Preparation of Highly Dispersed Cu on TiO_2 Using Cu(II) Complexes

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TiO_2-supported Cu samples were prepared by using several Cu precursors, and isolated Cu^{2+} ions and their behavior of thermal reduction were evaluated by means of ESR spectroscopy. Only 50% of Cu^{2+} were reduced to Cu^+ or Cu^0 by using cupric nitrate as a precursor. Highly dispersed Cu ions on TiO_2 could be obtained by using Cu^{2+} complexes ($Cu(acac)_2$ and $Cu(dbm)_2$) as a precursor.

TiO_2-supported Cu shows a catalytic activity for methanol-reforming,[1] NO and N_2O decomposition,[2-5] combustion of soot particles,[6] etc. For these reaction systems, it is summarized that reduced Cu ions, *e.g.*, Cu^+ and Cu^0, act as the active center, and the support-interaction between Cu and TiO_2 is very effective for stabilizing reduced Cu species. However, formation of highly dispersed Cu species on the support-oxide is difficult because Cu ions tend to aggregate to form Cu-cluster species by means of general preparation method. In the case of Cu ion-exchanged zeolites such as Cu-ZSM-5 and Cu-Y, Cu ions can be stabilized in the channel of frameworks dispersively, and well-dispersed Cu ions can be obtained.[8-10] These Cu ions show a high catalytic activity for *de*NO_x reactions because Cu ions can easily be reduced thermally.[11] In the case of cupric nitrate precursor, almost Cu^{2+} ion could not be reduced, because Cu^{2+} cluster was formed. Since strong cation-exchange site does not exist on the oxide supports used widely (such as TiO_2, ZrO_2, ZnO, SiO_2, etc.), the preparation of highly dispersed Cu ions on the support is necessary to obtain a novel catalyst exhibiting high redox activity.

In this study, we attempted to prepare highly dispersed Cu ions on TiO_2 support. It is reported that highly dispersed NbOx species are formed on TiO_2 by using Nb^{5+} complex ($Nb(dbm)_4{}^+$-Cl^-, Hdbm : 1,3-diphenyl-1,3-propanedione).[12] By use of Cu^{2+} complex with bulky ligands, dispersion of Cu ions can be expected. We employed two Cu^{2+} complexes in preparing Cu/TiO_2 to form isolated Cu^{2+}species on TiO_2. The state of Cu ions and their behavior of thermal reduction were appreciated by means of ESR spectroscopy.

The Cu/TiO_2 samples were prepared by impregnation of ultra-fine TiO_2 particle (IT-S; Idemitsu Kosan Co., Ltd.) support which calcined at 600 °C for 6h with an aqueous solution of $Cu(NO_3)_2 \cdot 3H_2O$ or methyl chloride solution of Cu^{2+} complexes. The synthesized complexes used in this study are bis-(acetylacetonato)-copper(II) ($Cu(acac)_2$) and bis-(1,3-diphenyl-1,3-propanedionato)-copper(II) ($Cu(dbm)_2$). The Cu-loading is 0.1 wt% in all the samples. The impregnated samples were then dried at 120 °C for overnight and calcined at 600 °C for 3 h. In this paper, the samples prepared from $Cu(NO_3)_2 \cdot 3H_2O$, $Cu(acac)_2$, and $Cu(dbm)_2$ were designated as Cu(N)/TiO_2, Cu(A)/TiO_2, and Cu(D)/TiO_2, respectively. All the samples consisted of anatase type TiO_2, because of calcined at 600 °C. Each sample (0.05 g) was set to the *in situ* quartz cell and evacuated at given temperature between 100 and 500 °C for 1 h prior to ESR measurement. ESR spectra (X-band) were recorded with JEOL JES-ME3X spectrometer at room temperature. The *g*-values and the signal intensity were evaluated by use of Mn^{2+}-marker as an internal standard and $CuSO_4 \cdot 5H_2O$ as a reference of Cu^{2+} sample. The surface areas of samples were increased with evacuated temperature from 45 to 60 m^2/g.

For all Cu/TiO_2 samples after evacuation, ESR signal of Cu^{2+} can be seen definitely at g=2.040 as a center. This Cu^{2+} signal exhibits different intensity between the samples prepared. The relation between the evacuation temperature and signal intensity in Cu(N)/TiO_2, Cu(A)/TiO_2, and Cu(D)/TiO_2 is shown in Figure 1. In the case of low evacuation temperature at 100–300 °C, the intensity of Cu^{2+} signal in Cu(N)/TiO_2 is lower than those in Cu(A) and Cu(D)/TiO_2. It can be explained that the loss of the signal intensity is due to the dipole-dipole interaction of Cu^{2+} clusters.[8] Thus, the Cu ions in Cu(N)/TiO_2 contain aggregated Cu^{2+} cluster species. It supports the several works that Cu ions on TiO_2 tend to aggregate by use of cupric nitrate as a precursor.[1,13,14] For Cu(A)/TiO_2 and Cu(D)/TiO_2, about 83% of Cu^{2+} is ESR-visible even after evacuation at 100

