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Comparative Performance between Cu/Na -ZSM-5 and Cu/H-ZSM-5 in NO Abatement

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Abstract

The activities of Cu/Na-ZSM-5 and Cu/H-ZSM-5 in NO abatement were investigated. The different activities between both catalysts were observed only under oxygen deficiency. NO decomposition reaction over Cu/H-ZSM-5 produces more NO_2 than the one over Cu/Na-ZSM-5. Also Cu/H-ZSM-5 is more active than Cu/Na-ZSM-5 in NO reduction by propane in the absence of oxygen. This might be due to a high formation of NO_2, a crucial intermediate in NO reduction by hydrocarbon, in the reaction over Cu/H-ZSM-5. No significant differences in acidity and coke deposition between Cu/Na-ZSM-5 and Cu/H-ZSM-5 were detected. Although total amount of copper in both catalysts was the same, Cu/H-ZSM-5 have Cu^{1+} had more than Cu/Na-ZSM-5. Cu^{1+} plays an important role in NO decomposition to N_2 and O_2 which is likely to be the first step in NO reduction without oxygen.

Keywords: NO, propane, Cu/Na-ZSM-5, Cu/H-ZSM-5

Introduction

Cu/ZSM-5 was proposed as an active catalyst by Iwamoto *et al.* (Iwamoto, *et al.* 1988; and Iwamoto, *et al.* 1990) for NO decomposition over years ago. Its activity is still outstanding compared to other catalysts that have been studied so far. Furthermore, Cu/ZSM-5 catalyst is one of the most active catalysts for the selective catalytic reduction (SCR) of nitrogen monoxide by hydrocarbon and has been one of most widely studied catalysts in recent years (Iwamoto, *et al.* 1992 (a); Petunchi, *et al.* 1993; Grunert, *et al.* 1994; Iwamoto, 1994; Shelef, 1995; and Amiridis, *et al.* 1996).

In general, Cu/ZSM-5 zeolite is prepared by ion-exchange of copper ions into either Na- or H-ZSM-5. So far, the choice of the primary form of ZSM-5 used by researchers seems to have been arbitrary. For example, in order to avoid the effect of Na^+ ions, H-ZSM-5 would seem to be the preferred (Iwamoto, 1994). On the other hand, Na^+ on catalyst surface can be exchanged with copper ions easier than copper with a proton, so that, sometimes, Na-ZSM-5 would be used. Although overexchanged Cu/ZSM-5, which is the most active catalyst for SCR of NO by a hydrocarbon (Iwamoto, *et al.* 1992 (a)), has a degree of Cu^{2+} exchange above 100%, based on the assumption that one Cu^{2+} ion exchanges with two Na^{+} ions or two protons, this catalyst still has a significant amount of cations remaining on the surface (Shelef, 1995; and Zhang, *et al.* 1995).

It was found that Na -ZSM-5 is not active in the SCR of NO (Iwamoto, *et al.* 1992 (a); and Hamada, *et al.* 1990) while H-ZSM-5 is moderately active (Hamada, *et al.* 1990; and Hamada, *et al.* 1991). This must be due to the difference of cations on both catalysts. Therefore, a difference between Cu/Na-ZSM-5 and Cu/H-ZSM-5 might be expected. To clarify the different performance between Cu/Na-ZSM-5 and Cu/H-ZSM-5, NO decomposition and NO reduction on both catalysts were investigated. Furthermore, to study the adsorption behaviour of the reactions, the transient experiments would be carried out. Since proton on zeolite surfaces act as Bronsted acid sites but Na ion does not, acidity between Cu/Na-ZSM-5 and Cu/H-ZSM-5 was studied by using pyridine as a probe molecule (Parry, 1963). The characteristics of Cu ion on both catalysts were examined. It has been known that CO could adsorb only on Cu^{1+} (Iwamoto, *et al.* 1991 (b); Iwamoto, *et al.* 1991 (a); Piepapu, 1965; and Szanyi, *et al.* 1996), CuO and Cu metal (Szanyi and Paffett, 1996), however, no evidence of the existence of CuO and Cu metal in Cu/ZSM-5 thus was found (Szanyi and Paffett, 1996). O adsorption thus was applied to quantify the Cu^{1+} on the catalyst surface (Iwamoto, e*t al.* 1991 (b); and Iwamoto, *et al.* 1991 (a)).

