

Reduction of NO over TiO₂-Supported Cu Catalysts

2. Structure of Active Cu Species Studied by Cu K-Edge XAFS

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The active species of Cu supported on TiO₂, which were prepared by impregnation method with cupric nitrate and acetate, is investigated by means of Cu K-edge XAFS. The XAFS and UV-VIS spectra showed that the H₂ pretreatment of the samples at 473 K brings about the formation of Cu⁰ micro particles with several hundred angstroms of particle size, and the particle on TiO₂ prepared from cupric acetate is more stable than that from cupric nitrate. It is concluded that the Cu⁰ particle with pertinent size, which coexists with cations such as Cu²⁺, is the active species for NO reduction.

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INTRODUCTION

Development of a catalytic system for removing nitrogen oxides, NO_x, is an important problem in environmental catalysis. It is well known that supported and ion-exchanged Cu catalysts are active for *de*NO_x reaction. For instance, Cu-ion-exchanged ZSM-5 is one of the most reactive catalysts as reported by many workers. The active species for the reaction have been characterized recently by FT-IR (1–6), ESR (2–4), STEM (7), XAFS (8–10). Although, the reaction mechanism and mobility of Cu ions in the reaction are proposed in these studies, they conflict with each other. The reaction mechanism of *de*NO_x reaction and the structure of reactive Cu-species have been studied so far, and more detailed study is called for. It is widely accepted that Cu⁺ ions stabilized strongly in the cation hole of ZSM-5 play a major role in selective decomposition of NO through Cu⁺-dinitrosyl species as a pathway (1, 6), whereas the Cu-dimer species, (Cu–O–Cu)²⁺, also plays a role for the active species, as reported by several groups (2, 10, 11). Thus, the characterization of active Cu species for *de*NO_x reaction has been in progress.

However, it is generally accepted that redox performance of Cu ions relates to the catalytic activity. In the case of supported Cu catalysts, the redox of Cu ions correlates strongly to the support. If the oxide-support is easily affected by the redox treatment, it is expected that the redox mobility

of Cu ions is more enhanced. In the present study, TiO₂-supported Cu (Cu/TiO₂) catalysts are chosen, because Ti⁴⁺ ions in TiO₂ are easily reduced to Ti³⁺, even by thermal treatment *in vacuo* at more than 573 K (12). In fact, it is reported that the Cu/TiO₂ catalyst has high reactivity for selective oxidation of ammonia (13) and combustion of soot particles (14). In this manner, TiO₂ has a peculiar effect on supported Cu ions, and this effect is expected to bring about the high reactivity for the *de*NO_x reaction.

We have studied the catalytic reactivity for reduction of NO with H₂ over supported Cu catalysts reacted in a closed system. In the previous report (15) it is found that Cu/TiO₂ has a higher reactivity for reduction of NO at 473 K than Cu supported on other oxides. For the characterization of Cu/TiO₂ by ESR, XANES, and UV-VIS spectroscopy, it is also found that both Cu and Ti ions are reduced easily by the treatment with hydrogen at 473 K to form reduced ions, and Cu ions on TiO₂ are stabilized as small metal particles after the treatment (15). However, the correlation between the local structure and/or valence of Cu ions and catalytic activity is still unclear. In order to clarify the structure of Cu ions which act as active species for NO reduction, Cu K-edge XAFS study is presented in this paper. By obtaining information of the local structure around Cu ions, we discuss the effect of TiO₂ support and the structural change of Cu ions on TiO₂ during the reaction.

EXPERIMENTAL

Preparation of the Samples

Supported Cu samples are prepared by the method as follows. The samples were obtained by impregnation of TiO₂ (P25, Degussa) with an aqueous solution of cupric nitrate (Cu(NO₃)₂·3H₂O) or cupric acetate (Cu(CH₃COO)₂·4H₂O), followed by drying at 353 K and calcination at 773 K for 3 h. The TiO₂ support was calcined at 773 K prior to impregnation. The loading amount is 1–8 wt% as Cu for each sample. Reduced samples were

carried out by the treatment with 100 Torr of H₂ at 473 K for 1 h after evacuation at the same temperature. As pretreatment before each reaction or measurement, the sample was evacuated at 473 K for 1 h. The reaction of NO with supported Cu-catalysts was carried out in a closed system as described in the previous paper (15).

Measurement of X-Ray Absorption Spectra at Cu K-Edge

The Cu K-edge XANES/EXAFS spectra were collected by a facility of BL-7C station at Photon Factory in the National Laboratory for High Energy Physics (KEK-PF), with 2.5 GeV of ring energy and 250–360 mA of stored current, in a fluorescence mode at room temperature. The measurements, Si(111) double crystal monochromator ($d=3.13551$ Å) was used. Incident X-ray flux and fluorescent emission were measured with ionization chambers in which 100% nitrogen and 100% argon gases, respectively, are flowing at 1 atm. Each reduced and/or used sample was moved to the polyethylene bag, and it was sealed in the glove box filled with Ar gas to prevent the sample from exposing to air.

Computational analyses for the spectra were performed with the FACOM M1800 computer system at the Data Processing Center of Kyoto University. Each spectrum was normalized to the height of the McMaster curve which is an approximation of absorption by a free atom after removal of the contribution from absorption other than the K-edge absorption, as described elsewhere (16). The k^3 -weighted EXAFS spectra were obtained from normalized EXAFS spectra, and Fourier-transformations were performed within the range $\Delta k=3\text{--}12$ Å⁻¹ without any phase shift correction. Curve-fitting analyses were performed with the empirical parameters extracted from Cu foil for Cu–Cu shells and from Cu₂O for Cu–O shells.

