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Study on the supported Cu-based catalysts for the low-temperature water–gas shift reaction

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Abstract

This paper presents a study on the influence of support (Al_2O_3, MgO, SiO_2-Al_2O_3, SiO_2-MgO, β-zeolite, and CeO_2) of Cu-ZnO catalysts for the low-temperature water–gas shift reaction. Supported Cu-ZnO catalysts were prepared by the conventional impregnation method, followed by the H_2 reduction. The activity of Cu-ZnO catalysts for the water–gas shift (WGS) reaction was largely influenced by the kind of support; Cu-ZnO catalysts supported on Al_2O_3, MgO, and CeO_2 showed high activity, while those on SiO_2-Al_2O_3, SiO_2-MgO and β-zeolite showed less activity in the temperature range 423–523 K. XRD analysis demonstrated that the copper species were highly dispersed on the supports used in the present study, except for a MgO support. TPR results of a series of supported CuO-ZnO catalysts suggest that the reducibility of CuO is one of the important factors controlling the activity of the WGS reaction over the supported catalysts.

Keywords: Water–gas shift reaction; Carbon monoxide; Supported catalyst; Copper; Zinc oxide

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1. Introduction

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) operated at low-temperature because CO is irreversibly adsorbed on the platinum electrode of a PEFC. 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). The most promising catalyst for the WGS reaction is Cu/ZnO-based mixed oxide prepared by the coprecipitation method [1–5].

Supported copper-based catalysts have been also reported to be active for the WGS reaction [6–10]. Eguchi and co-workers [9] have reported that 5 wt.%Cu-5 wt.%ZnO/Al_2O_3 catalyst prepared by the impregnation method was highly active for the WGS reaction. Recently, we have reported that Cu catalyst supported on Al_2O_3, which was calcined at 1073 K, showed high activity for the WGS reaction [10]. However, little is known about an influence of support of Cu-based catalysts on the catalytic activity of the WGS reaction. In this work, Cu-ZnO catalysts supported on several oxides with high surface area (Al_2O_3, MgO, SiO_2-Al_2O_3, SiO_2-MgO, β-zeolite, and CeO_2) were prepared by the impregnation method and successfully applied to the WGS reaction. In addition, XRD and TPR studies of supported catalysts were carried out to elucidate the dispersion and the reducibility of CuO supported on oxides.

2. Experimental methods

Al_2O_3 (JRC-ALO-1, -2, -3, -5, and -8), MgO (JRC-MGO-3, and -4), SiO_2-Al_2O_3 (JRC-SAH-1), SiO_2-MgO (JRC-SM-1), and β-zeolite (JRC-Z-B25) supports were supplied from Catalysis Society of Japan. CeO_2 support was prepared by the precipitation method with cerium nitrate solution and ammonia solution. The abbreviations of supports used in the present study are listed in Table 1. Supported Cu-metal oxide catalysts were prepared by a conventional impregnation method using the mixed aqueous solution of $Cu(NO_3)_2{\cdot}3H_2O$ (Wako

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Table 1
Catalytic activity of Cu(4 wt.%)-ZnO(5 wt.%) supported on various metal oxides

Support	Abbreviation of support	Surface area ($m^2 g^{-1}$)	Conversion of CO (%)		
			423 K	473 K	523 K
Al_2O_3					
JRC-ALO-1	ALO1	129	0	0	1
JRC-ALO-2	ALO2	188	0	1	5
JRC-ALO-3	ALO3	98	42	67	87
JRC-ALO-5	ALO5	163	1	3	7
JRC-ALO-8	ALO8	125	59	92	100
MgO					
JRC-MGO-3	MGO3	44	6	17	52
JRC-MGO-4	MGO4	35	3	19	66
SiO_2-Al_2O_3					
JRC-SAH-1	SAH1	263	0	0	1
SiO_2-MgO					
JRC-SM-1	SM1	333	0	5	7
β-Zeolite					
JRC-Z-B25	ZB25	332	0	0	1
CeO_2					
	CeO	40	16	55	86

Reaction condition: CO = 2.5 vol.%, H_2O = 50.0 vol.%, N_2 = 47.5 vol.%, and gas hourly space velocity = 12,000 h^{-1}. The catalysts were reduced by flowing 20%H_2/He at 523 K for 2 h prior to the activity test.