Experimental

CATALYST PREPARATION

The preparation of parent Na-ZSM-5 zeolite with Si/Al ratio of 40 has been synthesized by the method obtained from the literature (Inui, *et al.* 1984). The zeolite prepared was analyzed by XRD to confirm the structure of ZSM-5. Na-ZSM-5 was exchanged with ammonium nitrate solution at 80 °C twice and then calcined in air at 540 °C for 3.5 hrs. to form H-ZSM-5. Cu/Na-ZSM-5 and Cu/H-ZSM-5 were prepared by exchangingNa-ZSM-5 and H-ZSM-5 respectively with copper (II) nitrate solution overnight in an appropriate pH level condition (~8.5-9.5) to achieve a high degree of loading. The powder samples obtained were washed with de-ionized water (~5 times) and then dried in an oven. Finally, the catalysts were calcined in air at 540 °C for 3.5 hrs. The amounts of Cu, Na in the catalysts and specific surface area of catalysts were determined by X-Ray Fluorescence and the BET method respectively and respectively; the results are summarized in Table 1. The catalyst powder was pelletized, crushed into granular form, then sized between 8-20 mesh by sieving for using in this study.

TRANSIENT EXPERIMENT

Transient experiments were accomplished in a fixed bed flow reactor. Nitrogen gas or a reactant gas mixture of about 50 ml/min were switched by valves to pass through a 10 mm quartz tube reactor filled with 1.2 g of the granular catalyst and glass beads. The reactions were carried out between 300 - 400 °C. The outlet gas was directed to a light pipe (IR gas cell) built into a Mattson Galaxy 5022 FT-IR. Composition of the outlet stream was thus analyzed by IR which measured the absorbances of NO, NO_2, N_2O, CO_2 and propane simultaneously. However, neither N_2 nor O_2 could be detected. From a blank test, the transport lag at a total gas flow of around 50 ml/min. at 350 °C, from the switching valve to the detector, was approximately 12 sec. The absorption band used for each gas detected is summarized in Table 2.

Tablel Composition and surface area of catalysts

Catalyst	**Si/Al**	**BETsurface area (m^2/g cat.)**	**Cu content (wt %)**	**Na content (wt %)**
Cu/Na-ZSM-5	37	353.6	1.06	0.38
Cu/H-ZSM-5	39	370.6	1.09	<0.09

Table 2 IR Band of gases

Gas species	**appearance peak (cm^{-1})**
NO	1905(xl), 1850(1)
NO_2	1630(x1), 1600(x1), 1750(1), 1263(1)
N_2O	2225(x1), 1290(1)
C_3H_8	2970
CO_2	2362

Note : x1= extra large, 1= large

Table 3 Amount of Cu^{1+} in catalysts estimated by CO adsorption method

Catalyst	**Amount of CO adsorbed (µ mol/g,cat)**	**Number of Cu^{1+} (x 10^{19} site/g.cat.)**
Cu/Na-ZSM-5	1.121	1.35
Cu/H-ZSM-5	2.247	2.71