Measurement of UV-VIS Spectroscopy

UV-VIS spectra were recorded in a diffuse reflectance mode at room temperature with a Perkin-Elmer LAMBDA-19, using an *in situ* cell.

RESULTS AND DISCUSSION

(1) Comparison between Cu/TiO₂ Prepared from Nitrate and Acetate on Reactivity for NO Reduction

In our previous report (15), it is shown that TiO₂-supported Cu (2 wt% as Cu) catalyst prepared from nitrate and pretreated with H₂ at 473 K exhibits higher activity for the NO reduction than Cu supported on other supports, such as Al₂O₃, SiO₂, MgO, and ZnO. As for the pretreatment temperature with H₂, it has been found that 473 K is the optimum temperature for NO reduction at 303 K (15).

The relation between reactivity for NO reduction and H₂ treatment temperature over the Cu/TiO₂ samples prepared

TABLE 1

Effect of Pretreatment Temperature on Activity of NO Reduction with H₂ over 2 wt% Cu/TiO₂^a

Sample	H ₂ pretreatment temperature/K	NO conversion/%	
		Reacted at 303 K ^b	Reacted at 473 K ^c
Cu/TiO ₂ from nitrate	None	28	57
	373	44	70
	473	91	76
	573	78	75
	673	15	72
Cu/TiO ₂ from acetate	None	8	44
	373	47	77
	473	75	75
	573	36	76
	673	12	76

^a Catalyst 0.1 g; reacted for 1 h.

^b Reactant: NO and H₂ (28 μmol, each).

^c Reactant: NO and H₂ (88 μmol, each).

from cupric nitrate and acetate was investigated. The result is shown in Table 1. In the case of the reaction at 303 K, NO conversion is maximized when H₂ pretreatment temperature is 473 K in the samples prepared from nitrate and acetate. It suggests that 473 K is also the optimum temperature for NO reduction over the samples from acetate, and the reactivity is similar to that over the samples from nitrate. However, in the reaction at 473 K, NO conversion (88 μmol of NO) is kept 70–76% over both samples from nitrate and acetate in the range 373–673 K of H₂ pretreatment temperature.

To compare the reactivity between the Cu/TiO₂ samples prepared from nitrate and acetate, the reactions were carried out at various reaction temperatures. The result is shown in Fig. 1. At 303 K, the sample from nitrate is

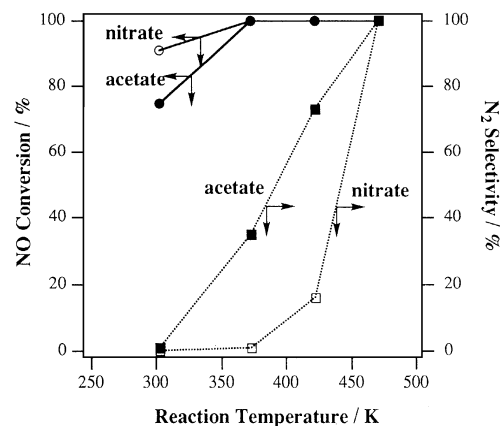


FIG. 1. Relationship between reaction temperature and the activity on NO reduction over 2 wt% Cu/TiO₂ prepared from cupric nitrate and acetate. Catalyst 0.1 g, pretreated with H₂ at 473 K. Reactant NO and H₂ (28 μmol, each); reacted for 1 h.

more active than that from acetate, and the formation of N_2 was observed in neither sample. In the reaction above 373 K, NO conversion reaches 100% in both samples. For the samples prepared from acetate, the selectivity of N_2 becomes larger with an increase in reaction temperatures above 373 K, while for the sample from nitrate, formation of N_2 is definitely seen above 423 K. For the sample from nitrate. The selectivity reached 100% at 473 K as did that for the sample from acetate. In the region of 373–423 K of reaction temperature, N_2 selectivity is found to be higher in the sample from acetate than that from nitrate. Thus, the activity of Cu/TiO_2 samples prepared from acetate for NO reduction to produce N_2 is higher than that of the samples from nitrate at relatively low temperatures.

Table 2 shows the results of NO reduction (NO 88 μmol) at 473 K over Cu/TiO_2 with various Cu loadings. In the case of the samples from nitrate, NO conversion increased with an increase in Cu loading less than 4 wt%, and it is kept about 82% in the region of 4–8 wt% of Cu loading. The selectivity of N_2 also increased with an increase in Cu loading up to 4 wt%, and it reaches about 94% in higher Cu amount than 4 wt%. For the samples from acetate, NO conversion is increased with the increase of Cu less than 6 wt%, and it reaches about 82% in 6–8 wt% Cu. The conversion in the samples from acetate is almost similar to that in the samples from nitrate, indicating that the effect of Cu loading is almost the same for Cu/TiO_2 samples prepared from nitrate and acetate.

In order to clarify the difference of reactivity, the time courses of the reaction (NO 65 μmol) over these samples were investigated. The results are shown in Fig. 2. In this reaction condition, the conversion of NO is reached 100% over the whole samples within 1 h. The pathways proceed from the reduction of NO to N_2 , and N_2O is seen at the

TABLE 2

Effect of Cu-Loading on Activity and Selectivity for NO Reduction over Cu/TiO_2 (Pretreated with H_2 at 473 K)^a

Sample (Cu loading)	NO conversion/%	N_2 selectivity/%
<i>Cu/TiO₂ from nitrate</i>		
1 wt%	34	76
2 wt%	76	89
4 wt%	82	94
6 wt%	81	94
8 wt%	83	95
<i>Cu/TiO₂ from acetate</i>		
1 wt%	51	78
2 wt%	75	93
4 wt%	78	92
6 wt%	83	98
8 wt%	82	98

^a Catalyst: 0.1 g; reactant: NO and H_2 (88 μmol , each). Reacted at 473 K for 1 h.

