

Spinel CuFe₂O₄: a precursor for copper catalyst with high thermal stability and activity

Satoshi Kameoka^{a,*}, Toyokazu Tanabe^b and An Pang Tsai^{a,c}

^aInstitute of Multidisciplinary Research for Advanced Materials, Tohoku University, 2-1-1 Katahira, Aoba-ku, Sendai, 980-8577 Japan

^bGraduated School of Materials Science and Technology, Tokyo University of Science, 2641 Yamazaki, Noda, Chiba, 278-0022 Japan

^cNational Institute for Materials Science, 1-2-1 Sengen, Tsukuba, Ibaraki, 305-0047 Japan

Received 9 July 2004; accepted 15 November 2004

Spinel CuFe₂O₄ has been studied as a precursor for copper catalyst. The spinel CuFe₂O₄ was effectively formed on the SiO₂ by calcination in air at 800 °C with the atomic ratio of Fe/Cu = 2. The spinel CuFe₂O₄ on the SiO₂ was reduced to fine dispersion of Cu and Fe₃O₄ particles by the H₂ reduction at 240 °C. After H₂ reduction at 600 °C, sintering of Cu particles over the CuFe₂O₄/SiO₂ (Fe/Cu = 2) was inhibited significantly, while fatal sintering of Cu particles over the Cu/SiO₂ (Fe/Cu = 0) occurred. The CuFe₂O₄/SiO₂ catalyst exhibited much higher activity and thermal stability for steam reforming of methanol (SRM), compared with the Cu/SiO₂ catalyst. The spinel CuFe₂O₄ on the SiO₂ can be regenerated after an intentional sintering treatment by calcination in air at 800 °C where the activity is also restored completely. Based on these findings, we propose that spinel CuFe₂O₄ is an effective precursor for a high performance copper catalyst in which the immiscible interaction between Cu and Fe (or Fe oxide) plays an important role in the stabilization of Cu particles.

KEY WORDS: CuFe₂O₄; spinel; immiscible; thermal stability; regeneration; methanol steam reforming.

1. Introduction

Copper-based catalysts are extensively studied due to their good catalytic performance in many reactions such as methanol synthesis and water gas shift reactions [1,2]. It is also well known that copper-based catalysts reveal high selectivity for steam reforming of methanol (SRM: CH₃OH + H₂O → 3H₂ + CO₂), i.e. Cu catalysts are most promising for the SRM reaction [3–7]. However, difficulty of homogeneous dispersion of Cu particles on supports and poor thermal stability have been major drawbacks [3, 6]. To overcome these problems, several preparation methods for copper catalysts have been challenged [3–9]. Copper-containing spinel oxides possessing high performance in steam reforming of methanol [7], water gas shift reaction [8], CO oxidation [9] and removal of NO_x [10] have been reported. Matsukata *et al.* [7] reported that CuAl₂O₄ catalysts prepared by the coprecipitation method showed a high activity for steam reforming of methanol due to the formation of highly dispersed copper induced by reduction of CuAl₂O₄. Tanaka *et al.* [8] reported that Cu/MnO catalysts prepared via reduction of CuMn₂O₄ spinel oxide showed high activity in water gas shift reaction. In the previous literature, it has been commonly indicated that active sites responsible for reactions are copper species generated from Cu-containing spinel oxide (e.g.,

CuM₂O₄ type spinel). However, regeneration process of the copper species generated from the Cu-containing spinel oxide after the reduction and/or oxidation treatments have not been sufficiently investigated.

From the point of view of metallurgy, the interaction of second constituent metal (M) with copper involved in the CuM₂O₄ type spinel oxide seems to be a key factor for the formation and the catalytic redox process. However, little detailed work with respect to preparation of catalyst has been performed from this viewpoint. Recently, Tsai and Yoshimura [11] reported that an Al–Cu–Fe quasicrystal leached in NaOH aqueous solutions reveals excellent activity for steam reforming of methanol. Leaching leads to selective dissolution of Al, and consequently Cu and Fe segregate at the surface of quasicrystal. It was then claimed that the high catalytic activity was due to the immiscibility of Fe with Cu [11]. Actually, according to the Cu–Fe equilibrium phase diagram, Cu and Fe are neither form compounds nor mutually dissolve in the solid state [12]. Very recently, we have observed that calcination in air at 600 °C for the leaching Al–Cu–Fe quasicrystal furthermore improved the stability and activity [13]. We suppose that spinel CuFe₂O₄ might be important in this improvement. Therefore, we study catalytic activity of an oxide, spinel CuFe₂O₄, and the role of immiscibility between Cu and Fe in the oxide.