Chem.) and metal nitrate (Zn, Mg, Al, and Ce; Wako Chem.). The catalysts were dried at 383 K for 24 h and calcined at 773 K for 8 h in air. The surface area of catalyst was measured by the BET method using N_2 adsorption.

The WGS reaction was carried out in a fixed-bed continuous flow reactor at 423–573 K. Prior to the activity test, the catalyst was reduced by flowing 20 vol.%H_2/N_2 gas at a flow rate of 30 $cm^3 min^{-1}$ at 423–623 K for 2 h to yield metallic copper which was considered to be active species for the WGS reaction [9,10]. The reactant gas, 2.5 vol.% of CO and 50.0 vol.% of H_2O (N_2 balance), was fed into the Pyrex glass reactor. The total flow rate was 30 $cm^3 min^{-1}$ and the volume of the catalyst bed was 0.15 cm^3 (gas hourly space velocity = 12,000 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 Cu Kα radiation. Temperature-programmed reduction (H_2-TPR) was carried out by flowing 5 vol.%H_2/Ar (30 $cm^3 min^{-1}$) in the temperature range 373–773 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 the gas chromatograph (Shimadzu, GC-8AIT).

3. Results and discussion

3.1. Activity of Cu-ZnO supported on various oxides

Fig. 1 shows the effect of the coexistence of metal oxide on the catalytic activity of Cu(4 wt.%)/ALO8, where the loading amount of metal oxide added was unified to be 5 wt.%. As shown in Fig. 1, the addition of ZnO resulted in the enhancement of the catalytic activity of Cu/ALO8 in the temperature range 423–523 K, while the addition of CeO_2, Al_2O_3, and MgO showed the negative effect. Therefore, the catalytic performance of Cu-ZnO catalyst supported on metal oxides was investigated in more detail.

It is interesting to compare the WGS activity of Cu(4 wt.%)-ZnO(5 wt.%)/ALO8 to that of a commercial catalyst, CuO/

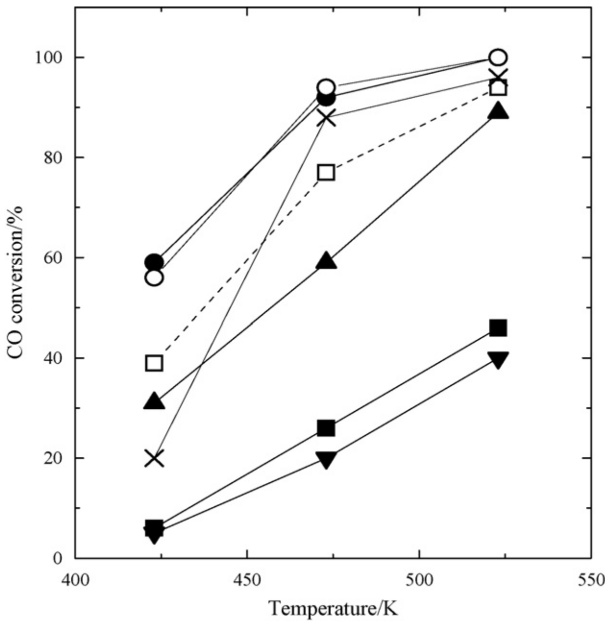

Fig. 1. Catalytic activities of Cu(4 wt.%)-MO(5 wt.%)/ALO8 catalysts and (*X*) a commercial CuO/ZnO/Al_2O_3 catalyst. MO = (●) ZnO(5 wt.%), (○) ZnO(10 wt.%), (▲) CeO_2, (■) Al_2O_3, (▼) MgO, and (□) none. Reaction conditions: CO = 2.5 vol.%, H_2O = 50.0 vol.%, N_2 = 47.5 vol.%, and gas hourly space velocity = 12,000 h^{-1}.