TABLE 3

Effect of Cu-Loading on Activity and Selectivity for NO Reduction over Cu/TiO_2 (Pretreated with H_2 at 473 K) in the Initial Stage^a

Sample (Cu loading)	NO conversion/%	N_2 selectivity/%
<i>Cu/TiO₂ from nitrate</i>		
1 wt%	29	43
2 wt%	47	77
4 wt%	34	61
6 wt%	40	68
8 wt%	47	86
<i>Cu/TiO₂ from acetate</i>		
1 wt%	32	62
2 wt%	48	84
4 wt%	41	77
6 wt%	42	76
8 wt%	45	73

^a Catalyst: 0.1 g; reactant: NO and H_2 (55 μmol , each). Reacted at 473 K for 2.5 min.

initial stage of the reaction. The composition of N_2O is almost constant apparently until the NO is consumed. After disappearance of the NO, the reduction of N_2O to produce N_2 proceeds. It is concluded that NO reduction undergoes *via* direct N_2 formation and the reaction path *via* the N_2O intermediate is minor.

For the samples from nitrate as shown in Fig. 2, the NO consumption rate at the initial stage decreased with an increase in Cu loading amount to less than 8 wt%. The results of reactivity in the initial stage (reacted for 2.5 min) are shown in Table 3. In comparison between various Cu loading samples in 1–6 wt%, the 2 wt% Cu-loading sample exhibits the highest activity for both NO conversion and N_2 selectivity. It suggests that the sample with 2 wt% Cu is relatively the most active for NO reduction to produce N_2 . On the other hand, NO consumption rates at the initial stage are larger in the samples from acetate than those from nitrate in the whole range of Cu loading amounts. In addition, the composition of N_2O at the initial stage is smaller than that of the samples from nitrate, as shown in Table 3. These results indicate that the samples from acetate are more active for NO reduction to N_2 than those from nitrate. In the comparison between the samples from acetate with various Cu-loading, the 2 wt% sample exhibits the highest activity for both NO conversion and N_2 selectivity. This result is similar to that for the samples from nitrate. In the case of the samples from acetate with 6 and 8 wt% Cu, selectivity to N_2 reached 100% after 50 min from starting the reaction. For these samples, NO is perfectly consumed within 20 min from starting the reaction. After the disappearance of NO, converting N_2O to N_2 is significantly faster than in case of other samples from acetate with lower Cu content, while it is not clear whether or not N_2 is produced catalytically. In the case of the samples from acetate with higher Cu