In this study, the catalytic behavior of spinel CuFe₂O₄ on an SiO₂ support for the SRM reaction has been examined. Validity of spinel CuFe₂O₄ used as a

*To whom correspondence should be addressed.

E-mail: kameoka@tagen.tohoku.ac.jp

precursor compound for a high catalytic performance copper catalyst, i.e. high catalytic activity and thermal stability, is discussed.

2. Experimental

An SiO₂ support (Japan Aerosil Co. Ltd., SIO-50) had been precalcined in air at 900 °C (BET surface area: 50 m²/g) to avoid structural change during the consequent high-temperature calcinations. Cu–Fe/SiO₂ catalysts were prepared by the impregnated method (incipient wetness) using Cu(NO₃)₂ (aq) and/or Fe(NO₃)₃ (aq) (atomic ratio of Fe/Cu = 0.5, 1, 2, 3; the weight loading of Cu was 10 wt%), and dried in air at 110 °C overnight. For comparison, 10 wt% Cu/SiO₂ (Fe/Cu = 0) and 10 wt% Fe/SiO₂ (Fe/Cu = ∞) were also prepared with the same method. All impregnated catalysts were calcined in air at 800 °C for 5 h. List of the samples is given in table 1.

The steam reforming of methanol (SRM) experiments were carried out in a conventional flow reactor at 100 kPa. Inlet partial pressure of methanol, water and nitrogen were 35.5, 52.7 and 13.2 kPa, respectively (LHSV of CH₃OH/H₂O mixture: 30 h⁻¹). Here nitrogen was used as diluent. All the sample was pretreated at 240 °C with H₂ for 1 h in a flow reactor before SRM. The products were monitored by an on-line gas chromatograph [11]. The catalytic activity for the steam reforming of methanol was evaluated by the H₂ 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 phase identification of each sample was performed by X-ray diffraction (Rigaku RINT 2500) using Cu Kα (λ = 1.543 Å) radiation. The crystallite sizes of Cu were estimated from the XRD peak widths using the scherrer equation. The N₂O titration measurements were carried out with a conventional method as described previous report [14]. The H₂-TPR measurements were carried out using 50 mg of the catalyst from room

temperature to 600 °C at a heating rate of 2 °C/min in a 30 mL/min flow of 5% H₂/Ar.

3. Results and discussion

Figure 1 shows the XRD patterns of Cu–Fe/SiO₂ catalysts with various Fe/Cu atomic ratio after calcination in air at 800 °C for 5 h. As shown in figure 1, the peaks responsible for spinel CuFe₂O₄ were observed for the Cu–Fe/SiO₂ catalysts (Fe/Cu = 0.5, 1, 2, 3) [15]. Additionally, the CuO was observed in the samples of Fe/Cu < 2, while the Fe₂O₃ was observed in the samples of Fe/Cu > 2. CuO and Fe₂O₃ were solely observed on Cu/SiO₂ (Fe/Cu = 0) and Fe/SiO₂ (Fe/Cu = ∞) catalyst, respectively. The list and the crystalline phases of each catalyst sample are summarized in table 1. From these results, it was found that the optimal value of the atomic ratio (Fe/Cu) for the formation of CuFe₂O₄ is consistent with the stoichiometry of the CuFe₂O₄ compound (Fe/Cu = 2). It should be noted that the spinel CuFe₂O₄ was formed from the mixture of CuO and Fe₂O₃ under high temperature, e.g., 700 °C [10,16].

Figure 2 shows the dependence of the fraction of Cu, i.e., Cu_{atom}/(Cu_{atom} + Fe_{atom}), on the rate of H₂ production in the steam reforming of methanol (SRM) over the different catalysts after H₂ reduction at 240 °C. For all Cu–Fe/SiO₂ catalyst, the rate of H₂ production increases with increasing reaction temperature (240–360 °C). As shown in figure 2, the rate of H₂ production varies with the fraction of Cu and it becomes clear at higher temperatures. Maxima of activity were observed around the stoichiometry of CuFe₂O₄ compound (Cu_{atom}/(Cu_{atom} + Fe_{atom}) = 0.33; Fe/Cu = 2), whereas the catalytic activities of the Cu/SiO₂ and the Fe/SiO₂ catalysts are very low even at 360 °C. This result indicates that the catalytic activity is significantly improved by coexistence of copper and iron, and the formation of CuFe₂O₄ compound is a key factor dominating catalytic activity.

