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Catalysis Today 50 (1999) 117–123

CATALYSIS TODAY

Higher activity of $CuCl_2$/HZSM-5 prepared by dispersion method in selective catalytic reduction of NO by propylene (SCR-HC) at lower temperature

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Abstract

A series of samples have been prepared from high dispersion of $CuCl_2$ into NaZSM-5 and HZSM-5 zeolites, and characterized by X-ray diffraction (XRD), differential thermal analysis (DTA), hexane isotherms, and IR spectroscopy. The catalytic activity in selective reduction of NO shows that $CuCl_2$/HZSM-5 catalyst exhibits higher conversion at 300°C than that of CuZSM-5 prepared from an ion-exchange method. Correlation of catalytic data with infrared spectra for $CuCl_2$/HZSM-5, $CuCl_2$/NaZSM-5, and CuZSM-5 samples suggested that the catalytic sites can be assigned to synergetic effect of protons and copper species. © 1999 Elsevier Science B.V. All rights reserved.

Keywords: Selective catalytic reduction of NO (SCR-HC); Dispersion; $CuCl_2$; ZSM-5 zeolite; Infrared spectroscopy

1. Introduction

Copper ion-exchanged ZSM-5 (CuZSM-5) zeolites have been reported to have exceptionally high activity for the NO decomposition and selective catalytic reduction of NO by hydrocarbons (SCR-HC) [1–6]. Catalytic data show that the activity and selectivity are strongly influenced by the copper loading in ZSM-5 zeolites. Campa et al. [5] showed that the activity of 100% exchanged CuZSM-5 was 100 times more than that of the 80% exchanged one. Moretti et al. [6] reported the turn over frequency of NO conversion on CuZSM-5 had linear relationship with the Si/Al ratio when the ion-exchange level was 90% or more. Notably, preparation of copper catalysts is usually carried out by the ion-exchanged [1–6] or excessively ion-exchange method [1,4] with Cu/Al ratio from 0 to near 1.0, and it is difficult to prepare CuZSM-5 with a high Cu content (Cu/Al>1.0) due to the limitation of the ion-exchange amount in zeolites [1–6].

Recently, we have prepared high copper loading in zeolites by dispersion method under the condition of microwave radiation for 5–20 min at an ambient temperature or heating at 400–450°C for 12–24 h [7–9], as compared with that by ion-exchange method. For example, inorganic copper salts could highly disperse into channels of (M)ZSM-5 (M=H, Na^+, Cu^{2+},...) zeolites with weight ratio of Cu^{2+}/ZSM-5 at 0–0.2 g/g, in which the highest copper loading was

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PII: S0920-5861(98)00468-4

of 10 times more than ion-exchanged method. The goal of this work is to study the catalytic performance of various copper catalysts prepared from ion-exchange and dispersion methods, and to investigate the nature of the active sites in these catalysts.

2. Experimental

NaZSM-5 zeolite was synthesized by reacting an aluminosilicate gel containing Na^+ and tetrapropylammonium (TPA) cations. The parameters of NaZSM-5 are as follows: Si/Al=40, surface area of 450 m^2/g, crystallinity over 95%, and $H^+/Na^+<0.03$. HZSM-5 was prepared from ion-exchange of NaZSM-5 with NH_4Cl solution, followed by calcination for 4 h at 550°C.

Three preparation methods of ZSM-5 supported copper catalysts were used in this study. The first method was ion-exchanged of Cu^{2+} with NaZSM-5 (HZSM-5), forming CuZSM-5 (CuHZSM-5). The second method was mechanical mixture of inorganic copper salt with NaZSM-5 ($CuCl_2$+NaZSM-5) or HZSM-5 ($CuCl_2$+HZSM-5) zeolite at 25°C with weight ratio of Cu^{2+}/ZSM-5 at 0.018–0.15 g/g. The third method was the mechanical mixture of copper salt with ZSM-5 at 25°C, followed by calcination at 400–450°C for 24 h ($CuCl_2$/NaZSM-5 or $CuCl_2$/HZSM-5). The samples were characterized by X-ray diffraction (D/max-IIIA, Rigaku) and differential thermal analysis (DTA) (PE-1700, programmed heating rate of 10 K/min).

