TPR STUDY ON DIFFERENTLY PREPARED COPPER MORDENITES

Myung-Suk Kim, Chang-Yong Lee and Baik-Hyon Ha*

Department of Chemical Engineering, Hanyang University, Seoul 133-791, Korea

Abstract — Three kinds of copper mordenite such as copper ion-exchanged, impregnated and physically mixed hydrogen mordenites were prepared and TPR study was carried out. For the fresh ion-exchanged mordenite, two distinct reduction processes were observed; one for the reduction of Cu(II) ion to Cu(I) ion at 225°C and the other for the reduction of Cu(I) to copper metal at 480°C, respectively. Successive TPR/oxygen-treatment lowered the first reduction temperature to 200°C and raised the hydrogen consumption. However, the second peak at 480°C for Cu(I) to copper metal was diminished. The reduction peak at 200°C may be an indicative of the newly formed ionic compounds such as cluster of copper ions. Impregnation of cupric salts leads to the formation of similar cluster of copper ions as those appeared in ion-exchanged mordenite. The treatments of CuO-mixed mordenite also decreased the reduction temperature due to the well dispersed CuO particles on the crystal surface and also formed the same cluster copper ions as appeared in the ion-exchanged one. The cluster of copper ions on the crystal surface created the higher activity for CO oxidation.

INTRODUCTION

The role of copper for the copper/zeolites has been mainly studied for the copper-ion-exchanged Y-type zeolites [1-9]. However it is only a beginning step for the copper/mordenites studies. Iwamoto [10] reported the redox mechanism of copper ions on Cu-NaM by using TPR/TPO techniques with hydrogen and oxygen as redox agents. Kucherov et al. [11] proposed the identification of isolated and clustered ions on CuHM through the ESR studies. Slinkin and Kucherov [12] have also studied the ion-exchange properties of copper when they mixed copper oxide in solid state with hydrogen mordenite, calcined under the vacuum, and reoxidized with oxygen. Miro et al. [13] studied the oxidation of carbon monoxide on Cu-NaM which was redox-treated with carbon monoxide and oxygen, and discussed the role of newly formed copper oxide.

However, no studies for the redox behavior of the copper/mordenites have been carried out by changing the preparation method. Also the status of copper ions and newly formed copper oxides after the redox treatment have not been elucidated yet. Therefore in this study, the role of copper in the copper/mordenites,

which are prepared by three different methods, has been studied with the TPR technique which has been known as a useful tool for the characterization of the redox nature of cations on zeolites.

EXPERIMENTALS

1. Preparation of Copper/Mordenites
1-1. Ion-Exchanged Mordenites

NaM from Norton(Zeolon-900) was ion-exchanged three times with 1 N NH₄Cl solution at 80°C to obtain NH₄M and then followed with $Cu(NO_3)_2$ solution to obtain CuNH₄M. After washing and drying CuNH₄M, it was calcined in oxygen atmosphere at 500°C to prepare CuHM. This is designated as CuHM-32, where 32 denotes an ion-exchange percent.
1-2. Impregnated Mordenites

NH₄M was calcined at 500°C to prepare HM and impregnated with $Cu(NO_3)_2$ solution. It is then dried at 120°C. These samples are also designated as Cu/HM (3), Cu/HM(14), where 3 and 14 in parenthesis denote the impregnated copper content by weight percent.
1-3. Physically Mixed Mordenites

The copper oxide was physically mixed with the fine powder of 60/80 mesh HM. These are designated as CuO//HM(1) or CuO//HM(3), where 1 and 3 in parenthesis represent the weight percent of copper

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*To whom all correspondence should be addressed.

oxide in the mixed catalysts.

2. Experimental Measurements

2-1. Temperature Programmed Reduction(TPR)

Five vol.% of hydrogen balanced with nitrogen was used as a reducing gas. Flow rate was 10 ml/min and temperature increasing rate was 10°C/min one hundred mg of 60/80 mesh powder was mounted in a quartz tube and calcined in oxygen atmosphere at 500 °C for 30 min as a first step and cooled down to ambient temperature in nitrogen atmosphere. To remove the moisture of gases, solid NaOH trap was used. The amount of hydrogen measured with TCD.

2-2. X-Ray Diffraction(XRD)

To confirm the presence of copper or copper oxide on catalyst surface, XRD(Rigaku Geigerflex, D-Max 3A) was used.