Figure 3 shows the rate of H₂ production as a function of reaction temperature in the SRM over CuFe₂O₄/SiO₂ (Fe/Cu = 2) and Cu/SiO₂ catalysts after H₂ reduction at 600 °C. The activity of the CuFe₂O₄/SiO₂ catalyst decreased (process [I]) after H₂ reduction at 600 °C. The activity could not be detected even at 360 °C for the Cu/SiO₂ catalyst (figure 3(d)). Surprisingly, the activity could be recovered completely after the retreatment at 800 °C in air for the CuFe₂O₄/SiO₂ catalyst (process [III]) but entirely not for the Cu/SiO₂ catalyst. Obviously, the re-oxidation treatment brings about the reversible change in activity. The deactivation and the possible regeneration in the catalytic activities of the CuFe₂O₄/SiO₂ catalyst are correlated well with redox behaviors of the spinel CuFe₂O₄, which will describe below.

To understand the redox behavior of spinel CuFe₂O₄, we performed characterization on catalysts treated in

Table 1
List of each catalyst sample and initial crystalline phases

Catalyst Fe/Cu atomic ratio	Atomic fraction of Cu (Cu _{atom} /(Cu _{atom} + Fe _{atom}))	Observed crystalline ^a (phase)
0 ^b (10 wt% Cu/SiO ₂)	1	CuO
0.5 ^b	0.67	CuO, CuFe ₂ O ₄
1 ^b	0.50	CuO, CuFe ₂ O ₄
2 ^b	0.33	CuFe ₂ O ₄
3 ^b	0.25	CuFe ₂ O ₄ , Fe ₂ O ₃
∞ ^c (10 wt% Fe/SiO ₂)	0	Fe ₂ O ₃

^aXRD measurement for the catalyst sample after air calcination at 800 °C for 5 h.

^bConstant as 10 wt% Cu loading.

^c10 wt% Fe loading alone.

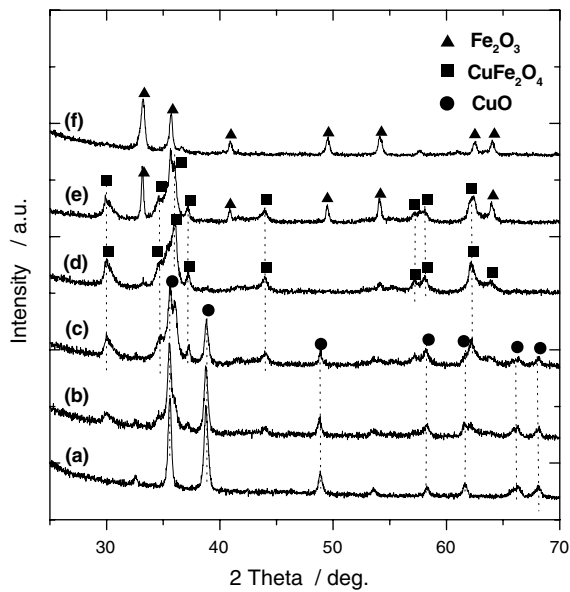


Figure 1. Powder X-ray diffraction patterns for Cu-Fe/SiO₂ catalysts with different Fe/Cu atomic ratio after air calcination at 800 °C for 5 h. (a) Fe/Cu = 0 (Fe = 0; Cu: 10 wt%), (b) Fe/Cu = 0.5, (c) Fe/Cu = 1, (d) Fe/Cu = 2, (e) Fe/Cu = 3 and (f) Fe/Cu = ∞ (Cu = 0; Fe: 10 wt%).