The *n*-hexane isotherms on various samples were carried out by using a Cahn-2000 electron recording balance. At first, 0.20 g of the sample was placed into the sample cell, and evacuated at 300°C for 3 h. After the sample was cooled down to 25°C, *n*-hexane was exposed to the sample and the weight change of the sample was recorded.

Infrared spectra of ν_{OH} in the region of 3000–4000 cm^{-1} were measured with a Nicolet Impact 410 IR spectrometer. The samples were pressed into thin wafers (5 mg/cm^2), and were placed into a quartz cell equipped with CaF_2 windows. After the sample discs were evacuated at 320°C for 2 h (10^{-5} Torr), the IR spectra were recorded.

Catalytic measurements were carried out in a fixed bed flow reactor operated at atmospheric pressure and temperature at 300°C. Prior to each experiment, the catalyst was heated at 320°C in Ar for 2 h, and then cooled to the desired temperature in Ar. A typical reaction mixture contained 1600 ppm NO, 1370 ppm propylene, 2.0 vol% oxygen, with the balance of Ar. A 0.5 g sample of the catalyst was used with a total flow rate of 100 ml/min, and the conversion of NO was based on the amount of N_2 formed. The gas products were analysed by gas chromatography using Porapak Q (N_2O, CO_2, and hydrocarbons) and molecular sieve 5 Å (O_2, N_2, NO, CH_4, and CO) columns.

3. Results and discussion

3.1. X-ray diffraction (XRD)

The dispersion of inorganic copper salts into the channels of ZSM-5 zeolites was characterized by X-ray diffraction. As observed in Fig. 1(a), the XRD

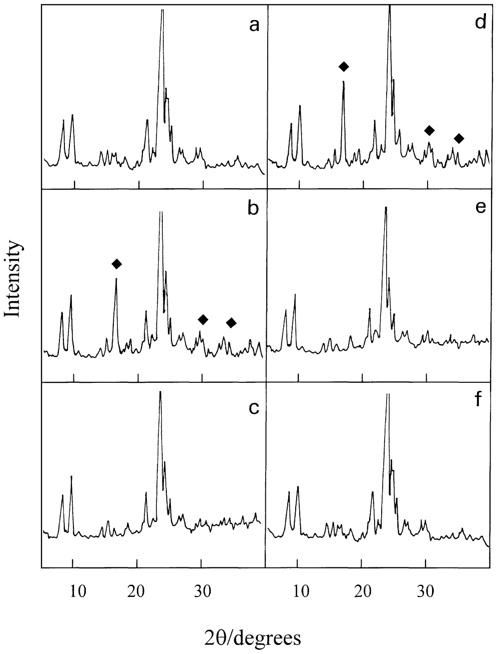

Fig. 1. X-ray diffraction patterns of zeolites and $CuCl_2{\cdot}2H_2O$ at various conditions (◆: characteristic peaks of $CuCl_2{\cdot}2H_2O$): (a) NaZSM-5; (b) mechanical mixture of NaZSM-5 with $CuCl_2{\cdot}2H_2O$ (Cu^{2+}/NaZSM-5=0.048 g/g); (c) after (b), the sample was heated for 24 h at 400°C; (d) mechanical mixture of HZSM-5 with $CuCl_2{\cdot}2H_2O$ (Cu^{2+}/HZSM-5=0.048 g/g); (e) after (d), the sample was heated for 24 h at 400°C; (f) CuZSM-5.

pattern gives rise to peaks at 7.9, 8.9, and 23.1, being characteristic of NaZSM-5. The mechanical mixture of $CuCl_2{\cdot}2H_2O$ and NaZSM-5 (Cu^{2+}/NaZSM-5= 0.048 g/g) shows the XRD peaks at 16.3, 21.9 and 34.0, assigned to $CuCl_2{\cdot}2H_2O$ crystalline, in addition to those of NaZSM-5 zeolite (Fig. 1(b)). However, the characteristic peaks assigned to $CuCl_2{\cdot}2H_2O$ crystalline completely disappear when the mixture is heated for 24 h at 400°C, suggesting that the copper salts highly disperse into NaZSM-5 channels, where $CuCl_2{\cdot}2H_2O$ no longer exists in crystalline state [7–9]. Similarly, the treatment of mechanical mixture of crystalline $CuCl_2{\cdot}2H_2O$ in HZSM-5 zeolite at 400°C for 24 h resulted in disappearance of the XRD peaks of crystalline $CuCl_2{\cdot}2H_2O$, which is also explained by the high dispersion of $CuCl_2{\cdot}2H_2O$ in the channels of HZSM-5 zeolite.

