# Methanol Synthesis from $CO_2$ and $H_2$ over CuO–ZnO Catalysts Combined with Metal Oxides under 13 atm Pressure

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The synthesis of methanol from $CO_2$ and $H_2$ in a flow reactor was studied over CuO–ZnO catalysts combined with $ZrO_2$, MgO, $Al_2O_3$, or $Cr_2O_3$ under a presssure of 13 atm. CuO–ZnO–$Al_2O_3$, CuO–ZnO–$ZrO_2$, and CuO–ZnO–MgO showed higher activity and higher selectivity for methanol than did CuO–ZnO. The selectivity for methanol formation became higher as the reaction temperature was lower, or any of the $H_2/CO_2$ ratio, the pressure and the space velocity were higher. On the basis of analyses by XRD, XPS, and ultraviolet diffused reflectance spectroscopy, the active centers of CuO–ZnO–$ZrO_2$ seem to be a $Cu^+$–ZnO species stabilized by $ZrO_2$.

Methanol synthesis from $CO_2$ and $H_2$ has recently been studied over various mixed oxide catalysts. The binary mixed oxides used were CuO–$Al_2O_3$,[1,2] CuO–ZnO,[2,3] CuO supported on MgO, $La_2O_3$, $Sm_2O_3$, $ThO_2$–K, and $ZrO_2$[2] and ZnO supported on MgO, $Al_2O_3$, $SiO_2$, $TiO_2$, $ZrO_2$, and $Nb_2O_5$.[4] The ternary mixed oxides used were CuO–ZnO–$Al_2O_3$,[2,3,5,6] CuO–ZnO–$Cr_2O_3$,[3] and CuO–ZnO supported on MgO, $Y_2O_3$, $In_2O_3$, $La_2O_3$, $Nd_2O_3$, $ThO_2$, and $SiO_2$.[6] Among these catalysts, CuO–ZnO–MgO, CuO–ZnO–$Al_2O_3$, CuO–ZnO–$La_2O_3$, and CuO–ZnO–$ThO_2$ showed high catalytic activity and selectivity for methanol formation. In the present work, CuO–ZnO–$ZrO_2$ was examined and the activity and selectivity of CuO–ZnO–$ZrO_2$ compared with those of CuO–ZnO–MgO, CuO–ZnO–$Al_2O_3$, and CuO–ZnO–$Cr_2O_3$; further, the active sites on CuO–ZnO–$ZrO_2$ were studied by means of XRD, XPS, and ultraviolet diffused reflectance spectroscopy.

## Experimental

**Catalyst.** CuO-ZnO catalysts with different compositions were prepared by the hydrolysis of a mixed solution of $Cu(NO_3)_2$ and $Zn(NO_3)_2$ with an aqueous solution of $Na_2CO_3$, followed by thoroughly washing the co-precipitates with distilled water and drying overnight. The dried catalysts were calcined in air at 350 °C for 3 h and then at 500 °C for 1 h.

CuO-ZnO-$ZrO_2$, CuO-ZnO-MgO, CuO-ZnO-$Al_2O_3$, and CuO-ZnO-$Cr_2O_3$ catalysts with different compositions were prepared by directly adding $Zr(OH)_4$, $Mg(OH)_2$, $Al(OH)_3$, and $Cr(OH)_3$, respectively, to the $Cu(OH)_2$–$Zn(OH)_2$ co-precipitates obtained above, followed by drying and calcining, as described above. Zirconium tetrahydroxide was obtained by the hydrolysis of $ZrOCl_2$ with aqueous ammonia and $Mg(OH)_2$, $Al(OH)_3$, and $Cr(OH)_3$ were prepared by hydrolysis of the respective nitrates with an aqueous solution of $Na_2CO_3$.

Catalysts after being sieved to 20—40 mesh size were reduced with $H_2$ at 300 °C for 6 h in a reactor and subjected to evaluation.

**Preparation of Standard Samples.** A standard sample of $Cu^0$ was obtained by etching a pure Cu metal plate with $Ar^+$ ions at an electric current of 20 μA for 10 min until the $O_{1s}$ lines in the XPS spectra disappeared. Pure CuO sample was prepared by calcining a pure Cu metal plate at 500 °C for 3 h in air. Pure $Cu_2O(Cu^+)$ was obtained by etching the pure CuO with $Ar^+$ ions in an ultra high vacuum at a lower electronic current (15 μA) for 10 min.[7]

**Reaction Procedures.** A reaction of $CO_2$ with $H_2$ was carried out in a flow reactor. A mixture containing $H_2$ and $CO_2$ at a mole ratio 3:1 was fed through a constant volume of catalyst (1.8 $cm^3$) at a total pressure of 13 atm. The products were analyzed by gas chromatography with a Porapak Q column.

