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Al–Cu–Fe quasicrystals for steam reforming of methanol: a new form of copper catalysts

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Abstract

Alloy catalysts were prepared by leaching various structures of Al–Cu–(Fe) alloys (quasicrystal (QC), beta- or theta-phase) in NaOH and Na_2CO_3 aqueous solutions. Comparison of the catalytic properties for steam reforming of methanol (SRM) on different Al–Cu–(Fe) alloy phases (quasicrystalline versus crystalline phase) was made. At high temperatures (e.g., 360 °C), the catalytic activity of the QC catalyst (5% Na_2CO_3-leached) for the SRM was much higher than that of other phase catalysts. No sintering of highly dispersed copper particles on QC catalyst was observed by XRD measurements even after the SRM reaction at 360 °C. We propose that the high catalytic activity and the excellent thermal stability of copper particles on QC catalyst are due to the immiscibility of Fe with Cu and the interaction with QC surface.

Keywords: Quasicrystal; Quasicrystalline catalyst; Al–Cu–Fe alloy; Leaching; Immiscible; Thermal stability; Methanol steam reforming

1. Introduction

Quasicrystal (QC) discovered by Shechtman et al. in 1984 [1] are a novel form of matter, which are neither crystalline nor disordered. QCs exhibit diffraction patterns with sharp diffraction peaks but forbidden symmetry (five-fold) indicating the presence of an unusual atomic structure with a long-range order [2]. Therefore, due to their unique structures, QCs have been anticipated to exhibit unusual physical and/or chemical properties. From the point of view of the catalysis, it is of interest to study the catalytic properties at QCs surfaces. Some fundamental studies of adsorption and/or reactivity of simple molecules such as CO and CH_3OH on QC surfaces such as Al–Pd–Mn QC and Al–Ni–Co QC have been reported [3–5]. However, little work has been performed with respect to the chemical properties and performance of QC alloys as practical catalyst materials. Recently, Tsai and Yoshimura [6,7] reported that an Al–Cu–Fe quasicrystal leached in NaOH aqueous solutions reveals excellent activity for steam reforming of methanol (SRM). Cu catalysts are most promising for the SRM reaction [6–11], but poor thermal stability due to sintering of Cu particles at elevated temperatures has been a major drawback. This has not yet been overcome in NaOH-leached Al–Cu–Fe quasicrystal as well as Cu-based catalysts. In order to develop high activity and thermally stable copper catalysts, correlation between the leaching treatment in alkaline aqueous solution and the catalytic properties of different Al–Cu–(Fe) alloy phases (i.e., QC, beta-, and theta-phase) have been examined. We propose that the Al–Cu–Fe QC catalyst is promising as a new form of copper catalyst.

2. Experimental

Quasicrystalline (QC: $Al_{63}Cu_{25}Fe_{12}$) and crystalline beta-phase (Beta: $Al_{55}Cu_{25}Fe_{20}$) alloys were prepared from pure elements with purities of 99.9 wt.% Al, 99.9 wt.% Cu and 99.9 wt.% Fe, in an electric arc furnace in Ar atmosphere. The prepared alloy samples were annealed at 800 °C for 24 h, and subsequently crushed to particle sizes of interest ($<150\,\mu m$) in a ball mill. The detailed preparation method of the alloy samples are described in previous papers [6,7,12]. Crystalline theta-phase (Theta: Al_2Cu) was supplied by Kawaken Fine Chemical Corp. Surface area of particle was determined by BET analysis. The sample powders were leached in a 5 wt.% alkaline aqueous solution

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(Na_2CO_3 and NaOH), kept in the aqueous solution for 4 h at room temperature, and then filtered out and thoroughly washed with distilled water until no alkali was detected in the filtrate. The concentration of dissolved metal ions in the leaching solution was analyzed by ICP measurement. The crystal structure of each sample was confirmed by X-ray diffraction (Rigaku RINT 2500) using Cu Kα ($\lambda = 1.543$ Å) radiation. The steam reforming of methanol experiments were carried out in a conventional flow reactor at 100 kPa. The sample was pretreated at 240 °C with H_2 for 1 h in a flow reactor. Inlet partial pressure of methanol, water and nitrogen were 35.5, 52.7 and 13.2 kPa, respectively (LHSV of CH_3OH/H_2O mixture: 30 h^{-1}). Here nitrogen was used as dilutent. The products were monitored by an on-line gas chromatograph [6,7]. The catalytic activity for the steam reforming of methanol was evaluated by the H_2 production rate (ml STP min^{-1} g-cat^{-1}). The data in the catalytic activity measurements were recorded when the reaction reached steady state after 30 min.

