Catal Lett (2008) 124:233–237
DOI 10.1007/s10562-008-9504-7

Promotion Effect of FeO_x Addition on the Catalytic Activity of Supported Cu Catalysts for the Water–gas Shift Reaction

Hidenori Yahiro · Kunimasa Sagata · Tetsuya Yamamoto · Kazuhiko Saiki · Makiko Asamoto · Hiroyuki Yamaura

Received: 2 March 2008 / Accepted: 24 April 2008 / Published online: 15 May 2008

Abstract Among the supported Cu–FeO_x catalysts, Al_2O_3-supported Cu–FeO_x catalyst exhibited the highest activity for WGS reaction. The enhancement of the catalytic activity by adding FeO_x to Cu/Al_2O_3 could be interpreted by the two possibilities; one is the formation of highly dispersed Cu^0 and the other is the participation of reduced FeO_x in WGS reaction in the presence of Cu^0.

Keywords Water–gas-shift reaction · Carbon monoxide · Supported catalyst · Copper · Iron oxide

1 Introduction

It is well-known that the removal of carbon monoxide (CO) in the hydrogen fuel produced by reforming of hydrocarbon sources is indispensable to attain high and stable performances of polymer electrolyte fuel cells (PEFCs). The low-temperature water–gas-shift (WGS) reaction, $CO + H_2O = H_2 + CO_2$, has been used in industry to achieve the removal of CO in the relatively high concentration range (ca. 7–10% CO). Cu-based mixed oxide catalysts [1–5] and supported Cu catalysts [6–11] have been reported to exhibit the high activity for the WGS reaction.

Recently, we have reported that Cu/Al_2O_3 catalysts calcined at relatively high temperature, 1073 K, contain both highly dispersed Cu and $CuAl_2O_4$ spinel and the former species act as active sites for the WGS reaction [10]. Eguchi and co-workers [9] have reported that 5 wt%Cu–5 wt%ZnO/Al_2O_3 catalyst prepared by the impregnation method was active for the WGS reaction. In this case, ZnO plays a role as the promoting additive. In the present study, supported Cu catalysts with iron oxide-promoter were prepared by the impregnation method and successfully applied to the WGS reaction. In particular, the catalytic performance of Cu–FeO_x/Al_2O_3 having the highest catalytic activity for WGS reaction among supported Cu–FeO_x catalysts used in the present study was investigated as functions of Fe loading and calcination temperature. In addition, XRD and H_2-TPR studies were carried out to characterize the supported catalysts.

2 Experimental Methods

The support materials, SiO_2 (JRC-SIO-6), SiO_2–MgO (JRC-SM-1), SiO_2–Al_2O_3 (JRC-SAH-1), Al_2O_3 (JRC-ALO-8), ZrO_2 (JRC-ZRO-3), and MgO (JRC-MGO-4), were supplied from Catalysis Society of Japan. Supported Cu–FeO_x catalysts were prepared by a conventional impregnation method using the mixed aqueous solution of $Cu(NO_3)_2 \cdot 3H_2O$ (Wako Chem.) and $Fe(NO_3)_3 \cdot 9H_2O$ (Wako Chem.). The catalysts were dried at 383 K for 1 h and calcined at 873–1073 K for 8 h in air. The loading of Cu was unified to be 12 wt%, while that of Fe was changed from 0 to 11 wt%. The surface area of catalyst was measured by the BET method using N_2 adsorption. The samples are abbreviated as Cu–FeO_x/Al_2O_3(1.0) (Cu–FeO_x/support (Fe/Cu molar ratio)).

The WGS reaction was carried out in a fixed-bed continuous flow reactor at 473–523 K. Prior to the activity test, the catalyst was reduced by flowing 20 vol%H_2/He gas at a flow rate of 30 cm^3 min^{-1} at 523 K for 2 h. The reactant

---

H. Yahiro (✉) · K. Sagata · T. Yamamoto · K. Saiki · M. Asamoto · H. Yamaura
Department of Materials Science and Biotechnology, Graduate School of Science and Engineering, Ehime University, Matsuyama 790-8577, Japan
e-mail: hyahiro@eng.ehime-u.ac.jp

gases contained 9.5 vol% of CO, 27.7 vol% of H_2O, 56.0 vol% of H_2, and 6.8 vol% of CO_2. The total flow rate was 96 cm^3 min^{-1} and the weight of the catalyst bed was 0.5 g (gas hourly space velocity = 7500–13000 h^{-1}). The effluents were analyzed by on-line gas chromatography (Shimadzu, GC-8AIT) using an active carbon column.