**XPS Measurement.** XPS spectra were measured by the use of an ESCALAB MK spectrometer (V. G. Scientific Ltd., UK) equipped with an in-situ reaction cell and a pretreatment chamber, using Mg $K\alpha$ radiation ($h\nu$=1253.6 eV). Catalyst specimens were prepared by pressing powder samples to a small plate, followed by evacuation at room temperature of about $10^{-9}$ Torr in the pretreatment chamber. After being transferred to a small reactor equipped inside the pretreatment chamber, each specimen was reduced with $H_2$ (1 atm) at 300 °C for 2 h (a mixture of 25% $CO_2$+75% $H_2$ (1 atm) was adsorbed on it at room temperature) and then evacuated to $10^{-3}$ Torr at 250 °C. The specimen was cooled down, and transferred back to the pretreatment chamber, evacuated to about $5\times10^{-8}$ Torr, and then transferred to the analyzing chamber for an XPS measurement. The charging effects of various specimens were minimized by taking the binding energy of the Zn($2p_{2/3}$) level at 1021.7 eV as the internal standard.

**XRD Measurement.** The X-ray powder diffraction patterns were recorded by using a Rigaku D/MAX III-A X-ray diffractometer with Cu $K\alpha$ (0.15418 nm) radiation. Samples were mounted on a glass slide by using double-seal tape and inserted into the sample holder.

**UDRS Measurements.** Ultraviolet diffused reflectance spectra were measured by utilizing a UV-240 spectrometer in the range of 250—800 nm; $BaSO_4$ was used as a standard. Samples were reduced for 6 h and then placed in infrasil front-window cells without exposure to air, either by transfer under nitrogen or by direct reduction in a closed system.

## Results and Discussion

**Catalytic Activity and Selectivity.** Table 1 shows both the activity and selectivity of CuO–ZnO catalysts with different compositions. Only CuO showed a very low activity ($CO_2$ conversion), no methanol being formed; only ZnO showed low activity and formed

Table 1. Activity and Selectivity of CuO-ZnO Catalysts in $CO_2+H_2$ Reaction[a)]

| Catalyst | SV | Reac. temp | $X_{CO_2}$[b)] | Selectivity/% | | | $Y_{CO_2}$[c)] |
|---|---|---|---|---|---|---|---|
| | $h^{-1}$ | °C | % | $CH_3OH$ | CO | $CH_4$ | % |
| ZnO | 3500 | 240 | 6.0 | 16.9 | 74.7 | 8.5 | 1.0 |
| CuO/ZnO (10/90) | 3600 | 220 | 7.2 | 13.5 | 79.1 | 7.3 | 1.0 |
| | | 240 | 15.1 | 12.1 | 82.3 | 5.6 | 1.8 |
| CuO/ZnO (30/70) | 3600 | 220 | 20.0 | 42.6 | 53.8 | 3.7 | 8.5 |
| | | 240 | 32.4 | 20.6 | 76.5 | 2.9 | 6.7 |
| CuO/ZnO (47/53) | 3600 | 220 | 21.2 | 56.7 | 40.3 | 3.1 | 12.0 |
| | | 240 | 31.6 | 38.9 | 56.5 | 4.0 | 12.3 |
| CuO/ZnO (90/10) | 3600 | 220 | 19.1 | 41.0 | 56.2 | 2.8 | 7.8 |
| | | 240 | 33.5 | 28.3 | 67.7 | 4.0 | 9.5 |
| CuO | 3600 | 240 | 1.7 | 0 | 81.0 | 19.0 | 0 |

a) Reaction conditions: mole ratio of $H_2/CO_2=3/1$, total pressure 13 atm. The catalyst of 1.8 $cm^3$ was used after reduction with $H_2$ at 300 °C for 6 h. b) $X_{CO_2}$=Conversion of $CO_2$. c) $Y$=yield.

Table 2. Activity and Selectivity of CuO-ZnO-$ZrO_2$ Catalysts in $CO_2+H_2$ Reaction[a)]