2-3. Electron Spin Resonance(ESR)

In order to examine the status of copper ion such as Cu(II) or its clustered form, ESR(Varian E-4 Spectrometer) spectra of copper ion were obtained at ambient temperature.

2-4. CO Oxidation Activities

The reactants consisting of 5 vol.% oxygen and 5 vol.% carbon monoxide balanced with nitrogen, was used at a flow rate of 40 ml/min for 200 mg of catalyst. Product stream was analysed with gas chromatograph equipped with a column packed with Porapac Q and molecular sieve 13 X. The catalytic activity was expressed in terms of the reaction temperature where 50% conversion is obtained, T_{50}.

RESULTS

1. Ion-exchanged Mordenites

TPR spectra for the ion-exchanged Cu(II)HM-32 are shown in Fig. 1. The TPR spectrum (a) is for the fresh catalyst treated at 500°C in oxygen atmosphere for 2 hrs. The spectrum (a) consists of two peaks appeared at about 225°C and 480°C. The spectra (b), (c) and (d) are obtained from the sample of spectrum (a) by successive redox-treatment at 500°C for 1 hr. When the procedure was repeated, it was found that the first hydrogen consumption for the peak at 225°C increased with the temperature shift to 200°C, and the second peak at 480°C was diminished. The new reduction processes were appeared at 265°C in (c) and at 278°C as a shoulder in (d), respectively.

The reduction treatment by carbon monoxide at 500 °C instead of hydrogen gives spectrum (e) which shows only one peak at 480°C. The previous result [14] presents that the reduction of Cu(II)HM by CO at 500°C changed only Cu(II) into Cu(I). The peak at 480°C ap-
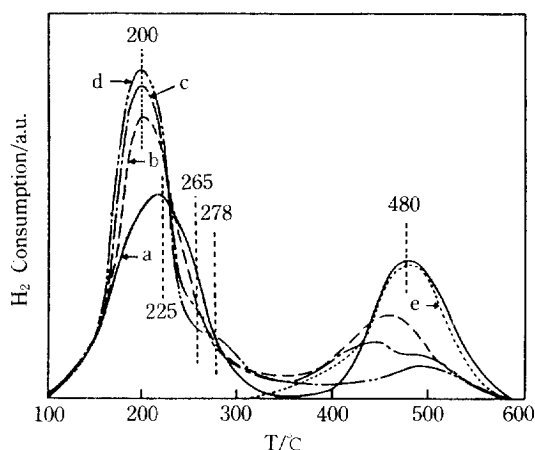

Fig. 1. TPR spectra of Cu(II)HM.
  a: fresh sample, treated by O_2 at 500°C for 2 hr;
  b: reoxidized at 500°C for 1 hr after TPR of (a);
  c: reoxidized at 500°C for 1 hr after TPR of (b);
  d: reoxidized at 500°C for 1 hr after TPR of (c);
  e: treated by CO at 500°C for 2 hr.

peared in Fig. 1(a) indicates that Cu(I) may have been changed to metal and the appearence of peak at 225°C is due to the reduction from Cu(II) to Cu(I).

The XRD powder patterns of Cu(II)HM-32, which is pretreated by hydrogen for 2 hrs and by oxygen for 1 hr, are shown in Fig. 2. Copper oxide crystal diffraction peak appeared. The gradual increase is observed as the redox treatment is repeated. These results indicate the migration of copper ions to the external surface of the mordenite crystals because the particle size of CuO detected by XRD is too large to locate in the pore of mordenite. Iwamoto [10] also reported the formation of CuO from the redox treatment of Cu(II)NaM in which one half of the copper metal changed to CuO after oxidizing treatment. Therefore, newly appeared reduction peaks at 265 and 278°C after the redox treatment, as shown in Fig. 1, are attributed to the reduction of CuO formed by the reoxidation of copper metal.