3.2. *Differential thermal analysis (DTA)*

Fig. 2 shows the curves of DTA for various samples. The sample of NaZSM-5 shows one peak at 88°C in the DTA curves (Fig. 2(a)), which is assigned to the desorption of water adsorbed on NaZSM-5. The DTA curve of $CuCl_2{\cdot}2H_2O$ shows two peaks at 127°C and 500°C (Fig. 2(b)), which are attributed to the dehydration of $CuCl_2{\cdot}2H_2O$ and melting point of $CuCl_2$, respectively. The mechanical mixture of $CuCl_2{\cdot}2H_2O$ with NaZSM-5 gives strong peaks at 117°C and 350°C (Fig. 2(c)). The peak at 117°C is very similar to the peak at 127°C assigned to the dehydration of $CuCl_2{\cdot}2H_2O$ in Fig. 2(b). The peak at 350°C may be assigned to the dispersion of $CuCl_2$ in the NaZSM-5. Similar phenomena have been studied extensively by Xie et al. [9]. It is interesting to note that after heating of $CuCl_2{\cdot}2H_2O$+NaZSM-5 for 24 h at 400°C, the sample profile exhibits only a peak at 110°C (Fig. 2(d)) assigned to the dehydration of the sample, and the peak at 350°C in Fig. 2(c) and the peak at 500°C in Fig. 2(b) completely disappeared, which may be assigned to the high dispersion of $CuCl_2$ into the channels of NaZSM-5 zeolite. Similarly, the high dispersion of $CuCl_2$ into HZSM-5 zeolite is shown in Fig. 2(e).

3.3. *Hexane isotherms*

As shown in Fig. 3, the hexane isotherms on various samples exhibit Langmuir-type isotherms, indicating that these samples are microporous materials [10]. As shown in Fig. 3(a), (b), and (c), the hexane isotherms for NaZSM-5, CuZSM-5, and HZSM-5 are the same, indicating that NaZSM-5, CuZSM-5, and HZSM-5 have similar channels and surface areas. The shape of the hexane isotherm for mechanical mixture of $CuCl_2{\cdot}2H_2O$ with NaZSM-5 (Fig. 3(d)) is the same as that of NaZSM-5, but the adsorption amount of hexane is reduced, which is well consistent with the theoretical value for the $CuCl_2{\cdot}2H_2O$+NaZSM-5 sample estimated by the isotherm of NaZSM-5, where only NaZSM-5 can adsorb hexane. Notably, after heating of $CuCl_2{\cdot}2H_2O$+NaZSM-5 sample for 24 h at 400°C, the hexane isotherm (Fig. 3(e)) shows that hexane adsorption requires a higher pressure to reach saturated adsorption, as compared with those on NaZSM-5, CuZSM-5, and HZSM-5, and mechanical mixture of $CuCl_2{\cdot}2H_2O$+NaZSM-5. Similar phenomenon is also observed in the sample of $CuCl_2{\cdot}2H_2O$/