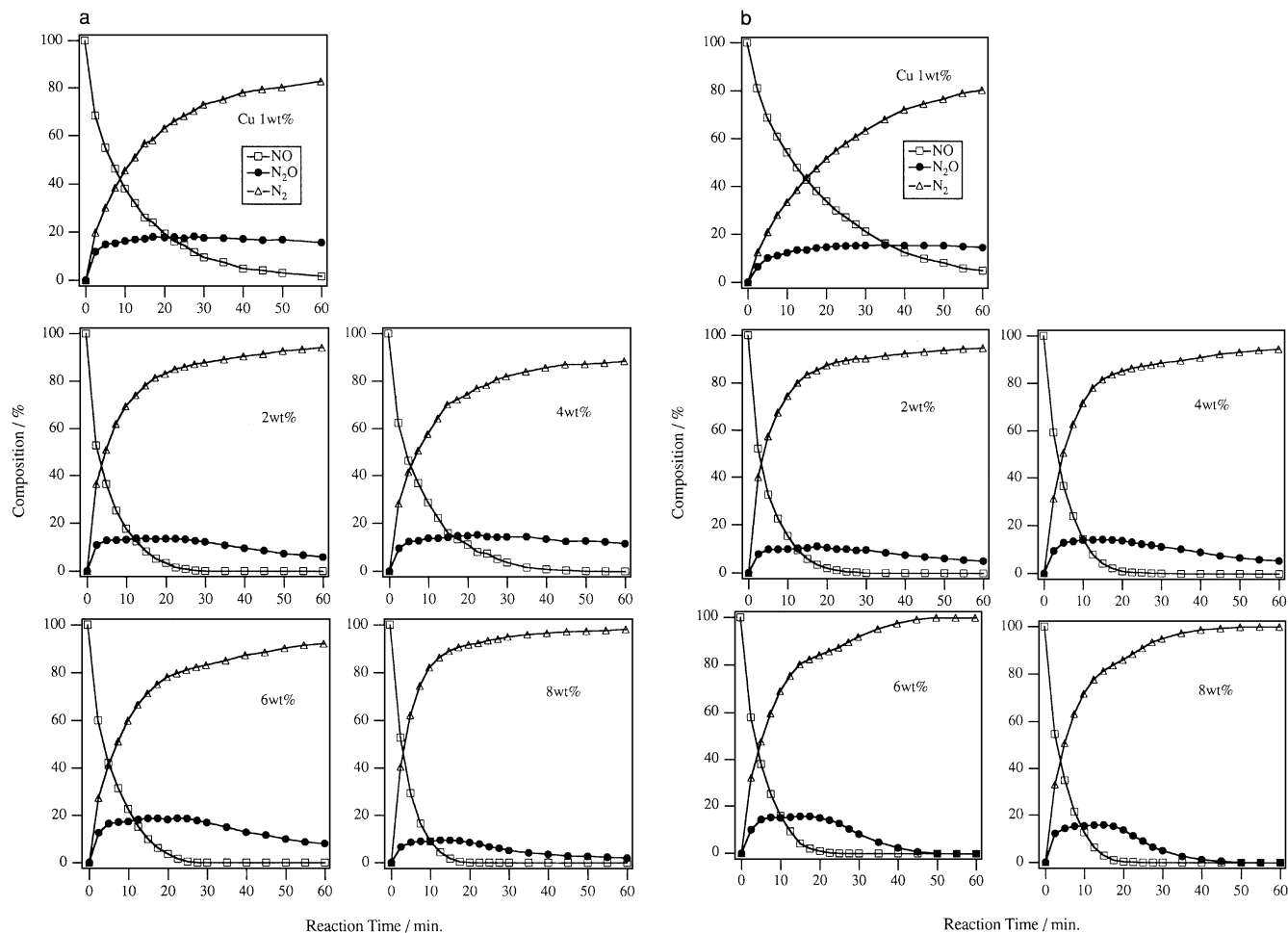


FIG. 2. Time course of NO reduction with H_2 over Cu/TiO_2 prepared from (a) nitrate with various Cu loading; (b) acetate with various Cu loading. Reactant NO and H_2 ($65 \mu\text{mol}$, each); reacted at 473 K.

loadings, the formation of N_2O is larger and the reduction of N_2O is faster after the disappearance of NO. From these results, it is summarized that the samples prepared from acetate exhibit more appropriate reactivity for NO reduction to produce N_2 than those from nitrate. Higher amounts of Cu loading (6–8 wt%) show lower activity for NO reduction to N_2 and/or N_2O but higher activity for N_2O reduction to N_2 than lower Cu loading (1–4 wt%). The 2 wt% sample exhibits the highest activity in the initial stage of the reaction.

The result of the successive reaction of NO and H_2 over the samples from nitrate and acetate with 2 wt% Cu loading ($315 \mu\text{mol} \cdot (\text{g-sample})^{-1}$ as Cu) is shown in Table 4. The reactions take place catalytically. It is deduced that the decrease of activation for the sample from acetate is less than that for the sample from nitrate by successive reaction. It indicates that the sample from acetate possesses more appropriate reactivity for NO reduction than that from nitrate and suggests that a higher stability of the catalytic species of the acetate sample is shown than that of the nitrate sample.

(2) Cu K-edge XAFS Study of Cu/TiO_2

In our previous report (15), it is concluded in 2 wt% Cu/TiO_2 samples prepared from nitrate that the treatment with hydrogen at 473 K brings about the formation of Cu

TABLE 4

Successive Reactions of NO with H_2 over 2 wt% Cu/TiO_2 from Nitrate and Acetate (Pretreated with H_2 at 473 K)^a

Run ^b	NO conversion/%	
	From nitrate	From acetate
1	76	75
2	62	70
3	50	61

^a Catalyst 0.1 g; reacted at 473 K for 1 h. Reactant NO and H_2 ($88 \mu\text{mol}$, each).

^b The reactor was evacuated (not treated with H_2) at 473 K between each reaction.

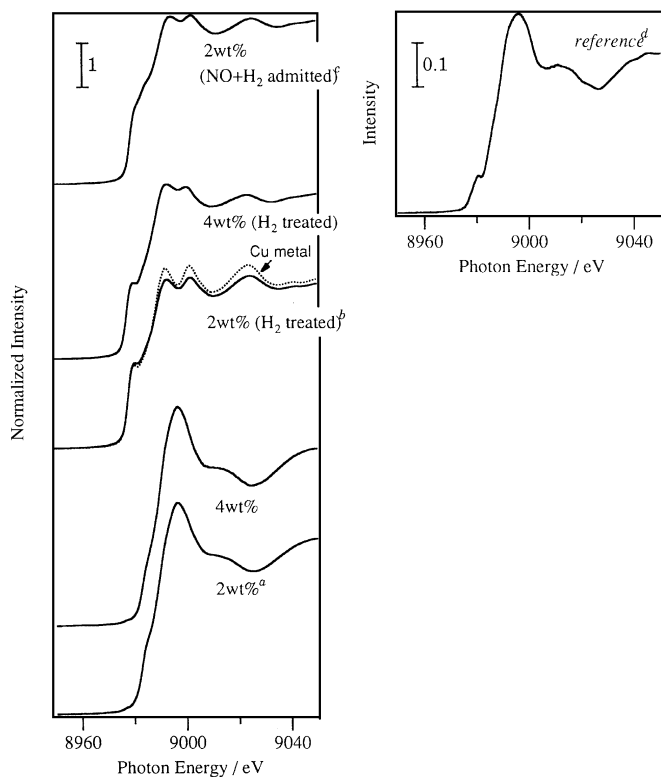


FIG. 3. Cu *K*-edge XANES spectra of Cu/TiO₂ samples prepared from nitrate: *a*, calcined at 773 K; *b*, treated with H₂ at 473 K for 1 h; *c*, after admission of (NO + H₂) to sample *b* at 473 K for 1 h; *d*, reference spectrum: {(4 wt% H₂ treated) – (2 wt% H₂ treated)} × 0.8.

metal particles and promotes the reduction of Ti ions studied by XANES, UV-VIS, and ESR spectroscopies. The extent of the reduction of TiO₂ supporting Cu is much higher than that of TiO₂ itself. NO has a role for oxidizing both Cu and Ti ions even at room temperature, and H₂ has a role for reducing both ions. It is revealed that the active Cu-species of Cu/TiO₂ from nitrate is the CuO particle with a Cu metal core.