X-ray powder diffraction (XRD) analysis was performed to determine the crystalline phase of the catalysts using a Rigaku RINT2200HF diffractometer with CuK_α radiation. Temperature-programmed reduction (H_2-TPR) was carried out by flowing 5 vol%H_2/N_2 (30 cm^3 min^{-1}) in the temperature range of 373–1173 K. The sample temperature increased with a rate of 2 K min^{-1} and the amount of H_2 consumed was monitored by a thermal conductivity detector of a gas chromatograph (Shimadzu, GC-8AIT). The accessible Cu fraction was measured by N_2O decomposition method described elsewhere [10, 12, 13].

3 Results and Discussion

The catalytic activities of supported Cu–FeO_x catalysts (Fe/Cu = 1.0) were largely dependent on the kind of supports. The catalytic activities of supported Cu–FeO_x and Cu catalysts measured at 523 K are summarized in Table 1. The calcination temperature was unified to be 973 K. For all the samples, the catalytic activity was enhanced by the addition of FeO_x. The specific surface areas of each catalyst are also shown in Table 1. The specific surface areas of supported Cu catalysts were decreased by the addition of FeO_x except for Cu/SiO_2–Al_2O_3. The order of surface area was disagreement with that of catalytic activity, indicating that the specific surface area is not the main factor controlling the catalytic activity.

Among the catalysts listed in Table 1, Cu–FeO_x/Al_2O_3 catalyst exhibited the highest catalytic activity for WGS reaction. The reason why the Al_2O_3 support was favorable for WGS reaction was not clear from the present study. In general, it was agreed that the reactants, CO and H_2O, were individually activated on metal and support, respectively, for the supported metal catalysts [14]. Therefore, it is expected that H_2O was highly activated on Al_2O_3 compared to the other supports used in the present study.

Table 1 Catalytic activity[a] and specific surface area of Cu–FeO_x (Fe/Cu = 1.0) and Cu catalysts supported on different oxides

Support	Conversion of CO at 523 K/% (specific surface area/m^2 g^{-1})	
	Cu–FeO_x	Cu
SiO_2	39(233)	32(336)
SiO_2–MgO	19(121)	3(248)
SiO_2–Al_2O_3	49(104)	6(51)
Al_2O_3	87(78)	65(106)
ZrO_2	38(15)	19(26)
MgO	73(10)	56(17)

[a] Experimental condition: 9.5 vol% of CO, 27.7 vol% of H_2O, 56.0 vol% of H_2, and 6.8 vol% of CO_2: the total flow rate = 96 cm^3 min^{-1}: the weight of the catalyst bed = 0.5 g (gas hourly space velocity = 7500–13000 h^{-1})

Since Al_2O_3-supported Cu–FeO_x catalysts showed the highest catalytic activity for WGS reaction as mentioned above, their catalytic performances were investigated in more detail. Figure 1 shows the catalytic activities of Cu–FeO_x/Al_2O_3 (1.0) and Cu/Al_2O_3 as a function of calcination temperature. The less change in the catalytic activity of Cu/Al_2O_3 was observed in the range of 873–1073 K of calcination temperature, as reported previously [10]. On the other hand, the catalytic activity of Cu–FeO_x/Al_2O_3 increased with calcination temperature, reached a maximal value at 973 K, and then decreased with further increasing calcination temperature. It should be noted that the enhancement of the catalytic activity by FeO_x addition was pronounced for the catalytic reaction performed at higher temperature, 523 K. This may be due to the change in the reaction mechanism or the increase in the number of active site at elevated temperature.

