New Catalytic System for Producing Pure Hydrogen -Water-gas-shift Reaction of Supported Copper Catalysts-

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ABSTRACT

The catalytic activities of the low-temperature water-gas-shift (WGS) reaction were investigated for Al2O3-supported Cu catalysts containing CrOx, MnOx, FeOx, CoOx, or NiOx. The catalytic activity of Cu/Al2O3 catalyst at 423 K was enhanced by the addition of transition metal oxide. FeOx and MnOx additives additionally gave the enhancement in the catalytic activity at 523 K. The preparation conditions concerning calcination temperature and MOx/Cu molar ratio were optimized for Cu-FeOx/Al2O3 and Cu-CoOx/Al2O3 catalysts. The reason why the catalytic activity was enhanced by adding FeOx and CoOx to Cu/Al2O3 was proposed on the basis of XRD and H2-TPR results.

Keywords: hydrogen, copper catalyst, wgs reaction, iron oxide.

1 INTRODUCTION

It is well-known that 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 + H2O = H2 + CO2, 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 [1-4] and supported Cu catalysts [5-10] have been reported to exhibit the high activity for the WGS reaction.

Recently, we have reported that Cu/Al2O3 catalysts calcined at relatively high temperature contain both highly dispersed Cu and CuAl2O4 spinel and the former species act as active sites for the WGS reaction [9]. Here, we wish to report the influences of transition metal oxide additives on the catalytic activity of Cu/Al2O3 for WGS reaction. In particular, the catalytic performances of Cu-FeOx/Al2O3 and Cu-CoOx/Al2O3 catalysts having the highest catalytic activity for WGS reaction at low and high temperature, respectively, were investigated.

2 EXPERIMENTAL

Al2O3 support was supplied from the Catalysis Society of Japan (JRC-ALO-8). Cu/Al2O3 catalysts containing FeOx were prepared by a conventional impregnation method using the mixed aqueous solution of Cu(NO3)2·3H2O (Wako Chem.) and Fe(NO3)3·9H2O (Wako Chem.). Cu/Al2O3 catalysts containing other transition metal oxides were prepared by a similar way. 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 15 wt%. The surface area of catalyst was measured by the BET method using N2 adsorption. Al2O3-supported catalysts with and without H2 reduction at 523 K are abbreviated as Cu-FeOx/Al2O3 [973](1.0) (Cu-transmission metal oxide (MOx)/Al2O3 [calcination temperature] (MOx/Cu molar ratio) and CuO-FeOx/Al2O3 [973](1.0), respectively.

The WGS reaction was carried out in a fixed-bed continuous flow reactor at 423-523 K. Prior to the activity test, the catalyst was reduced by flowing 20 vol%H2/He gas at a flow rate of 30 cm3·min⁻¹ at 523 K for 2 h. The reactant gases contained 9.5 vol% of CO, 27.7 vol% of H2O, 56.0 vol% of H2, and 6.8 vol% of CO2. The total flow rate was 96 cm3·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 CuKα radiation. Hydrogen temperature-programmed reduction (H2-TPR) was carried out by flowing 5 vol%H2/N2 (30 cm3·min⁻¹) in the temperature range 343-1173 K. The sample temperature increased with a rate of 2 K·min⁻¹ and the amount of H2 consumed was monitored by a thermal conductivity detector of a gas chromatograph (Shimadzu, GC-8AIT). The DRIFT-IR spectra were recorded with FT-IR spectrometer (Perkin Elmer, Spectrum One) equipped with MCT detector.

3 RESULTS AND DISCUSSION

3.1 Supported Cu-MOx Catalysts

The catalytic activities of Cu-MOx/Al2O3[973](1.0) catalysts are summarized in Table 1. A unique promotive effect of MOx additives on the catalytic activity of Cu/Al2O3 was observed. For Cu/Al2O3 catalyst, no catalytic activity was observed at temperature as low as 423 K. However, the catalytic activity of Cu/Al2O3 catalyst was enhanced by MOx additives at 423 K. In addition, FeOx and MnOx additives gave the enhancement of the catalytic
activity at high temperature (523 K). As can be seen in Table 1, no relation between catalytic activities of WGS reaction and BET surface area was observed.