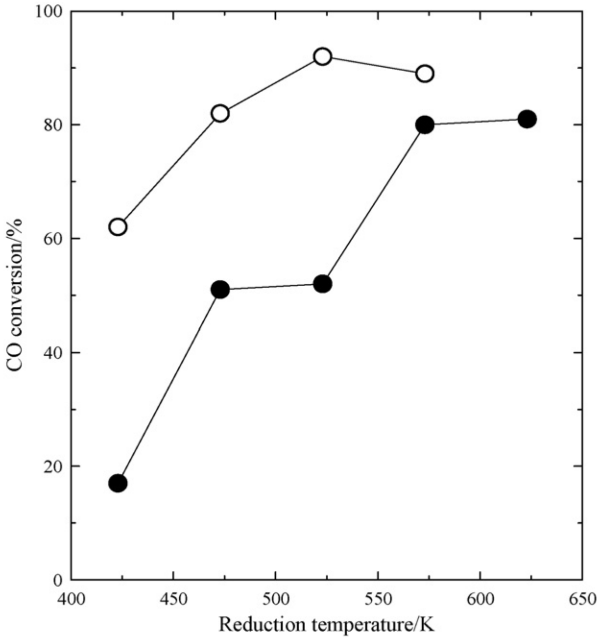

Fig. 2. Catalytic activity of (○) Cu(4 wt.%)-ZnO(5 wt.%)/ALO8 and (●) Cu(4 wt.%)-ZnO(5 wt.%)/MGO3 as a function of reduction temperature. Reaction conditions: CO = 2.5 vol.%, H_2O = 50.0 vol.%, N_2 = 47.5 vol.%, temperature = 523 K, and gas hourly space velocity = 12,000 h^{-1}.

ZnO/Al_2O_3, with the weight ratio 43:49:8. Under the present conditions, the catalytic activities of the latter catalyst were 88 and 96% at 473 and 523 K, respectively. The activity of Cu-ZnO/ALO8 was comparable to that of the oxide catalyst; however, considering that the copper content of the latter catalyst was ca. 8 times larger than that of the former catalyst, the activity per copper content in Cu-ZnO/ALO8 was much higher than that in the oxide catalyst.

The dependence of the amount of ZnO added to Cu(4 wt.%)/ALO8 on the catalytic activity of the WGS reaction is also shown in Fig. 1. The catalytic activity of Cu(4 wt.%)-ZnO(5 wt.%)/ALO8 was almost same as that of Cu(4 wt.%)-ZnO(10 wt.%)/ALO8, suggesting that the amount of ZnO added has no or less influence on the catalytic activity. A similar result was reported by Eguchi and co-workers [9].

The catalytic activities of Cu (4 wt.%)-ZnO(5 wt.%) supported on various metal oxides are summarized in Table 1 as a function of reaction temperature. All the catalysts were calcined at 773 K, followed by the H_2 reduction at 523 K for 2 h prior to the WGS reaction. Cu-ZnO catalysts supported on ALO3 and ALO8 were very active for the WGS reaction, while Cu-ZnO catalysts on ALO1, ALO2, and ALO5 showed less active. The BET surface areas of the supported catalysts are listed in Table 1. The order of BET surface area of the Al_2O_3-based supported catalysts was ALO2 > ALO5 > ALO1 ≈ ALO8 > ALO3. The Cu-ZnO/ALO8 and Cu-ZnO/ALO3 catalysts showed a high activity in spite of the lower BET surface area than those for Cu-ZnO/ALO2 and Cu-ZnO/ALO5 catalysts.

For the other supports, it was found that MgO (MGO3 and MGO4) and CeO were effective supports for Cu-ZnO catalyst in the WGS reaction. By contrast, SAH1, SM1, and ZB25 supports were less effective, as shown in Table 1.

