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Water Tolerance of DeNO$_x$ SCR Catalysts Using Hydrocarbons: Findings, Improvements and Challenges

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Abstract−The recent developments on the effect of H_2O on deNO$_x$ performance of a variety of SCR catalysts selectively removing NO$_x$ by hydrocarbons in excess oxygen have been reviewed. In particular, the water tolerance of the catalyst is summarized to illustrate a common deactivation behavior of SCR catalyst for the reduction of NO by hydrocarbons under wet feed gas mixture. Earlier proposals elucidating the possible cause of the catalyst deactivation under wet conditions are discussed, focusing mainly on the catalyst characteristics. A promising way, which can improve the water tolerance and the hydrothermal stability of zeolite-based SCR catalyst, is also described.

Key words: NO$_x$ Reduction, Water Tolerance, Hydrocarbon, Deactivation, SCR, DeNO$_x$ Catalyst, Zeolite, Mordenite, Ferrierite

INTRODUCTION

Selective catalytic reduction (SCR) is one of the most effective technologies for lowering NO$_x$ from a high temperature combustion process. With strict emission standards for NO$_x$ emissions from stationary and mobile sources, combustion measure and modification technology will be no longer appropriate for reducing NO$_x$; therefore, post-treatment deNO$_x$ technology will be unavoidable. Commercially proven deNO$_x$ technology including NH$_3$-SCR for catalytic NO$_x$ removal and the purification of automotive exhausts using three-way catalytic converter are currently available; however, there are a few limitations in their commercial application. The deNO$_x$ SCR using NH$_3$ over a V_2O_5-WO_3/TiO_2 may be the most technically advanced technology for effectively removing NO$_x$ from large and small scale combustion processes, but still contains disadvantages such as NH$_3$-slip by unreacted and/or excess NH$_3$ and high cost of facilities and operation. A Pt-Pd-Rh system is capable of reducing NO$_x$ from gasoline engines. This technology, however, may hardly reduce NO$_x$ from diesel and lean burn gasoline engines due to huge amounts of excess O_2, which can easily transfer the rhodium to an inactive phase, rhodium oxide during the course of the reaction.

This would be the reason why a new catalytic system is required for removing diluted NO$_x$ from stationary and oxygen-rich mobile sources. Catalytic decomposition is essentially the simplest and best approach for NO$_x$ removal, and an ultimate goal in the development of deNO$_x$ technology. Up to now, Cu-exchanged zeolite-based catalyst is known as the best catalyst for NO decomposition; however, a catalyst containing consistently high removal activity for the decomposition has not been developed yet. Since the selective reduction of NO$_x$ by hydrocarbons (HC) in the presence of excess oxygen was successfully established with Cu-zeolites [Held et al., 1990; Iwamoto, 1990], the use of HCs as an alternative reductant to NH$_3$ has received great attention as the most promising deNO$_x$ technology for stationary and oxygen-rich mobile sources. There have been numerous investigations on the selective reduction of NO$_x$ by HCs with excess oxygen. Based on the earlier works, the SO$_2$ effect on NO removal activity was moderate, whereas H_2O resulted in serious catalyst deactivation even with small amounts. Not only would high catalytic activity be essential for a commercial application, but water and sulfur tolerances of the catalyst must also be required from the view of catalyst life.

In the early 1990s, an extensive review of research in this area mainly concerning the catalysts and their activity for the reduction had been made [Truex et al., 1992; Iwamoto and Mizuno, 1993]. The reaction mechanism for the reduction of NO by HCs, has been reviewed by Iwamoto and Yahiro [1994], Smits and Iwasawa [1995], and Adelman et al. [1996]. More than 200 patents and their applications in the present deNO$_x$ technology have been summarized by Tabata et al. [1994]. Recently, Parvulescu et al. [1998] published an extensive review of catalytic NO$_x$ removal where the catalysts and their catalytic property were covered in a part. The present review will focus on the issues, particularly relating to the effect of H_2O on the catalytic reduction of NO$_x$ by HCs over a variety of catalysts, an approach to improve the water tolerance and the hydrothermal stability from knowledge-based understandings on predominant factors in determining it. For this purpose, recent studies, efforts and attempts on the present topic in the literature will be mainly covered in the present review.