| Catalyst | SV | Reac. temp | $X_{CO_2}$[b)] | Selectivity/% | | | Rate of reaction[d)] | | | $Y_{CH_3OH}$[c)] |
|---|---|---|---|---|---|---|---|---|---|---|
| | $h^{-1}$ | °C | % | $CH_3OH$ | CO | $CH_4$ | CO | $CH_3OH$ | $CO_2$ | % |
| CuO/ZnO/$ZrO_2$ (47/53/0) $A_1$ | 3600 | 220 | 21.2 | 56.7 | 40.3 | 3.1 | 3.3 | 4.7 | 8.2 | 12.0 |
| | | 240 | 31.6 | 38.9 | 56.5 | 4.6 | 6.9 | 4.8 | 12.2 | 12.3 |
| CuO/ZnO/$ZrO_2$ (45/50/5) $A_2$ | 3600 | 220 | 12.5 | 68.9 | 27.4 | 3.8 | 1.5 | 3.7 | 5.4 | 8.6 |
| | | 240 | 19.8 | 60.7 | 34.9 | 4.4 | 3.0 | 5.2 | 8.55 | 12.0 |
| CuO/ZnO/$ZrO_2$ (42/47/11) $A_3$ | 3600 | 160 | 5.4 | 94.8 | 4.4 | 0.8 | 0.1 | 2.3 | 2.4 | 5.1 |
| | | 180 | 9.4 | 88.8 | 10.3 | 0.9 | 0.4 | 3.8 | 4.3 | 8.4 |
| | | 200 | 17.9 | 73.0 | 26.0 | 1.0 | 2.1 | 6.0 | 8.2 | 13.1 |
| | | 220 | 29.1 | 59.9 | 38.4 | 1.6 | 5.1 | 8.0 | 13.3 | 17.4 |
| | | 240 | 37.1 | 39.6 | 56.5 | 3.9 | 8.7 | 6.8 | 17.2 | 14.9 |
| | | 260 | 39.3 | 22.8 | 69.5 | 7.7 | 12.5 | 4.1 | 17.9 | 9.0 |
| | | 280 | 42.8 | 18.6 | 72.4 | 8.9 | 14.2 | 3.6 | 19.5 | 8.0 |
| CuO/ZnO/$ZrO_2$ (32/35/33) $A_4$ | 3600 | 220 | 21.6 | 72.4 | 25.7 | 1.9 | 3.0 | 8.6 | 11.8 | 15.6 |
| | | 240 | 27.5 | 51.4 | 46.6 | 2.0 | 7.0 | 7.8 | 15.1 | 14.1 |
| CuO/ZnO/$ZrO_2$ (21/24/55) $A_5$ | 3600 | 220 | 20.5 | 68.3 | 29.3 | 2.3 | 4.3 | 9.9 | 14.6 | 14.0 |
| | | 240 | 29.7 | 46.4 | 50.3 | 3.2 | 10.6 | 9.8 | 21.1 | 13.8 |
| CuO/ZnO/$ZrO_2$ (11/12/77) $A_6$ | 3600 | 240 | 6.9 | 78.7 | 17.0 | 4.3 | 0.8 | 3.6 | 4.6 | 5.4 |

a) Reaction conditions: mole ratio of $H_2/CO_2=3/1$, total pressure 13 atm. The catalyst of 1.8 $cm^3$ was used after reduction with $H_2$ at 300°C for 6 h. b) $X_{CO_2}$=Conversion of $CO_2$. c) $Y$=yield. d) mmol $g^{-1}$ $h^{-1}$.

methanol, its selectivity being 17%. However, the mixed oxides, CuO-ZnO, showed much higher activity for $CO_2$ conversion and much higher selectivity for the formation of methanol than did CuO or ZnO alone. A CuO-ZnO catalyst with a molar ratio=47/53 showed the higher yield (12.3%) of methanol at 240 °C, the $CO_2$ conversion and methanol selectivity being 31 and 39% at 240 °C, respectively.

The results for the reaction of $CO_2$ with $H_2$ over CuO-ZnO-$ZrO_2$ catalysts of different compositions are given in Table 2. The selectivities for methanol were high for all of the CuO-ZnO-$ZrO_2$ catalysts, compared with that for CuO-ZnO. A CuO-ZnO-$ZrO_2$ catalyst with a molar ratio of 42/47/11 exhibited the highest yield (17.4%) of methanol at 220 °C, and the highest selectivity (94.8%) for methanol at 160 °C. The lower was the reaction temperature, the higher was the methanol selectivity. On the other hand, the conversion of $CO_2$ and the selectivity for CO or $CH_4$ increased with increasing the reaction temperature.

The effects of the $H_2/CO_2$ ratio, pressure, and space velocity on the activity and selectivity of CuO-ZnO-

$ZrO_2$ (42/47/11) are shown in Figs. 1, 2, and 3, respectively. With an increase in the $H_2/CO_2$ ratio, the $CO_2$ conversion and methanol selectivity increased linearly, and the CO selectivity decreased. With an increase in the pressure, the $CO_2$ conversion and methanol selectivity increased, and the CO selectivity decreased. With an increase in the space velocity, and methanol selectivity increased over an SV range smaller than 3600 $h^{-1}$, while a small increase was observed above 3600 $h^{-1}$; CO selectivity decreased considerably.

Since the addition of $ZrO_2$ to CuO–ZnO caused a high yield of methanol, we attempted to examine the additive effect of MgO, $Al_2O_3$, or $Cr_2O_3$ on the activity and selectivity of CuO–ZnO. As shown in Table 3, the methanol yield was found to be highest over CuO–ZnO–$Al_2O_3$. The addition of $Cr_2O_3$ resulted in a marked decrease in the activity. No reaction was appreciable over CuO–ZnO–$Cr_2O_3$ below 300 °C. Although the amount of $Cr_2O_3$ was higher than those of the other catalyst supports, the decrease in the activity was so great that it cannot be explained by the amount of support. Thus, the order of methanol yield over verious catalysts is CuO–ZnO–$Al_2O_3$>CuO–ZnO–$ZrO_2$>CuO–ZnO–MgO>CuO–ZnO≫CuO–ZnO–$Cr_2O_3$.