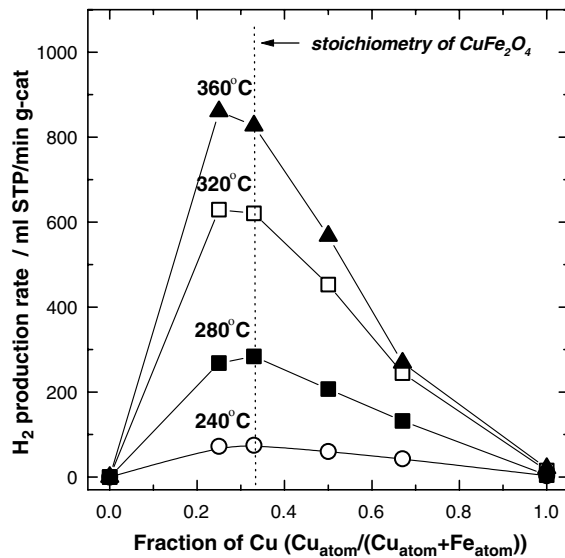


Figure 2. The rate of H₂ production versus fraction of Cu atom ($\text{Cu}_{\text{atom}}/(\text{Cu}_{\text{atom}} + \text{Fe}_{\text{atom}})$) in the steam reforming of methanol for catalysts given in figure 1. Reaction at (○) 240 °C, (■) 280 °C, (□) 320 °C and (▲) 360 °C.

each process. Figure 4 shows the H₂-TPR profiles of Cu/SiO₂, CuFe₂O₄/SiO₂ (Fe/Cu=2) and Fe/SiO₂ catalysts after calcination in air at 800 °C. Additionally, figure 5 shows the XRD patterns of Cu/SiO₂ and CuFe₂O₄/SiO₂ (Fe/Cu=2) catalyst after air calcination at 800 °C followed by H₂ reduction at 240, 360 and 600 °C. As shown in figure 4(a), two reduction peaks around 190 and 220 °C observed for the Cu/SiO₂

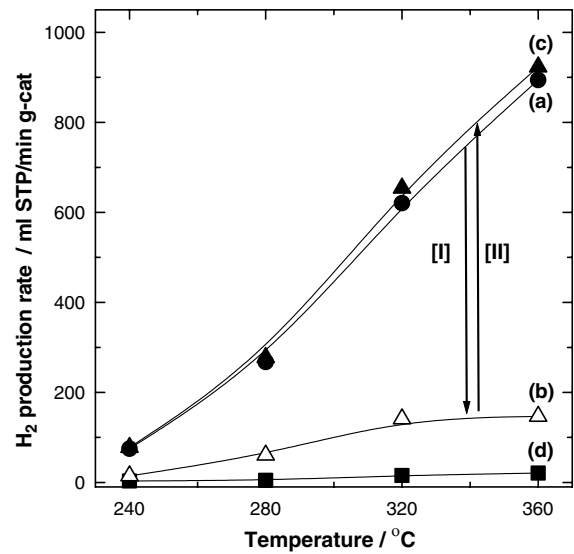


Figure 3. The rate of H₂ production versus reaction temperatures in the steam reforming of methanol for the CuFe₂O₄/SiO₂ (Fe/Cu = 2) catalyst. (●): a) air calcinations at 800 °C followed by H₂ reduction at 240 °C, (△): b) (a) followed by H₂ reduction at 600 °C, (▲): c) (b) followed by air recalcinations at 800 °C for 1 h and (■): d) Cu/SiO₂ catalyst after air calcinations at 800 °C for 5 h followed by H₂ reduction at 600 °C.

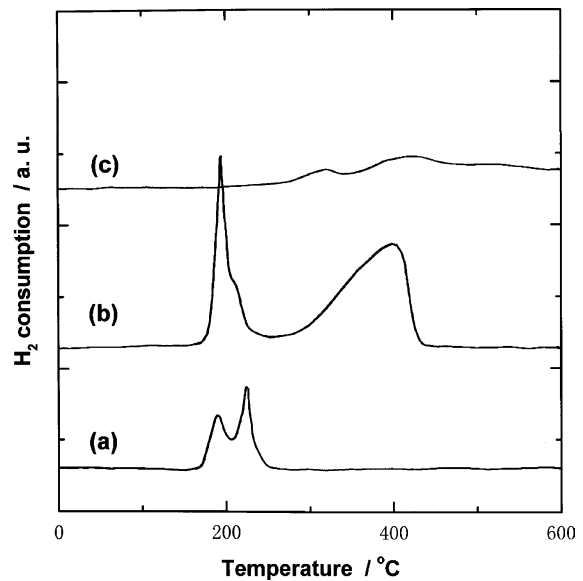


Figure 4. H₂-TPR profiles of the different catalysts after air calcinations at 800 °C. (a) Cu/SiO₂ (Fe/Cu = 0), (b) CuFe₂O₄/SiO₂ (Fe/Cu = 2) and (c) Fe/SiO₂ (Fe/Cu = ∞); TPR conditions: heating rate 2 °C/min in 5% H₂/Ar.