Figure 2a shows the catalytic activities of Cu–FeO_x/Al_2O_3 catalysts calcined at 973 and 1073 K as a function of Fe/Cu molar ratio. The catalytic activity was initially decreased by the addition of FeO_x to Cu/Al_2O_3; however, the catalytic activity was recovered for Cu–FeO_x/Al_2O_3 catalysts with Fe/Cu = 0.5. The activity of Cu–FeO_x/Al_2O_3 with Fe/Cu > 0.5, calcined at 973 K, exceeded the

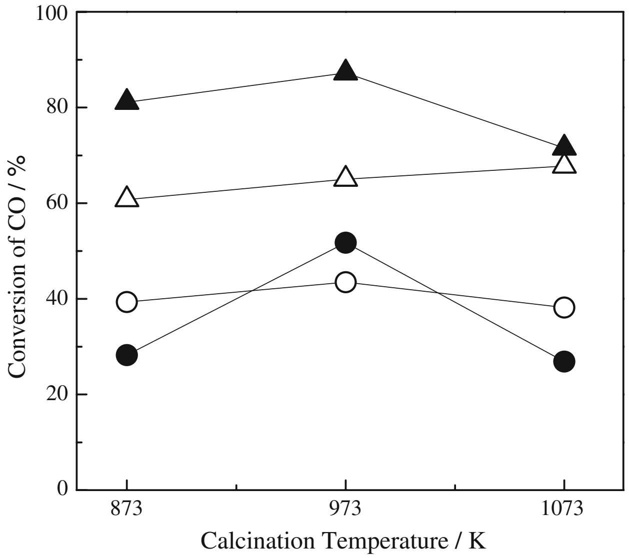

Fig. 1 Catalytic activities of (▲, ●) Cu–FeO_x/Al_2O_3 (Fe/Cu = 1.0) and (Δ, ○) Cu/Al_2O_3, measured at (▲, Δ) 523 and (●, ○) 473 K, as a function of calcination temperature

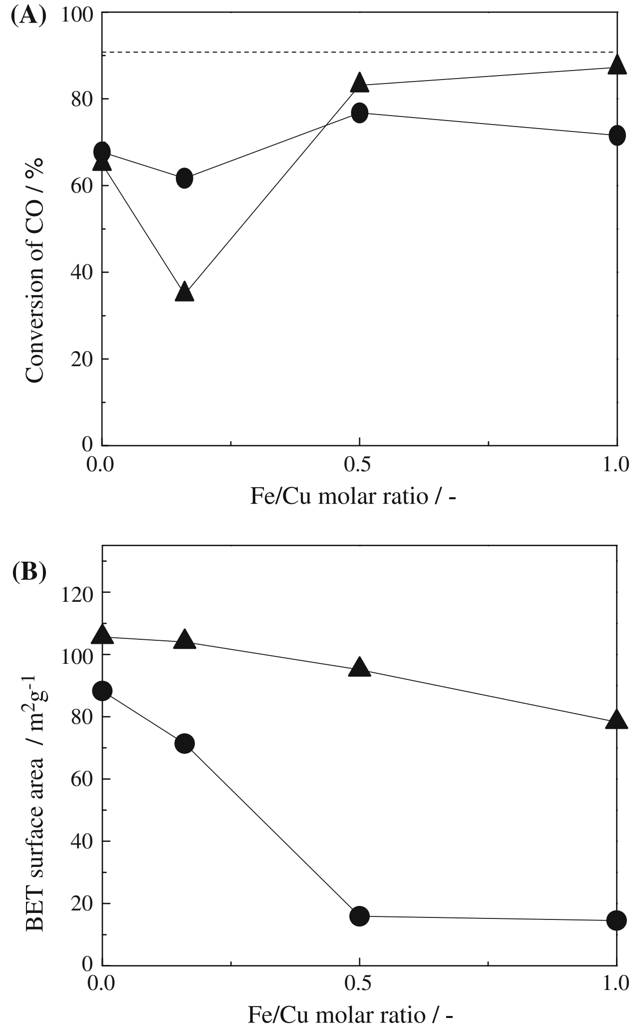

Fig. 2 (**a**) Catalytic activities and (**b**) BET surface areas of Cu–FeO_x/Al_2O_3 catalysts calcined at (▲) 973 and (●) 1073 K. The dotted line indicates the activity of a commercial composite oxide catalyst, CuO/ZnO/Al_2O_3, with 43:48:9 of the molar ratio. Reaction conditions: temperature = 523 K, CO = 9.5 vol%, H_2O = 27.7 vol%, H_2 = 56.0 vol%, CO_2 = 6.8 vol%, and gas hourly space velocity = 6000 h^{-1}

initial value (Cu/Al_2O_3) and was comparable to the activity of a commercial catalyst, CuO/ZnO/Al_2O_3, with the weight ratio 43:49:8 (dotted line).