1. Advent of NO$_x$ SCR by HCs

There have been earlier studies investigating the use of HCs for replacing NH$_3$ in the SCR process. Representative examples can be found from the work to clean up the tail gas from nitric acid pro-

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duction plant *via* ammonia oxidation. The tail gas stream generally contains 0.1 to 0.5% NO_x and 3 to 4% O_2 [Cohn et al., 1961; Adlhart et al., 1971]. A major fraction of NO_x exists in the form of NO_2, so that the stack plume from nitric acid plants is associated with yellow to red color. The color of the stack gas is distinctive compared to the colorless one including the equivalent amounts of other pollutants without NO_2; therefore, initial efforts were mainly directed toward eliminating the color of the flue gas rather than NO_2 itself. One of the most frequently employed methods removing NO_2 was to convert it into colorless NO through a commercial decolorizing process for “purely public relations purposes” [Adlhart et al., 1971]. The catalytic decolorization of such tail gases over alumina-supported Pt, Pd and Rh can be typically described as:

$$4NO_2+CH_4 \rightarrow 4NO+CO_2+2H_2O \quad (1)$$

Reaction (1) is easily accomplished by introducing an excessive stoichiometric amount of fuel, referred to as CH_4, to the feed gas stream. During the decolorizing reaction, the combustion of fuel should also occur:

$$2O_2+CH_4 \rightarrow CO_2+2H_2O \quad (2)$$

Subsequently, NO removal can take place by Reaction (3).

$$4NO+CH_4 \rightarrow 2N_2+CO_2+2H_2O \quad (3)$$

This reaction might provide a conceptual guideline for the development of NO_x by HCs, although methane is one of the most difficult molecules to activate.

An earlier attempt to establish the catalytic technology for removing NO_x by using HCs was made mainly with metal oxides and supported-noble metals. Ault and Ayen [1971] utilized a barium-promoted copper chromite for the reduction of NO by C_1-C_8 hydrocarbons including alkenes and alkanes. Numerous metal oxides including MnO_2, Fe_2O_3, V_2O_5, Cr_2O_3, WO_3, ZnO, SnO_2, Co_3O_4, CdO, MoO_3, NiO, Cu_2O and TiO_2 have been examined for NO reduction using C_3H_6 [Murakami et al., 1977]. Among them, Fe_2O_3 and MnO_2 were the most active catalyst for this reaction system. Few, if any, kinetic and mechanistic studies have been made on the catalytic NO reduction by HCs. The catalytic reduction of NO by CH_4 over an alumina-supported Rh could be well illustrated by a Langmuir-Hinshelwood mechanism [Hardee and Hightower, 1984]. These earlier studies, however, may not be so attractive from the view of commercial application, since they have been mainly examined in oxygen-free streams and/or excess NO and HCs feed concentrations.