Figure 1 shows the XRD patterns of as-calcinated CuO-MO\(_2\)/Al\(_2\)O\(_3\) [973](1.0) catalysts before H\(_2\)-reduction at 523 K. CuO/Al\(_2\)O\(_3\) [973](1.0) catalyst provided the XRD pattern consisting of the intense and the broad peaks assigned to CuO (2\(\theta\) = 35.3 and 38.5 degree) and \(\gamma\)-Al\(_2\)O\(_3\) (2\(\theta\) = 31.7, 37.2, and 45.4 degree), respectively (Fig. 1(a)). When MO\(_x\) were added to CuO/Al\(_2\)O\(_3\), the peak intensity of CuO more or less decreased, suggesting that MO\(_x\) additives were reacted with CuO and/or made CuO particles highly dispersed state. In the following sections, the catalytic performances of Al\(_2\)O\(_3\) supported Cu-FeO\(_x\) and Cu-CoO\(_x\) catalysts will be presented as instances.

![XRD patterns of CuO-MO\(_2\)/Al\(_2\)O\(_3\) [973](1.0) catalysts. M = (a) none, (b) Cr, (c) Mn, (d) Fe, (e) Co, and (f) Ni.](image)

### Table 1: Catalytic activities and BET surface areas of Cu-MO\(_x\)/Al\(_2\)O\(_3\) [973](1.0) catalysts.

<table>
<thead>
<tr>
<th>M</th>
<th>423 K Conversion of CO / %</th>
<th>473 K Conversion of CO / %</th>
<th>523 K Conversion of CO / %</th>
<th>BET surface area / m(^2)g(^{-1})</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cr</td>
<td>20</td>
<td>59</td>
<td>69</td>
<td>71</td>
</tr>
<tr>
<td>Mn</td>
<td>7</td>
<td>46</td>
<td>74</td>
<td>82</td>
</tr>
<tr>
<td>Fe</td>
<td>4</td>
<td>52</td>
<td>87</td>
<td>78</td>
</tr>
<tr>
<td>Co</td>
<td>13</td>
<td>38</td>
<td>25</td>
<td>83</td>
</tr>
<tr>
<td>Ni</td>
<td>16</td>
<td>38</td>
<td>48</td>
<td>91</td>
</tr>
<tr>
<td>None</td>
<td>0</td>
<td>44</td>
<td>65</td>
<td>105</td>
</tr>
</tbody>
</table>

Experimental condition: 9.5 vol% of CO, 27.7 vol% of H\(_2\), 56.0 vol% of H\(_2\)O, 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\(^{-1}\)).

3.2 Supported Cu-FeO\(_x\) Catalysts

The catalytic activities of Cu-FeO\(_x\)/Al\(_2\)O\(_3\) and Cu/Al\(_2\)O\(_3\) are summarized in Table 2, as functions of calcination temperature and FeO\(_x\)/Cu molar ratio. The less change in the catalytic activity of Cu/Al\(_2\)O\(_3\) was observed at 873-1073 K of calcination temperature. On the other hand, the catalytic activity of Cu-FeO\(_x\)/Al\(_2\)O\(_3\) increased with calcination temperature, reached a maximal value at 973 K, and then decreased with further increasing calcination temperature. When the catalytic activity of Cu-FeO\(_x\)/Al\(_2\)O\(_3\) [973](1.0) was compared with that of Cu/Al\(_2\)O\(_3\) [973], it was found that the enhancement of the catalytic activity by FeO\(_x\) addition was pronounced for the catalytic reaction performed at higher temperature, 523 K.

The catalytic activities of Cu-FeO\(_x\)/Al\(_2\)O\(_3\) catalysts calcined at 973 K were dependent on FeO\(_x\)/Cu molar ratio, as shown in Table 2. The catalytic activity was increased by the addition of FeO\(_x\) to Cu/Al\(_2\)O\(_3\). It should be noted that the activity of Cu-FeO\(_x\)/Al\(_2\)O\(_3\) with FeO\(_x\)/Cu > 0.5 exceeded the initial value (Cu/Al\(_2\)O\(_3\)). FeO\(_x\)/Al\(_2\)O\(_3\) catalysts calcined at 873-1073 K exhibited no catalytic activity for the WGS reaction at 473 and 523 K; therefore, the increase in the catalytic activity by FeO\(_x\) additive may be due to the synergistic effect of co-existence of Cu and FeO\(_x\).