The changes in the specific surface areas of Cu–FeO_x/Al_2O_3 catalysts are depicted in Fig. 2b. The specific surface areas of Cu–FeO_x/Al_2O_3 calcined at 973 K decreased monotonously with the increase in the Fe/Cu molar ratio. A similar trend was observed for Cu–FeO_x/Al_2O_3 calcined at 1073 K; however, its specific surface area was steeply decrease by adding FeO_x with more than Fe/Cu = 0.17. This may be due to the phase transition of alumina support, as described later. FeO_x/Al_2O_3 catalysts calcined at 873–1073 K exhibited no catalytic activity for the WGS reaction at 473 and 523 K; therefore, the catalytic activity of Cu–FeO_x/Al_2O_3 could not be explained by adding the catalytic activity of FeO_x/Al_2O_3 to that of Cu/Al_2O_3.

The XRD patterns of Cu–FeO_x/Al_2O_3 catalysts as-calcined at 973 K are shown in Fig. 3a. Cu/Al_2O_3 catalyst calcined at 973 K gave the diffraction lines assigned to CuO as well as the broad diffraction lines from γ-Al_2O_3 [10]. The addition of FeO_x to Cu/Al_2O_3 catalysts resulted in the decrease in the intensity of diffraction lines of CuO. When more than 5 wt% FeO_x (Fe/Cu > 0.5) was added to the Cu/Al_2O_3, the two sets of diffraction lines were observed at 33.2, and 35.6° for Fe_2O_3 and 31.0 and 36.5° for $FeAl_2O_4$ produced by the reaction between FeO_x and Al_2O_3 support.