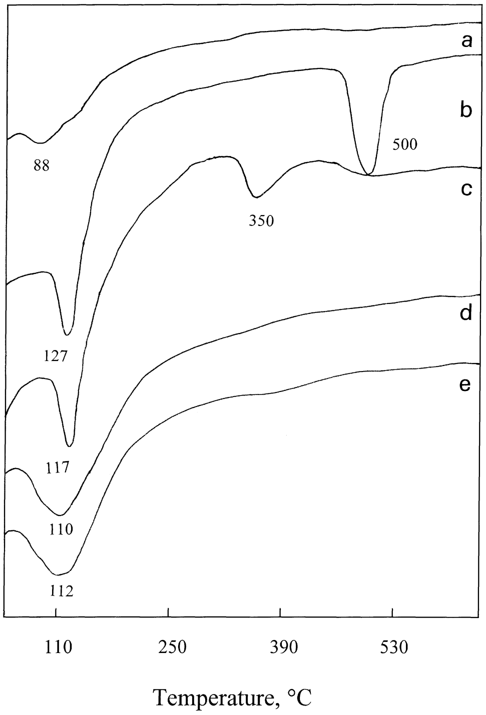

Fig. 2. DTA curves of (a) NaZSM-5; (b) $CuCl_2{\cdot}2H_2O$; (c) mechanical mixture of NaZSM-5 with $CuCl_2{\cdot}2H_2O$ (Cu^{2+}/NaZSM-5=0.048 g/g); (d) after (c), the sample was heated for 24 h at 400°C; (e) mechanical mixture of HZSM-5 with $CuCl_2{\cdot}2H_2O$ (Cu^{2+}/HZSM-5=0.048 g/g), followed by heating for 24 h at 400°C.

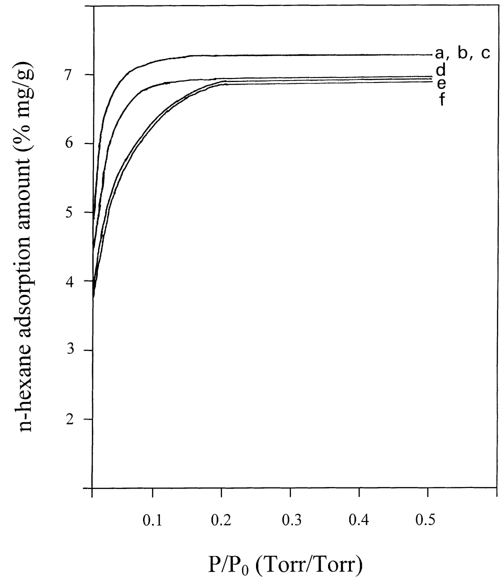

Fig. 3. Hexane isotherms of: (a) NaZSM-5; (b) CuZSM-5; (c) HZSM-5; (d) mechanical mixture of NaZSM-5 with $CuCl_2 \cdot 2H_2O$ (Cu^{2+}/NaZSM-5=0.048 g/g); (e) after (d), the sample was heated for 24 h at 400°C; (f) mechanical mixture of HZSM-5 with $CuCl_2 \cdot 2H_2O$ (Cu^{2+}/HZSM-5=0.048 g/g), followed by heating for 24 h at 400°C.

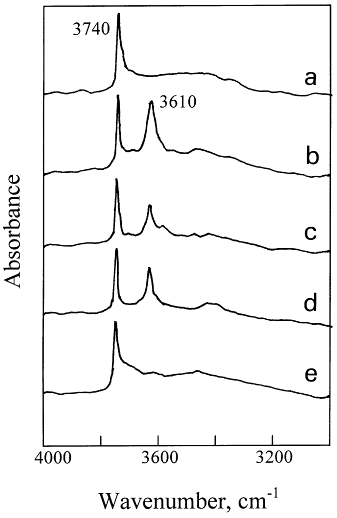

Fig. 4. IR spectra for ν_{OH} in the region of 3000–4000 cm^{-1} on: (a) NaZSM-5; (b) HZSM-5; (c) CuZSM-5; (d) mechanical mixture of HZSM-5 with $CuCl_2 \cdot 2H_2O$ (Cu^{2+}/HZSM-5=0.048 g/g), followed by heating for 24 h at 400°C; (e) mechanical mixture of NaZSM-5 with $CuCl_2 \cdot 2H_2O$ (Cu^{2+}/NaZSM-5=0.048 g/g), followed by heating for 24 h at 400°C.

HZSM-5 (Fig. 3(f)). These results may be interpreted by different arrangement of channels in various samples. The heating effect for the $CuCl_2 \cdot 2H_2O$+NaZSM-5 sample may result in the high dispersion of $CuCl_2$ into NaZSM-5, leading to a change in channel shape in the zeolite, which strongly influences the adsorption of hexane on the samples.