1-1. Initial Efforts in Germany

In the middle of the 1980s, a number of zeolite catalysts were developed to catalytically reduce NO_x by using hydrocarbons in an exhaust gas containing excess oxygen through a cooperative research with Volkswagen AG and Bayer AG in Germany [Held and Konig, 1987]. Transition metal ion-exchanged zeolites such as MOR, MFI and FAU (X and Y) structures were quite active for NO reduction at 100 to 700 °C of the reaction temperature and 10,000 to 50,000 h^{-1} of the reactor space time [Held and Konig, 1987; Held et al., 1988], where the MOR, MFI and FAU represent mordenite, ZSM-5 and faujasite zeolites, respectively. Cu-MOR catalyst exhibited 66% of NO conversion within the temperature range from 150 to 230 °C when C_2H_4 was used as a reducing agent in the absence of H_2O. The catalytic activity of 50% in terms of NO conversion at 350 °C was observed for Cu-MFI catalyst, but other metal-exchanged MFI catalysts were relatively less active [Held and Konig, 1987]. The capability of MFI zeolite to reduce NO at 300 °C strongly depends on metal ions exchanged in the zeolite; for example, Ir-, Pt-, Rh-, Ni- and Co-MFI catalysts revealed lower activity than Cu-MFI. FAU type zeolite exchanged with Cu, Fe, Mn, Ni, Co, Ag, V and Cr also revealed the deNO_x performance with C_2H_4 and C_3H_6 but their NO removal activity was mainly less than 20% of NO conversion in the range of the reaction temperature from 300 to 600 °C. In a wet condition, the activity maintenance of Cu-MFI catalyst for NO reduction with C_2H_4 was stronger than Cu-MOR catalyst. These findings have been mainly observed over a conventional monolith coated with Cu-MFI to remove NO from a lean-burn engine [Held and Konig, 1987; Held et al., 1988]. It has been believed that Held and coworkers at Volkswagen AG in Germany were first aware of the present selective reduction technology to remove NO by HCs.

1-2. Pioneering Work in Japan

In the research undertaken by Toyota Motor Corporation and Iwamoto and coworkers in Japan, an extensive screening test for the effective catalytic decomposition of NO_x contained in automotive engine exhausts was conducted at the end of 1980s [Fujitani et al., 1988; Tanaka et al., 1989; Iwamoto, 1990]. Among the catalysts examined, Iwamoto and coworkers found that Cu-MFI was the most active catalyst for the decomposition [Iwamoto, 1990; Iwamoto et al., 1991]; for example, the activity of Cu-MFI catalyst was 80% of NO conversion at 500 °C and 3,000 h^{-1}, depending on the Si/Al ratio and copper loading of the catalyst. After this pioneering finding, the subsequent effect of O_2, CO_2, SO_2, H_2O, CO and HCs on the removal of NO was systematically examined to confirm if any change in the catalytic activity could be accompanied, since automotive engine exhaust also contains gas components besides NO [Fujitani et al., 1988; Tanaka et al., 1989; Iwamoto et al., 1991; Iwamoto and Hamada, 1991].

In the presence of O_2, the catalytic removal activity of NO decreased and a similar trend was also observed by the addition of either SO_2 or H_2O in the feed gas stream. However, it dramatically increased according to the presence of either CO or HCs. It has been believed that the significant enhancement should be mainly related to the role of HCs similar to the result observed for the decolorizing reaction described before [Fujitani et al., 1988; Tanaka et al., 1989]. The decomposition of NO over Cu-MFI catalyst in the presence of *stoichiometric amounts* of HCs as well as of excess O_2 could occur [Fujitani et al., 1988; Tanaka et al., 1989]. In addition, this NO removal reaction was later designated as not “Decomposition” but “Selective Catalytic Reduction” [Iwamoto, 1990]. From this history for NO_x SCR by HCs, the advent of SCR technology came coincidently into the world “*during the survey of the effect of coexisting gases on the catalytic activity of copper ion-exchanged zeolites for the decomposition of NO*” as Iwamoto and Mizuno [1993] described.

2. Catalyst and Reductant

2-1. HC-SCR DeNO_x Catalyst

Since Held and Konig [1987], Held et al. [1988, 1990] and Iwamoto [1990] independently reported the selective catalytic reduction of NO_x by HCs over Cu-MFI catalyst on which the ppm level

Table 1. Literature-based catalysts for selective reduction of NO$_x$ by hydrocarbons