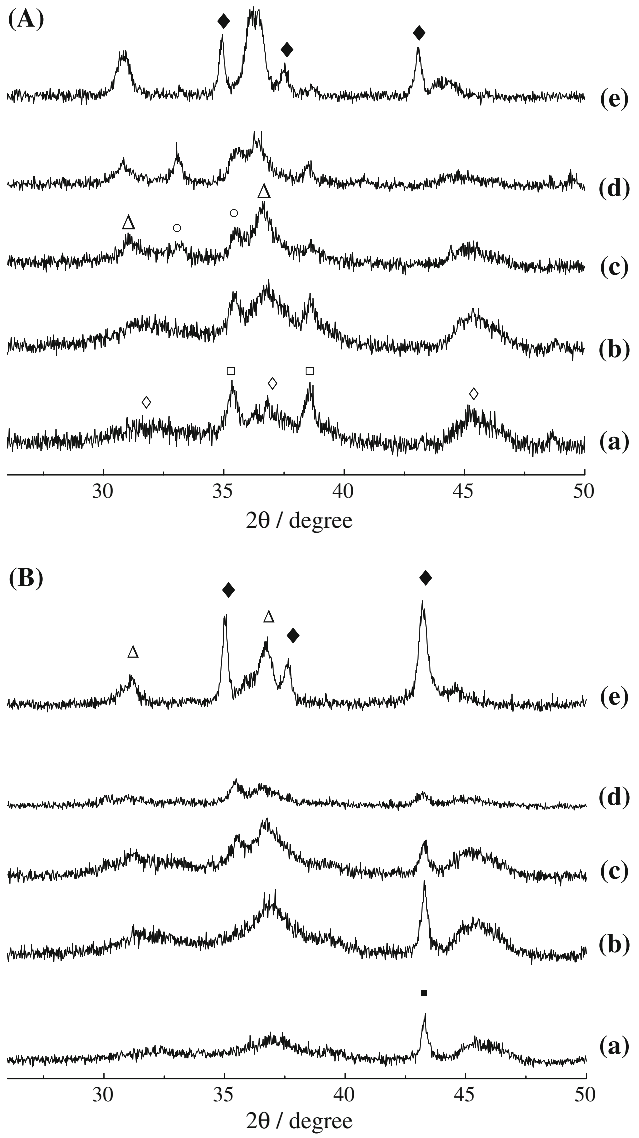

Fig. 3 X-ray powder diffraction patterns of (**A**) Cu–FeO_x/Al_2O_3 catalysts as-calcined at (**a**–**d**) 973 and (**e**) 1073 K and (**B**) followed by the H_2 reduction at 523 K for 2 h. Fe/Cu = (**a**) 0, (**b**) 0.17, (**c**) 0.5, and (**d**, **e**) 1.0. (□) CuO, (■) Cu^0, (○) Fe_2O_3, (Δ) $FeAl_2O_4$, (◇) γ-Al_2O_3, and (♦) α-Al_2O_3

Figure 3e shows the XRD pattern of Cu–FeO_x/Al_2O_3 catalysts calcined at 1073 K for 8 h. The intense diffraction lines assigned to α-Al_2O_3 appeared at 35.2, 37.8, and 43.3°. This indicates that FeO_x plays a role in accreting phase transformation from γ-Al_2O_3 to α-Al_2O_3. It is known that the BET surface area of α-Al_2O_3 is smaller than that of γ-Al_2O_3; therefore the steeper decrease in BET surface areas of Cu–FeO_x/Al_2O_3 calcined at 1073 K, as shown in Fig. 2b, is due to the phase transformation of Al_2O_3.

When the Cu–FeO_x/Al_2O_3 samples were reduced by H_2 at 523 K, metallic copper (Cu^0) species were formed as shown in Fig. 3b. The intensity of Cu^0 diffraction line increased by the small amount of FeO_x added; however, it decreased with further increase in the amount of FeO_x added. The intensity of peaks assigned to Fe_2O_3 slightly decreased after H_2 reduction at 523 K, suggesting that Fe_2O_3 was partially reduced to FeO_x with lower valence of Fe. Such a decrease in peak intensity of Fe_2O_3 was not observed in the absence of Cu^0.

Our previous H_2-TPR measurements demonstrated that the highly dispersed CuO species was formed in Cu/Al_2O_3 catalysts calcined at 1073 K [10]. Figure 4 shows TPR profiles of Cu/Al_2O_3 and Cu–FeO_x/Al_2O_3 calcined at 973 K. A large peak in the range 400–550 K was observed for Cu/Al_2O_3 catalyst (Fig. 4a), being assigned to the reduction of CuO to Cu^0 [10]. On the other hand, FeO_x/Al_2O_3 exhibited a very broad peak in the temperature range 493–1050 K (not shown in Fig. 4). When the content of Fe additive increased, an additional peak was observed at ca. 530 K just after the reduction peak attributable to CuO, as shown in Fig. 4d. This additional peak was tentatively assigned to the reduction of Fe_2O_3 strongly interacted with Cu^0. A similar TPR profile was reported for Cu–FeO_x/SiO_2 [15] and copper ferrite spinel [16].

The effect of Fe additives on the catalytic activity of Cu/Al_2O_3 will be briefly discussed on the basis of XRD and H_2-TPR results. We are considering the two possibilities for interpretation of the enhancement of the catalytic activity by adding FeO_x to Cu/Al_2O_3. One is the formation of highly dispersed Cu^0 formed by Fe additives. As shown in Fig. 3b, from the XRD patterns of Cu–FeO_x/Al_2O_3 catalysts, the addition of FeO_x to Cu/Al_2O_3 catalysts resulted in the decrease in the intensity of diffraction lines of Cu^0. This may be correspondence to the formation of Cu^0 fine particles. As the catalytic activity of WGS reaction depended on the surface area of Cu^0 [10], it is expected that the formation of such fine particles leads to enhance the catalytic activity. It has been reported that FeO_x in Cu–FeO_x/SiO_2 and Cu–FeO_x/ZrO_2 inhibits the sintering and/or aggregation of Cu^0 particles [15, 17, 18], supporting above idea. The other possibility is the participation of reduced FeO_x in WGS reaction in the presence of metallic Cu. FeO_x has reported to be active for high temperature-WGS reaction (ca. 623–723 K) [19]. In this case, it is considered that the redox property between Fe_2O_3 and Fe_3O_4 was important for WGS reaction. The present XRD and TPR studies suggest that the Fe_2O_3 was reduced to FeO_x with lower valence of Fe in the presence of Cu^0 at the low temperature region. From the present results, it is not clear that the reoxidaion process of FeO_x succeeded in WGS reaction at low temperature.