Kucherov et al. [11] reported that at lower concentration of Cu(II) ion[8% ion-exchanged Cu(II)HM], Cu(II) ion existed as isolated ion even after the reduction by carbon monoxide at 400°C. However, at higher concentration of Cu(II) ions[51% ion-exchanged Cu(II) HM], Cu(II) ions formed the cluster which could be easily reduced to metal by CO at temperature ranging from 300°C to 400°C. Cu(II)HM-32 studied in this work which has an intermediate concentration of copper ion, may have a part of ion cluster. The diminution of sec-
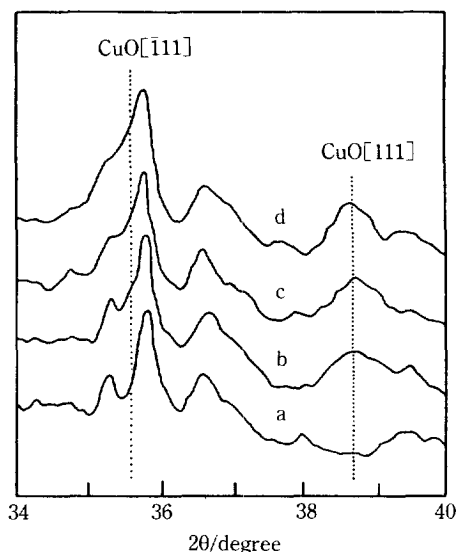
Fig. 2. XRD powder patterns of Cu(II)HM.
a: fresh sample; b: treated by H_2/O_2 at 500℃(2 hr/1 hr) redox cycle; c: treated by 2 H_2/O_2 at 500℃ (2 hr/1 hr) redox cycles; d: treated by 3 H_2/O_2 at 500℃(2 hr/1 hr) redox cycles.

Fig. 4. T_{50} of CO oxidation after successive redox treatment for Cu(II)HM.
a: reduced with H_2 at 500℃(2 hr). reoxidized with O_2 at 500℃(1 hr); b: reduced with CO at 500℃(2 hr). reoxidized with O_2 at 500℃(1 hr); □: fresh sample, treated by O_2 at 500℃ for 2 hr; ○: reduction; ●: reoxidation.

first and second peaks should have the same area, because the amount of hydrogen consummed during the two reduction steps, that is, the reduction of Cu(II) to Cu(I) and the reduction of Cu(I) to copper metal, must be the same. However, the first peak due to the hydrogen consumption is actually larger than the second peak. It is considered that a part of Cu(II) ions directly changed to metallic state and/or some of cupric ions formed a cluster of ion.

The presence of such cluster of copper ions could be also confirmed by ESR studies as shown in Fig. 3. The ESR spectra of Cu(II) ion for the fresh (a) and redox-treated (b) are the same samples as (a) and (c) of TPR spectra in Fig. 1. Successive TPR/oxygen-treatment modified the ESR spectrum (a) of the fresh sample to more asymmetric form (b). The size of peak for Cu(II) ions is also reduced in spite of the increase of hydrogen consumption during the reduction process at 200℃ in TPR. It means the formation of cluster of ions, which are more easily reducible than isolated Cu(II) ions.

The activities of the oxidation of carbon monoxide as a function of T_{50} are shown in Fig. 4. The activities for two catalysts redox-treated by H_2/O_2 and CO/O_2 at 500℃ are appeared in (a) and (b), respectively. The

Fig. 3. ESR spectra of Cu(II)HM.
a: fresh sample, treated by O_2 at 500℃ for 2 hr; b: treated by the same condition to (d) in Fig. 1.

ond hydrogen consumption peak at 480℃ caused the enlargement of first consumption peak and decreased the reduction peak temperature to 200℃ by the successive redox treatment as shown in Fig. 1. Indeed, the
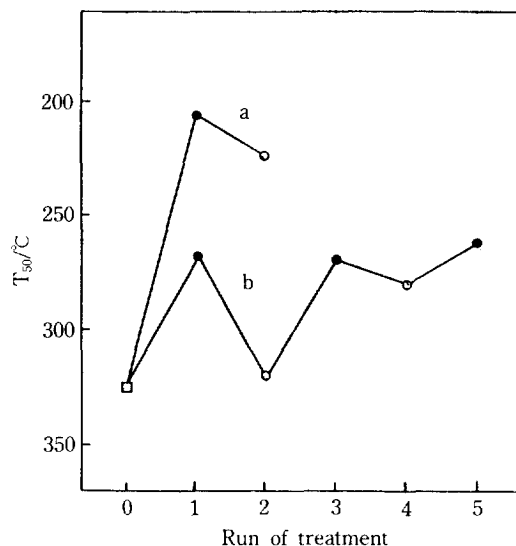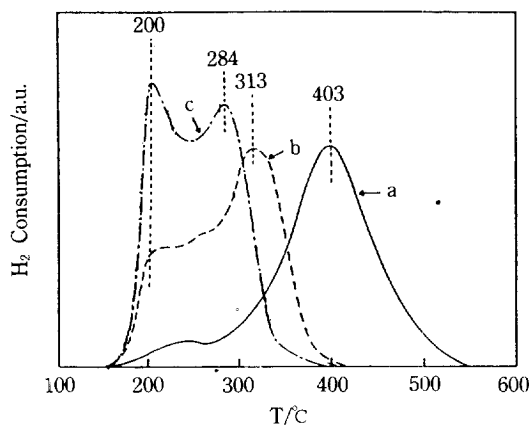
Fig. 5. TPR spectra of CuO//HM(3).
   a: fresh sample, treated by O_2 at 500℃ for 2 hr;
   b: treated by H_2/O_2 at 500℃(2 hr/1 hr) redox cy-
   cle; c: treated by 2 H_2/O_2 at 500℃(2 hr/1 hr) redox
   cycles.