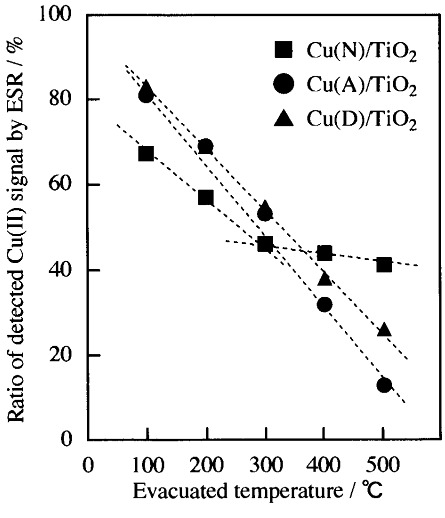
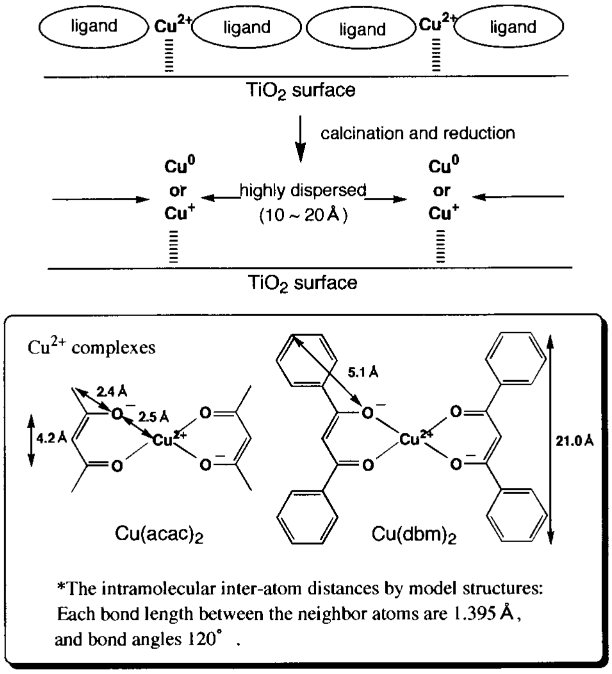


Figure 1. Relation between the intensity of Cu^{2+} ESR-signal and evacuated temperature (equimolecular $CuSO_4 \cdot 5H_2O$ as a reference of Cu^{2+}).

°C. In these samples, more than 90% of Cu^{2+} can be seen after evacuation at room temperature. These results show that well-dispersed Cu^{2+} ions on TiO_2 are obtained by use of Cu^{2+}-complexes as a precursor. With an increase of evacuated temperature, Cu^{2+} signal is reduced in all the samples. Since these samples were calcined sufficiently at 600 °C before evacuation, aggregation of Cu ions during the evacuation is not reasonable. The disappearance of the signal is assigned to the thermal reduction of Cu^{2+} ions to form Cu^+.[15] In the case of Cu(N)/TiO_2, low evacuation temperature up to 300 °C, the slope of signal reduction is almost as similar as those in Cu(A)/TiO_2 and Cu(D)/TiO_2. However, it is remarkable that the slope becomes low above 300 °C. It is inferred that isolated Cu^{2+} in Cu(N)/TiO_2 is reduced below 300 °C, and most of thermally reducible Cu^{2+} ions are occupied by the ESR-inactive cluster species above 300 °C. It is reported that aggregated Cu^{2+} cluster can hardly be reduced to Cu^+ below 500 °C,[14] and thus, reduction of Cu^{2+} in Cu(N)/TiO_2 may scarcely proceed at 300–500 °C. On the other hand, the signal intensity in Cu(A)/TiO_2 and Cu(D)/TiO_2 decreased monotonously with increasing of evacuation temperature up to 500 °C. It has been accepted that isolated Cu^{2+} can easily be reduced thermally for Cu/SiO_2 and Cu ion-exchanged zeolites.[9,16,17] It is appropriate that Cu^{2+} ions in Cu(A)/TiO_2 and Cu(D)/TiO_2 also be reduced thermally because of isolation of Cu ions. The difference of the slope between Cu(A)/TiO_2 and Cu(D)/TiO_2 is still unclear, however, it is likely that the molecular size of $Cu(dbm)_2$ is too large to exceed the full coverage of TiO_2 surface slightly.



*The intramolecular inter-atom distances by model structures: Each bond length between the neighbor atoms are 1.395 Å, and bond angles 120° .

Scheme 1. Formation of surface structure of Cu(A) or Cu(D)/TiO_2 catalyst.

As described above, highly dispersed Cu ions on TiO_2 can be prepared by use of Cu^{2+} complexes as a precursor than that of Cu^{2+} nitrite. The isolated Cu^{2+} ions can reduced thermally up to 500 °C.

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