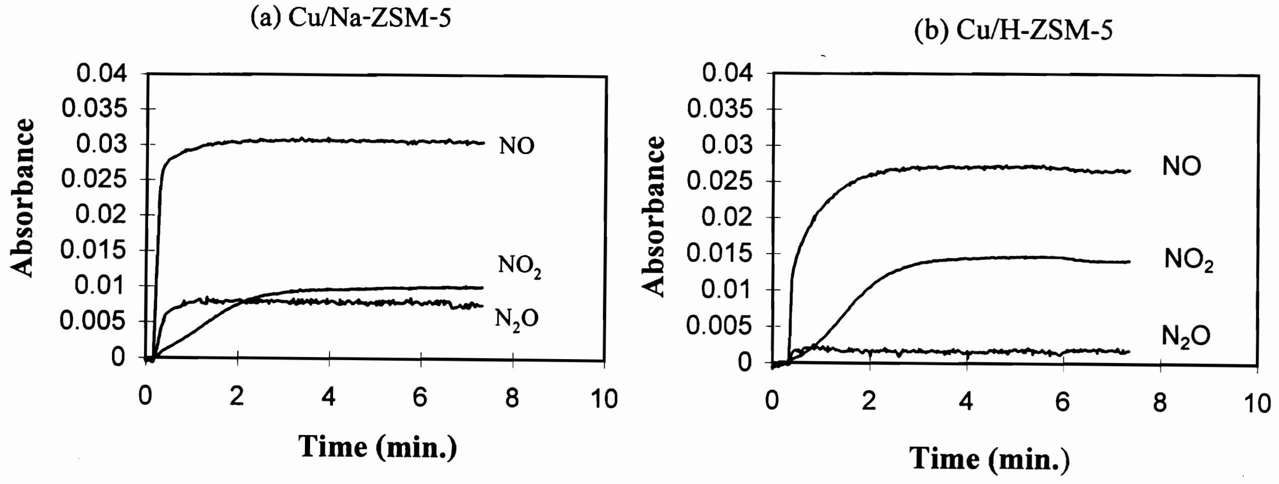

Figure1 Absorbance of gaseous species after switching from N_2 to 1.2% NO+N_2 at 400°C over (a) Cu/Na-ZSM-5 and (b) Cu/H-ZSM-5

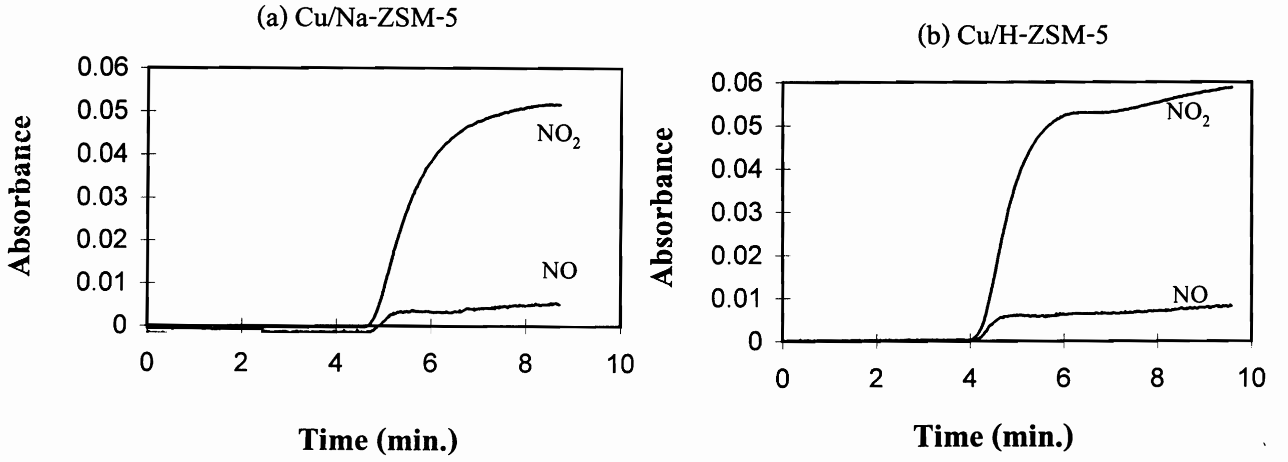

Figure 2 Absorbance of gaseous species after switching from N_2 to 1.2% NO+10% O_2+N_2 at 350°C over (a) Cu/Na-ZSM-5 and (b) Cu/H-ZSM-5