**Structure and Surface Area.** The XRD powder pattern of a calcined CuO–ZnO sample showed that it comprises of tetragonal CuO and hexagonal ZnO. When a small amount (11 mol%) of $ZrO_2$ was added, the pattern of CuO–ZnO was not changed, as is shown in Fig. 4, indicating that $ZrO_2$ forms an amorphous

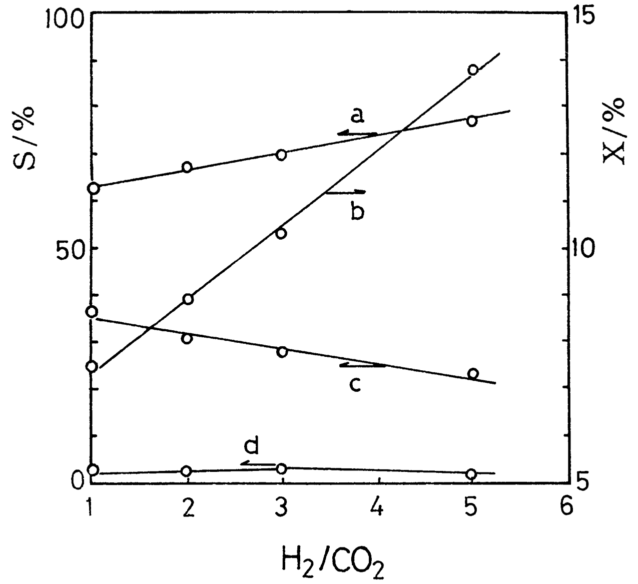

Fig. 1. Effect of $H_2/CO_2$ ratio on activity and selectivity of CuO–ZnO–$ZrO_2$ (42/47/11) catalyst. (a: $S_{CH_3OH}$, b: $X_{CO_2}$, c: $S_{CO}$, d: $S_{CH_4}$).

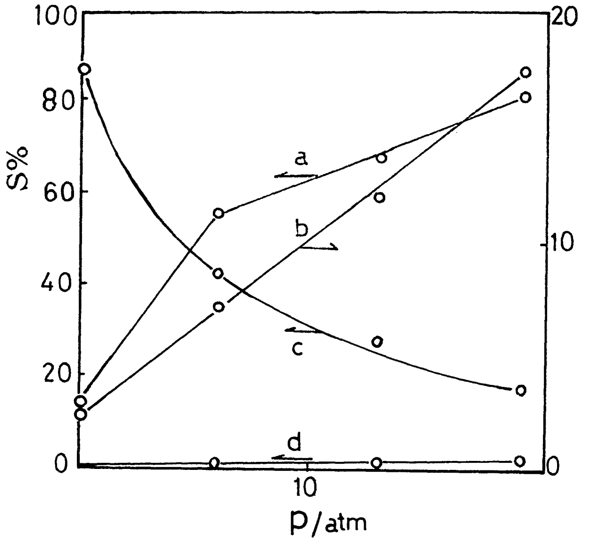

Fig. 2. Effect of pressure on activity and selectivity of CuO–ZnO–$ZrO_2$ (42/47/11) catalyst. (a: $S_{CH_3OH}$, b: $X_{CO_2}$, c: $S_{CO}$, d: $S_{CH_4}$).

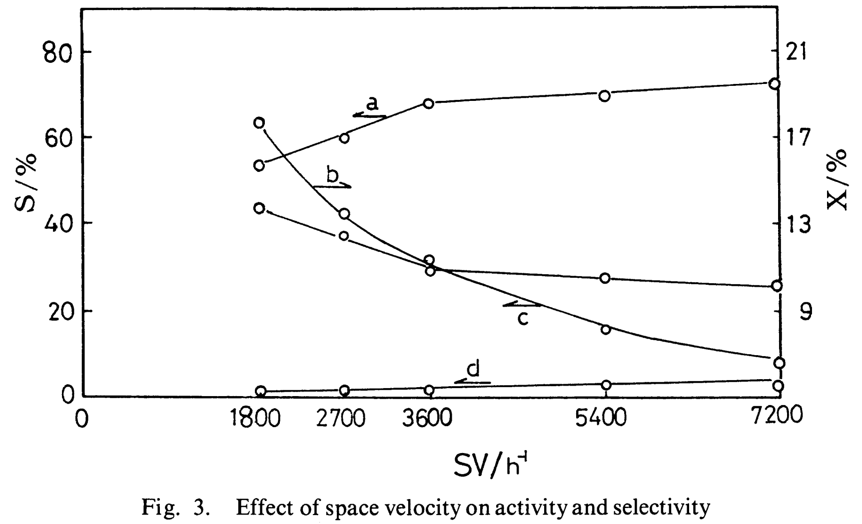

Fig. 3. Effect of space velocity on activity and selectivity of CuO–ZnO–$ZrO_2$ (42/47/11) catalyst. (a: $S_{CH_3OH}$, b: $X_{CO_2}$, c: $S_{CO}$, d: $S_{CH_4}$).