catalyst, which are attributed to the reduction of dispersed copper oxide species and the bulk CuO, respectively [16, 17]. Total amount of H₂ consumed (H₂/Cu ratio) was 0.994, which is corresponding to the reduction of CuO to Cu (i.e., $\text{CuO} + \text{H}_2 \rightarrow \text{Cu} + \text{H}_2\text{O}$). Results of physical measurements of Cu/SiO₂ catalyst are given in table 2. As shown in figure 5 (f, g), only sharp diffraction peaks from Cu were observed after H₂

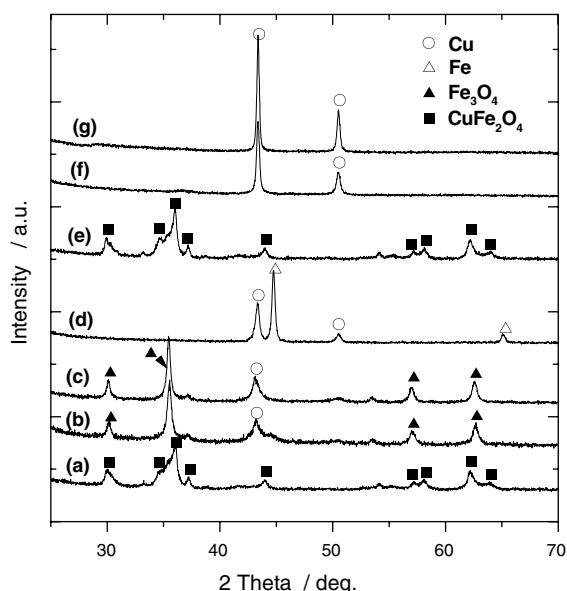


Figure 5. Powder X-ray diffraction patterns for CuFe₂O₄/SiO₂ catalyst (Fe/Cu = 2) and Cu/SiO₂ catalyst (Fe/Cu = 0). (a) CuFe₂O₄/SiO₂ catalyst after air calcination at 800 °C for 5 h, (b) (a) followed by H₂ reduction at 240 °C, (c) (a) followed by H₂ reduction at 360 °C, (d) (a) followed by H₂ reduction at 600 °C, (e) (d) followed by air calcinations at 800 °C for 1 h, (f) Cu/SiO₂ catalyst after air calcination at 800 °C followed by H₂ reduction at 360 °C and (g) (f) followed by H₂ reduction at 600 °C.

reduction at 360 and 600 °C, indicating that severe sintering of Cu particles readily occurs over the Cu/SiO₂ catalyst.

On the other hand, as shown in figure 4 (b), two pronounced reduction peaks were observed at 180–220 and 300–420 °C regions for the CuFe₂O₄/SiO₂ catalyst. Figures 5(a) and 5(b) show that the CuFe₂O₄ compound is reduced to Cu⁰ and Fe₃O₄ particles below 240 °C. Subsequently, Fe₃O₄ particles is reduced to Fe⁰ particles at higher temperatures (~600 °C: figure 5(d)). According to these results, it is clear that the reduction peak at lower temperature region in figure 4(b) is responsible for the reduction of CuFe₂O₄ species to Cu and Fe₃O₄ and that at higher temperature region in figure 4(b) is responsible for the reduction of Fe₃O₄ to Fe. The total amount of H₂ consumed (H₂/Cu ratio) was

3.90, which is consistent with that for the reduction of CuFe₂O₄ to Cu and Fe (*i.e.*, CuFe₂O₄ + 4H₂ → Cu + 2Fe + 4H₂O). The changes in XRD patterns in a series of reduction treatments are unambiguously interpreted with the TPR profile for the CuFe₂O₄/SiO₂ catalyst. Results of N₂O titration and crystallite size of Cu particles estimated from XRD peaks are also summarized in table 2. Amount of O(a) species by N₂O titration for the CuFe₂O₄/SiO₂ is almost one order larger than that for the Cu/SiO₂. The crystallite size of copper particles for the CuFe₂O₄/SiO₂ catalyst even after the H₂ reduction at 600 °C is much smaller than that of copper particles over the Cu/SiO₂ catalyst. These results suggest that fine dispersion of Cu particles is performed by the reduction of CuFe₂O₄ in H₂ flow, and severe sintering of Cu particles is inhibited by the presence of iron even in the H₂ flow at high temperature (*e.g.*, ~600 °C). Interestingly, as shown in figure 5(e), the spinel CuFe₂O₄ can be regenerated by treatment in air at 800 °C even after an intentional sintering of copper and iron particles. Consequently, the catalytic activity is restored to its original level (figure 3(c)).