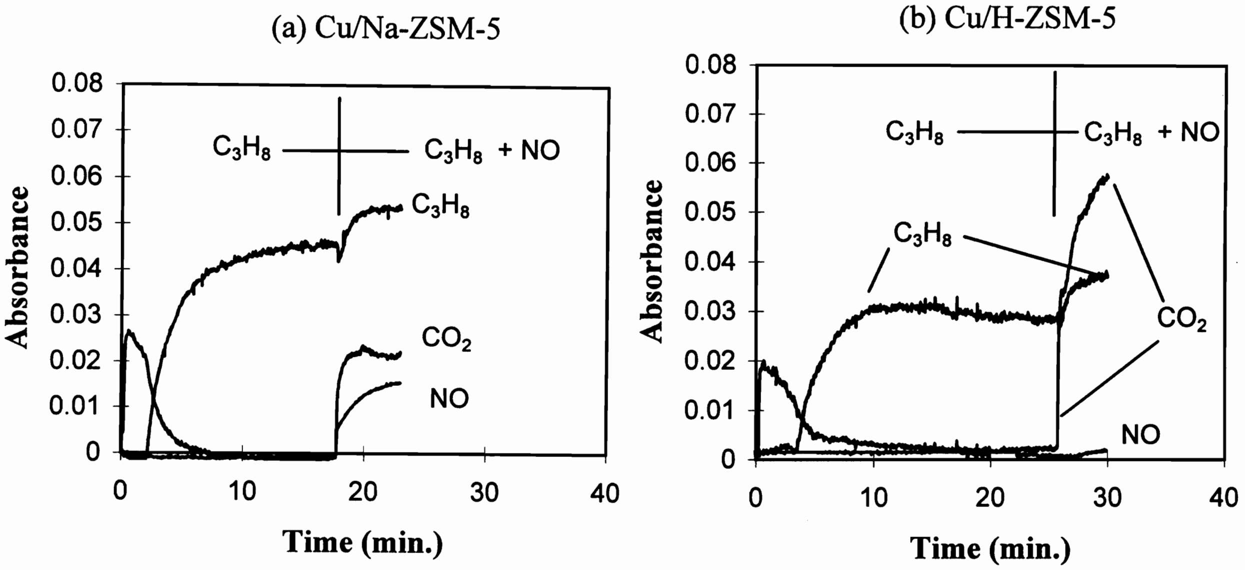

Figure 3 Absorbance of gaseous species after switching from N_2 to 0.4%C_3H_8+N_2 and to 0.4% C_3H_8+0.5% NO+N_2 at 400°C over (a) Cu/Na-ZSM-5 and (b) Cu/H-ZSM-5

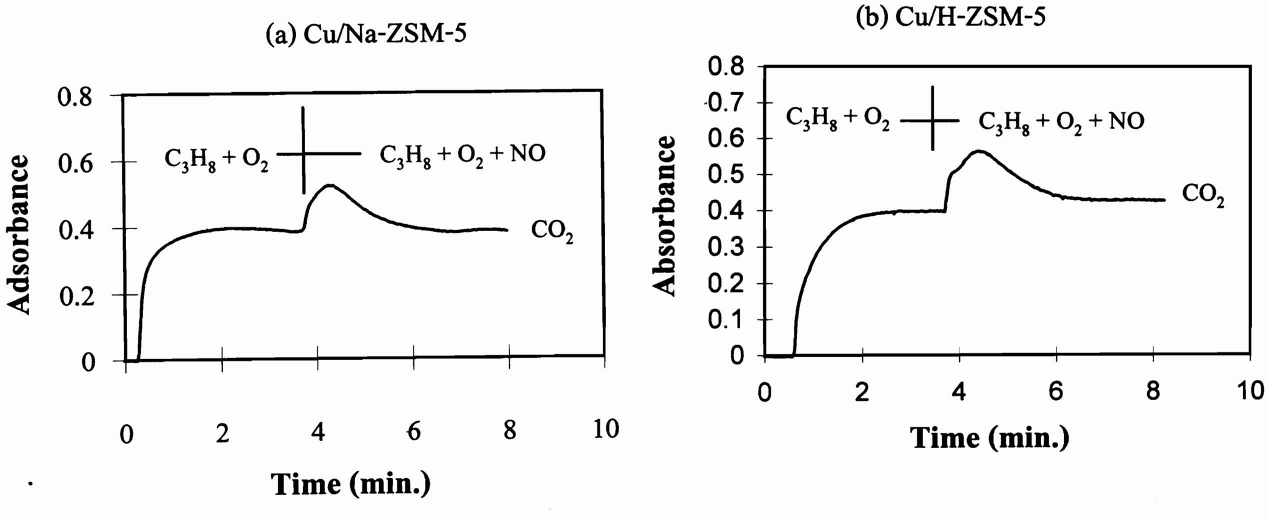

Figure 4 Absorbance of gaseous species after switching from N_2 to 0.4%C_3H_8+12%O_2+N_2 and to 0.4% C_3H_8+12%O_2+ 0.5% NO+N_2 at 300°C over (a) Cu/Na-ZSM-5 and (b) Cu/H-ZSM-5

