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Temperature Programmed Reduction of Copper-Silica Catalysts Prepared by Ion Exchange Method[1)]

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Temperature programmed reduction (TPR) has been used to study copper–silica catalysts which were prepared by ion exchange method and the effects of preparation of catalysts upon their reducibilities were elucidated. Three peaks appeared with maxima at 265—300 °C (α), 400 °C (β), and 650—800 °C (γ) over the catalysts calcined at 500 °C. Highly dispersed cupric oxide clusters were reduced to metallic copper, giving α peak. Isolated copper(II) ions which were strongly interacted with silica surface were reduced stepwise to metallic copper through copper(I) ion species, giving α and γ peaks. However, isolated copper(II) ions which were weakly interacted with the support gave α and β peaks. When the catalysts were precalcined above 800 °C, the fourth peak (α′) appeared at 330—350 °C and α, β, and γ peaks diminished. This was assigned to the reduction of bulk CuO which was crystallized from species described above. The reducibility of copper–silica catalyst was found to depend strongly upon the conditions of preparation.

Characterization of catalysts is one of the important initial steps for catalyst design.[2)] In our previous work,[3)] copper–silica catalysts prepared by ion exchange method were characterized by means of a variety of analytical methods such as DTA, TG, UV, XPS, AES, and XRD and it was shown that the precursor states of the catalysts depended sensitively upon copper loading and the calcination temperature. The activity and selectivity of methanol steam reforming $CH_3OH+H_2O=CO_2+3H_2$ were found to be strongly influenced by the preparation of the catalysts[4—6)] and metallic copper formed in the course of the reaction was suggested to be active sites for the reaction. The reducibility of the catalyst was also closely associated with the preparation conditions of the catalyst.[7)] Recently, TPR method has been successfully applied for the characterization of supported metal catalysts[8,9)] and TPR peaks obtained are found to reflect sensitively the states of the catalysts such as valence of active species and metal-support interaction. In these connections, the copper-silica catalysts were reduced by hydrogen under temperature programmed conditions and their reducibilities were extensively studied in relation to the states of the precursor species.

Experimental

Catalysts. The catalysts were prepared in a manner similar to that employed in the previous work.[3)] Hydroxyl protons on silica gel (Nihon Chromato. Co., 60—80 mesh in granules) were exchanged at a pH=11—12 overnight with tetrammine copper(II) cations which had been prepared from copper(II) nitrate (Wako Pure Chemicals, extra pure grade) and an aqueous ammonia solution. The ion exchange silica gel was filtered, washed with distilled water and dried at 110 °C for 12 h, and were further calcined in air under various conditions covering temperature range of 500—900 °C and calcination time of 3 min to 3 h. Copper loading in catalyst was estimated from the concentrations of the mother solution and of the filtrate. These were determined by titration with EDTA solution of known concentration by use of PAN as an indicator. Copper loading thus determined varied in the range of 0.5—13.0 wt% copper. As previously stated,[3,5)] no nitrate anion was held on the surface as revealed by XPS of the catalysts and chemical analysis of the solution.

Temperature Programmed Reduction (TPR). A hydrogen–nitrogen mixture (4% hydrogen) was passed over the catalyst at a total flow rate of 50 ml/min. TPR runs were carried out at a heating rate of 10 °C/min with a programming temperature controller (Muto HM 53) and hydrogen consumption was monitored by thermal conductivity cell attached to a gas chromatograph (Ohkura Electric Co. Model 701). The reactor was made of quartz tubing of 12 mm in diameter and the catalyst sample of 0.5—3.0 g was mount ed on loosely packed quartz wool. The temperature was simultaneously recorded with hydrogen concentration on a multipen recorder (Hitachi 056) using a chromel-alumel thermocouple.

Results and Discussion

Copper Loading and TPR Spectra. Figure 1 illustrates TPR spectra obtained over the catalysts which had been prepared by calcination at 500 °C for 3 h in air. Three peaks are seen with maxima at 265—300 °C (referred to as α-peak), 440 °C (β-peak) and 665—800 °C (γ-peak), and these peak areas depend markedly upon copper loading. On the catalysts with high copper loading (10.4 and 13.0 wt% copper), α peak appears predominantly with a small β peak on its shoulder. Three peaks α, β, and γ are seen separately on the catalysts with medium loading (5 wt% copper), while only α and γ peaks are perceptible on the catalyst with copper loading below 2 wt%. The amounts of hydrogen consumed were estimated from the peak area and were plotted against copper loading in Fig. 2. The total amount of hydrogen consumed was found to be practically equal to that of hydrogen required for complete reduction of cupric oxide to metallic copper. α-Peak increases monotonically with the increase of copper loading while β and γ peaks attain to the maximum and decrease as the loading is increased. In Fig. 3, peak area ratio α/γ is plotted against copper loading. It is seen that α/γ decreases and tends to approach unity as the loading is lowered.