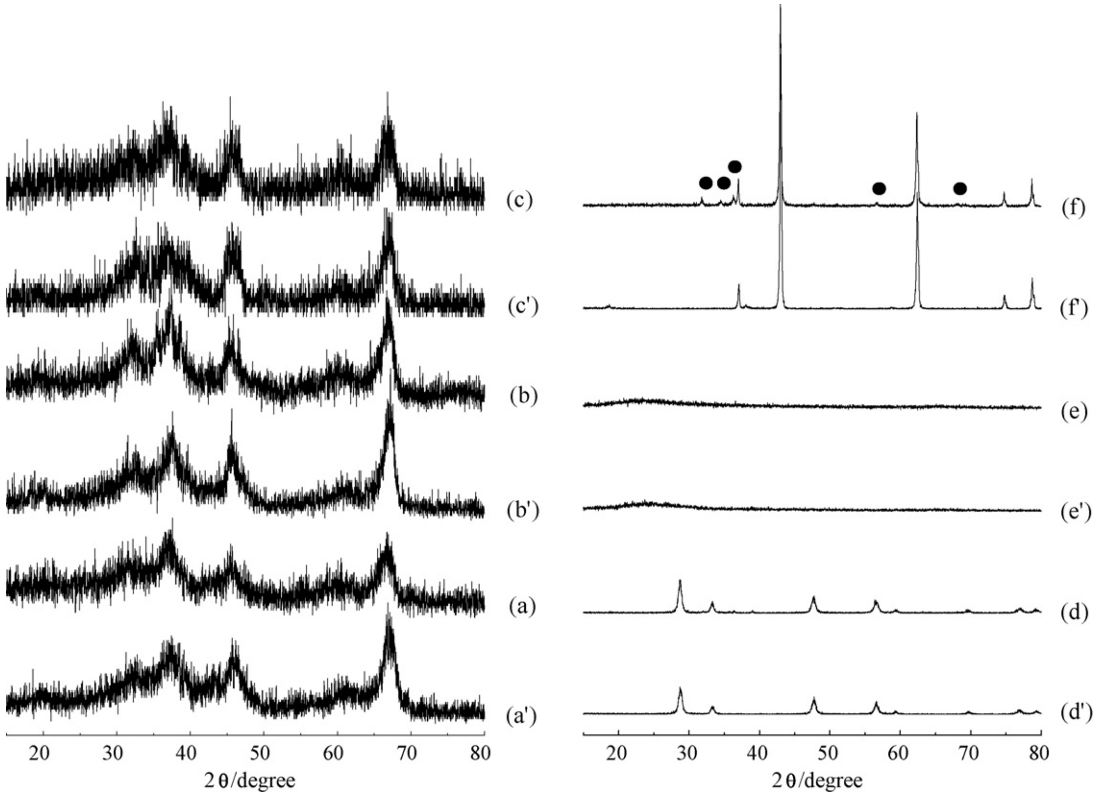

Fig. 3. Powder X-ray diffraction patterns of (a)–(f) supported CuO(5 wt.%)-ZnO(5 wt.%) catalysts and (a′)–(f′) pure supports. Support = (a) and (a′) ALO1, (b) and (b′) ALO3, (c) and (c′) ALO8, (d) and (d′) CeO, (e) and (e′) SAH1, and (f) and (f’) MGO3 (●) ZnO.

The catalytic activities of supported catalysts depended on the temperature of H_2 reduction. Fig. 2 shows the dependence of the reduction temperature on the catalytic activities of Cu-ZnO/ALO8 and Cu-ZnO/MGO3 that showed the relatively high activity among the supported catalysts tested in the present study. For Cu-ZnO/ALO8 catalyst, the activity gradually increased with reduction temperature, reached a maximal value at 523 K of the reduction temperature, and then slightly decreased with further increasing the reduction temperature. On the other hand, the activity of Cu-ZnO/MGO3 was significantly lower than that of Cu-ZnO/ALO8 in the low reduction temperature region. However, the increases in the activity of Cu-ZnO/MGO3 were observed in the temperature regions, 423–473 and 523–573 K. These results suggest that the most appropriate reduction temperature strongly depended on the kind of support; the appropriate reduction temperature of Cu-ZnO/ALO8 was lower than that of Cu-ZnO/MGO3. Considering that metallic copper is an active site [10], the difference of the catalytic activities between Cu-ZnO/ALO8 and Cu-ZnO/MGO3 catalysts at lower reduction temperature may correspond to the difference of the amount of metallic copper formed by H_2 reduction of CuO at a given reduction temperature. Details of the reduction behavior of supported catalysts will be given in the later section.

3.2. XRD analysis of CuO-ZnO catalysts supported on various oxides

The XRD patterns of supported CuO(5 wt.%)-ZnO(5 wt.%) catalysts are presented in Fig. 3. The XRD patterns of pure supports are also shown for comparison. No or less detectable diffractions of both copper oxide and zinc oxide crystallites can be distinguished for CuO-ZnO catalysts supported on ALO1, ALO3, ALO8, SAH1, and CeO (Fig. 3(a–e)), suggesting that both copper oxide and zinc oxide are highly dispersed. Similar results were obtained for CuO-ZnO catalysts supported on ALO2, ALO5, SM1 and ZB25. On the other hand, CuO-ZnO catalysts supported on MGO3 with a low surface area provided the diffraction lines assigned to zinc oxide (Fig. 3(f)). A similar result was observed for CuO-ZnO/MGO4.