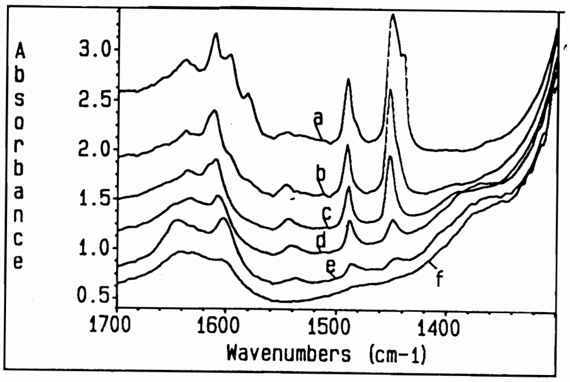

Figure 5 Spectra of pyridine adsorption on Cu/Na-ZSM-5 at (a) rt., (b) 100°C, (c) 200°C, (d) 300°C, (e) 400°C and (f) 450°C

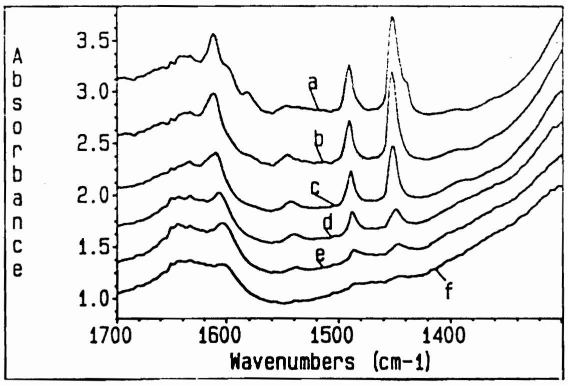

Figure 6 Spectra of pyridine adsorption on Cu/H-ZSM-5 at (a) rt., (b) 100°C, (c) 200°C, (d) 300°C, (e) 400°C and (f) 450°C

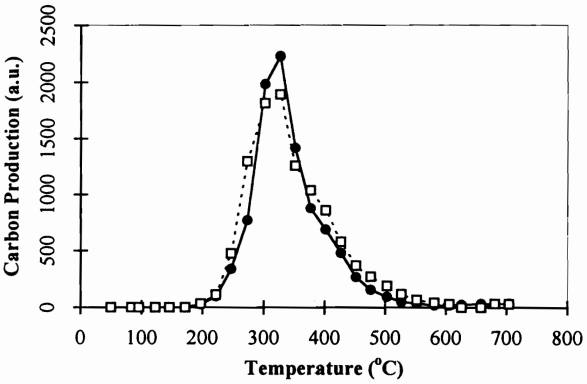

Figure 7 Temperature programmed oxidation of Cu/Na-ZSM-5(●) and Cu/H-ZSM-5 (□) after used in the transient experiment of switching from 0.4%C_3H_8 to 0.4%C_3H_8 + 0.5%NO

CHARACTERIZATION

Temperature programmed oxidation (TPO) was employed to characterize carbonaceous deposits on the catalyst surface. Measurement was carried out in a quartz tube reactor packed with the spent catalyst. The catalyst was pretreated in the reactor in 30 ml/min of He at 250 °C for about 4 hrs. and then cooled down to an ambient temperature before starting measurement. The TPO process began by heating up the catalyst in 30 ml/min. of 1% O_2 in He at a rate of 5 °C/min. to 700 °C. A Shimadzu 8A gas chromatography with Porapak QS column was used every 5 minutes to measure the amount of CO_2 produced from coke combustion.

The pyridine adsorption apparatus was composed of a Pyrex glass line connected to a quartz IR gas cell mounted in a FT-IR Nicolet Model Impact 400. A 15-20 mg/cm^2 self-supported sample disk was placed in a sample holder in the IR gas cell. After the system was well evacuated, pyridine was evaporated into the system at room temperature. To achieve complete adsorption, the pyridine vapor was circulated in the system for at least 0.5 hr. The IR gas cell was evacuated again in order to eliminate the pyridine vapor and also any physisorbed pyridine. IR spectra were recorded under vacuum from room temperature up to a temperature at which all pyridine desorbed.

The amount of Cu^{1+} was determined by CO adsorption. 0.2 g of the catalyst sample was packed in an 4 mm. stainless steel tube. The catalyst bed was pretreated in 50 ml/min. of He at 450 °C for 1hr. Then, the catalyst bed was cooled down to room temperature for adsorption. Injections of 0.2 ml of CO to the bed were carried out until the adsorption was complete. Unadsorbed CO in downstream of the catalyst bed was detected by TCD. The quantity of Cu^{1+} was calculated on the basis that one site of Cu^{1+} can adsorb one molecule of CO.