In our previous work,[3)] the precursor states of copper–silca catalyst which was prepared by ion exchange method were characterized with the help of a variety of analytical methods and it was shown that when copper(II) ions were held no silica gel support, various states of the precursors appeared. Relative amounts

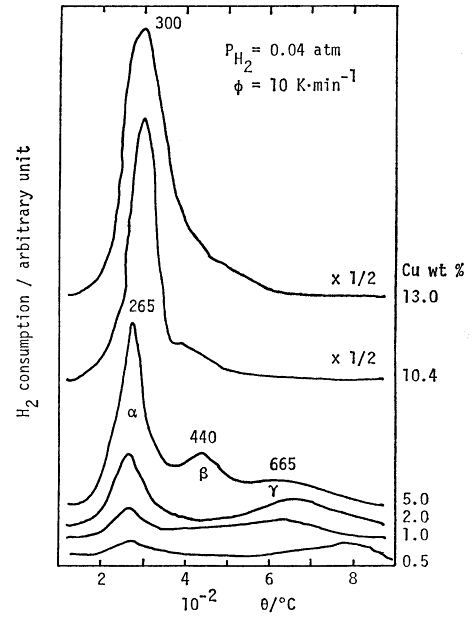

Fig. 1. TPR spectra of Cu/SiO$_2$ catalysts calcined at 500 °C for 3 h.

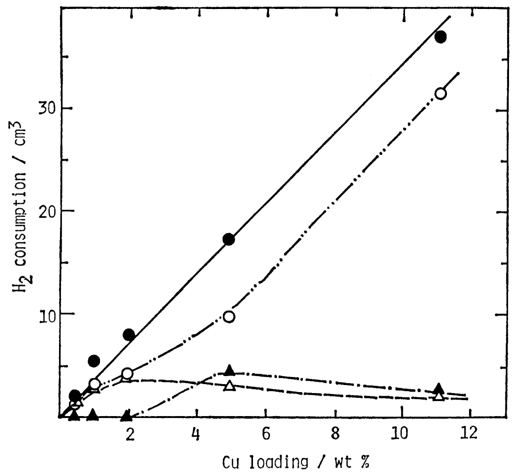

Fig. 2. Cu-loading and the amounts of consumed hydrogen in the course of TPR runs.
(—●—), Total amount of consumed hydrogen. (—○—), Amount of consumed hydrogen which gave α-peak. (—▲—), Amount of consumed hydrogen which gave β-peak. (—△—), Amount of consumed hydrogen which gave γ-peak.

of these species were found to be sensitively affected by copper loading and calcination temperature. On the catalyst with copper loading below 0.5—1 wt%, the precursor which was calcined in the temperature range 300—720 °C existed as isolated copper(II) ions, while with higher copper loadings it existed as small clusters of CuO. When the catalyst was calcined above 720 °C, the latter species were crystallized into bulk CuO, while the former species were partly clustered but in part still remained as isolated copper(II) ions.

In the present work, a variety of TPR peaks were observed. α and β Peaks appeared with the same intensity at lower copper loading (below 2 wt%), while at higher copper loading (10.4 and 13.0 wt%), the

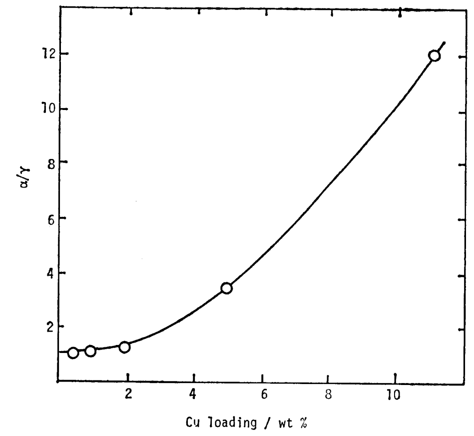

Fig. 3. The ratio of TPR peak areas α/γ against Cu-loading.