3.3. TPR studies of CuO-ZnO catalysts supported on various oxides

The H_2-TPR behavior of supported Cu-based catalyst is well documented in the literature to elucidate the state of copper oxide and metallic copper. Fig. 4 shows TPR profiles of a series of CuO-ZnO supported on Al_2O_3 used in the present study. As shown in Fig. 4, a large peak in the range 400–550 K was observed for CuO-ZnO catalysts supported on Al_2O_3. Such a large peak can be attributed to the reduction of CuO species because no reduction peak was observed for ZnO supported on Al_2O_3 in the temperature range 373–750 K. For all the catalysts shown in Fig. 4, the amount of H_2 consumed, which can be determined from the peak area, corresponded to the amount of copper loaded, i.e., the H_2/CuO molar ratio was close to unity, demonstrating that the following reaction, $CuO + H_2 \rightarrow Cu^0 + H_2O$, was completed below 550 K.

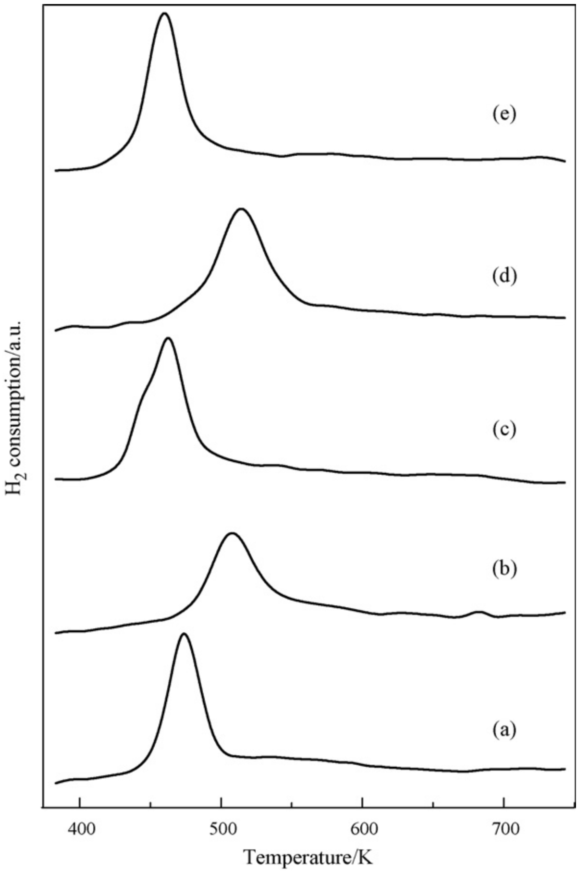

Fig. 4. H_2-TPR profiles of CuO(5 wt.%)-ZnO(5 wt.%)/Al_2O_3 catalysts. Support = (a) ALO1, (b) ALO2, (c) ALO3, (d) ALO5, and (e) ALO8.

The reduction temperature of CuO depended on the kind of Al_2O_3. It should be noted that the reduction temperature of CuO-ZnO/ALO8 and CuO-ZnO/ALO3 catalysts with high activity was lower than those of CuO-ZnO catalysts on the other Al_2O_3 supports. It might mean that the high reducibility of CuO was required for the catalysts showing high activity. Dow et al. [11] have reported that the shift of the reduction temperature of CuO was related with the crystalline size of CuO; the reducibility of CuO was promoted by decreasing the crystalline size of CuO. Therefore, the crystalline sizes of CuO in CuO-ZnO/ALO8 and CuO-ZnO/ALO3 might be smaller than those in CuO-ZnO/ALO1, CuO-ZnO/ALO2, and CuO-ZnO/ALO5, although the crystalline sizes among CuO-ZnO/Al_2O_3 catalysts could not be distinguished by XRD analysis. The order of the reducibility of CuO supported was ALO8 $\approx$ ALO3 > ALO1 > ALO2 $\approx$ ALO5, being not completely agreement with that of the catalytic activities of Al_2O_3-supported catalysts shown in Table 1. This result suggests that not only the reducibility of CuO but also another interaction between metallic copper and support should be considered for better understanding the catalytic performances of CuO-ZnO/Al_2O_3 catalysts.