Results and Discussion

The activity of Cu/Na-ZSM-5 and Cu/H-ZSM-5 was examined by transient observations of NO decomposition. NO_2 and N_2O were observed in a step change experiment over both catalysts (Figure 1). Unfortunately N_2 and O_2 could not be detected in the gas phase by IR. The NO_2 signal grew slower than NO and N_2O after appearing in the reactor outlet. These phenomena were also observed in the works of Iwamoto, *et al.* (1991 a), Li and Hall, (1990); and Pirone, *et al.* (1997).

The experiment on Cu/H-ZSM-5 produced more NO_2 but less N_2O than the one on Cu/Na-ZSM-5. Also, NO is more slightly consumed in the Cu/H-ZSM-5 system. The formation of NO_2 and N_2O indicate that not only NO decomposition occurred in these experiments. Iwamoto, *et al.* (1992 a) mentioned that O_2 from NO decomposition might further oxidize NO to produce NO_2. Pirone, *et al.* (1996) reported that NO disproportionation to N_2O and NO_2 would occur parallel with NO decomposition. Moreover, they suggested that N_2O can be formed by the reoxidizing of copper Cu^{2+} by NO (Pirone, *et al.* 1997). However, the formation of NO_2 does not parallel with N_2O over both catalysts. More NO_2 but less N_2O was formed in the test over Cu/H-ZSM-5. It is likely that, over Cu/H-ZSM-5, NO oxidation to NO_2 is a more likely occurrence compared to the reaction which produces N_2O.

From the result of the oxidation of NO experiment in Figure 2, it can be seen that both Cu/Na-ZSM-5 and Cu/H-ZSM-5 are active in NO oxidation. However, no differences between the catalysts were observed. The long lag time appeared in this results (Figure 2) indicate the high NO_2 adsorption capacity of Cu/ZSM-5. However, the different retention time of NO appearance between the results in Figure 1 and Figure 2 is due to the different NO concentration in feed. The tests of NO reduction by propane in the absence and presence of oxygen were carried out and the results are shown in Figure 3 and 4, respectively. After inert gas (N_2) flowing through the reactor was suddenly switched to propane, the response of propane in the reactor outlet gradually increased until a constant value was reached (Figure 3). This clearly establishes strong C_3H_8 adsorption over the Cu/ZSM-5 catalysts. Burch, *et al.* (1993), and Cho (1995) have observed a chromatographic effect when light hydrocarbon passes over these catalysts. The formation of CO_2 in the first few minutes after the step change to C_3H_8 is due to reaction between propane and extra-lattice oxygen or some residual adsorbed oxygen on the catalyst surface left from the washing step. Valyon and Hall (1993 a, b), and Larsen, *et al.* (1994) mentioned the existence of extra-lattice oxygen (ELO) which is carried out into the catalysts during the preparation step. Therefore, when oxygen on the surface is exhausted, CO_2 disappears from the reactor outlet. When NO is added to the gas feed, the reduction occurs. CO_2 emerged again. The appearance of CO_2 parallels NO appearance in the reactor outlet for both catalysts. Surprisingly, the propane signal also increased on the interaction of NO because hydrocarbon desorbed from the catalyst surface due to the competitive adsorption of NO. The NO consumption and CO_2 production over Cu/H-ZSM-5 was substantially higher than over Cu/Na-ZSM-5. In Figure 4, when the gas stream was changed from N_2 to the gas mixture of C_3H_8 and O_2, only CO_2 was observed. Complete combustion took place over both Cu/Na-ZSM-5 and Cu/H-ZSM-5. When NO was added into the feed, CO_2 formation rose rapidly and then gradually reduced until a steady state was reached. This overshooting could be observed in both catalyst systems. It is likely that the sudden existence of NO in the catalyst bed caused some CO_2 on the catalyst surface to desorb into the gas phase and gradually reach a new adsorption equilibrium. However, the explanation of this behavior is still unclear.