For the Fe/SiO₂ catalyst, broad reduction peaks were observed above 280 °C (figure 4 (c)), which are attributed to the reduction from Fe₂O₃ to Fe₃O₄ and partially from Fe₃O₄ to Fe. Fe₃O₄ could not reduce to Fe completely during the H₂-TPR experiment (up to 600 °C). As shown in figures 4(b) and 4(c), the reduction temperature of iron oxides (Fe₃O₄ → Fe) over CuFe₂O₄/SiO₂ shifted to lower temperatures, which indicates that reduction of iron oxides is promoted by the presence of copper. For this result, it is interpreted that the dissociative hydrogen atoms may migrate from the copper onto the iron oxides during H₂ treatment at high temperatures (*i.e.*, spillover phenomenon [18]). Subsequently, iron oxides are reduced to iron by the reaction with H(a) atoms.

Recently, addition of iron to supported Cu catalysts such as Cu/SiO₂ and Cu/ZrO₂ causes a dramatic increase in activity and thermal stability against deactivation, which have been reported by several research groups [19, 20]. Chen *et al.* [19] reported that a small amount addition of Fe provided the advantages for copper catalysts both in promoting activity and in

Table 2
Results of the characterization of the Cu/SiO₂ and the CuFe₂O₄/SiO₂ catalyst

Catalyst ^a (Fe/Cu atomic ratio)	N ₂ O titration ^b (μmol/g-cat)	H ₂ -TPR ^c		Crystalline size of Cu ^d	
		LT (mmol/g-cat)	HT (mmol/g-cat)	360 (nm)	600 (nm)
Cu/SiO ₂ (0)	41.6	1.56	—	29.7	52.8
CuFe ₂ O ₄ /SiO ₂ (2)	387.8	1.95	4.17	7.9	18.5

^aConstant as 10 wt% Cu loading (1.57 mmol Cu/g-cat).

^bTotal amount of N₂ produced by N₂O pulsed at rt after H₂ reduction at 240 °C.

^cCalculated from H₂-TPR profiles in the region of LT (< 240 °C) and HT (> 300 °C).

^dCalculated from XRD patterns after H₂ reduction at 360 and 600 °C using the Scherrer equation.

stabilizing catalyst dispersion. It was proposed that the iron species acts as a textural promoter to prevent copper sintering at high temperatures. Okamoto *et al.* [20] reported that the direct interaction between copper species and iron oxide clusters could form new species to inhibit sintering and enhance catalytic activity. However, the interaction between copper and iron in these catalyst systems is not sufficiently understood. In this study, we have shown a Cu catalyst with high thermal stability and revealing high catalytic activity where a spinel CuFe₂O₄ oxide acted as a precursor. The origin of high activity and high thermal stability is due to the formation of a composite structure induced by reduction of the CuFe₂O₄ where nano-scale Cu particles homogeneously dispersed within Fe₃O₄ (i.e., fine dispersion of copper particles). Phase separation between copper and iron (or iron oxide) at nano-scale may be induced effectively because copper and iron in the spinel CuFe₂O₄ compound are regularly bonding through oxygen; i.e., –O–Cu–O–Fe–O– [21]. Incorporating negligible solubility of oxygen in Cu and phase separation of Cu and Fe₃O₄ observed in figure 5(b), we may speculate that Cu is immiscible to Fe₃O₄. This is a key factor keeping high dispersion and high thermal stability of Cu particles. Moreover, as seen in the phase diagram of Cu–Fe binary system, Cu and Fe are immiscible [12], and when the CuFe₂O₄ fully reduced Cu and Fe particles maintain certain small size (~19 nm) as shown in table 2 and segregated on SiO₂. At this stage, although the activity decreases significantly, mixture with small grain size of Cu and Fe is favorable for the formation of CuFe₂O₄ at 800 °C in air. Through redox process, the phase transition from CuFe₂O₄ to Cu and Fe₃O₄, and to Cu and Fe and finally return to CuFe₂O₄, implying that CuFe₂O₄ is an ideal catalyst. Formation of spinel CuFe₂O₄ in which Cu and Fe are homogenous in atomic scale is the first key point. Immiscibility of Cu and Fe or Fe oxide is important in two ways; immiscibility of Cu and Fe₃O₄ sustains high dispersion of Cu particles and their stability, and that of Cu and Fe keeps Cu and Fe particles at certain small size which ensures quick regeneration of CuFe₂O₄ in air at 800 °C. By employing the similar concept, design of new catalyst is highly anticipated. Study in other CuM₂O₄ is in progress.