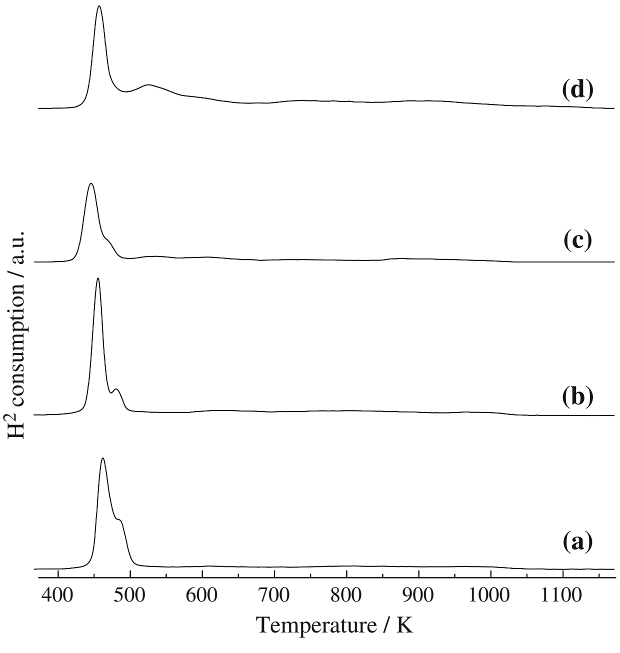

Fig. 4 H_2-TPR profiles of Cu–FeO_x/Al_2O_3 catalysts calcined at 973 K. Fe/Cu = (**a**) 0, (**b**) 0.17, (**c**) 0.5, and (**d**) 1.0

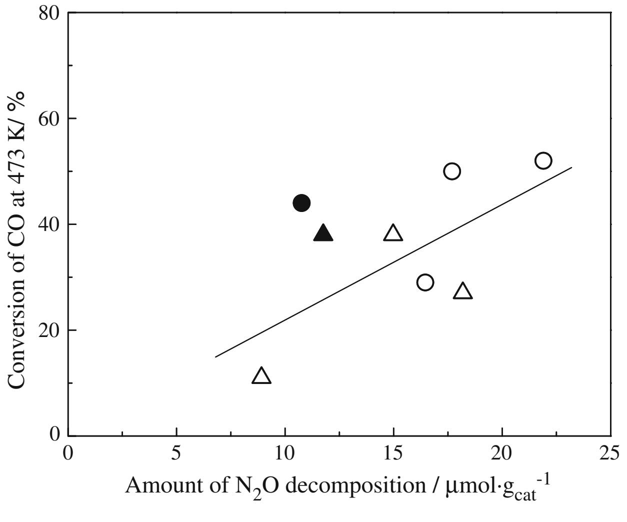

Fig. 5 Catalytic activities at 473 K as a function of the amount of N_2O decomposition over various Cu/Al_2O_3 and Cu–FeO_x/Al_2O_3 catalysts. (○) Cu–FeO_x/Al_2O_3 (0.17, 0.5, and 1.0) calcined at 973 K, (Δ) Cu–FeO_x/Al_2O_3 (0.17, 0.5, and 1.0) calcined at 1073 K, (●) Cu/Al_2O_3 calcined at 973 K, and (▲) Cu/Al_2O_3 calcined at 1073 K. Experimental conditions of N_2O decomposition method: temperature = 373 K, catalyst weight = 0.1 g, and N_2O = 10% (He balance)

However, considering the report that the oxygen on Cu^0 can rapidly diffuse to Fe surface [15], the redox process of FeO_x probably take place in the present condition, although further studies are needed.