3. Results and discussion

Fig. 1 shows the XRD patterns of the different Al–Cu–(Fe) alloys leached in the NaOH and Na_2CO_3 aqueous solutions. Each Al–Cu–(Fe) alloy before leaching was identified to consist of mostly a single phase [12–14]. As shown in Fig. 1, it is evident that leaching in the NaOH aq. solution results in more extensive leaching. The theta-phase in the Al_2Cu alloy disappeared completely, while the QC phase still remained in the $Al_{63}Cu_{25}Fe_{12}$ alloy even after the NaOH leaching. In the QC and the theta-phase catalyst, Cu and/or copper oxides came up after leaching in the NaOH aq. solution (Fig. 1(B)). The beta-phase was found to be resistant to caustic leaching. On the other hand, leaching in the Na_2CO_3 aq. solution did not lead to significant changes in XRD patterns of all Al–Cu–(Fe) alloys. No visible peaks from copper or copper oxides were observed after the Na_2CO_3 leaching treatment (Fig. 1(C)).

Table 1 shows the BET surface area (S_{BET}) of the different Al–Cu–(Fe) samples. The surface areas of Al–Cu–(Fe) alloy samples were drastically increased by the leaching in both the NaOH and the Na_2CO_3 aqueous solutions. Amounts of dissolution of Al from Al–Cu–(Fe) alloys into the leaching solutions were analyzed by ICP, and are also shown in Table 1. It should be noted that no Cu and Fe in any leaching solutions were detected by ICP analysis. Leaching in both the alkaline aqueous solutions results in the highly selective removal of aluminum from the alloys. In the case of the NaOH-leached samples, the dissolution of the Al from the alloys depends on the content of the Al in the alloys. On the other hand, the reactivity with Na_2CO_3 aq. for each alloy sample remains at the same level. The surface area of the QC phase catalyst was larger than that of other phase catalysts. From these results, it is found that the leaching activities of alloys are strongly dominated by the kind of alkaline aqueous solution and depend on the content of Al in the alloy and/or the structural stability of the alloy phase.

Fig. 2 shows the rate of hydrogen production as a function of reaction temperatures in the steam reforming of methanol (SRM) over the different Al–Cu–(Fe) alloy catalysts. For comparison, the activity of the QC ($Al_{63}Cu_{25}Fe_{12}$) alloy before the leaching is also presented. The catalytic activities of all the alloy samples were dramatically increased by the

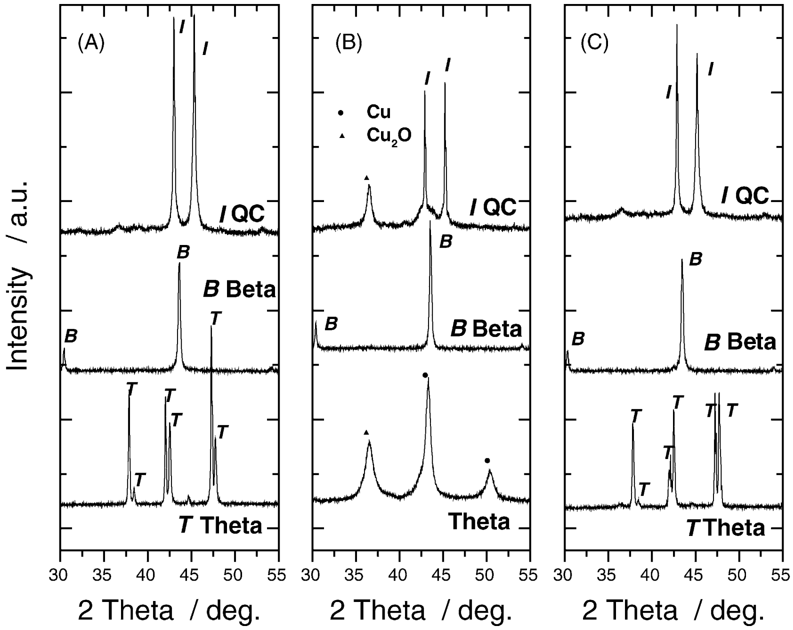

Fig. 1. Powder X-ray diffraction patterns of different Al–Cu–(Fe) alloys: (A) before leaching, (B) after leaching with 5% NaOH aq. and (C) after leaching with 5% Na_2CO_3 aq.

