Synthesis of Fe_2O_3 in the capillary-tube reactor

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These days microreactors are widely studied as a new reactor [1], because it has many advantages such as rapid heat transfer, rapid mixing, and so on. Organic syntheses and polymer syntheses in these reactors are reported by many researchers [2–5]. For example, Hiemer *et al.* [3] studied direct oxidation of benzene to phenol using Fe-ZSM-5-coated stainless-steel microreactor. Kestenbaum *et al.* [4] investigated exothermic epoxidation of ethylene to ethylene oxide in the middle of the explosive regime by Ag-catalyst in a microreactor. In contrast, not so many researches are seen in the field of inorganic synthesis [6–12]. One of the reasons would be the problem of plugging or blockage. To circumvent this problem, not a microreactor but a micro-mixer was used by Schur *et al.* [9].

In this letter, we report preliminary studies on the synthesis of Fe_2O_3 in the capillary-tube reactor by decomposition of ferric nitrate nonahydrate $(Fe(NO_3)_3 \cdot 9H_2O)$ dissolved in formamide. The influence of the properties of the capillary-tube reactors on the products obtained is mainly studied.

The capillary-tubes used are listed in Table I and the reactor system is shown in Fig. 1. Typically, a capillary-tube made of glass of diameter 0.32 mm and effective length 1.0 m was immersed in an oil bath maintained at 150 °C. $Fe(NO_3)_3 \cdot 9H_2O$ of 1.0 mol/l dissolved in formamide (b.p. 210 °C) was fed by a syringe pump. By changing the feed rate of the solution from 2 to 30 ml/hr, the reaction time was varied. A conventional autoclave was also used for comparison. Reagents were purchased and used without further treatment.

The solid products obtained after washing with water and drying at 120 °C overnight were characterized as follows. Crystalline structure was analyzed by X-ray diffraction (XRD), JEOL JDX-3530, using Cu Kα radiation at 40 KV and 30 mA. By Scherrer equation, a crystallite size was calculated. Thermogravimetric and differential thermal analyses (TG-DTA) was measured on Shimadzu DTG-60H under air flow. Morphology of particles was observed by transmission electron microscopy (TEM), JEOL JEM-2000FX, at 200 KeV.

As the as-received $Fe(NO_3)_3 \cdot 9H_2O$ powder decomposed in air at about 150 °C, this temperature 150 °C was adopted as the reaction temperature for decomposition in the capillary-tube reactor.

It was indicated by XRD (Fig. 2) that the solid product obtained by decomposition of $Fe(NO_3)_3 \cdot 9H_2O$ in the capillary-tube reactors was Fe_2O_3. In addition, no shift of peak position and no substantial change in relative peak intensity were observed regardless of the reactors used.

From the result of TG-DTA (not shown) of the products, it was revealed that there was no weight decrease up to about 200 °C, however, at around 250 °C a weight decrease accompanying exothermic peak was observed. This suggests that a small amount of formamide (b.p. 210 °C) interacting with Fe_2O_3 is included in the product and therefore the yield of the product indicated hereafter is calibrated taking this weight decrease into consideration.

Fig. 3a shows the relation between the yield of Fe_2O_3 and the reaction time for the capillary-tube reactor. Here, a variety of reactors were used to study influences of tube-materials and flow of the solution. The yield (%) of Fe_2O_3 was calculated on the basis of the amount (g) of obtained Fe_2O_3 and the theoretical amount (g) of Fe_2O_3 in the fed solution. As indicated, the yield of Fe_2O_3 increased linearly up to about 60% and thereafter it increased very gradually. Exception was a capillary-tube of wide diameter, 0.53 mm. It is surprising that the reaction rate in this reactor is roughly one-third of that in the 0.32-mm glass capillary-tube. This suggests that the size of the tube gives a strong influence on the decomposition rate. For comparison, when an autoclave was used as a reactor (Fig. 3b), it took roughly 2 hr to obtain the yield of 30%. This result means that the reaction rate in the capillary-tube reactors was about 2 orders faster than that in the autoclave.

