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A novel catalyst fabricated from Al–Cu–Fe quasicrystal for steam reforming of methanol

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Abstract

The optimum preparation condition of Al–Cu–Fe quasicrystalline (QC) catalyst with excellent catalytic performance for steam reforming of methanol (SRM) has been investigated. The QC alloy is superior to the other crystalline Al–Cu–(Fe) alloys (i.e., beta and theta phase) as a catalyst material because of the brittle nature of QC. The wet milling process (in ethanol) for the QC powders is much better than the dry milling process to obtain fine particles with high surface area. The QC powder prepared by the wet process followed by leaching in Na_2CO_3 aq. at 323 K exhibited the highest catalytic performance (activity and stability) in the present study. From these findings, it is clear that the QC catalyst with the excellent catalytic performance could be obtained by controlling the initial grain size of the QC powder and the leaching temperature.

Keywords: Quasicrystal; Al–Cu–Fe alloy; Wet milling process; Leaching; Na_2CO_3; Methanol steam reforming

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1. Introduction

Quasicrystals (QC) have well-ordered structure without periodicity, and exhibit non-crystallographic rotational symmetries (i.e. 5- and 10-fold symmetries). Since they were first reported in 1984 by Shechtman et al. [1], over 100 binary, ternary and quaternary alloy systems have been found to contain quasicrystalline phases [2]. Intensive efforts have been dedicated to the studies of alloy synthesis, structure and physical properties over the last two decades. No longer mere academic pursuits, recent works have focused on trying to exploit the novel properties of these materials for commercial applications. The most promising application is catalysis. Due to brittle nature [3,4], quasicrystalline powders of the thermodynamically stable materials are made readily by cast and crush methods and, at least in the case of Al–Cu–Fe QC, are available at low cost.

Some fundamental studies of adsorption and/or reactivity of simple molecules like CO and CH_3OH on the surfaces of QCs such as Al–Pd–Mn QC and Al–Ni–Co QC were reported [5–7]. However, none had been performed with respect to the catalytic performance for QC alloys as practical catalyst materials. Recently, Tsai and Yoshimura [8,9] reported that an Al–Cu–Fe QC leached in NaOH aqueous solutions reveals excellent activity for the steam reforming of methanol (SRM). The Cu catalysts are most promising for the SRM reaction [8–13], but poor thermal stability due to sintering of Cu particles at elevated temperatures has been a major drawback. This was not improved in NaOH-leached Al–Cu–Fe QC as well as Cu-based catalysts. More recently, we reported that the sintering of copper particles on the Na_2CO_3-leached Al–Cu–Fe QC has been significantly suppressed even after the SRM reaction at 633 K [14]. The catalytic activity for the SRM reaction at high temperature (e.g., 633 K) is much superior to that of other Al–Cu–(Fe) crystalline catalysts [14]. However, the catalytic activity at lower temperatures (e.g., 513 K) is not as high as those of the normal Cu-based catalysts. The activity is attributed to the copper particles at the surfaces of QC grains which were generated by leaching treatment. The leaching

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depth of the Na_2CO_3-leached QC was around ∼200 nm. Therefore, the most copper in the core of the QC did not contributed to the activity. The present work is aiming at improving catalytic activity at low temperature region by controlling initial grain size and leaching parameter for the Al–Cu–Fe QC catalyst. In this work, we show that the Na_2CO_3-leached QC catalyst is promising as a new form of copper catalyst.

2. Experimental

Quasicrystalline (QC: $Al_{63}Cu_{25}Fe_{12}$ (at.%)) and other Al–Cu–(Fe) alloys were prepared from pure elements with purities of 99.9 wt.% Al, 99.9 wt.% Cu and 99.9 wt.% Fe, in an arc furnace in Ar atmosphere. The alloy samples annealed for 24 h at 1073 K for the QC and the beta, and at 893 K for the theta, and subsequently were crushed into particle sizes (<150 μm) of interest in a ballmill with dry or wet (in ethanol) process for 5 min. The sample powders were leached in 5 wt.% Na_2CO_3 aqueous solution for 4 h at various temperatures, and then they were filtered out and thoroughly washed with distilled water until no alkali was detected in the filtrate. The concentration of dissolved metallic ions into the leaching solution was analyzed by ICP measurement. The specific surface area of the particles was determined by BET surface area measurement. The copper surface area and dispersion were determined by the H_2-TPR measurements of Cu oxidized by N_2O [15] at a heating rate of 2 °C/min in a 30 ml/min flow of 5% H_2/Ar. The bulk structure of each sample was confirmed by X-ray diffraction (Rigaku RINT 2500) using Cu Kα (λ = 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 513 K 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 = 2/3 mol ratio mixture: 65 h^{-1}). Here nitrogen was used as diluent. The products were monitored by an on-line gas chromatograph [8,9]. 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. The surface of the leached QC powders was observed by a scanning electron microscopy (LEO 982).