To compare the structure of the Cu species between the samples prepared from nitrate and acetate, the local structure around Cu ions and/or metals are investigated by means of Cu *K*-edge XANES/EXAFS. The XANES spectra of 2 wt% Cu/TiO₂ samples from nitrate are shown in Fig. 3. For the sample before the pretreatment with H₂, the spectrum is almost similar to that of Cu(OH)₂, indicating that Cu species on TiO₂ exist as Cu²⁺ ions centered in oxygen octahedra. After the treatment with H₂ at 473 K, the spectrum can be attributed to Cu metal (15). In comparison with the spectra of the 4 wt% Cu/TiO₂ sample from nitrate, they are similar to those for the 2 wt% sample before and after the pretreatment. After pretreatment with H₂, the total spectral feature for both the samples is that for Cu metals. However, careful observation of the peaks at the absorption edge tells the presence of oxide. The peaks are not so

well resolved as those for Cu metal due to the overlapping peaks of the oxide phase. These peaks for the 4 wt% sample are less clear than those for the 2 wt% sample, indicating that the spectrum of the 4 wt% sample has a smaller intensity of Cu metal than that of the 2 wt% sample. This is rationalized by the difference spectrum as shown in Fig. 3. The spectrum was obtained by subtraction of the spectrum for the 2 wt% sample multiplied by 0.8 from the spectrum for the 4 wt%. The feature of the difference spectrum is that of the oxide phase, indicating that the fraction of Cu⁰ in the spectrum of the pretreated 2 wt% sample is higher than that of the pretreated 4 wt% sample. It suggests that the Cu ions in the 2 wt% sample are reduced to Cu⁰ more easily than those in the 4 wt% sample in this condition of H₂ treatment. In our previous paper (15), it was proposed by XANES study that Cu metal species are oxidized by the admission of NO even at room temperature, and the metal species are oxidized completely to form octahedrally coordinated Cu²⁺ species by the admission of NO at 473 K for 1 h. In case the samples after admission of NO + H₂ mixed gases, the spectrum in Fig. 3 suggests the coexistence of Cu metal and its oxidized ions, indicating that Cu metal species are partially oxidized by the admission.

The spectra of the samples from acetate pretreated with H₂ at 473 K are shown in Fig. 4. For 1–2 wt% Cu loading, the spectra can be attributed to a mixture of Cu²⁺ ions and Cu⁺ and/or Cu⁰. The spectral feature around the postedge peak (due to electron transition of 1*s*–4*p*π (17)) is very similar to Cu(OH)₂ but the position of the adsorption threshold is lower than that for Cu²⁺, resulting in the lack of a preedge peak (due to 1*s*–3*d* transition (18)). However, for the spectrum of the 2 wt% Cu sample, the energy position of a

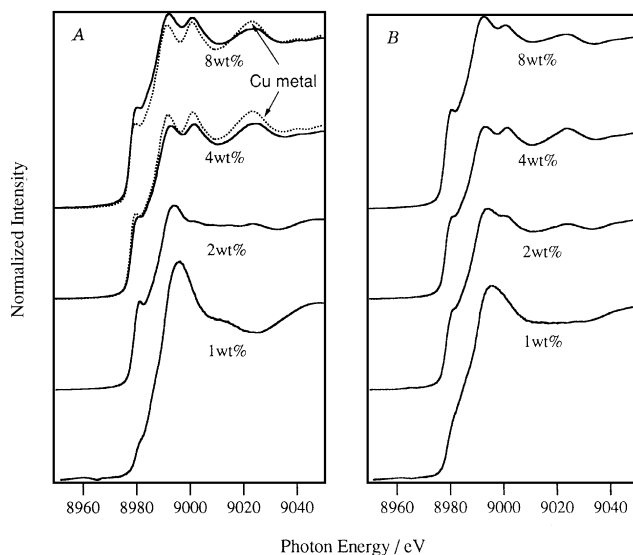


FIG. 4. Cu *K*-edge XANES spectra of Cu/TiO₂ samples from acetate treated with H₂ at 473 K (A) and after admission of (NO + H₂) to sample A at 473 K (B).

postedge peak is the same as that for Cu metal, suggesting that Cu^0 and Cu^{2+} ions coexist. In comparison between the samples prepared from nitrate and acetate in the 2 wt% of Cu loading, although, the H_2 treatment brings about the reduction of Cu ions in both samples; Cu metals are not definitely formed in the sample from acetate but they are formed in the sample from nitrate. It is determined that Cu ions in the sample from nitrate are reduced easier than those in the sample from acetate. The spectra of 4–8 wt% Cu show the formation of Cu metal species clearly. Comparison of these samples may suggest that the intensity of Cu metal in 4 wt% Cu is relatively higher than that in 8 wt%.

The changes of Cu species on TiO_2 before and after the reaction were investigated by means of EXAFS in 2 wt% Cu samples, which have high reactivity at the initial stage (Fig. 5). The k^3 -weighted EXAFS oscillations and Fourier-transformed EXAFS (FT-EXAFS) of the samples prepared from nitrate and acetate are shown in Fig. 6. In the whole cases, the oscillations strongly reflect the scattering of Cu–Cu in the local structure of Cu^0 metal species, which gives a peak at 2.3 Å in FT-EXAFS (shown in Fig. 6). In case of the sample from nitrate after H_2 treatment at