Table 3. Activity and Selectivity of CuO-ZnO-(MgO, $Al_2O_3$, or $Cr_2O_3$) Catalysts in $CO_2+H_2$ Reaction[a)]

| Catalyst | SV | Reac. temp | $X_{CO_2}$[b)] | Selectivity/% | | | Rate of reaction[d)] | | | $Y_{CH_3OH}$[c)] |
|---|---|---|---|---|---|---|---|---|---|---|
| | $h^{-1}$ | °C | % | $CH_3OH$ | CO | $CH_4$ | CO | $CH_3OH$ | $CO_2$ | % |
| CuO-ZnO (50/50) $B_1$ | 3600 | 160 | 4.4 | 78.4 | 21.5 | 0 | 0.2 | 0.7 | 0.9 | 3.4 |
| | | 180 | 8.2 | 57.2 | 42.8 | 0 | 0.7 | 0.9 | 1.7 | 4.7 |
| | | 200 | 14.6 | 40.6 | 59.4 | 0 | 1.6 | 1.2 | 3.0 | 6.0 |
| | | 220 | 27.3 | 31.9 | 68.1 | 0 | 3.8 | 1.8 | 5.5 | 8.7 |
| | | 240 | 35.9 | 22.2 | 77.8 | 0 | 5.7 | 1.6 | 7.3 | 8.0 |
| | | 260 | 39.7 | 21.1 | 78.9 | 0 | 6.3 | 1.7 | 8.0 | 8.4 |
| | | 280 | 39.9 | 15.4 | 84.6 | 0 | 6.8 | 1.2 | 8.1 | 6.2 |
| CuO/ZnO/MgO (47/47/6) $B_2$ | 3600 | 160 | 9.6 | 96.8 | 3.0 | 0 | 0.6 | 1.9 | 2.0 | 9.3 |
| | | 180 | 12.3 | 91.8 | 8.3 | 0 | 0.2 | 2.3 | 2.6 | 11.3 |
| | | 200 | 11.2 | 72.1 | 27.9 | 0 | 6.5 | 1.7 | 2.3 | 8.1 |
| | | 220 | 19.1 | 57.0 | 53.0 | 0 | 2.1 | 1.9 | 4.0 | 9.0 |
| | | 240 | 30.7 | 41.2 | 58.9 | 0 | 3.8 | 2.6 | 6.4 | 12.6 |
| | | 260 | 39.0 | 26.7 | 73.3 | 0 | 5.9 | 2.2 | 8.1 | 10.4 |
| | | 280 | 41.2 | 26.1 | 74.0 | 0 | 6.3 | 2.3 | 8.6 | 10.7 |
| CuO/ZnO/$Al_2O_3$ (47/47/6) $B_3$ | 3600 | 160 | 20.6 | 97.9 | 2.1 | 0 | 0.1 | 6.0 | 6.2 | 20.2 |
| | | 180 | 27.2 | 95.3 | 4.7 | 0 | 0.4 | 7.6 | 8.1 | 25.9 |
| | | 200 | 23.9 | 82.4 | 17.6 | 0 | 1.3 | 5.9 | 7.2 | 19.7 |
| | | 220 | 35.3 | 64.7 | 35.3 | 0 | 3.7 | 6.8 | 10.6 | 22.8 |
| | | 240 | 48.3 | 57.9 | 42.0 | 0 | 6.1 | 8.4 | 14.5 | 28.0 |
| | | 260 | 43.3 | 61.7 | 38.3 | 0 | 4.8 | 7.8 | 12.7 | 26.7 |
| | | 280 | 45.7 | 37.8 | 62.2 | 0 | 8.5 | 5.2 | 13.7 | 17.3 |
| CuO/ZnO/$Cr_2O_3$ (34.5/34.5/31) $B_4$ | 3600 | 300 | 2.4 | 31.1 | 51.1 | 0 | | | | 0.7 |
| | | 320 | 5.8 | 25.5 | 49.9 | 0 | | | | 1.6 |
| | | 340 | 11.0 | 14.8 | 73.2 | 0 | | | | 1.6 |
| | | 360 | 17.8 | 8.1 | 56.0 | 31.7 | | | | 1.4 |
| | | 380 | 27.0 | 4.0 | 0 | 95.5 | | | | 1.0 |

a) Reaction conditions: mole ratio of $H_2/CO_2=3/1$, total pressure 13 atm. The catalyst of 1.8 $cm^3$ was used after reduction with $H_2$ at 300°C for 6 h. b) $X_{CO_2}$=Conversion of $CO_2$. c) $Y$=yield. d) mmol $g^{-1}$ $h^{-1}$.