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>423 K Conversion of CO / %</th>
<th>473 K Conversion of CO / %</th>
<th>523 K Conversion of CO / %</th>
</tr>
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<tr>
<td>Cu-FeO(_x)/Al(_2)O(_3) <a href="1.0">873</a></td>
<td>0</td>
<td>28</td>
<td>81</td>
</tr>
<tr>
<td>Cu-FeO(_x)/Al(_2)O(_3) <a href="1.0">973</a></td>
<td>4</td>
<td>52</td>
<td>87</td>
</tr>
<tr>
<td>Cu-FeO(_x)/Al(_2)O(_3) <a href="1.0">1073</a></td>
<td>0</td>
<td>27</td>
<td>72</td>
</tr>
<tr>
<td>Cu-FeO(_x)/Al(_2)O(_3) <a href="0.5">973</a></td>
<td>1</td>
<td>50</td>
<td>83</td>
</tr>
<tr>
<td>Cu/Al(_2)O(_3) [873]</td>
<td>5</td>
<td>39</td>
<td>61</td>
</tr>
<tr>
<td>Cu/Al(_2)O(_3) [973]</td>
<td>0</td>
<td>44</td>
<td>65</td>
</tr>
<tr>
<td>Cu/Al(_2)O(_3) [1073]</td>
<td>3</td>
<td>38</td>
<td>68</td>
</tr>
</tbody>
</table>

Experimental conditions were the same as those in Table 1.

3.2 Supported Cu-FeO\(_x\) Catalysts

The XRD patterns of Cu-FeO\(_x\)/Al\(_2\)O\(_3\) catalysts calcined at 973 K in air, followed by the H\(_2\)-reduction at 523 K, are shown in Fig. 2. Cu/Al\(_2\)O\(_3\) catalyst calcined at 973 K gave the diffraction lines assigned to metallic copper (Cu\(^0\)) species as well as the broad diffraction lines from \(\gamma\)-Al\(_2\)O\(_3\). The intensity of Cu\(^0\) diffraction line decreased by the addition of FeO\(_x\), suggesting the formation of highly dispersed Cu\(^0\) particles. Interestingly, the diffraction lines assigned to FeO\(_x\) appeared in XRD pattern of Cu-FeO\(_x\)/Al\(_2\)O\(_3\), although no reduction of FeO\(_x\) to Fe\(_2\)O\(_3\) took place in the absence of copper species (probably Cu\(^0\)).

Figure 3 shows H\(_2\)-TPR profiles of Cu/Al\(_2\)O\(_3\) [973], FeO\(_x\)/Al\(_2\)O\(_3\) [973], and Cu-FeO\(_x\)/Al\(_2\)O\(_3\) [973](0.5 and 1.0). A large peak in the range 450-500 K was observed for Cu/Al\(_2\)O\(_3\) [973] catalyst (Fig. 3(a)), being assigned to the reduction of CuO to Cu\(^0\) [9]. On the other hand, FeO\(_x\)/Al\(_2\)O\(_3\) [973] exhibited a very broad peak in the
temperature range 493-1050 K (Fig. 3(d)). 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. 3(c). This additional peak was tentatively assigned to the reduction of Fe$_3$O$_4$ to Fe$_2$O$_3$ strongly interacted with metallic Cu. A similar H$_2$-TPR profile was reported for Cu-FeO$_x$/SiO$_2$ [11] and copper ferrite spinel [12].

From the present XRD and H$_2$-TPR results, we are considering the two possible interpretations of the enhancement in the catalytic activity by adding FeO$_x$ to Cu/Al$_2$O$_3$. One is the formation of highly dispersed Cu$^0$ formed by Fe additives. The XRD patterns of Cu-FeO$_x$/Al$_2$O$_3$ catalysts, as shown in Fig. 3, indicates that the addition of FeO$_x$ to Cu/Al$_2$O$_3$ 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$^0$ [9], it is appreciably expected that the formation of fine particles leads to enhance the catalytic activity.

The other explanation is the participation of the reduced FeO$_x$ to WGS reaction in the presence of Cu$^0$. FeO$_x$ has reported to be active for high temperature-WGS reaction (ca. 623-723 K) [13]. In this case, it is considered that the redox property between Fe$_3$O$_4$ and Fe$_2$O$_3$ was important for WGS reaction over FeO$_x$ catalysts. The present XRD and H$_2$-TPR studies proved that the Fe$_3$O$_4$ was easily reduced to Fe$_2$O$_3$ in the presence of Cu$^0$ at lower temperature. Considering the report that the oxygen on Cu$^0$ can rapidly diffuse to Fe surface [11], the redox process of FeO$_x$ sufficiently take place in the present condition.