Fig. 6. XRD powder patterns of Cu(II)HM.
   a: fresh sample; b: treated by H_2/O_2 at 500℃(2
   hr/1 hr) redox cycle; c: treated by 2 H_2/O_2 at 500℃
   (2 hr/1 hr) redox cycles.

activities of the former are higher than those of the latter. The activities of reduced Cu(II)HM by hydrogen or by CO at 500℃ are also higher than those of the reoxidized by oxygen. This is consistent with the previous work [14] of CO oxidation.

As mentioned above, treatment by carbon monoxide can not reduce the copper ions to metallic state at 500℃ within 1 or 2 hours and then most of Cu(I) ions stay in the pore and the reoxidation of the sample changes only ionic state of Cu(I) to Cu(II) in the pore. However, the strong reduction by hydrogen brings the copper ions to the external surface or to the shell of the mordenite crystal as metallic state. When it is reoxidized, most of copper will stay on its original location as ionic or oxidized copper compounds. Therefore, the significant difference of catalytic activities between the samples treated by H_2/O_2 and CO/O_2 can be related with the presence of cluster of copper ions and/or newly formed CuO on the catalyst crystal surface.

Oxidation activities of the samples redox-treated by CO/O_2 are nearly constant even if repeatedly redox-treated(Fig. 4b). Miro et al. [13] reported that redox treatment at 500℃ in CO and oxygen on Cu(II) NaM had not affected the activity of CO oxidation. Therefore, for the Cu(II)HM-32 treated by CO and oxygen, the distribution of Cu(II) ions could not be changed within only a few of number of redox treatment, but successive redox treatment changes the activities, as shown in Fig. 4b, due to the change of status of copper ion on the surface.
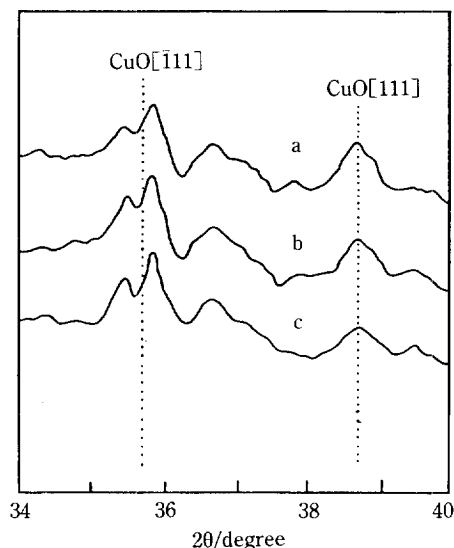
2. Physically Mixed Mordenites

The TPR spectra of CuO(3)//HM, which are prepared by 3% CuO powder mixing with HM, are shown in Fig. 5. The TPR spectrum for the fresh mixed sample 5(a) shows only one peak related to the reduction of CuO at 403℃. The TPR spectra (b) and (c) are for the samples treated once and twice with hydrogen for 2 hrs and with oxygen for 1 hr, respectively. Two distinctive peaks of hydrogen consumption at 313℃ and 200℃ are appeared in spectrum (b). A small peak also appears at 260℃. Spectrum (c) presents two peaks at 284℃ and at 200℃. The reduction peak at 200℃ is considered as the same peak as observed for ion-exchanged CuHM-32. The improvement of the contact between fine powder of CuO and external surface of the mordenite by the repeated redox treatment leads to the formation of ions on the outer surface of the mordenite crystals.