3.4. Infrared spectroscopy (IR)

Fig. 4 shows IR spectra for ν_{OH} in the region of 3000–4000 cm^{-1} on various samples. NaZSM-5 zeolite (Fig. 4(a)) shows a sharp peak at 3740 cm^{-1}, which is assigned to terminal SiOH [11–13]. HZSM-5 zeolite exhibits both 3740 and 3610 cm^{-1} (Fig. 4(b)), which are assigned to Brønsted acidic Si(OH)Al groups and terminal SiOH, respectively [11–13]. CuZSM-5 sample prepared from copper ion-exchanged method shows two peaks at 3740 and 3610 cm^{-1} (Fig. 4(c)), but the intensity of 3610 cm^{-1} band is weaker than that of HZSM-5 sample (Fig. 4(a)). The IR spectrum of the mechanically mixed and heated $CuCl_2$/HZSM-5 (Fig. 4(d)) gives a sharp band at 3610 cm^{-1} assigned to strong acidic OH groups, which is identical with that of HZSM-5 (Fig. 4(b)) [11–13]. On the contrary, we could not observe the band at 3610 cm^{-1} in the sample of $CuCl_2$/NaZSM-5 (Fig. 4(e)).

Accordingly, 100% ion-exchange of Cu^{2+} with NaZSM-5 and HZSM-5 would result in the formation of CuZSM-5 with a full removal of sodium ions and protons in ZSM-5 zeolite. Both HZSM-5 and CuZSM-5 prepared from $CuCl_2$ aqueous solution exhibit the band at 3610 cm^{-1}. Moreover, the highest value for ion-exchange of Cu^{2+} with NaZSM-5 and HZSM-5 is approximately 1.0 of Cu^{2+}/Al [1,4]. These results suggested that the Cu^{2+} ion-exchanged with NaZSM-5 and HZSM-5 at pH values of 6.5–7.0 to give [Cu(OH)]ZSM-5 [14], showing highest ion-exchanged value at 1.0 of Cu/Al. The band at 3610 cm^{-1} is possibly assigned to strong acidic OH in $[Cu(OH)]^+$ species [11]. The dehydration of $[Cu(OH)]^+$ at higher temperature gives to $[Cu–O–Cu]^{2+}$ oxocations [15,16].

3.5. Catalytic activity

Table 1 presents the conversion at 300°C in selective catalytic reduction of NO by propylene in the

Table 1
Catalytic activity in selective catalytic reduction of NO by propylene over zeolite-supported copper samples prepared from mechanical mixture, dispersion, and ion-exchange methods

Sample	Catalyst	Preparation method of catalyst	Copper loading (wt%)	Catalytic conversion[a] (%)	3610 cm^{-1} in IR band[b]
1	NaZSM-5	–	0	<5	N
2	HZSM-5	–	0	<5	Y
3	$CuCl_2$+NaZSM-5	Mechanica	4.8	<5	N
4	CuZSM-5	Ion-exchange	1.8	18	Y
5	CuHZSM-5	Ion-exchange	1.8	21	Y
6	$CuCl_2$/HZSM-5	Mechanical and heating	4.8	39	Y
7	$CuCl_2$/NaZSM-5	Mechanical and heating	4.8	<5	N
8	$CuCl_2$+CuHZSM-5	Mechanical and ion-exchange	4.8[c]	23	Y
9	NaCl/CuHZSM-5	Dispersion and ion-exchange	1.8	22	Y
10	$CuCl_2$/CuHZSM-5	Dispersion and ion-exchange	4.8[d]	36	Y

[a] Catalytic conversion was estimated on N_2 yield at 300°C.

[b] Y represents that the sample showed 3610 cm^{-1} band, and N means that no 3610 cm^{-1} band was observed in IR spectroscopy.

[c] 1.8 and 3.0 wt% of Cu loadings were prepared from Cu^{2+} ion-exchange and mechanical mixture of $CuCl_2$, respectively.