![Figure 2: XRD spectra of Cu-FeO$_x$/Al$_2$O$_3$ [973] (x) catalysts. x = (a) 0, (b) 0.5, and (c) 1.0. (□)Cu$^0$, (▲)Fe$_3$O$_4$, (△)FeAlO$_4$, and (◇)γ-Al$_2$O$_3$.](image)

![Figure 3: H$_2$-TPR profiles of (a) CuO/Al$_2$O$_3$[973], (b) CuO-FeO$_x$/Al$_2$O$_3$[973][0.5], (c) CuO-FeO$_x$/Al$_2$O$_3$[973][1.0], and (d) FeO$_x$/Al$_2$O$_3$[973].](image)

### 3.3 Supported Cu-CoO$_x$ Catalysts

The catalytic activities of Cu-CoO$_x$/Al$_2$O$_3$ are summarized in Table 3 as a function of CoO$_x$/Cu molar ratio. As shown in Table 1, Cu-CoO$_x$/Al$_2$O$_3$ exhibited the higher catalytic activity than Cu/Al$_2$O$_3$ at 423 K. The catalytic activity was significantly increased by the small amount of CoO$_x$ added; Cu-CoO$_x$/Al$_2$O$_3$ [973][0.05] catalyst was the most active for WGS reaction at 423 K among the Cu-MO$_x$/Al$_2$O$_3$ catalysts tested in the present study. However, the catalytic activity was slightly decreased by the further addition of CoO$_x$ to Cu/Al$_2$O$_3$.

![Table 3: Catalytic activities of Cu-CoO$_x$/Al$_2$O$_3$ catalysts](image)
large peak in the range 450-500 K; this profile was also essentially the almost same as that of Cu/Al\textsubscript{2}O\textsubscript{3}[973] catalyst. These results indicated the dispersion state of Cu\textsuperscript{0} was very similar to that of Cu/Al\textsubscript{2}O\textsubscript{3}. In order to elucidate the adsorption state of CO on Cu-CoO\textsubscript{x}/Al\textsubscript{2}O\textsubscript{3} catalyst, DRIFT-IR measurements were conducted. The spectra of Cu-CoO\textsubscript{x}/Al\textsubscript{2}O\textsubscript{3}[973](0.05) and Cu/Al\textsubscript{2}O\textsubscript{3}[973] are depicted in Fig. 4. When the Cu/Al\textsubscript{2}O\textsubscript{3}[973] and Cu-CoO\textsubscript{x}/Al\textsubscript{2}O\textsubscript{3}[973](0.05) samples were exposed to CO at 473 K, an intense IR peak assigned to Cu\textsuperscript{0}-CO was observed at 2108 cm\textsuperscript{-1}. It is clear that the intensity of Cu\textsuperscript{0}-CO peak was increased by the addition of CoO\textsubscript{x}. Assuming that the morphology of Cu\textsuperscript{0} (for example, particle size) was unchanged by the small amount of CoO\textsubscript{x} added, CoO\textsubscript{x} addition provides the enhancement in the adsorption ability of CO on Cu\textsuperscript{0} supported on Al\textsubscript{2}O\textsubscript{3}, although further studies are needed.

Figure 4: DRIFT-IR spectra of (a) Cu/Al\textsubscript{2}O\textsubscript{3}[973] and (b) Cu-CoO\textsubscript{x}/Al\textsubscript{2}O\textsubscript{3}[973](0.05) catalysts after the introduction of CO (5.0 vol\%, N\textsubscript{2} balance) for 60 min. Measurement temperature was 423 K.

4 CONCLUSION

The catalytic activities of the low-temperature WGS reaction were investigated for Al\textsubscript{2}O\textsubscript{3}-supported Cu catalysts containing various transition metal oxides. For Cu/Al\textsubscript{2}O\textsubscript{3} catalyst, no catalytic activity was observed at temperature as low as 423 K. However, the catalytic activity of Cu/Al\textsubscript{2}O\textsubscript{3} catalyst at 423 K was enhanced by the addition of transition metal oxide. Furthermore, the addition of FeO\textsubscript{x} and MnO\textsubscript{x} resulted in the enhancement in the catalytic activity at high temperature (523 K). The effect of FeO\textsubscript{x} additives on the catalytic activity may be explained by two possibilities; one is the formation of highly dispersed Cu\textsuperscript{0} formed and the other is the participation of reduced FeO\textsubscript{x} in WGS reaction in the presence of Cu\textsuperscript{0}. It was found that CoO\textsubscript{x} addition provides the increase in the adsorption ability of CO on Cu\textsuperscript{0} supported on Al\textsubscript{2}O\textsubscript{3}.

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REFERENCES