Table 1
Composition, phase, surface area and Al% extracted of different Al–Cu–(Fe) alloy samples

Catalyst (at.%)	Structure (phase)	Leaching[a]	S_{BET} (m^2 g-cat^{-1})		ICP analysis[b] (Al%)
			BR[c]	AR[d]	
$Al_{63}Cu_{25}Fe_{12}$	QC[e]	–	1.3	1.1	–
$Al_{63}Cu_{25}Fe_{12}$	QC[e]	NaOH	25.3	19.5	58.0
$Al_{63}Cu_{25}Fe_{12}$	QC[e]	Na_2CO_3	31.5	23.9	13.1
$Al_{55}Cu_{25}Fe_{20}$	Beta	NaOH	10.1	6.8	27.0
$Al_{55}Cu_{25}Fe_{20}$	Beta	Na_2CO_3	10.0	6.2	8.9
$Al_{67}Cu_{33}$	Theta	NaOH	20.1	5.1	91.8
$Al_{67}Cu_{33}$	Theta	Na_2CO_3	3.3	2.6	8.0

[a] Leached with 5 wt.% alkaline aqueous solutions for 4 h at rt.

[b] Amount of extracted Al (%) from Al–Cu–(Fe) alloys analyzed by ICP.

[c] Before SRM reaction.

[d] After SRM reaction at 360 °C.

[e] Icosahedral phase of quasicrystal.

leaching treatment with both the NaOH and the Na_2CO_3 aqueous solutions. It should be noted that the catalytic activities of all the alloy powders before the leaching were very low for the SRM reaction. This is due to low surface area and aluminum oxide cover of the alloy powders before leaching [15–17]. Therefore, the leaching treatment with NaOH or Na_2CO_3 aqueous solution is found to be an efficient method for activating the Al alloys by increase of the surface area and the removal of the aluminum oxide passivation layer.

Although the NaOH-leached QC and theta catalysts show high activities at low temperatures, degradation of activities at higher temperature are observed, as shown in Fig. 2(A). It should be noted that the catalytic activity of the NaOH-leached QC catalyst was almost comparable to that of the industrial Cu-based catalyst [6,7]. After the reaction at 360 °C, decrease in surface area and sharpening of the diffraction peaks of Cu in these samples were observed (Table 1, Fig. 3(A)). These results clearly indicate

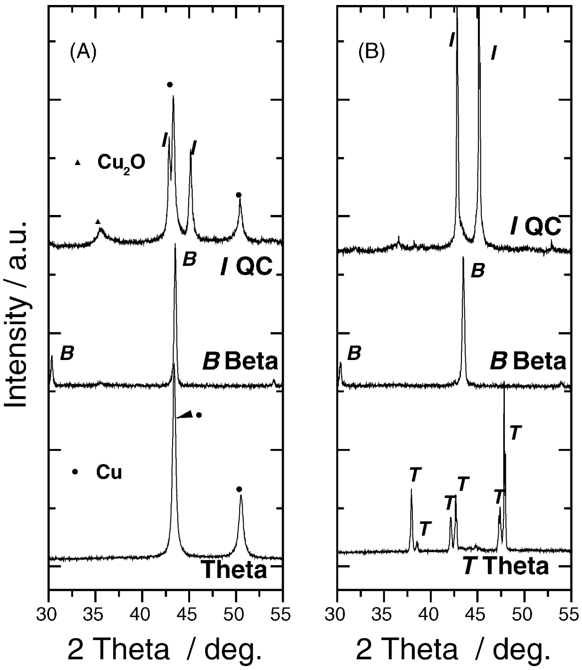

Fig. 3. Powder X-ray diffraction patterns of different Al–Cu–(Fe) alloy catalysts after SRM reaction at 360 °C: (A) 5% NaOH-leached alloy catalysts and (B) 5% Na_2CO_3-leached alloy catalysts.

