.

Fig. 3 compares the yield of octylsilane as a function of the reaction time. In the case of the Pt film catalyst, which is widely used in conventional microreactors, the initial yield reached 48%, but it decayed gradually and lost catalytic activity after 5 h. In the microreactor made by dropping the Pt salt directly on the channel wall, no reaction occurred. The catalyst prepared by deposition of the colloidal Pt nanoparticles on the channel wall showed 10% conversion, and lost catalytic activity in 1 h.



Scheme 1

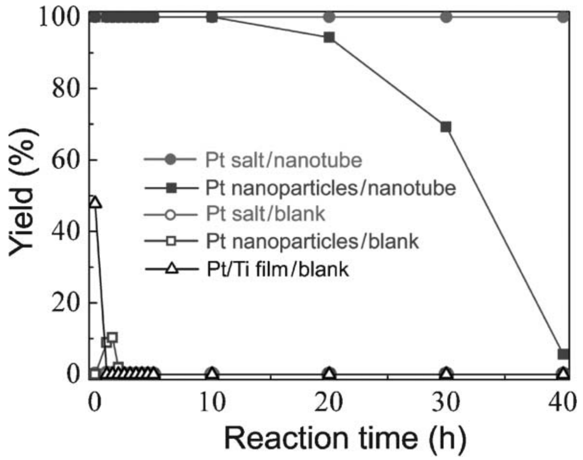


Fig. 3 Time dependence of the catalytic activity of the microreactors. (●): impregnated Pt deposited on aligned nanotube array, (■): Pt nanoparticles deposited on aligned nanotubes array, (○): impregnated Pt deposited on the channel wall, (□): Pt nanoparticles deposited on the channel wall, (△): Pt/Ti film deposited on the channel wall.

Remarkably, both the nanotube-based microreactor showed much higher initial catalytic activity, nearly 100% yield, and longer catalyst lifetime as long as 10 h, as compared with the conventional microreactors. We did not observe any by-products in the effluent solution. In the microreactor prepared by the impregnation method, the catalytic activity was retained for more than 40 h. No morphological change was observed for the aligned nanotubes after the reaction, because the buffer Al layer enhanced the adhesion of nanotubes to the Si substrate.

We suppose that the high catalytic activity of the Pt-supported nanotube arrays stems from the highly dispersed state of Pt nanoparticles on the nanotubes. In addition, the presence of nanotubes should be important to enhance the contact between the reactants and Pt nanoparticles through the diffusion of the reactant into the slits of the nanotube array. Although the reactants dissolved in toluene may not fully penetrate into the bottom of the reaction zone (*i.e.*, roots of nanotubes), the flow in the upper part of the reaction zone (near the tip of nanotubes) is sufficient to provide a high conversion yield, thus leading to dramatic enhancement of the catalytic reaction due to the aligned nanotubes. The stabilization of Pt nanoparticles on the nanotube surface, which prevents the nanoparticles from sintering, should contribute to the extended catalyst lifetime. The Pt concentration in the effluent solution was low, below the detection limit of an inductively coupled plasma-mass spectrometer (ICP-MS), indicating relatively strong interface bonding.

The Pt-supported nanotubes were characterized by X-ray photoelectron spectroscopy (XPS), and it was found that the Pt nanoparticles were mainly metallic for both samples. We speculate that the Pt nanoparticles prepared by the impregnation method preferentially adsorb on the structural defects of nanotubes which were formed during the CVD growth (see Fig. 1(d) inset), while the colloidal Pt nanoparticles attached on the nanotube surface simply through the adhesion of the surfactant. In other words, the interface bonding between Pt nanoparticles and nanotubes is weaker for the direct deposition method than the impregnation method. Therefore, it is likely that the colloidal Pt nanoparticles are more facile to sintering during the reaction, resulting in shorter catalyst lifetime (Fig. 3).

It has been reported that acid treatment generates the surface functional groups on nanotube surfaces, which anchors the nanoparticles more strongly.[1] In the present case, the acid treatment was not performed because it peeled off the nanotubes due to etching of the Al buffer layer. Note that no functional groups were detected for the as-grown nanotubes from the infrared (IR) absorption measurement. Therefore, appropriate modification of the nanotube surface may further improve the performance of the microreactor.

In summary, we have fabricated a microreactor having aligned multi-walled carbon nanotubes and studied the hydrosilylation of an olefin. The aligned nanotubes were found to greatly improve the catalytic activity as well as its lifetime. The present study may find applications for nanotubes as a support material in highly efficient microreactors.

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