Table 1
Composition, phase and surface area of different Al–Cu–(Fe) alloys crushed to particle sizes in ballmill with dry or wet process

Alloy (at.%)	Structure (phase)	BET surface area (m^2/g_{cat})	
		Dry milling process[a]	Wet milling process[b]
$Al_{63}Cu_{25}Fe_{12}$	QC[c]	0.6	2.5
$Al_{55}Cu_{25}Fe_{20}$	Beta	0.8	0.8
$Al_{67}Cu_{33}$	Theta	0.4	0.7

[a] 5 g samples crushed at rt for 5 min.
[b] 5 g samples crushed in ethanol 10 g at rt for 5 min.
[c] Quasicrystal.

3. Results and discussion

3.1. Effect of milling process of Al–Cu–(Fe) alloy powders on surface area

Table 1 shows the results of BET surface area of various Al–Cu–(Fe) alloys crushed into fine powder (<150 μm) in a ballmill with dry or wet (in ethanol) process. In the dry milling process, no significant difference in the surface area for all the Al–Cu–(Fe) alloys was observed. In the wet milling process, only the surface area of the beta alloy did not change. However, drastic increase in the surface area was only observed for QC, which is much higher than those of other alloys. It is suggested that the wet milling process is especially superior to the dry process for obtaining the finer powder with high surface area. On top of this, the brittle nature of QC is also playing a crucial role. Also, the drastic increase in surface area of QC by wet milling process might be attributed to the unusual wetting property of Al–Cu–Fe quasicrystal. Dubois [16] reported that the quasicrystalline phase exhibits a significantly lower wetting behavior in polar liquids than those of crystalline phases in Al–Cu–Fe system. There is a possibility that the low wetting in polar liquids of Al–Cu–Fe QC powder contributes to be readily crushed by wet milling process.

Table 2
Properties of Na_2CO_3-leached Al–Cu–Fe QC catalysts at various leaching temperatures

Catalyst	ICP[a] (Al%)	S_{BET} (m^2 g_{cat}^{-1})	S_{Cu}[b] (m_{Cu}^2 g_{cat}^{-1})	Dispersion (%)	H_2 production rate[c] (ml min^{-1} g_{cat}^{-1})	TOF[c] (10^{-1} s^{-1})
Before leaching[d]	–	0.6	–	–	–	–
273 K-leaching[d]	5.7	10	4.2	32.9	48	3.7
298 K-leaching[d]	13.1	32	9.5	25.6	173	5.8
323 K-leaching[d]	13.8	57	15.2	25.3	262	5.4
323 K-leaching[e]	–	89	45.2	44.2	677	4.8
Raney Cu[f]		32	30.0	5.8	181	1.9

[a] Amount of extracted Al (%) from the QC powders by the dry milling and the leaching treatment.
[b] 1.41×10^{19} copper atoms per m^2.
[c] Reaction temperature at 573 K.
[d] The QC powder was prepared by the dry milling process.
[e] The QC powder was prepared by the wet milling process.
[f] Commercial Cu catalyst (Kawaken fine Chemical Co.).