The XRD patterns for the mixed type CuO//HM are shown in Fig. 6. The peak height of XRD patterns for CuO decreased slightly as the redox-treatment proceeds. Therefore, TPR peaks at 284℃, 313℃ and 403℃ represent the direct reduction from CuO particles to copper metal. Generally, the growing of oxide particle lowers its reduction temperature. The decrease of reduction temperature of CuO from 403℃ to 284℃, as shown in Fig. 5, indicates the growth of CuO particles on mordenite crystal surface when the
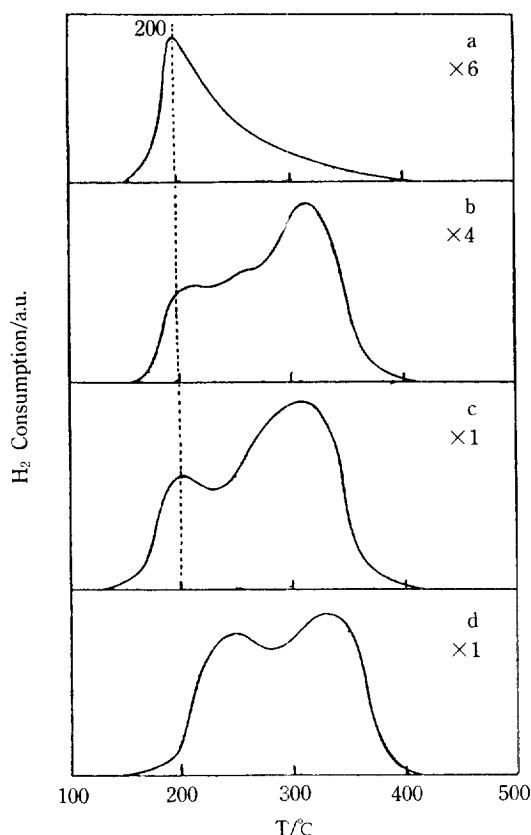
Fig. 7. TPR spectra of CuO//HMs and CuO//NaM treated by H₂/O₂ at 500°C(2 hr/1 hr) redox cycle.
a: CuO//HM(1); b: CuO//HM(3); c: CuO//HM(14); d: CuO//NaM(14).

Fig. 8. TPR spectra of Cu/HM(3).
a: fresh sample, treated by O₂ at 500°C for 2 hr;
b: treated by H₂/O₂ at 500°C(2 hr/1 hr) redox cycle.

redox treatment is repeated.

3. Effect of Copper Content for CuO//HM and CuO//NaM

In order to observe the redox behavior of the copper compounds on catalysts in terms of the copper content, 1%, 3%, and 14% of copper oxide are mixed with HM. As a support, NaM is also used to examine the formation of copper ion in the presence of sodium ions. The TPR spectra for these samples are shown in Fig. 7. The spectrum (a) for 1% copper oxide mixing with fine powder of HM, CuO(1)//HM gives only one asymmetric reduction peak at 200°C. However, 3% copper oxide mixing with HM, CuO(3)//HM, presents several overlapped peaks at higher temperatures. More increased mixing of copper oxide such as 14% with HM, CuO(14)//HM gives also similar reduction patterns as CuO(3)//HM did. However, copper oxide mixing of 14% CuO with NaM, CuO(14)//NaM shows no peaks at 200°C. In general, for sufficient copper
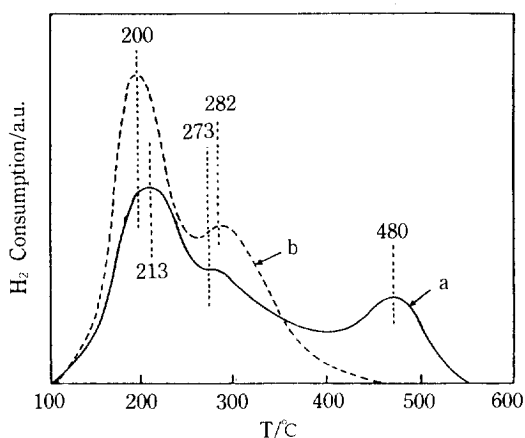
loading such as 14% CuO, a large reduction peak at 250-400°C appeared. For the temperature ranging from 200°C to 400°C, there are several overlapped reduction peaks. Therefore, the tailing part of the asymmetric peak in Fig. 7(a) is considered as an overlapped reduction peaks at higher temperature.

