PREPARATION OF POROUS GLASS-CERAMICS WITH A SKELETON OF NASICON-TYPE COPPER TITANIUM PHOSPHATE CRYSTAL

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Abstract A novel porous glass-ceramic with a skeleton of $\text{CuTi}_2(\text{PO}_4)_3$ was prepared by controlled crystallization of a glass with a nominal composition of $50\text{CuO}\cdot 20\text{TiO}_2\cdot 30\text{P}_2\text{O}_5$ (in mol%) and subsequent chemical leaching of the resulting dense glass-ceramic consisting of $\text{CuTi}_2(\text{PO}_4)_3$ and $\text{Cu}_3(\text{PO}_4)_2$ phases with CuO phase at the surface. By leaching the resultant glass-ceramic with dilute H_2SO_4 , $\text{Cu}_3(\text{PO}_4)_2$ and CuO thin layer were dissolved out selectively, leaving a crystalline $\text{CuTi}_2(\text{PO}_4)_3$ skeleton. The resulting porous glass-ceramic with large specific surface area ($\approx 45 \text{ m}^2\cdot\text{g}^{-1}$) showed some catalytic activities such as conversion of propene into acrolein.

INTRODUCTION

Porous glass-ceramics, utilizing spinodal-type phase separation in glass, have following advantages over conventional porous ceramics prepared by using a powder-sintering method: (1) this processing is relatively simple; (2) bulk materials which are controlled in shape and dimension can be obtained; (3) porous bodies with a large surface area and narrow width of pore-size distribution are obtained; (4) crystalline phases with active function can be also precipitated as the skeleton of the porous material. Since it has been reported in our laboratory that a microporous glass-ceramic with a skeleton of $\text{CaTi}_4(\text{PO}_4)_6$ crystals was prepared in 1989,¹ we have reported various porous glass-ceramics consisting of a functional titanium phosphate crystal.² We anticipate that this promising is in fabrication of catalysts with high activities. In the present work, a novel porous glass-ceramic with a skeleton of NASICON-type copper titanium phosphate crystal $\text{CuTi}_2(\text{PO}_4)_3$,³ was successfully obtained. The crystals have some catalytic activities such as oxidation of propene into acrolein.⁴

EXPERIMENTAL PROCEDURE

A batch with a composition of $50\text{CuO}\cdot 20\text{TiO}_2\cdot 30\text{P}_2\text{O}_5$ (in mol%) was melted at 1250°C for 1h in an alumina crucible in air. The melt was poured onto a stainless steel plate and quenched quickly by pressing in N_2 atmosphere. The resultant glassy plate was reheated at $520\text{--}590^\circ\text{C}$ for 24h in air. The dense glass-ceramic was then leached with $0.5N\text{-H}_2\text{SO}_4$ at room temperature for 3 days. As a result, a porous glass-ceramic was obtained.

The catalytic property of the resulting porous glass-ceramic was evaluated by conversion of propene into acrolein in a continuous-flow system under atmospheric pressure. A 100 mg of the resultant porous glass-ceramic was put into a reactor of a U-shaped Pyrex tube at 400°C . The reactant mixture consisting of C_3H_6 with air ($\text{C}_3\text{H}_6 / \text{air} = 30 / 70$) was flowed into the reactor at a rate of $10\text{ cm}^3\cdot\text{min}^{-1}$. The products by the reactions were analyzed by gas chromatography.

RESULTS AND DISCUSSION

Figure 1 shows a photograph of (A) as-prepared glass, (B) the dense glass-ceramic obtained after the heat treatment, and (C) the porous glass-ceramic prepared by acid-leaching. No serious cracking or deformation were seen in the specimen even after the acid-leaching. Figure 2 shows powder X-ray diffraction (XRD) patterns of the glass-ceramics before and after the acid leaching. The crystalline phases in the obtained glass-ceramic were identified as $\text{CuTi}_2(\text{PO}_4)_3$ containing cuprous(I) ions and $\text{Cu}_3(\text{PO}_4)_2$, and the dense glass-ceramic was covered by CuO thin layer. The mother glass contains a large amount of Cu^+ ions because it is obtained by quenching the melt at a high temperature.^{5,6} The existence of Cu^+ ions in the glass is essential for formation of $\text{CuTi}_2(\text{PO}_4)_3$ crystal. The dense glass-ceramic was leached with $0.5N\text{-H}_2\text{SO}_4$ at room temperature for 3 days. By this treatment, $\text{Cu}_3(\text{PO}_4)_2$ and CuO phases in the glass-ceramic were dissolved out selectively and, as a result, a microporous material with a skeleton of $\text{CuTi}_2(\text{PO}_4)_3$ crystal was prepared. Figure 3 is a scanning electron micrograph (SEM photo) of a fracture face, showing that numerous pores are distributed throughout the sample. The BET specific surface area was determined as $45\text{ m}^2\cdot\text{g}^{-1}$.

FIGURE 1. Photograph of (A) as-prepared glass, (B) the dense glass-ceramic, (C) the porous glass-ceramic. (numbers on the scale denote centimeters)

The excellent leachability up to approximately 40 volume percent (vol%) and rather small mean pore radius (≈ 9 nm) suggest that the phase separation occurs by spinodal decomposition prior to crystallization.

The porous glass-ceramics showed a catalytic activity in conversion of propene into acrolein and the conversion was improved by heating the resulting porous glass-ceramics in N_2 . The glass-ceramics heated at 700°C showed high conversion (≈ 40 mol%). The improvement may show increase in active sites for the removal of molecules adsorbed on the surface of the glass-ceramics.

It was found that another porous glass-ceramic composed of $\text{CuTi}_4(\text{PO}_4)_6$ skeleton containing cupric(II) ions can be also obtained by changing the acid solution for leaching the dense glass-ceramic from H_2SO_4 to HCl . This glass-ceramic showed a catalytic activity such as conversion of 2-propanol into acetone. Further work is in progress to investigate the some characteristic properties of the glass-ceramics and the formation mechanism of the $\text{CuTi}_4(\text{PO}_4)_6$ crystal, and will be reported in a near future.

FIGURE 2. Powder XRD patterns of glass-ceramics (a) before and (b) after acid leaching. (●) $\text{CuTi}_2(\text{PO}_4)_3$, (▽) $\text{Cu}_3(\text{PO}_4)_2$, and (□) CuO .

FIGURE 3. SEM photo of the resultant porous glass-ceramic.

SUMMARY

Porous $\text{CuTi}_2(\text{PO}_4)_3$ glass-ceramic with catalytic activity has been successfully prepared and its surface area, porosity, and mean pore radius were approximately $45 \text{ m}^2 \cdot \text{g}^{-1}$, 40 vol%, and 9 nm respectively. It may be expected that the preparing process of the porous glass-ceramics in this work have great potential in a field of preparation of novel catalysts.

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