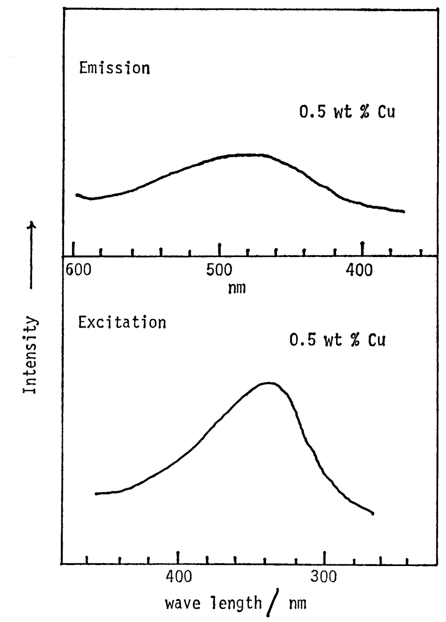

Fig. 4. Phosphorescence spectra of Cu/SiO$_2$ catalysts which were employed for TPR run to 400 °C.

former peak was exceedingly large compared to other TPR peaks. On the basis of the previous results as to the characterization of the catalyst,$^{3)}$ it is very likely that α-peak obtained on the catalyst with high copper loading is ascribed to the reduction of small clusters of CuO. These species were transformed to metallic copper as evidenced by the amount of the hydrogen consumption. On the catalyst with 0.5 wt% copper loading the phosphorescence spectra were obtained after a TPR run was carried out to 400 °C where α-peak was completed (Fig. 4). In both the emission and the excitation modes, the peaks due to copper(I) ions are seen at 340 and 490 nm, respectively. α-Peak obtained for the catalysts with low copper loading is, therefore, ascribable to the reduction of isolated copper(II) ions to copper(I) ions. In these respects, γ-peak is ascribed to the reduction of the formed copper(I) ions to metallic copper, so that the ratio of peak area α/γ approaches unity as the loading is lowered. Both isolated copper(II) ions and copper(I)

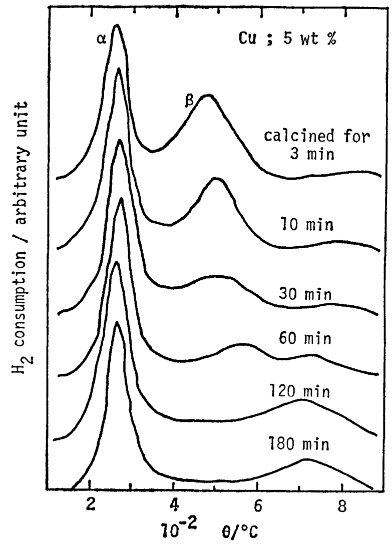

Fig. 5. TPR spectra of Cu/SiO_2 (5.0 wt% copper) catalyst calcined at 500 °C.

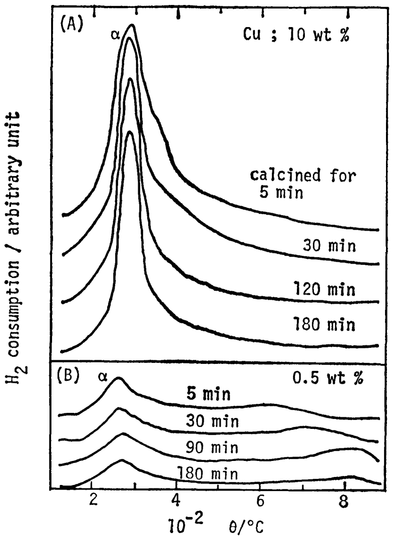

Fig. 6. TPR spectra of Cu/SiO_2 (10.0 wt% and 0.5 wt% copper) catalysts calcined at 500 °C.

ions formed were presumably interacted strongly with silica and stabilized on the support. The copper(II) ions were, therefore, reduced stepwise to metallic copper through the copper(I) ions. On the other hand, the results obtained at medium copper loading appeared to be puzzling in which β-peak was seen. It was tentatively concluded that copper(II) ions which were weakly interacted with silica were also reduced to copper(I) ions, giving α peak, and the formed copper(I) ions were then reduced to metallic copper at the temperature where β peak appeared.

Figure 5 illustrates TPR spectra of Cu/SiO_2 (5.0 wt%) catalysts which were calcined at 500 °C for different length of time. As the calcination time becomes longer, β-peak decreases but γ-peak increases. However, the intensity of α-peak remains practically unchanged. The interaction between copper(II) ions and silica was suggested to be strengthened during the course of calcination. Figure 6 illustrates TPR spectra which were obtained for the catalysts (10 and 0.5 wt% copper) calcined at 500 °C for different length of time. On the catalyst with 10 wt% copper small β-peak on α-peak diminishes with time and only α-peak is observed after 180 min. On the catalyst with 0.5 wt% copper the peaks are initially observed at 260 and 650 °C but γ-peak shifts to higher temperature when the calcination time is increased. This also indicates that the mutual interaction between isolated copper(II) ion and silica support is enhanced with the calcination time.