The primary crystallite size calculated by Scherrer equation was between 10 and 60 nm depending on the reactors. The secondary particle size was about a few micrometers and this is far smaller than the diameter of the capillary-tube. The dependence of the crystallite size on the yield of Fe_2O_3 was almost the same for the capillary-tube treated with trimethylsilyl chloride (TMS) and the polyimide tube. The products obtained using the autoclave resulted in a smaller crystallite size.

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TABLE I Properties of capillary-tubes

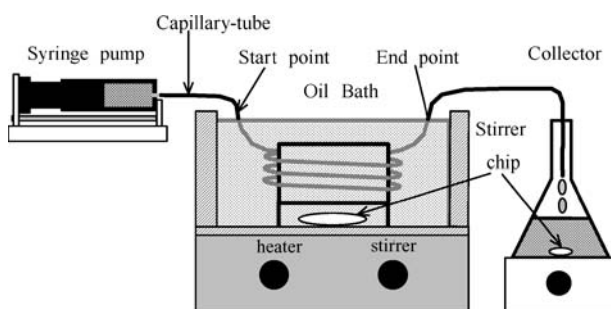| Material	Tube diameter	
	Inner (mm)	Outer (mm)
Glass	0.32	0.45
Glass (TMS)*	0.32	0.45
Glass	0.53	0.65
Polyimide	0.40	0.50

*Treated with Trimethylsilyl chloride.

Figure 1 Capillary-tube reactor system.
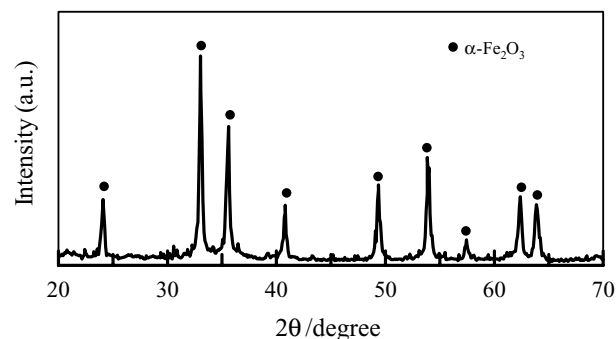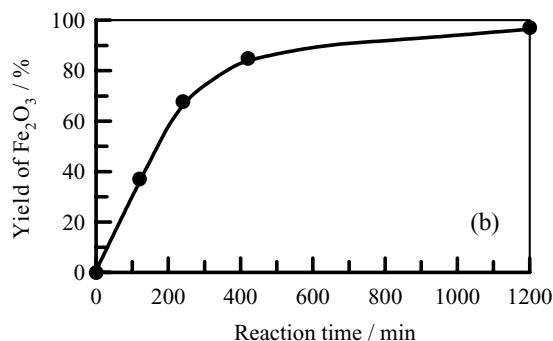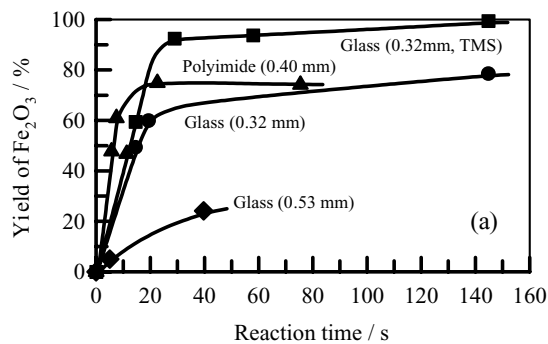

Figure 2 XRD pattern of the product prepared in the capillary-tube reactor.

Figure 3 Influence of the reaction time on the yield of Fe_2O_3 (a) capillary-tube reactors, (b) autoclave (50 ml).