[d] 1.8 and 3.0 wt% of Cu loadings were prepared from Cu^{2+} ion-exchange and dispersion of $CuCl_2$ into ZSM-5 zeolite (mechanical and heating), respectively.

presence of excessive oxygen over a series of zeolite-supported copper samples prepared from ion-exchange, mechanical mixture, and dispersion method. The samples of NaZSM-5, HZSM-5, $CuCl_2$+NaZSM-5, and $CuCl_2$/NaZSM-5 (samples 1–3 and 7) exhibit low conversion as compared with ion-exchanged samples of CuZSM-5 and CuHZSM-5 (samples 4 and 5). However, the sample prepared from the dispersion of $CuCl_2$ into HZSM-5 (sample 6) gives much higher conversion. In contrast, $CuCl_2$+CuHZSM-5 (sample 8) exhibits similar activity to CuHZSM-5 (sample 5). Furthermore, the activity of NaCl/CuHZSM-5 (sample 9) is closed to that of CuHZSM-5.

Dependence of NO conversion at 300°C on copper loading in $CuCl_2$/HZSM-5 is shown in Fig. 5, and obvious features are observed in the following:

1. NO conversion increased with copper loading in the region of 0–5.0 wt%;
2. further increase of copper loading leads to decrease of NO conversion, which was interpreted that at higher copper loading the pores of ZSM-5 are partially filled, and the catalytic reactions are partially limited.

These results suggest that copper species highly dispersed into channels of HZSM-5 with Cu loadings at 0–5.0 wt% are very effective for the improvement of the catalytic activity.

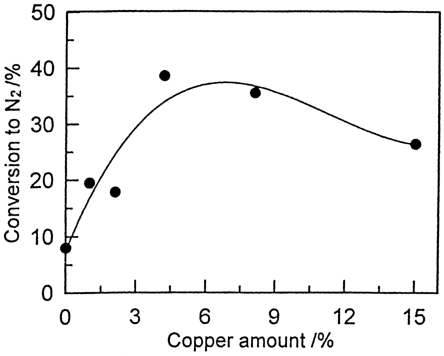

Fig. 5. NO conversion at 300°C as a function of copper loading over $CuCl_2$/HZSM-5.

Dependence of NO conversion on reaction temperature over $CuCl_2$/HZSM-5, $CuCl_2$/NaZSM-5, and CuZSM-5 zeolites is shown in Fig. 6. We observed obvious features in the following:

1. In the range of 300–600°C, $CuCl_2$/HZSM-5 and CuZSM-5 zeolites are catalytically active for NO reduction by propylene. In contrast, $CuCl_2$/NaZSM-5 sample is almost inactive.
2. At 300°C, catalytic activity of $CuCl_2$/HZSM-5 sample is much higher than that of CuZSM-5.
3. At 400–500°C, catalytic activity of $CuCl_2$/HZSM-5 sample slightly higher than that of CuZSM-5.

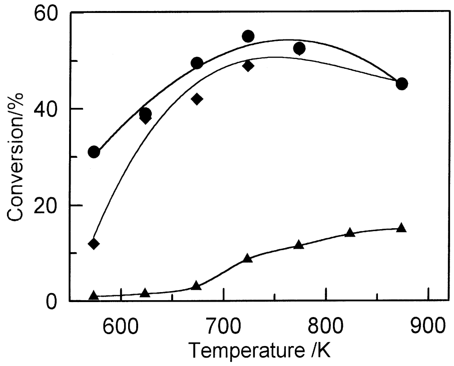

Fig. 6. NO conversion as a function of reaction temperature over $CuCl_2$/HZSM-5 (●) prepared from the mechanical mixture of HZSM-5 with $CuCl_2 \cdot 2H_2O$ (Cu^{2+}/HZSM-5=0.048 g/g), followed by heating for 24 h at 400°C, $CuCl_2$/NaZSM-5 (▲) prepared from the mechanical mixture of NaZSM-5 with $CuCl_2 \cdot 2H_2O$ (Cu^{2+}/NaZSM-5=0.048 g/g), followed by heating for 24 h at 400°C, and CuZSM-5 (◆) prepared from ion-exchanged method (Cu^{2+}/HZSM-5=0.024 g/g).