ESR study reveals that the small amount of ionic compounds is observed on NaM [12]. Therefore, the peaks at 200°C in Fig. 7(a), (b) and (c) clearly represent the reduction of ionic compounds. The peaks appeared at the temperature ranging from 250°C to 400°C, however, are considered for the reduction of copper oxide which is not influenced by the ability of ion-exchange. The overlapped and small peaks among them may represent the reduction for the small and well dispersed copper oxides created by the redox treatment.

4. Impregnated Mordenites

TPR spectra for the 3% CuO impregnated on HM, CuO(3)/HM are shown in Fig. 8. Spectrum (a) is for the samples oxidized at 500°C. The peaks appeared at 213°C and 480°C are related with reduction of Cu(II) ions formed by ion-exchange during the impregnation of cupric nitrate solution. At about 273°C, a shoulder like reduction peak for CuO appears after the calcination of impregnated mordenite. The TPR spectrum of (b) is for the catalyst redox-treated with hydrogen for 2 hrs and oxygen for 1 hr. The reduction peaks related to ionic compounds at 200°C are appeared, but the reduction peak at 480°C is clearly disappeared. It indicates that the easily reducible ionic compounds on impregnated mordenite have also created by the redox treatment.

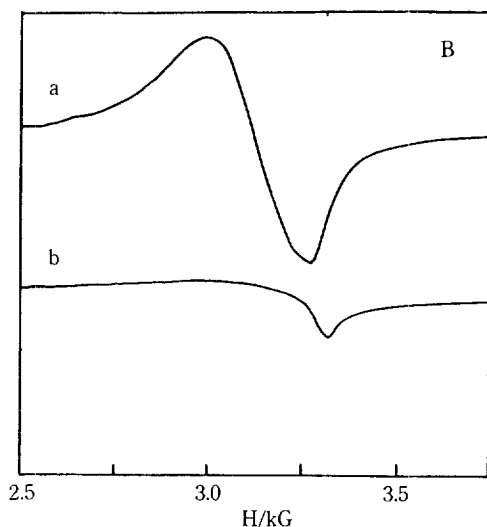ESR spectra for the impregnated samples are shown

Fig. 9. ESR spectra of Cu/HM(14).
　　a: fresh sample, treated by O_2 at 500℃ for 2 hr;
　　b: treated by 4 H_2/O_2 at 500℃(2 hr/1 hr) redox
　　cycles.

in Fig. 9. ESR spectrum (a) is for fresh Cu(14)/HM
and spectrum (b) is the result after redox-treatment
of (a) at 500℃. It informs the diminution of Cu(II)
ions and then the formation of the cluster of ions,
since the hydrogen consumption for the reduction
process at 200℃ increased as shown in Fig. 8.

5. Comparison with Other Supports

Copper oxide(14%) was loaded on HM, silicalite,
silica-gel by both impregnation with copper nitrate and
mixing with copper oxide. TPR spectra are shown in
Fig. 10 for these solids. The spectra (a) and (b) are
for mixed type, CuO//HM and impregnated type,
Cu/HM, respectively. For both samples, the similar
reduction temperatures are obtained. The peak at 200
℃ related with ionic compounds is clearly appeared.
It means that there is no differences in the formation
of copper ionic compounds which is reducible at 200℃
for both loading methods. The spectrum (c) of mixed
type with silicalite and spectrum (d) of the impreg-
nated one give one reduction peak only for CuO. The
peak related with ions reducible at 200℃ does not
appear. The TPR spectrum (e) of copper oxide mixed
with silica-gel shows one reduction peak and spectrum
(f) of impregnated one shows two reduction peaks. How-
ever, the peak at 200℃ does not appear too.