From the results of several transient reactions (Figure 1 - 4), significant differences in activity between Cu/Na-ZSM-5 and Cu/H-ZSM-5 were not observed in the NO reduction with propane in excess oxygen and in NO oxidation. On the contrary, Cu/H-ZSM-5 was more active than Cu/Na-ZSM-5 for the NO reduction with propane in the absence of oxygen and NO decomposition. Moreover, Cu/H-ZSM-5 produced NO_2 more rapidly than Cu/Na-ZSM-5 in NO decomposition. These indicate that the difference between Cu/Na-ZSM-5 and Cu/H-ZSM-5 can be observed in the reactions where oxygen was absent.

Since a significant amount of Na was observed in Cu/Na-ZSM-5 (Table 1), in the same way, Cu/H-ZSM-5 may have some protons remaining on the ZSM-5 surface. Protons on the zeolite surface normally act as Bronsted acid which may involve a reaction mechanism (Shelef, 1995). Thus, the acidic properties of Cu/Na-ZSM-5 and Cu/H-ZSM-5 should be compared. The acidity study, by using pyridine adsorption, is well known (Parry, 1963). The spectra of adsorbed pyridine on Cu/Na-ZSM-5 and Cu/H-ZSM-5 are shown as a function of temperature in Figure 5 and 6 respectively. The peaks at 1540 and 1640 cm^{-1} are assigned to pyridinium ion at Bronsted acid sites (Parry, 1963; Parrillo, *et al.* 1993; and Wachs, 1996). Pyridine coordinately bonded to surface Lewis acid sites shows peaks at 1450 and 1600 cm^{-1} (Parry, 1963; Parrillo, *et al.* 1993; and Wachs, 1996). The band at 1490 cm^{-1} represents all adsorbed pyridine species (Parry, 1963; and Raatz, *et al.* 1983). Both Bronsted and Lewis acid sites were found on both catalysts. Pyridine gradually desorbed at higher temperature is associated with the disappearance of a protonated pyridine peak and a nonprotonated pyridine peak. All pyridine species were removed at 450 ^{0}C on both Cu/Na-ZSM-5 (Figure 5) and Cu/H-ZSM-5 (Figure 6). The amount and strength of pyridine adsorbed on both catalysts were almost the same. Connerton, *et al.* (1995) also found that acid properties of Cu/ZSM-5 prepared by using Na form and H form of zeolites were very similar. This indicated that the residual protons on the Cu/H-ZSM-5 surface did not affect the acidity of Cu/H-ZSM-5.

Coke deposition of Cu/H-ZSM-5 and Cu/Na-ZSM-5 used in the transient experiment with NO and propane in the feed was also determined by the TPO method. Amounts of carbonaceous deposited on Cu/Na-ZSM-5 was 0.065 % carbon/g. of cat. and on Cu/H-ZSM-5 it was 0.060% carbon/g. of cat. The size and shape of the TPO peaks, depicted in Figure 7 for both catalysts, were quite similar. Both the amount and the characteristics of coke over both catalysts surfaces was identical. Since coke formation is closely relate to the acidity of a catalyst, the same coke deposition of both spent Cu/Na-ZSM-5 and Cu/H-ZSM-5 zeolite support the similarity in acidity of both catalysts.

Pyridine adsorption and TPO results are evidence that there is no acidity difference between Cu/Na-ZSM-5 and Cu/H-ZSM-5 although the amount of cations in both catalyst are not the same (Table 1). Indeed, Cu/H-ZSM-5 at a high level of copper exchange would have few protons left on the catalyst surface. Thus, acidity might come mainly from copper ion sites. Halasz and Brenner (Halasz, *et al.* 1995) studied the acidity of copper on ZSM-5 and suggested that the copper site exhibited Lewis acid properties rather than Bronsted acid ones. Moreover, Satsuma, *et al.* (1995) mentioned that acid properties of zeolites are not the major factor for performance in NO reduction.