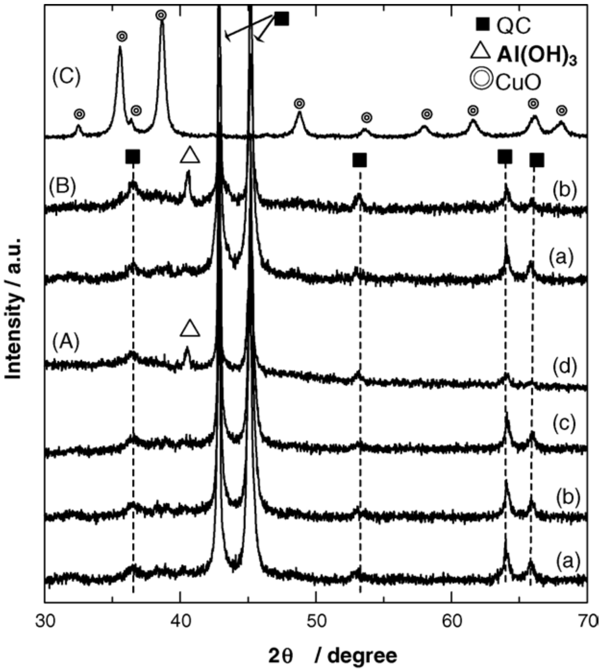

Fig. 1. Powder X-ray diffraction patterns of the Al–Cu–Fe QC leached in Na_2CO_3 at various leaching temperatures. (A) The Al–Cu–Fe QC powders crushed with dry process followed by leaching at various temperatures: (A-a) before leaching, (A-b) leaching at 273 K, (A-c) leaching at 298 K and (A-d) leaching at 323 K. (B) The Al–Cu–Fe QC powders crushed with wet process followed by leaching at 323 K: (B-a) before leaching and (B-b) leaching at 323 K. (C) Commercial Raney Cu catalyst.

3.2. *Effect of leaching temperature in the Na_2CO_3 aq. on surface area and catalytic activity of QC catalyst*

In order to obtain the high performance QC catalyst, we examined the effect of the leaching temperature (as a leaching parameter) on the surface area and the catalytic activity of the QC powder. Table 2 shows the physical properties for the QC powders leached in 5 wt.% Na_2CO_3 aqueous solution at various temperatures. The data of Raney copper catalyst are also shown for comparison. The BET and copper surface areas of the QC powders prepared by dry milling process were drastically increased due the leaching in the Na_2CO_3 aq. even at 273 K. The BET and copper surface areas of the QC powders remarkably increased with increasing the leaching temperature up to 323 °C. The leaching in the Na_2CO_3 aq. results highly selective removal of aluminum from Al–Cu–Fe QC alloys [14]. According to the ICP analysis of the leaching solutions, dissolution of Al from the QC powders led the increase in surface area of the QC powders (S_{BET} and S_{Cu} in Table 2). It is indicated that the amount of aluminum leached for the QC alloy increases with increasing the leaching temperature. From these results, it is clear that the leaching of the QC powders with Na_2CO_3 aq. at 323 K efficiently leads both high BET and copper surface area for the QC catalyst.

Fig. 1 shows the XRD patterns for the QC powders leached in Na_2CO_3 aq. at various leaching temperatures and Raney copper catalyst. Before leaching, the QC powders crushed both by dry and by wet milling process was identified to consist of a mostly single QC phase (Fig. 1(A-a) and (B-a)) [17,18]. As shown in Fig. 1(A) and (B), leaching in the Na_2CO_3 aq. did not lead to significant changes in XRD patterns of the QC catalysts. This means that QC phase of all the QC samples in this study remain in the core of the grains. Only the diffraction peak from $Al(OH)_3$ comes up after leaching at 323 K (Fig. 1(A-d) and (B-b)). The $Al(OH)_3$ formed on the QC surface during the leaching treatment: $NaAlO_2 + 2H_2O \rightarrow Al(OH)_3 + NaOH$. As shown in Fig. 1(C), only peaks from CuO were observed at Raney Cu catalyst. In contrast, no visible peaks from copper or copper oxides were observed at leached QC powder (Fig. 1(A) and (B)), even then the copper surface area were larger than Raney Cu (see Table 2).

Fig. 2 shows the SEM images of Raney copper catalyst and the QC catalyst at same magnification. Surface of Raney copper catalyst reveals skeletal structure aggregating from particles of Cu and/or CuO (Fig. 2(A)). On the other hand, the surface of the QC catalyst consists of porous Al oxides, which was determined by the EDX measurement [19], and the visible copper oxides particles was hardly observed (Fig. 2(B)). In addition, the copper metal dispersion in the QC catalyst was much higher than that of