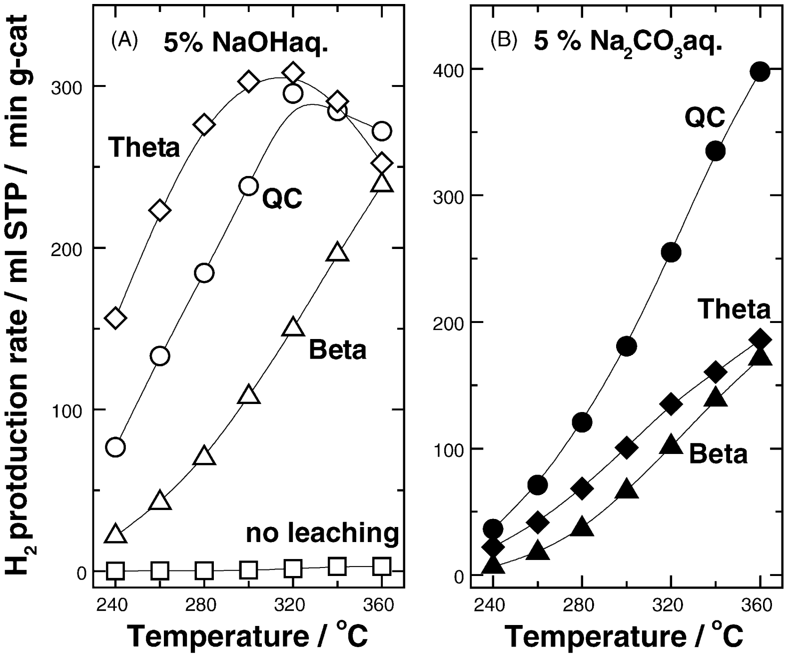

Fig. 2. The rate of H_2 production versus reaction temperatures in the steam reforming of methanol for QC, beta- and theta-phase alloys: (A) after leaching with 5% NaOH aq and (B) after leaching with 5% Na_2CO_3 aq. The results of the no leaching QC is also shown as a reference (☐).

that a sintering of copper particles generated on the surfaces. On the other hand, one should note that activities of the Na_2CO_3-leached catalysts keep increasing linearly till 360 °C (Fig. 2(B)). Especially, the activity of the Na_2CO_3-leached QC catalyst at 360 °C is much higher than that of other catalysts. Interestingly, as shown in Fig. 3(B), no sintering of Cu particles but significant decrease in surface area on the Na_2CO_3-leached QC catalyst was observed even after SRM reaction at 360 °C (Table 1). This result indicates that the highly dispersed copper particles over the Na_2CO_3-leached QC catalyst are very stable. This is an evidence that the Na_2CO_3-leached QC catalyst have potential to be thermally stable copper catalyst when it is treated with an adequate leaching condition.

It is well known that the sintering of copper particles on the conventional Cu catalysts readily proceeds even below 300 °C [8]. From the results of the surface area after SRM reaction at 360 °C (Table 1), thermal stability of copper on the NaOH-leached QC catalyst is found to be much higher than that on the NaOH-leached theta catalyst. This result suggests that Fe may play an important role in thermal stability of the dispersed copper particles on the QC catalyst. Fe is immiscible with Cu, i.e., they neither form compounds nor mutually dissolves in the solid state [6]. In the leaching process, Al would dissolve selectively and the excess Cu and Fe would be easily segregated. Therefore, sintering of Cu particle on the QC catalyst surface would be inhibited by the presence of Fe and/or Fe oxides. Although the sintering of copper particles on all the Na_2CO_3-leached catalysts was hardly observed even after the SRM reaction (Fig. 3(B)), the catalytic activity of the Na_2CO_3-leached QC catalyst was much higher than that of the other catalysts (Fig. 2). The high thermal stability of the dispersed copper particles on the QC catalyst also might be attributed to the chemical interaction between Cu particles and the leached QC surface which acts as a support [18]. Recently, Fournée et al. [19] studied deposition of Pd on pseudo-10-fold surface of a ξ-AlPdMn approximant crystal (like QC) by using STM/STS and photoemission spectroscopy. Deposited Pd atoms formed clusters with a size about 3 nm, reveals high thermal stability that Pd clusters persist even after a short annealing to 920 K [19]. This result indicates that strong interaction between the deposited metal nanoparticles and the approximant phase support stabilizes the clusters at high temperature. High thermal stability would be expected on QC surfaces.

There are several advantages of QC as catalyst materials: (1) thermodynamically stable phase, (2) ease of production of QC, (3) brittle nature of the QC and (4) low cost of the raw materials, i.e., Al, Cu and Fe [6,7]. Even if a conventional leaching treatment is performed on the Al–Cu–Fe QC alloy, we could prepare novel skeletal metal catalysts which are much different from the conventional Raney-type catalysts, by having highly dispersed copper particles and with excellent thermal stability. The QC alloys exhibit quasi-periodic structure and include the catalytic active metals (e.g., Cu, Co, Pd) and/or the immiscible metal system (e.g., Cu–Fe, Cu–Co) [20]. Therefore, the Al–Cu–Fe QC catalyst and the other Al-alloy QC systems (e.g., Al–Cu-Co, Al–Pd–Mn, Al–Ni–Co, etc.) deserve further attention to expand into more detailed studies including the catalytic properties and the interaction between dispersed metal particles and QC supports.

In conclusion, the catalytic activities of the QC catalysts for the steam reforming of methanol at high temperature (e.g., 360 °C) were higher than those of the beta- and the theta-phase catalysts. The copper particles on the Na_2CO_3-leached QC catalyst revealed the excellent thermal stability. These properties were ascribed to the immiscibility of Fe with Cu and the interaction with QC surface.

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