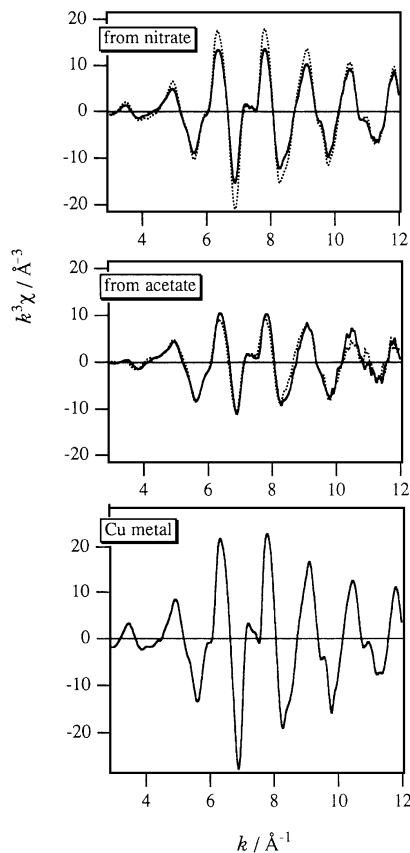


FIG. 5. EXAFS oscillations of 2 wt% Cu/TiO_2 prepared from nitrate and acetate before and after reaction: dotted lines, after pretreatment of H_2 at 473 K prior to admission; solid lines, after admission of $(\text{NO} + \text{H}_2)$ at 473 K for 1 h.

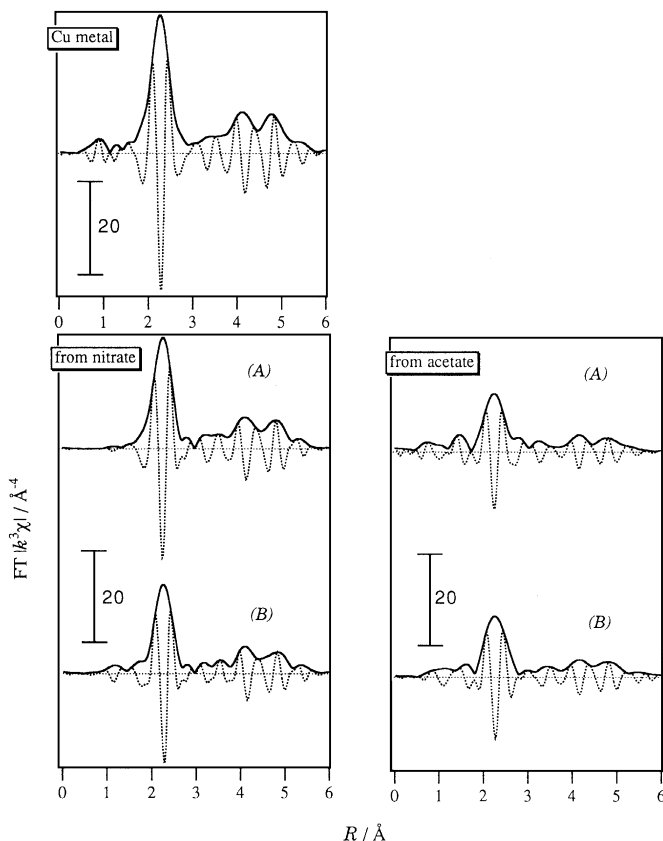


FIG. 6. Fourier-transformed EXAFS of 2 wt% Cu/TiO_2 prepared from nitrate and acetate before and after reaction: (A) after pretreatment with H_2 at 473 K prior to admission; (B) after admission of $(\text{NO} + \text{H}_2)$ at 473 K for 1 h.

473 K, the intensity of the oscillation due to the scattering of Cu–Cu metal is smaller than that of Cu metal, exhibiting that micro particles of Cu metal are stabilized. For the sample from acetate after H_2 treatment, the Cu–Cu scattering is also observed, while the Cu metal is less observed by XANES spectrum. It is remarkably shown that the intensity of Cu–Cu scattering in the sample from nitrate is larger than that in the sample from acetate before and after $(\text{NO} + \text{H}_2)$ admission at 473 K. This suggests that Cu^0 metal species formed after pretreatment with H_2 have a larger particle size for the nitrate sample than those for the acetate sample. For the samples from nitrate, the Cu–Cu scattering becomes less intense by the admission of $(\text{NO} + \text{H}_2)$, indicating that Cu metal particles become smaller in size. On the other hand, the Cu–Cu intensity for the samples from acetate is less changed by the admission. There is a definite difference between the samples prepared from nitrate and from acetate. In these results, it can be considered that the Cu metal particles in the sample from nitrate are oxidized in the near-surface region, but a Cu metal core remained which has a smaller particle size. In the case of the sample from acetate, the metal species are more stable for $(\text{NO} + \text{H}_2)$ admission than those of the sample from nitrate.

For FT-EXAFS shown in Fig. 6, a peak at 2.3 Å, due to Cu–Cu scattering, and a small peak at around 1.8 Å, possibly due to Cu–O scattering, are observed for each sample. The intensity of the Cu–Cu peak relates to that of the oscillation wave as mentioned above. For the samples from nitrate, the Cu–Cu peak at 2.3 Å becomes less intense by (NO + H₂) admission at 473 K. On the other hand, for the samples from acetate, the Cu–O peak at around 1.8 Å are investigated definitely even after H₂ pretreatment. It supports the coexistence of Cu metallic species and the oxidized ones in this sample. After admission of (NO + H₂) at 473 K, the Cu–Cu peak is less intense and the Cu–O peak is more intense. It is deduced that the effect of the admission for Cu species on TiO₂ is different between the samples prepared from nitrate and acetate, i.e., Cu-metal particle size is reduced by the admission for the nitrate sample, but it is a little enlarged for the acetate sample.