Zeolites and related materials
- (1) Bare zeolites: MFI, MOR, FER, FAU, CLI
- (2) Metal ion-exchanged zeolites:
  - MFI with Cu, Fe, Co, Ce, Ga, Ag, Na, Zn, Ni, Mn, Mg, Mo, V, Cr, Ca, La, Pr, Nd, Ln, In, Ir, Pb, Pt, Rh, Ru and Pd
  - MOR with Cu, Fe, Co, Pt, Rh, Ru, Pd, Ti, W, Mo, Ce, Mg, Zr, Sn, Na, V, Cr, Ni, Zn, Ca, Ga, Sr, Ba and La
  - FER with Cu, Fe, Co, Cr, V, Zn, Pt, Pd, Mn and Ni
  - FAU with Cu, Co, Fe, Ce and Ga
  - LTL with Cu, Co and Fe
  - BEA with Cu and Co
  - CLI with Fe, Cr, Ni and Mn
- (3) Metallosilicates: Cu-, Fe-, Ga-, Al-, Co-, Ni-, Mn-, Mo-, Ti-silicate
- (4) Silicoaluminophosphates: Cu-, H-, Ca-, Pd-SAPO, H-MAPO, ALPO
- (5) Cordierites
- (6) Mullites

Metal oxides and related materials
- (1) Single metal oxides: Al_2O_3, SnO_2, TiO_2, ZrO_2, La_2O_3, Fe_3O_4 and Ag_2O
- (2) Mixed metal oxides: Al_2O_3-BaO, Al_2O_3-La_2O_3, ZnO-SiO_2, TiO_2-Al_2O_3, SiO_2-Al_2O_3, ZrO_2-TiO_2 and ZrO_2-Al_2O_3
- (3) Sulfate-promoted single and mixed metal oxides: Al_2O_3, TiO_2, ZrO_2, Fe_2O_3, ZrO_2-Al_2O_3 and ZrO_2-TiO_2
- (4) Metal oxides supported on (1) to (3): Cu, Co, Ag, V, Ni, La, Mn, Ga, Cr, Ba, Ca, Sr, Mg, Zr, Cs, Sm, Mo, Ce and Fe
- (5) Perovskites

Noble metals
- (1) On zeolites: MFI, MOR, FER and FAU
- (2) On metal oxides: Al_2O_3, SiO_2, TiO_2, ZrO_2, La_2O_3, CeO_2, Cr_2O_3, ZnO, TiO_2-Al_2O_3, ZrO_2-TiO_2, TiO_2-ZrO_2-Al_2O_3, $AlPO_4$ and $AlBO_3$

of NO$_x$ concentration is readily reduced by HCs even in the presence of excess oxygen, numerous catalysts listed in Table 1 have been reported in the literature. Representatively, transition metal ion-exchanged zeolites [Iwamoto et al., 1991; Sato et al., 1991, 1992; Teraoka et al., 1992; Li et al., 1993; Kim et al., 1994, 1995; Ohtsuka and Tabata, 1999; Lee et al., 2001], H-zeolites [Hamada et al., 1990, 1991; Sato et al., 1991, 1992; Kim et al., 1994, 1995], supported noble metals [Hamada et al., 1991; Hamada, 1994], supported metals [Hamada et al., 1991; Hosose et al., 1991; Sato et al., 1992; Torikai et al., 1991], metal oxides [Hamada, 1994; Kintaichi et al., 1990; Sato et al., 1992; Maunula et al., 1998, 2000], solid acids [Hamada et al., 1991; Hamada, 1994; Hosose et al., 1991; Kintaichi et al., 1990; Torikai et al., 1991; Sato et al., 1992] and perovskites [Sato et al., 1992; Hong et al., 1997], have been suggested to be active for SCR reaction using HCs.

NO removal activity significantly depends on the catalyst and reductant, except the reaction condition including the concentrations of NO, HCs and O_2. Generally, transition metal-exchanged zeolites such as MFI, MOR, FER (ferrierite), LTL (L-zeolite) and FAU contain higher deNO$_x$ efficiency than the other type of the catalyst. It is widely accepted that MFI and MOR type zeolite catalysts are currently the best support material for NO reduction by HCs in the presence of oxygen [Sato et al., 1992]. Note that FER zeolite is the best catalyst support for the reduction of NO when reduced by CH_4 [Li and Armor, 1994; Witzel et al., 1994; Lee et al., 2001].