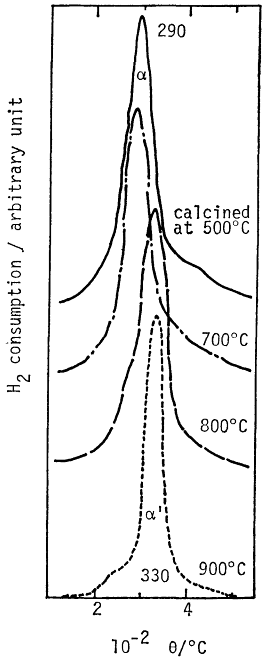

Fig. 7. TPR spectra of Cu/SiO_2 (10.4 wt% copper) catalysts and calcination temperature.

Calcination Temperature and TPR Spectra. Figure 7 illustrates TPR spectra obtained over Cu/SiO_2 catalyst (10 wt%) which was calcined at different temperatures for 3 h in air. α-Peak predominates on the catalyst calcined below 700 °C, but when the catalysts is calcined at 800 or 900 °C, this peak decreases to a considerable extent and a new peak (referred to as α′-peak) appears at 330 °C. As previously examined[3] by XRD, no CuO patterns were observed on the catalyst precalcined below 720 °C, but they grew when the catalyst was precalcined above this temperature. α′-Peak is, therefore, ascribed to the reduction of the bulk CuO. In fact, support-free CuO gave a peak at 340 °C.

Figure 8 shows TPR spectra obtained for the catalysts with lower copper loadings (2.0 and 0.5 wt% copper) which were calcined at various temperatures. The spectra are somewhat complicated compared to those obtained on the catalysts with higher copper loadings. When the cataylsts with 2 wt% copper is calcined at 900 °C, α′ peak grows evidently at the expense of α and γ peaks. On the catalyst with 0.5 wt% copper, however, α′ peak is also observed while α peak grows slightly but γ peak decreases. This indicates that isolated copper(II) ion precursors transform into CuO clusters and the latter species further transform into

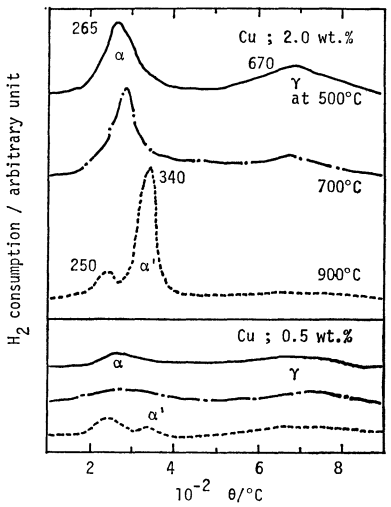

Fig. 8. TPR spectra of Cu/SiO_2 (2.0 and 0.5 wt% copper) catalysts and calcination temperature.

bulk CuO when the catalyst is precalcined at 900 °C. This substantially coincided with the previous results obtained by UV diffuse reflectance spectroscopy in which it was shown that the isolated species became partially clustered but in part still retained its orginal state.

Conclusion

TPR technique has been used to study copper–silica catalysts with varying copper loading and calcination. Four peaks were observed with maxima at 265—300 °C (α), 400 °C (β), 650—800 °C (γ), and 330—350 °C (α'). Relative peak intensities of these peaks depended upon copper loading and calcination temperature. It was concluded that α peak was ascribed to the reduction of highly dispersed CuO clusters and isolated copper(II) ions which were either strongly or weakly held on the support. The CuO clusters were easily reduced to metallic copper, while the isolated species were merely reduced to copper(I) ions when α peak was completed. These isolated copper(II) ions were concluded to be reduced stepwise to metallic copper and consequently β and γ peaks were ascribed to the reduction of intermediate copper(I) ions to metallic copper. When the catalyst was calcined at 900 °C, CuO clusters transformed into bulk CuO to a considerable extent and gave α' peak in TPR runs. On the other hand, the copper ions in the catalyst with lower copper loading are only partly transformed into bulk CuO clusters even after calcination at 900 °C.

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Added in Note: After the present work was presented at the Chemical Society of Japan Meeting, April 3, 1981 and at Catalysis Society Meeting, October 15, 1981, Okayama, the TPR work [S. J. Gentry and P. T. Walsh, *J. Chem. Soc., Faraday Trans. 1*, **78**, 1515 (1982)] was recently published for copper catalysts which were prepared by impregnation on silica and alumina. The results shown are practically in accord with those obtained in the present work in which the TPR peaks obtained are reported to be greatly affected by calcination temperature and copper loading.

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