phase. With the addition of a larger amount (77 mol%) of $ZrO_2$, almost all of the patterns of CuO and ZnO disappeared. This disappearance of the patterns is considered to be due to a high dispersion of CuO and ZnO over $ZrO_2$. The surface area (29 $cm^2$ $g^{-1}$) of CuO-ZnO (47/53) increased to 37 $cm^2$ $g^{-1}$ for CuO-ZnO-$ZrO_2$ (42/47/11) and 42 $cm^2$ $g^{-1}$ for CuO-ZnO-$ZrO_2$ (21/24/55). The activation energy for $CO_2$ conversion decreased from 71.2 kJ $mol^{-1}$ over CuO-ZnO (47/53) to 61.1 kJ $mol^{-1}$ over CuO-ZnO-$ZrO_2$ (42/47/11) and 47.2 kJ $mol^{-1}$ over CuO-ZnO-$ZrO_2$ (21/24/55). These changes seem to be due to the high dispersion of CuO-ZnO over $ZrO_2$.

**Active Centers.** Figure 5 shows the ultraviolet diffused reflectance spectra of reduced CuO, ZnO, CuO-ZnO, and CuO-ZnO-$ZrO_2$. The absorption edges of $ZrO_2$, ZnO, and $Cu^0$ were confirmed to be 330, 360, and 560 nm, respectively. The spectral feature of ZnO was observed for CuO-ZnO and CuO-ZnO-$ZrO_2$, but that of $ZrO_2$ was not found for those samples. The spectra characteristic of $Cu^0$ were shifted toward lower frequencies in CuO-ZnO and CuO-ZnO-$ZrO_2$. The shape of the spectra also changed. The characteristic edge (600—800 nm) of $Cu^0$ in CuO increased its intensity in CuO-ZnO and CuO-ZnO-$ZrO_2$ up to 55% of the $ZrO_2$ content. With increasing the $ZrO_2$ content to 77%, the characteristic edge of $Cu^0$ became close to that in CuO. This trend corresponds to a difference in the catalytic activity for methanol formation over CuO and CuO-ZnO-$ZrO_2$ catalysts with the different $ZrO_2$ contents shown in Tables 1 and 2. The visible absorption edge of the reduced catalysts was different from those of $Cu_2O$(610 nm),[8)] Cu(560 nm), CuO(850 nm),[9)] and $Cu^{2+}$ existing in a $Cu^{2+}$-ZnO solid solution. This characteristic absorption edge was reported to be caused by $Cu^+$ which existed in $Cu^+$-ZnO solid solution.[10)] Since $Cu^+$ and $Zn^{2+}$ are isoelectric ions, the replacement of $Zn^{2+}$ by $Cu^+$, and resulting dissolution of $Cu^+$ in ZnO, may be possible. The addition of high valent $Zr^{4+}$ may supply positive charge to $Cu^+$, thus making dissolution easy. As a result, the intensity of the absorption edges for Cu' is considered to increase.

According to an XPS measurement, the $Cu2p_{3/2}$ peak in CuO has two strong shoulders toward its high-energy side called a "satellite shake up peak".[11)] Although the $Zn2p_{3/2}$ and $Zr3d_{5/2}$ peaks in CuO-ZnO-$ZrO_2$ were very similar to those of ZnO and $ZrO_2$, respectively, the two $Cu2p_{3/2}$ shoulder peaks were slightly wider and weaker in intensity than those in CuO. It can be said that Cu ions are located in a center of more distorted symmetry as the intensity ratio of the satellite-to-main peak

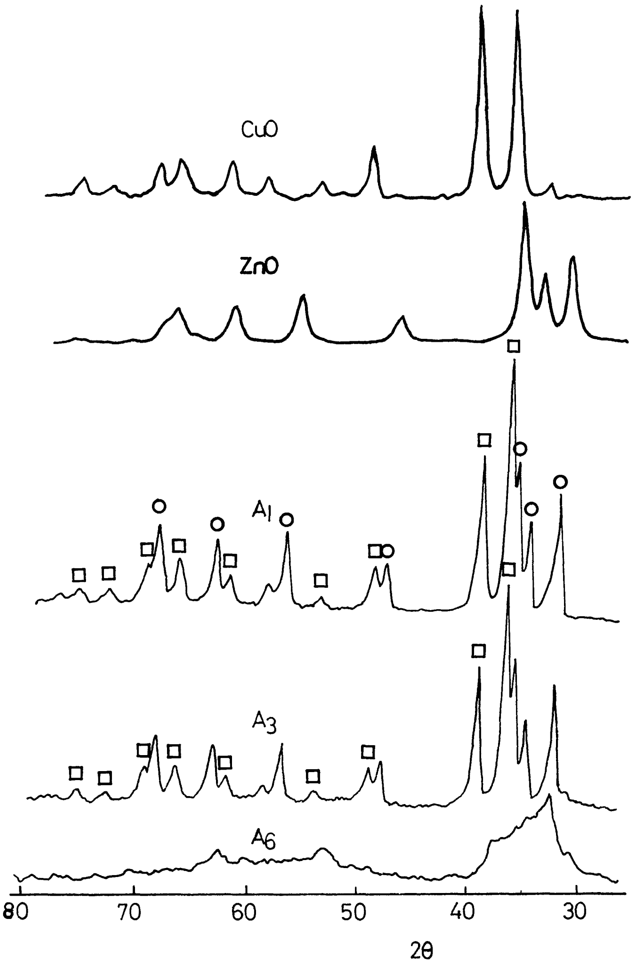

Fig. 4. XRD spectra of pure CuO and calcined samples (CuO-ZnO-ZrO$_2$) A$_1$, A$_3$, A$_6$. ○; ZnO, □; CuO.