The TPR profiles of CuO-ZnO catalysts supported on the other oxides are illustrated in Fig. 5. TPR profiles shown in

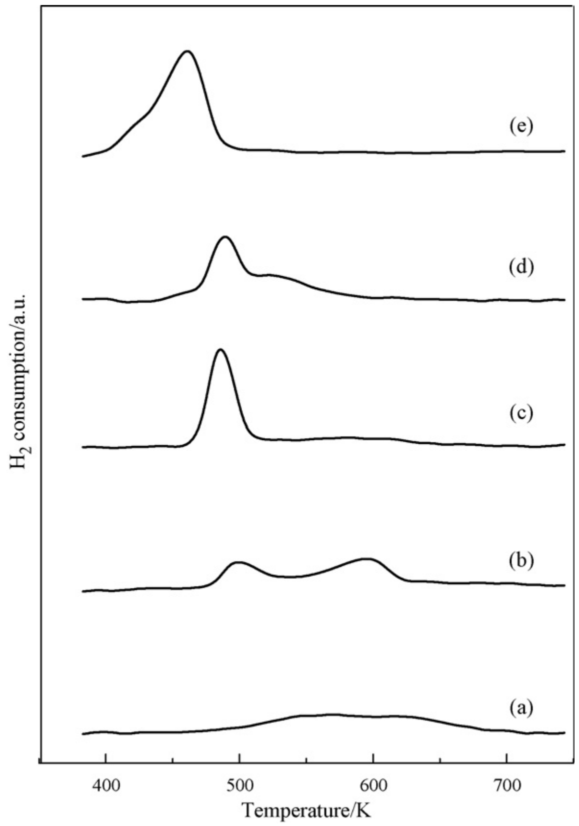

Fig. 5. H_2-TPR profiles of supported CuO(5 wt.%)-ZnO(5 wt.%) catalysts. Support = (a) SAH1, (b) MGO3, (c) SM1, (d) ZB25, and (e) CeO.

Fig. 5 consisted of two or more peaks, indicating that the reduction processes of CuO for the supported catalysts were more complicated than CuO-ZnO/Al_2O_3 catalysts shown in Fig. 4. Note that the CuO-ZnO/CeO catalyst gave the TPR peaks in the low-temperature region. This result is consistent with our hypothesis that the catalyst with the high reducibility of CuO is active for the WGS reaction. However, CuO-ZnO/MGO3 is not the case; although the TPR profile of CuO-ZnO/MGO3 gives two reduction peaks at relatively high-temperature, 500 and 590 K, CuO-ZnO/MGO3 catalyst is active for the WGS reaction (Table 1). The reason why the CuO-ZnO/MGO3 catalyst is active for the WGS reaction is not clear in the present study. Recently, Shishido et al. [12] have reported that the addition of MgO to Cu/ZnO oxide catalyst enhanced the activity of the WGS reaction and they considered that the active species were stabilized by MgO. This may be an important result for understanding the enhancement of the activity of Cu-ZnO catalyst by supporting on MgO.

The recent papers have reported that the catalytic activity for WGS reaction is closely related to the surface area of metallic copper [10,13]. The dependence of surface areas of metallic copper for the catalysts used in the present study on the catalytic activity for WGS reaction are under investigation.

4. Conclusion

The activities of the low-temperature WGS reaction were investigated for Cu-ZnO catalysts supported on Al_2O_3, MgO, SiO_2-Al_2O_3, SiO_2-MgO, β-zeolite, and CeO_2. The activity of Cu-ZnO catalysts for the WGS reaction was largely influenced by both the kind of support and the reduction temperature. The order of the activities of supported Cu-ZnO catalysts was $\mathrm{ALO8} > \mathrm{ALO3} \approx \mathrm{CeO} > \mathrm{MGO4} \approx \mathrm{MGO3} \gg \mathrm{SM1} \approx \mathrm{ALO5} \approx \mathrm{ALO2} \approx \mathrm{ALO1} \approx \mathrm{SAH1} \approx \mathrm{ZB25}$; the highest activity was obtained over Cu-ZnO/ALO8. Such an order was not consistent with that of BET surface area. TPR results of supported catalysts suggest that the reducibility of CuO is one of important factors controlling the activity of the WGS reaction for the supported catalysts.

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