These catalyst surfaces would consist mainly of copper ion sites which are believed to be the main active sites of Cu/ZSM-5 catalysts for the SCR reaction (Iwamoto, *et al.* 1992 (a); Petunehi, *et al.* 1993; Grunert, *et al.* 1994; Iwamoto, 1994; Shelef, 1995; and Amiridis, *et al.* 1996). However, although the total copper content in Cu/H-ZSM-5 and Cu/Na-ZSM-5 are the same (Table 1), the form or amount of active form of copper in both catalysts may be different. The difference of activity between both catalysts may due to the difference in the characteristics of the copper site. There have been many reports concerning types of copper on ZSM-5 surface (Grunert, *et al.* 1994; Valyon and Hall, 1993 (a, b); and Larsen, *et al.* 1994). Forms of copper on zeolite generally are cuprous (1+) ions and cupric (2+) ions (Shelef, 1995; Iwamoto, *et al.* 1991 (b); Iwamoto, *et al.* 1991 (a); Pieapu, *et al.* 1995; Szanyi, *et al.* 1996; Valyon and Hall, 1993 (b); Valyon and Hall, 1993 (a); and Larsen, *et al.* 1994). However, many authors (Iwamoto, *et al.* 1991 (b); Iwamoto, *et al.* 1991 (a); Pieapu, *et al.* 1995; Szanyi, *et al.* 1996; Dedecek, *et al.* 1994; Anpo, *et al.* 1994; and Cilambelli, *et al.* 1996) accepted that Cu^{2+} can be reduced to Cu^{1+} or even Cu^{0} in suitable conditions (Dedecek and Wichterlova, 1994). Copper in different states has the different properties and activities. CO adsorption is an easy method to investigate the quantity of Cu^{1+} (Iwamoto, *et al.* 1991 (a, b)).The amount of CO adsorp on Cu/Na-ZSM-5 and Cu/H-ZSM-5 is shown in Table 3. The amount of CO adsorp on the catalyst surface represents the amount of Cu^{1+} on the surface. The amount of Cu^{1+} in Cu/H-ZSM-5 is about double that of the one in Cu/Na-ZSM-5. Since the total copper content of the two catalysts was equal, Cu/H-ZSM-5 had a higher Cu^{1+}/Cu^{2+} ratio. The difference in Cu^{1+}/Cu^{2+} might have had an affect on the activity in both catalysts.

In the NO reduction by propane, in the absence of oxygen, the first step in the reaction would be NO decomposition to produce oxygen and the oxygen would be the limiting reactant of the reaction. It was found that NO conversion in NO decomposition over Cu/H-ZSM-5 is slightly more than that over Cu/Na-ZSM-5. Thus, possibly more oxygen in Cu/H-ZSM-5 would be generated. Furthermore, it is well known that NO_2 is reduced more easily than NO (Petunchi and Hall, 1993) and it is also suggested that it is the intermediate of the NO reduction by hydrocarbon (Shelef, *et al.* 1994; Beutel, *et al.* 1993; Chajar, *et al.* 1994; and Guyon, *et al.* 1994). The Cu/H-ZSM-5 system produced much more NO_2 than the Cu/Na-ZSM-5 system. This NO_2 might be the factor that caused the reduction over Cu/H-ZSM-5 to occur more.

There have been many reports mentioning about the role of Cu^{1+} active site for NO decomposition involving redox cyclic (Iwamoto, *et al.* 1991 (a); Iwamoto, *et al.* 1992 (b); Spoto, *et al.* 1994; and Cheung, *et al.* 1996) whereas Cu^{2+} has been proposed as an active site for NO reduction by hydrocarbon (Shelef, 1995; Shpiro, *et al.* 1994; and Hwang, *et al.* 1996). The result that Cu/H-ZSM-5 is slightly more active than Cu/Na-ZSM-5 is probably due to the higher amount of Cu^{1+} in Cu/H-ZSM-5. Small amounts of Na^{+} remaining in Cu/Na-ZSM-5 would not affect any mechanism in NO reaction because Na-ZSM-5 is not active for NO decomposition and NO reduction (Iwamoto, 1990; Iwamoto, *et al.* 1992 (a); and Hamada, *et al.* 1990). However, further study for confirmation should be conducted.

Conclusions

Activities in NO oxidation and NO reduction by propane in excess oxygen over Cu/Na-ZSM-5 and Cu/H-ZSM-5 was identical. On the other hand, Cu/H-ZSM-5 was more active than Cu/Na-ZSM-5 in NO decomposition and NO reduction by propane without oxygen. No difference in acidity and coke deposition between both catalysts was observed. In contrast, Cu/H-ZSM-5 had a higher Cu^{1+}/Cu^{2+} ratio than Cu/Na-ZSM-5.

The different activity in oxygen deficient reactions between both catalysts is probably due to the different characteristics of the copper sites, Cu^{1+}/Cu^{2+} ratio, rather than to the difference of residual cations, Na^{+} and H^{+}.

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