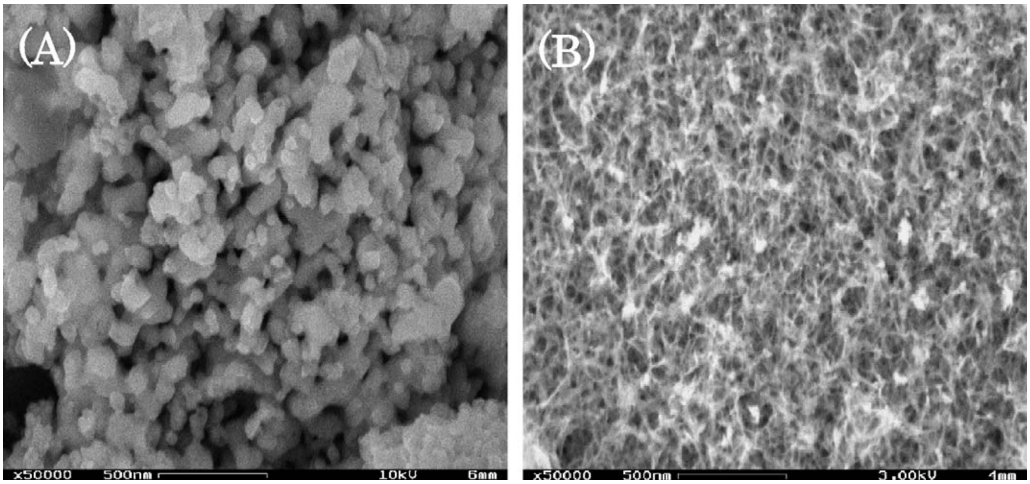

Fig. 2. SEM images of (A) Raney Cu and (B) QC catalyst prepared by the leaching with Na_2CO_3 aq. at 298 K.

Raney Cu catalyst (Table 2). From these results, it is concluded that highly dispersed copper particles, which cannot be observed by XRD, exist in the porous Al oxides on the QC surface. The formation of porous Al oxides during the leaching treatment leads to highly dispersed copper particles on the QC surface, and it is expected to contribute the increase in both the BET and copper surface area of QC catalyst.

Fig. 3 shows the rate of hydrogen production for the SRM reaction as a function of surface area of copper particles over the QC catalysts prepared at various leaching conditions. As shown in Fig. 3, the rate of H_2 production increased with increasing the surface area of copper particles and it becomes clear at higher reaction temperatures. This result indicates that the surface area of copper is a key factor for enhancing the activity is prepared by controlling the milling process (initial gain size of the QC powders) and the leaching temperature. From these findings, we combined the leaching in the Na_2CO_3 aq. at 323 K and the wet milling process for the QC powder. Consequently, we could obtain the QC catalyst with the highest copper surface area and dispersion (i.e., $45.2\,m^2_{Cu}\,g^{-1}_{cat}$, $D = 0.442$) at this leaching condition (see Table 2).

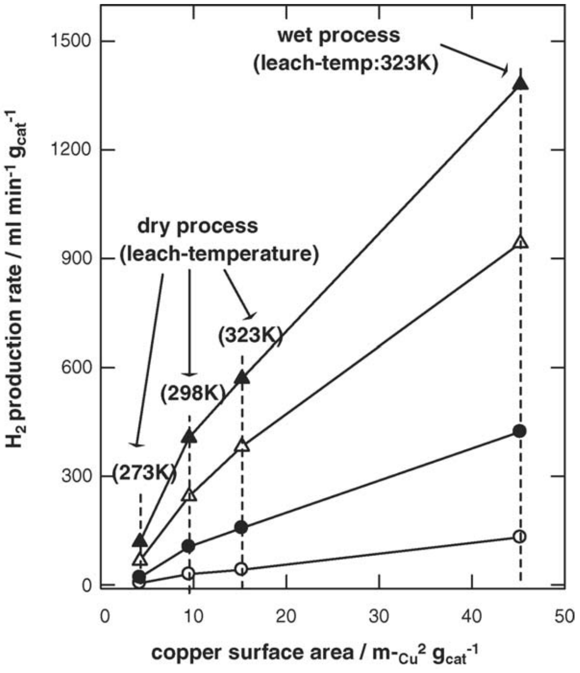

Fig. 3. The rate of H_2 production for the steam reforming of methanol vs. the copper surface area of the Al–Cu–Fe QC catalysts crushed by wet or dry process followed by leaching at various temperatures: the reaction temperature at 513 K (○) at 553 K (●), at 593 K (△) and at 633 K (▲).

3.3. Catalytic performance of the optimum Na_2CO_3-leached QC catalyst for SRM

Good catalytic performances of the QC catalyst treated with optimal condition have been obtained and were compared with those of commercial Cu catalyst (i.e., Raney Cu) tested in the same conditions for the SRM reaction. Fig. 4(A) shows the rate of hydrogen production for SRM as a function of reaction temperature for QC catalysts prepared with dry or with wet process followed by leaching at 323 K. At lower temperature range (e.g., below 533 K), the activity of the QC catalyst treated by dry milling process was lower than that of Raney Cu while the activity of the QC catalyst with wet milling process was almost comparable to Raney Cu. Above 573 K, both the activities of the QC catalysts were much higher than those of Raney Cu. Fig. 4(B) shows the XRD patterns of the QC catalysts and Raney Cu catalyst after the SRM reaction. After the reaction at 633 K, the sharpening of the diffraction peaks of