It was reported for copper-based catalysts that the catalytic activity of WGS reaction is related with the amount of N_2O decomposition which is responsible to the accessible Cu fraction [10]. The catalytic activities of Cu–FeO_x/Al_2O_3 and Cu/Al_2O_3 calcined at various temperatures were plotted against the amount of N_2O decomposition, as depicted in Fig. 5. For the catalysts with and without Fe, a linear correlation was observed between the catalytic activity and the amount of N_2O decomposition, although some data were slightly deviated from the linear correlation. This result suggests that the catalytic activity was dependent on the accessible Cu (and Fe in the case of Cu–FeO_x catalysts) fraction on catalysts, i.e., the accessible Cu fraction is one of the factors controlling the activity even for Cu–FeO_x catalysts, similar to Al_2O_3-supported Cu catalysts [10].

4 Conclusion

The activities of the low-temperature WGS reaction were investigated for Cu–FeO_x catalysts supported on SiO_2, SiO_2–MgO, SiO_2–Al_2O_3, Al_2O_3, ZrO_2, and MgO. For all the samples used in the present study, the catalytic activity of supported Cu catalyst was enhanced by the addition of FeO_x. The Cu–FeO_x/Al_2O_3 catalyst was optimized; maximum activity was achieved for the Cu–FeO_x/Al_2O_3 catalyst calcined at 973 K and with $Cu/Fe = 1.0$. The pronounced effect of FeO_x addition to Cu/Al_2O_3 was observed at the higher measurement temperature of WGS reaction. XRD and H_2-TPR results provided the two possibilities for interpretation of the enhancement of the catalytic activity by adding FeO_x to Cu/Al_2O_3. One is the formation of highly dispersed Cu^0 formed and the other is the participation of reduced FeO_x in WGS reaction in the presence of Cu^0.

Acknowledgement This study was partially supported by the New Energy and Industrial Technology Development Organization (NEDO), Japan.

References

1. Newsome DS (1980) Catal Rev Sci Eng 21:275
2. Rhodes C, Hutchings GJ, Ward AM (1995) Catal Today 23:43
3. Ginés MJL, Amadeo N, Laborde M, Apesteguía CR (1995) Appl Catal A 131:283
4. Ruettinger W, Ilinich O, Farrauto R (2003) J Power Source 118:61
5. Ghenciu AF (2002) Curr Opin Solid State Mater Sci 6:389
6. Utaka T, Sekizawa K, Eguchi K (2000) Appl Catal 194–195:21
7. Li Y, Fu Q, Stephanopoulos MF (2000) Appl Catal B 27:179
8. Regina T, Souza O, Brito SNO, Andrade HMC (1999) Appl Catal A 178:7
9. Tanaka Y, Utaka T, Kikuchi R, Sasaki K, Eguchi K (2003) Appl Catal A 238:11
10. Yahiro H, Nakaya K, Yamamoto T, Saiki K, Yamaura H (2006) Catal Commun 7:228
11. Yahiro H, Murawaki K, Saiki K, Yamamoto T, Yamaura H (2007) Catal Today 126:436
12. Evans JW, Wainwright MS, Bridgewater AJ, Young DJ (1983) Appl Catal 7:75
13. Jensen JR, Johannessen T, Livbjerg H (2004) Appl Catal A 266:117
14. Azzam KG, Babich IV, Seshan K, Lefferts L (2007) J Catal 251:153
15. Chen C-S, Cheng W-H, Lin S-S (2004) Appl Catal A 257:97
16. Faungnawakij K, Tanaka Y, Shimoda N, Fukunaga T, Kikuchi R, Eguchi K (2007) Appl Catal B 74:144
17. Kameoka S, Tanabe T, Tsai AP (2005) Catal Lett 100:89
18. Okamoto Y, Kubota T, Gotoh H, Ohto Y, Aratani H, Tanaka T, Yoshida S (1998) J Chem Soc, Faraday Trans 94:3743
19. Khan A, Chen P, Boolchand P, Smirniotis PG (2008) J Catal 253:91