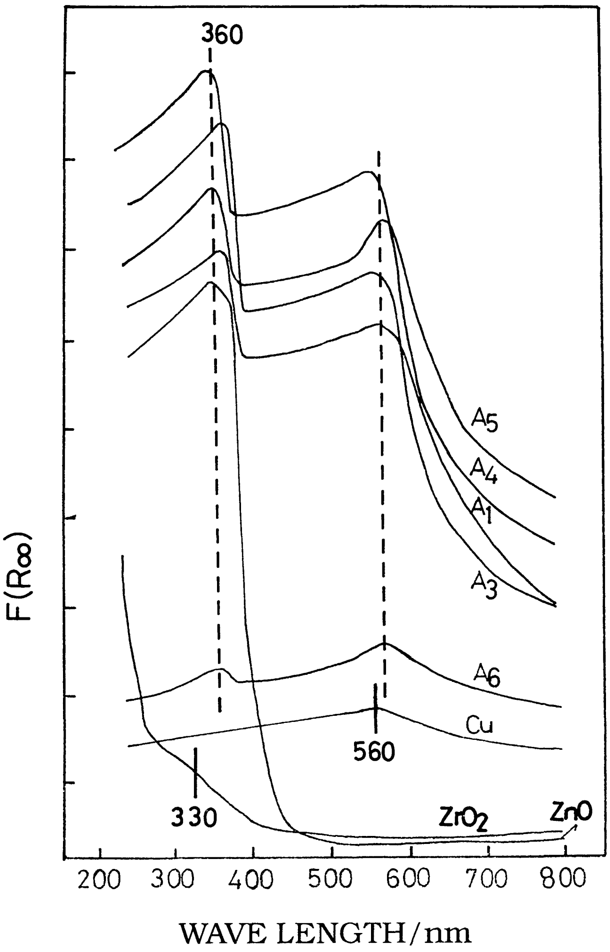

Fig. 5. Ultraviolet diffused reflectance spectra of the CuO-ZnO-ZrO$_2$ catalyst.

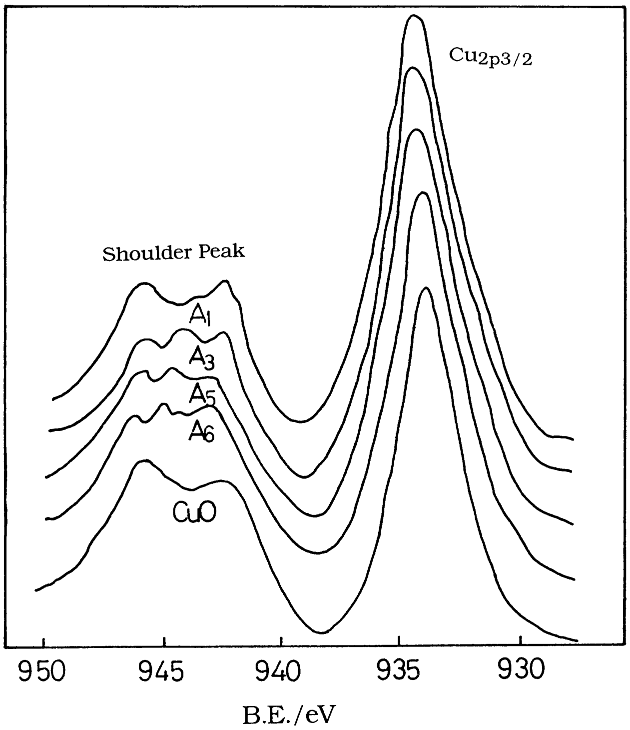

Fig. 6. XPS spectra of Cu2p$_{3/2}$ region for calcined samples. (CuO-ZnO-ZrO$_2$).