4. Conclusions

A Cu catalyst with fine dispersion of copper particles and high thermal stability can be prepared by

the H₂ reduction at 240 °C for the spinel CuFe₂O₄ on the SiO₂ support. The catalytic activity of the CuFe₂O₄/SiO₂ catalyst for the steam reforming of methanol at high temperature (e.g., 360 °C) is much higher than those of the Cu/SiO₂ and the Fe/SiO₂ catalysts. These properties are ascribed to the reduction of the spinel CuFe₂O₄ and the subsequent immiscible interaction between Cu and Fe (or Fe oxide). Additionally, the spinel CuFe₂O₄ was readily regenerated by calcination in air at 800 °C even after the sintering of Cu by H₂ reduction at 600 °C. The present study demonstrates the validity of spinel CuFe₂O₄ as a precursor for a high catalytic performance copper catalyst.

References

- [1] K. Klier, *Adv. Catal.* 31 (1980) 275.
- [2] D.S. Newsome, *Catal. Rev. Sci. Eng.* 21 (1980) 275.
- [3] N. Takezawa and N. Iwasa, *Catal. Today* 36 (1997) 45 and references therein.
- [4] C.J. Jiang, D.L. Trimm, M.S. Wainwright and N.W. Cant, *Appl. Catal.* 93 (1993) 245.
- [5] B.A. Peppley, J.C. Amphlett, L.M. Kearns and R.F. Mann, *Appl. Catal. A* 179 (1999) 21.
- [6] T. Takeguchi, Y. Kani, M. Inoue and K. Eguchi, *Catal. Lett.* 83 (2002) 49.
- [7] M. Matsukata, S. Uemiyu and E. Kikuchi, *Chem. Lett.* (1988) 761.
- [8] Y. Tanaka, T. Utaka, R. Kikuchi, T. Takeguchi, K. Sasaki and K. Eguchi, *J. Catal.* 215 (2003) 271.
- [9] F. Severino, J.L. Brito, J. Laine, J.L.G. Fierro and A.L. Agudo, *J. Catal.* 177 (1998) 82.
- [10] W.F. Shangguan, Y. Teraoka and S. Kagawa, *Appl. Catal. B* 8 (1996) 217.
- [11] A.P. Tsai and M. Yoshimura, *Appl. Catal. A* 214 (2001) 237.
- [12] T.B. Massalski (Editor-in-Chief), *Binary Alloy Phase Diagrams*, 2nd ed., Vol.2 (ASM International, USA, 1990), p. 1408.
- [13] S. Kameoka, M. Terauchi and A.P. Tsai, to be published.
- [14] J.W. Evans, M.S. Wainwright, A.J. Bridgewater and D.J. Young, *Appl. Catal.* 7 (1983) 75.
- [15] X-ray powder diffraction data file, PDF#34-0425.
- [16] L. Dong, Z. Liu, Y. Hu, B. Xu and Y. Chen, *J. Chem. Soc., Faraday Trans.* 94 (1998) 3033.
- [17] W.-P. Dow, Y.-P. Wang and T.J. Huang, *J. Catal.* 160 (1996) 155.
- [18] W.C. Conner Jr., G.M. Pajonk and S.J. Teichner, *Adv. Catal.* 34 (1986) 1.
- [19] C.-S. Chen, W.-H. Cheng and S.-S. Lin, *Appl. Catal. A* 257 (2004) 97.
- [20] Y. Okamoto, T. Kubota, H. Gotoh, Y. Ohto, H. Aritani, T. Tanaka and S. Yoshida, *J. Chem. Soc., Faraday Trans.* 94 (1998) 3743.
- [21] S. Krupicka and P. Novak, in: *Handbook on Ferromagnetic Materials*, E.P. Wohlfarth (ed.) Vol. 3 (North-Holland publishing Co., Amsterdam, 1982)..