To estimate the particle size of the Cu metallic species, we performed curve fitting of Cu–O and Cu–Cu shells by inverse-FT after FT-filtered EXAFS in the range of $\Delta R = 1.1\text{--}2.7$ Å. The results are shown in Table 5. In Fig. 7, the best fits for 2 wt% Cu/TiO₂ samples from nitrate and acetate are shown as examples. For all the samples, two-shell-fitting of both Cu–O and Cu–Cu bonds gave the satisfactory result. For the 2 wt% Cu/TiO₂ sample from nitrate, the coordination number (CN) of Cu is estimated to be

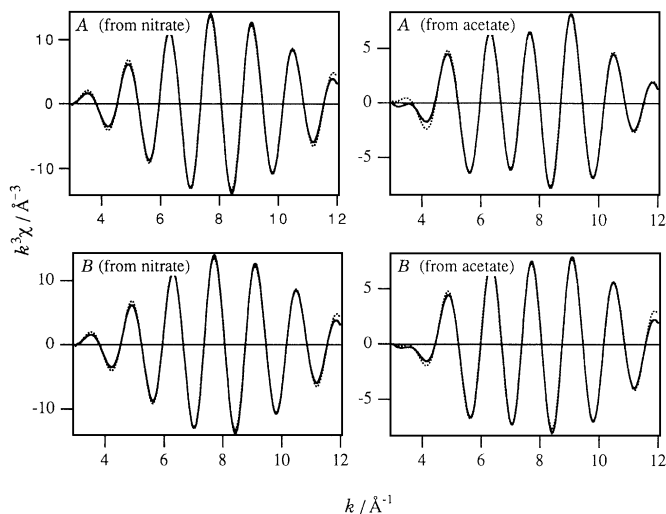


FIG. 7. The best fitting of Fourier back-filtered EXAFS oscillations in the range $\Delta R = 1.1\text{--}2.7$ Å: solid lines, isolated EXAFS; dotted lines, model EXAFS obtained by 2-shell fitting of Cu–O and Cu–Cu. A, treated with H₂ at 473 K for 1 h prior to admission; B, after admission of (NO + H₂) at 473 K for 1 h.

10.6 before (NO + H₂) admission, supporting the idea that Cu metal species exist as a small metal particle because of smaller number than that of the Cu metal sample. The CN decreased evidently to 7.5 by (NO + H₂) admission. It

TABLE 5

Results of EXAFS Analysis by Curve-Fitting of 2-Shells (Cu–O and Cu–Cu) at $\Delta R = 1.7\text{--}2.7$ Å

Sample	Shell	$N_{(CN)}$	$R/\text{Å}$	$\Delta\sigma^2/10^{-3}\text{Å}^2$	R-factor/%	
Cu metal	Cu–Cu	12	2.56			
2 wt% Cu/TiO ₂ from nitrate	A	Cu–O	2.7 (1.6)	2.00 (0.03)	8.5 (16.5)	3.9
		Cu–Cu	10.6 (0.9)	2.55 (0.01)	0.7 (1.3)	
	B	Cu–O	2.5 (1.1)	1.96 (0.02)	5.2 (6.0)	4.8
		Cu–Cu	7.5 (0.7)	2.56 (0.01)	0.0 (5.7)	
2 wt% Cu/TiO ₂ from acetate	A	Cu–O	1.7 (0.5)	1.85 (0.01)	–1.6 (1.3)	6.6
		Cu–Cu	6.3 (0.5)	2.56 (0.01)	1.1 (0.5)	
	B	Cu–O	3.4 (0.8)	1.89 (0.01)	8.3 (4.4)	6.0
		Cu–Cu	6.2 (0.5)	2.55 (0.01)	0.4 (0.6)	
4 wt% Cu/TiO ₂ from acetate	A	Cu–O	2.8 (1.3)	1.98 (0.05)	8.4 (7.5)	2.4
		Cu–Cu	10.2 (1.0)	2.55 (0.01)	0.1 (0.7)	
	B	Cu–O	4.6 (1.2)	1.94 (0.03)	19.1 (11.0)	4.8
		Cu–Cu	8.6 (0.5)	2.55 (0.01)	0.1 (0.7)	
8 wt% Cu/TiO ₂ from acetate	A	Cu–O	2.5 (1.2)	2.00 (0.02)	4.5 (7.5)	4.0
		Cu–Cu	10.6 (1.0)	2.55 (0.01)	0.8 (0.7)	
	B	Cu–O	3.9 (1.0)	1.91 (0.01)	17.5 (14.0)	5.2
		Cu–Cu	8.0 (0.7)	2.55 (0.01)	0.8 (0.7)	

Note. The values in parentheses are the standard deviations. A: after H₂ pretreatment at 473 K for 1 h prior to admission; B: after admission of (NO + H₂) at 473 K for 1 h.

substantiates that the metal particle becomes smaller. The CNs for oxygen as well as the Debye-Waller factors include large errors and we cannot discuss the size of the oxidized layer on the basis of the CN. But the bond distance between Cu and oxygen shows that the Cu ions are divalent. For the 2 wt% sample from the acetate, the CNs before and after admission are almost similar to each other, supporting the idea that Cu metal particle is stable for (NO + H₂) mixed gases. In these results, the active Cu species in 2 wt% Cu/TiO₂ samples consists of Cu-metal particles and oxidized species. Again, we cannot discuss the CN of oxygen but the shorter bond distances than those found in the case of 2 wt% Cu/TiO₂ sample from nitrate suggests that the Cu ions are monovalent. Thus, it is deduced that the admission of (NO + H₂) at 473 K brings about the formation of Cu metal species having a suitable particle size for the reduction of NO.