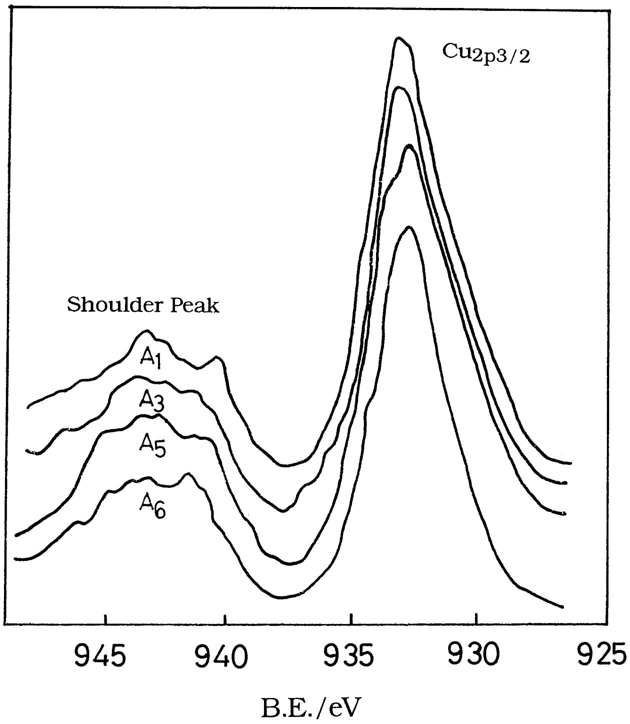

Fig. 7. XPS spectra of Cu2p$_{3/2}$ region for the samples (CuO-ZnO-ZrO$_2$) after reaction.

($S/M$) becomes large.[11)]

The $Zn2p_{3/2}$ and $Zr3d_{5/2}$ peaks of the used catalysts were the same as those of unused ones, and the $Cu2p_{3/2}$ peak shifted by approximately lev, similar to that of Cu. In contrast, Cu(LMM) Auger electron energy was different from that of Cu and similar to that of $Cu_2O$. The XPS spectra in the region of $Cu2p_{3/2}$ for the catalysts after calcination and after use for the reaction are shown in Figs. 6 and 7, respectively. Compared with the calcined catalysts, and used catalysts exhibited lower $S/M$ values for the calcined catalysts ($A_1$, $A_3$, $A_5$, and $A_6$): 0.46, 0.46, 0.41, and 0.42, respectively; they changed to 0.25, 0.20, 0.34, and 0.31, respectively.

The decrease in the $S/M$ value of $Cu2p_{3/2}$ is considered to be due to the formation of a solid solution comprising of $Cu^{2+}$ and ZnO.[12)] In used catalysts, although two shoulder peaks of $Cu2p_{3/2}$ also existed, their binding energy shifted toward lower energy, indicating that $Cu^{2+}$ was reduced to lower valencies. However, the similarity of Cu(LMM) of the used catalysts to that of $Cu_2O$ seems to suggest that the reduced Cu is partially oxidized and that the surface is partly converted with oxygen to prevent any further oxidation of Cu.[13)] The shoulder peaks are usually observed for CuO, but not for $Cu_2O$ and Cu. However, $Cu^{2+}$ was not detected for the used catalysts in the present work. Therefore, the shoulder peaks of $Cu2p_{3/2}$ are considered to be due to the formation of $Cu^+$ in a $Cu_2O$–ZnO solid solution. During the prereduction condition, $Cu^{2+}$ is easily reduced to $Cu^+$ and dissolved into ZnO, resulting in the formation of a $Cu_2O$ and ZnO solid solution, making it difficult for any further reduction to take place since $Cu^+$ and $Zn^{2+}$ are isoelectric ions. This result is in agreement with that obtained by UDRS. Thus, $Cu^+$ and ZnO in $Cu_2O$–ZnO solid solutions are suggested to be active centers under the reaction conditions.

## References

1) V. N. Ipatieff and G. C. Monroe, *J. Am. Chem. Soc.*, **67**, 2168 (1945).

2) B. Denise and R. P. A. Sneeden, *Appl. Catal.*, **28**, 235 (1986).

3) T. Tagawa, G. Pleizier, and Y. Amenomiya, *Appl. Catal.*, **18**, 285 (1985).

4) T. Inoue, T. Iizuka, and K. Tanabe, *Bull. Chem. Soc. Jpn.*, **60**, 2663 (1987).

5) Y. Amenomiya and T. Tagawa, "Proc. 8th Intern. Congr. Catalysis," Verlag Chemie, Weinheim (1984), Vol. II, p. 557.

6) E. Ramaroson, R. Kieffer, and A. Kiennemann, *Appl. Catal.*, **4**, 281 (1983).

7) G. Panzner, B. Egert, and H. P. Schmidt, *Surf. Sci.*, **151**, 400 (1985).

8) J. Bloem, *Phillips Res. Rep.*, **13**, 167 (1958).

9) F. S. Stone, *Bull. Soc. Chim. Fr.*, **1966**, 819.

10) R. G. Herman, K. Klier, G. W. Simmons, B. P. Finn, and J. B. Bulko, *J. Catal.*, **56**, 407 (1979).

11) D. Brigge, "Handbook of X-Ray and Ultraviolet Photoelectron Spectroscopy," ed by D. Briggs, Heyden & Son Ltd., London (1977), p. 190.

12) F. Garbassi and G. Petrini, *J. Catal.*, **90**, 106 (1984).

13) O. Ruggeri, F. Trifieo, and A. Vaccari, *J. Solid State Chem.*, **42**, 120 (1982).