4. At 500–600°C, catalytic activity of $CuCl_2$/HZSM-5 sample is close to that of CuZSM-5.

3.6. *Nature of catalytic active sites*

Correlation of catalytic data with infrared spectra shows that the samples with a strong acidic OH groups appearing at 3610 cm^{-1} band exhibited relatively high catalytic conversion (samples 4–6 and 8–10) as compared with that of the samples without 3610 cm^{-1} band (samples 1, 3, and 7). In addition, $CuCl_2$/HZSM-5 and $CuCl_2$/CuHZSM-5 with higher copper loading (samples 6 and 10) gave higher catalytic conversion (36–39%, 300°C) than that (18–21%, 300°C) of CuZSM-5 and CuHZSM-5 (samples 4 and 5), and $CuCl_2$+CuHZSM-5 (sample 8) showed similar catalytic conversion with CuHZSM-5 (sample 5). These results suggested that both highly dispersed copper species and protons in ZSM-5 zeolite are very important for selective catalytic reduction of NO by propylene, which might be related to synergetic effect of protons and copper species in these catalysts.

The catalytic active sites by which hydrocarbons reduce NO over CuZSM-5 prepared from ion-exchange method have largely been investigated by reaction kinetics and IR spectroscopy [17–19], suggesting that the catalytic active sites were from copper species. Notably, there was no discussion on the effect of acidic sites in CuZSM-5, which are not consistent with the results described in this study. Therefore, we proposed that the reaction mechanism would be as follows:

1. Propylene would be activated by strong acidic sites because the propylene is easily adsorbed on a strong acidic site.
2. NO would be activated by copper species because the NO is easily adsorbed on copper species.
3. The samples of $CuCl_2$/HZSM-5 and CuZSM-5 have strong acidic sites and copper species, adsorbing both propylene and NO simultaneously.
4. The NO adsorbed on copper species reacted with nearby propylene adsorbed on strong acidic site in the presence of excessive O_2 to form nitrogen and oxygenated carbon compounds.
5. Furthermore, the oxygenated carbon compounds reacted with excessive O_2 to form CO_2 and H_2O.

According to this mechanism, we attempted to design and prepare catalysts of $CuCl_2$/MCM-41(silicalite) and $CuCl_2$/MCM-41(aluminosilicate) [20,21]. Catalytic data in selective reduction of NO by propylene in the range 300–600°C show that the activity for $CuCl_2$/MCM-41(aluminosilicate) with a strong ν_{OH} at 3610 cm^{-1} is much higher than that for $CuCl_2$/MCM-41(silicalite) without the 3610 cm^{-1} bands [21,22], and details will be reported in the future.

4. Conclusion

1. A series of samples such as $CuCl_2$/NaZSM-5 and $CuCl_2$/HZSM-5 have been prepared from high dispersion of $CuCl_2$ into NaZSM-5 and HZSM-5 zeolites, which have been verified by X-ray diffraction (XRD), differential thermal analysis (DTA), hexane isotherms, and IR spectroscopy.
2. Catalytic activities in selective reduction of NO by propylene at 300°C show that the samples of NaZSM-5, HZSM-5, $CuCl_2$+NaZSM-5, and $CuCl_2$/NaZSM-5 exhibit low conversion, as compared with those of ion-exchanged sample of CuZSM-5. However, the sample ($CuCl_2$/HZSM-5) prepared from the dispersion of $CuCl_2$ into HZSM-5 zeolite gives much higher conversion.
3. Infrared spectroscopy shows that the samples of $CuCl_2$/HZSM-5 and CuZSM-5 exhibit a band at

3610 cm^{-1} assigned to strong acidic OH groups. In contrast, no band at 3610 cm^{-1} is observed for $CuCl_2$/NaZSM-5 sample. Correlation of catalytic data with IR spectra suggested that the catalytic sites can be assigned to synergetic effect of acidic sites and copper species.

Acknowledgements

This work was supported by National Natural Science Foundation of China, Foundation of Education Ministry of China, National Advanced Materials Committee of China, and Foundation of Key Laboratory of Inorganic Synthesis and Preparative Chemistry.

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