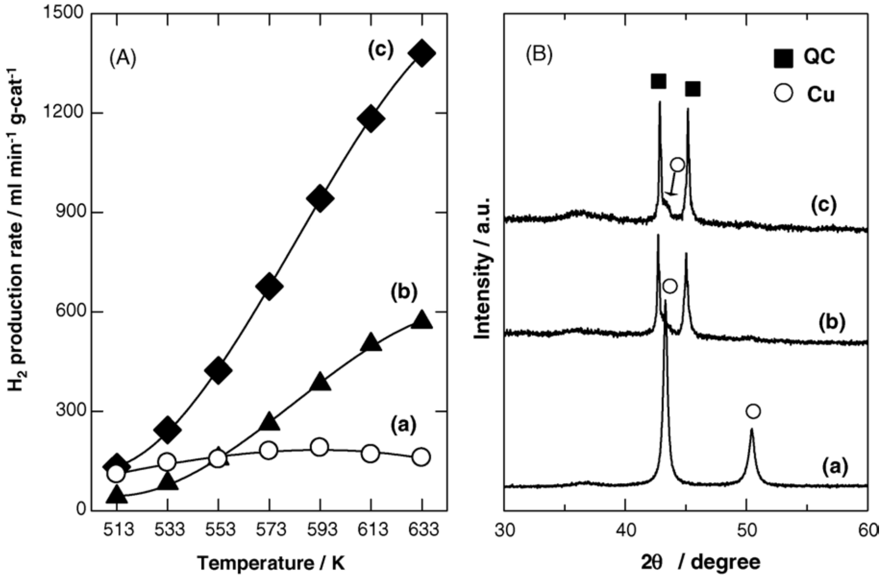

Fig. 4. (A) The rate of H_2 production for the steam reforming of methanol vs. the reaction temperatures for the Al–Cu–Fe QC catalysts leaching in the Na_2CO_3 aq. and (B) Powder X-ray diffraction patterns after the SRM reaction at 633 K: (a) Raney Cu (commercial Cu-based catalyst), (b) QC catalyst crushed by dry milling process followed by leaching at 323 K, (c) QC catalyst crushed by wet milling process followed by leaching at 323 K.

Cu was observed in the XRD (Fig. 4(B-a)). This is the evidence that the sintering of copper particles occurred at the surfaces, which is responsible for the degradation of activity at high temperature. The sintering of copper particles on the conventional Cu catalysts readily proceeds even below 527 K [10]. In contrast, only a very broad diffraction peak of Cu was observed for the QC catalyst even after reaction as shown in Fig. 4(B-b) and (B-c), indicating that Cu particles are kept definitely in small sizes. Consequently, the catalytic activity for the QC catalyst increased linearly with temperature up to 633 K. In other words, the highly dispersed copper particles over the Na_2CO_3-leached QC catalyst are remarkably stable.

In the present study, we have found that the catalytic performance (i.e., activity and stability) of the QC catalysts is much higher than that of Raney copper catalyst. One possible explanation is that Fe plays an important role in thermal stability of the highly dispersed copper particles. Fe is immiscible with Cu, i.e. they neither form compound nor mutually dissolve in the solid state. During leaching treatment, Al would dissolve readily, 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. Also, we cannot exclude the possibility that the high catalytic performance of the dispersed copper particles and QC catalyst is attributed to the chemical interaction between copper particles and QC surface which acts as a support. The TOF values of the QC catalysts are higher than that of Raney copper catalyst (Table 2). Moreover, the catalytic activity and stability of the QC catalyst were much higher than those of other phase Al–Cu–(Fe) alloy catalysts (e.g., beta- and theta-phase) [14]. More detailed interaction between dispersed Cu particles and QC surface is not clear at this stage, but here we show that the Na_2CO_3-leached QC catalyst have possibility of being copper catalyst stable at high temperature. The study of high thermal stability of Cu particles is in progress.

4. Conclusion

We have developed a QC catalyst with high catalytic performances capable with excellent activity and thermal stability for the SRM reaction by incorporating the wet milling process (in ethanol) and leaching in Na_2CO_3 aq. at 323 K. The brittle nature of QC is favorite to obtain fine grain powder with high surface area. Increase in the leaching temperature of the Na_2CO_3 aq. up to 323 K promoted efficiently the surface area. Based on these findings, we reached the optimum preparation condition of the QC catalyst.

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