As a reference, the curve-fitting results of EXAFS spectra for the samples from the acetate with higher Cu loading are shown in Table 5. Before the admission of (NO + H₂), the CNs are 10.2 and 10.6 in 4 and 8 wt% Cu loading, respectively. It suggests that the particle size is larger than that in the 2 wt% sample and the particle size for the 4 and 8 wt% Cu samples is almost the same for each. After admission of (NO + H₂), the size becomes smaller in both samples, but the reduction of the size is less in the 4 wt% than in the 8 wt%. This evidence is similar to that of the sample from the nitrate. It strongly suggests that admission of (NO + H₂) gives oxidation of the Cu metal particles in the surface region to form smaller particles, but the degree of oxidation depends on the particle size. Suitable particle size for NO reduction is formed by the admission. Therefore, this species exists as an active one for NO reduction. If it is justified, the acetate sample is more stable than the nitrate sample for the reaction in 2 wt% Cu. By means of UV-VIS spectroscopy in a diffuse reflectance mode shown in Fig. 8, the spectra in both the nitrate and the acetate samples with 2 wt% Cu have an observed peak centered at around 580 nm. This absorption is due to the existence of Cu-metal micro particles with 100–300 Å of particle size, as reported in the study of Cu metal colloids (19, 20). After admission of (NO + H₂), the absorption band becomes less intense in the samples from the acetate, although it still remains. For the sample from the nitrate, the band almost disappears and a new band is seen, centered at 700 nm, which is attributed to be octahedrally coordinated Cu²⁺, as found in case of Cu(OH)₂ (21, 22). It is to be noted that the absorption bands in the region of 200–300 nm are different between the samples prepared from nitrate and acetate. In the case of the sample from nitrate, both (A) and (B) exhibit the similar feature to the reduced TiO₂. On the contrary, in case of the sample from acetate, both (A) and (B) exhibit the similar one to TiO₂ in the oxidized state. The presence of Cu in the nitrate samples urged the reduction of TiO₂, but

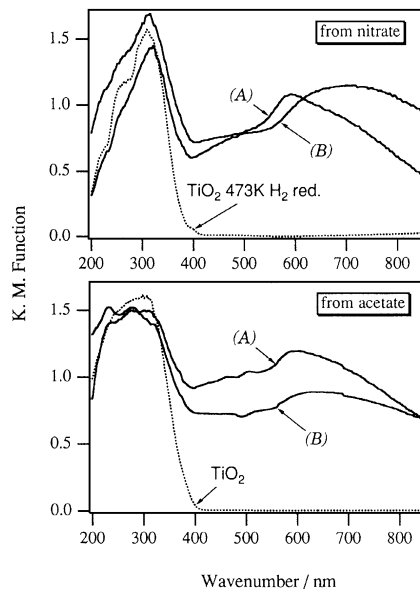


FIG. 8. Diffuse reflectance UV-VIS spectra of 2 wt% Cu/TiO₂ prepared from nitrate and acetate before and after reaction: (A) after pre-treatment with H₂ at 473 K prior to admission; (B) after admission of (NO + H₂) at 473 K for 1 h.

that in the acetate sample does not affect the TiO₂ at all. The feasibility of TiO₂ reduction may dominate the stability of Cu particles. This evidence relates to that of EXAFS. However, the Cu–Cu CN for the 2 wt% sample from acetate is 6.2–6.3 which corresponds to the 8–20 Å diameter of the Cu cluster, provided that Cu cluster is spherical (23). This is inconsistent with the size predicted by the UV-VIS spectrum. If the spherical cluster was so small, then the peaks due to the presence of Cu atoms in the third and fourth shells at longer distances in FT-EXAFS in Fig. 6 should have been invisible. The small CN and the clear peaks at long distances show that the Cu cluster in the 2 wt% sample from acetate are not spherical. It is likely that the cluster is raft-like with a few atomic layers. If a monolayer cluster of Cu(111) is assumed, CN is always less than 6 and the number of Cu atoms in the third shell becomes extremely small. If the two-layer cluster is assumed, the CN, 6.2–6.3, corresponds to the 20–100 Å particle size, which depends on the shape of the cluster. In any case, the Cu cluster presumably has the thin-layered raft-like structure. The spectral feature of XANES proves that the electronic band structure is very similar to that of bulk Cu. In such a case, the behavior of free electrons in the Cu cluster is expected to be similar to that of bulk Cu: the narrow VIS absorption peak at 580 nm is due to the presence of a fairly large Cu raft-like cluster. The suitable Cu metal particle for NO reduction has particle size *ca* 100 Å.

CONCLUSION

From the results mentioned above, it is concluded that the Cu metal species with suitable metal particle size for

NO reduction and oxidized Cu ions exist partly as active ones. In this species, Cu ions exist as Cu⁰ in a core and Cu²⁺ (and Cu⁺, partly) in the near-surface region. By means of UV-VIS spectroscopy, the presence of octahedrally coordinated Cu²⁺ is observed and Cu⁺ is not found definitely in the 2 wt% Cu/TiO₂ sample from nitrate, and the sample from acetate exhibited a similar phenomenon. Thus, it is possibly deduced that the coexistence of Cu⁰ and Cu²⁺ relates to generating the active species. By means of EXAFS studies, the suitable particle size of Cu metal leads to the active center.

In the case of TiO₂-supported with Cu metal particles, it can be considered that the redox performance is enhanced by other effects, such as SMSI. In fact, it is shown that both Cu and Ti ions show a redox behavior easier than TiO₂ only by means of ESR study (15). However, how metal species (and oxidized Cu²⁺) play a role for an active center for NO reduction is still unclear and is now in progress.

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