Morphology of products observed by TEM is shown in Fig. 4. Morphology differed among reactors used. In the case of untreated glass capillary-tube (Fig. 4a), aggregates of spherical particles having diameter of roughly 40 nm were observed. On the other hand, the glass capillary-tube treated with TMS gave aggregates of rod-like particle of typical diameter 3 nm and length 20 nm (Fig. 4b). In the case of the autoclave (Fig. 4c), bigger particles than those obtained by the former two capillary-tubes were observed. However, if we see the particles minutely, it is clear that the spherical particle itself in Fig. 4a is also composed of smaller parts. As to the products obtained by the autoclave, the same phenomenon was observed from TEM photos taken at higher resolution (not shown). Therefore, the particles observed by TEM are not the primary ones and this is the reason why size from TEM and information from XRD patterns differed. As to this discrepancy, at this moment we do not have proper explanations and this subject is to be studied further in the future.

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The fact that morphology of products could be varied simply by the choice of microreactors is very interesting. Formation of rod-like Fe_2O_3 is reported by Radtchenko *et al.* [13] and Woo *et al.* [14] and that of rod-like ZnO is reported by Li *et al.* [15]. In the case of Fe_2O_3, capsules of polyelectrolyte multilayers composed of poly(styrenesulfonate) and poly(allylamine hydrochloride) are used to give the space for precipitation [13]. In the case of ZnO nanorod [15], reverse micelles in complicated solvent system was adopted. These examples suggest that in order to arrange the morphology of inorganic materials the control of the precipitation reaction system is very important. In Contrast to these examples, the present study is suggesting that merely the choice of microreactor can arrange the morphology of obtained products and therefore the microreactor system is very useful for preparation of inorganic materials of unique properties.

Both the specific surface area of the reactor normalized by the reactor volume and the relative reaction rate were calculated and it was, as a general trend, indicated that the reaction rate increased as the specific surface area increased. Especially, the polyimide-tube reactor presented much higher reaction rate. These observations suggest that the inner surface of the tube reactors and probably diffusion of primary products from the surface to the reaction medium would play very important roles on the solid materials obtained. To understand these subjects deeply, it is necessary to study further the interaction between the metal salt and the inner surface of the capillary-tube.

In summary, fine Fe_2O_3 particles were obtained by the decomposition of $Fe(NO_3)_3 \cdot 9H_2O$ in formamide in the capillary-tube reactor. It was suggested that the surface properties of the reactor played a very important
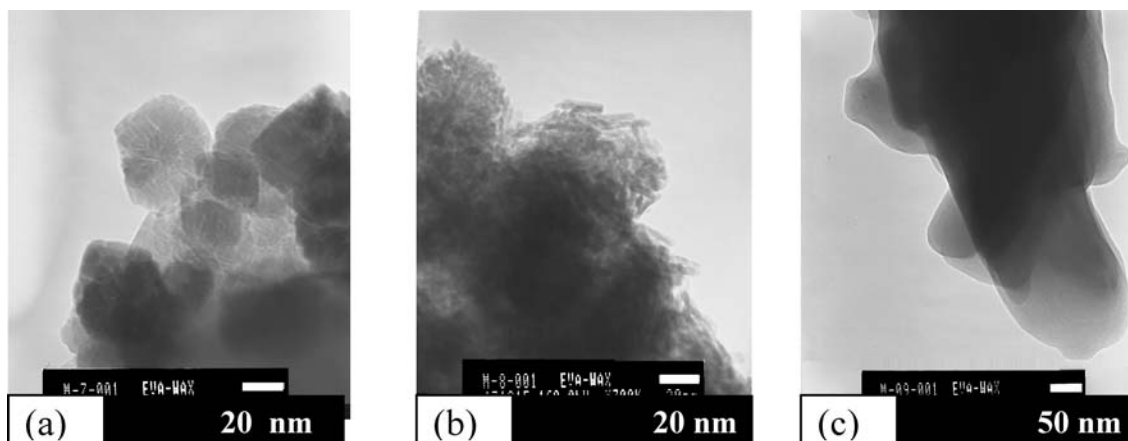
Figure 4. TEM images of the products (a) glass capillary, (b) glass capillary (TMS), and (c) autoclave (50 ml).

role on the properties of particles obtained. A mere choice of microreactors affected the morphology of products.

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