Such a TPR result is well agreed with the ESR re-
sult [15]. In Fig. 10(a) and (b), the reducibility of CuO
over the impregnated samples are slightly better than
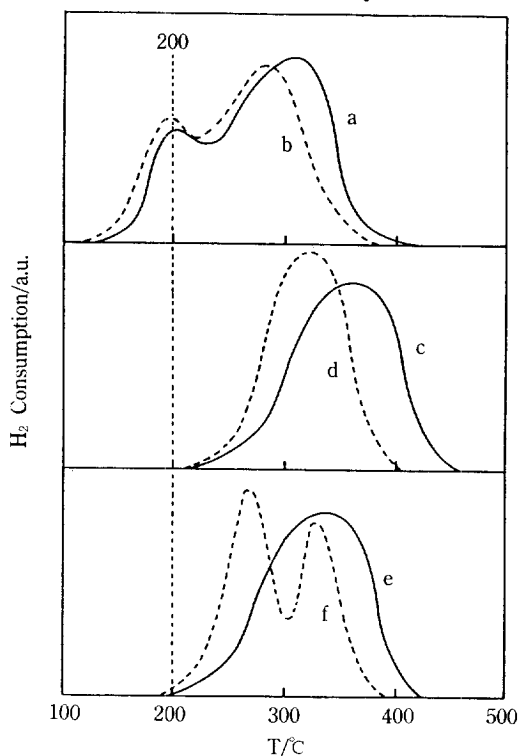that for the mixed samples since the growth and/or

**Fig. 10. TPR spectra of mixed samples and impregnated
　　samples with copper content of 14%, treated by
　　H_2/O_2 at 500°C(2 hr/1 hr) redox cycle.**
　　a: CuO//HM; b: Cu/HM; c: CuO//silicalite; d:
　　CuO/silicalite; e: CuO//silica-gel; f: Cu/silica-gel.

aggregation of CuO on solid surface over the impreg-
nated sample is much easier than that for the mixed
sample attributing to the difference of the copper dis-
persion.

DISCUSSION

Herman et al. [2] studied the reduction of copper
ions on CuNaY. They pointed out that copper metal
formed during the reduction process in the cage of
zeolite structure can be easily converted to Cu(II) ion,
but the metals on the external surface of zeolite crys-
tal can become partly Cu(II) ions at the interface be-
tween copper metal and the zeolite crystal surface and
the remaining copper metals converted to CuO par-
ticles. When CO is used as a reducing agent, the forma-
tion of $[Cu-O-Cu]^{2+}$ species is observed [5,15]. Hong
and Fung [16] studied the activity of Ni(II)Y for CO
oxidation and observed isolated ions as well as the
cluster of nickel ions which is linked by oxygen and

newly formed NiO. Cluster type nickel ions are the active sites for CO oxidation.

Mordenite, one of the high silica zeolite, has high silica/alumina ratio. So the formation of $[Cu-O-Cu]^{2+}$ in Cu(II)M was considered to be difficult [10]. Minachev et al. [11]. pointed out that in CuZSM-5 the presence of ions cluster is negligible even at high level of ion-exchange. Kagawa et al. [17] discussed the stability of Cu(I) ions which are formed from the Cu(II) and obtained the stability order as ZSM-5<mordenite<zeolite Y. This informs that the formation of ion cluster depends on the silica/alumina ratio. In high silica zeolite the distance between two tetrahedral aluminum sites is too long to form the cluster. Therefore, the stability of Cu(I) ion is much higher than that of the low silica zeolite.

However, most metals may stay on the external surface when copper oxide is reduced, because mordenite has a straight type pore structure which has not cages. It is different from the result for zeolite Y [2]. As the catalyst sample is redox-treated, the copper ions and copper oxide on external surface of crystals are concentrated. Therefore, it is possible to form the long chain of cluster ions like $[Cu-O-Cu]_n^{2-}$ as well as CuO crystallites. Especially excess impregnation or mixing of copper oxide with mordenite generates the high concentration of copper ions or oxides at the external surface of crystals by linking of oxygen like Ni(II)Y [16] as mentioned earlier. It is considered that such oxygen containing clusters play a role for the active sites for CO oxidation.

CONCLUSIONS

Regardless of the preparation methods for copper on mordenites such as ion-exchanged, impregnated and physically mixed, copper ions and oxides are distributed on the crystal surface of mordenite and the reduction temperatures of copper oxides are lowered by successive redox treatment. Reduction treatment in hydrogen atmosphere much increased the activity of CO oxidation than that obtained by carbon monoxide treatment. The strong reducing effect of hydrogen leads to the copper concentrated as cluster of cop-

per ions and oxides particles on the external surface when the reduction/reoxidation is repeated. The cluster of copper ions like $[Cu-O-Cu]_n^{2-}$ on the crystal surface created the higher activity for CO oxidation.

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