2-2. Hydrocarbons and Related Compounds

Hydrocarbons could be a useful reducing agent and replace NH_3 regarded as the best reductant for commercial SCR process. A variety of hydrocarbons and related compounds have been employed for the reduction of NO$_x$, as summarized in Table 2. Iwamoto and Hamada [1991] have classified the reductant into two categories, selective (C_2H_4, C_3H_6, C_3H_8 and C_4H_8) and non-selective (CH_4 and C_2H_6), based upon the amount of the consumption of the reductant during the course of the reaction, and a similar result has been also observed for light hydrocarbons [Truex et al., 1992]. It is of interest to note that such a classification may be valid for the non-selective reduction of NO$_x$ by CH_4 and C_2H_6 over Cu-MFI and Al_2O_3. How-

Table 2. Literature-based hydrocarbons and related compounds for selective reduction of NO$_x$ over SCR catalysts

Hydrocarbons
- (1) Saturated hydrocarbons: CH_4, C_2H_6, C_3H_8, C_4H_{10}, C_5H_{12}, C_6H_{14}, C_7H_{16}, C_8H_{18}, C_9H_{20}, $C_{10}H_{22}$ and $C_{16}H_{34}$
- (2) Unsaturated hydrocarbons: C_2H_4, C_3H_6 and C_4H_8

Related compounds
- (1) Alcohols: CH_3OH, C_2H_5OH, C_3H_7OH and C_4H_9OH
- (2) Common fuels: liquified petroleum gas, natural gas, diesel oil and gasoline
- (3) Others: acetone, kerosene, dioxane, methylethylketone, toluene, benzene, xylene, ether, ether acetone, dimethylether, diethylether, formaldehyde, acetoaldehyde, formic acid, acetic acid and methyl formate

Table 3. Water tolerance of numerous catalysts for the selective reduction of NO_x by HCs

Catalyst[a]	HC	H_2O (%)	Conversion of NO_x (%)[b]							Reference
			Reaction temperature (°C)							
			300	350	400	450	500	550	600	
Cu-MFI	C_2H_4	10		50 (37)						[Held et al., 1990]
		16		50 (23)						
Cu-MOR	C_2H_4	10		37 (17)						[Held et al., 1990]
Cu-MFI-157	C_3H_6	3.9					75 (40)			[Iwamoto et al., 1992]
Co-MFI-98	CH_4	2.0					40 (29)	27 (28)	21 (22)	[Li and Armor, 1993]
Co-FER-78	CH_4	2.0					60 (28)	50 (40)	40 (32)	[Li and Armor, 1993]
Co-MFI-140	CH_4	2.0				47 (23)	33 (31)			[Li et al., 1993]
Co-MOR-94	CH_4	2.0				33 (25)	28 (25)			[Li et al., 1993]
Mn-MFI-106	CH_4	2.0				31 (23)	39 (36)			[Li et al., 1993]
Ni-MFI-140	CH_4	2.0				26 (19)	21 (19)			[Li et al., 1993]
H-MFI	CH_4	2.0				16 (5)	24 (2)			[Li et al., 1993]
Cu-MOR-46	C_3H_8	3.0				24 (10)				[Mabilon and Durand, 1993]
		5.0				24 (2)				
Cu-MFI-87	C_3H_8	14			61 (19)	77 (45)	78 (55)			[Gopalakrishnan et al., 1993]
Al_2O_3	C_3H_6	10			42 (4)	71 (9)	79 (24)			[Miyadera, 1993]
CoO_x/Al_2O_3	C_3H_6	10			76 (20)	60 (42)	43 (44)			[Miyadera, 1993]
AgO_x/Al_2O_3	C_3H_6	10			81 (40)	77 (71)	62 (62)			[Miyadera, 1993]
CuO_x/Al_2O_3	C_3H_6	10			31 (13)	23 (10)	14 (5)			[Miyadera, 1993]
Ga-MFI-162	CH_4	2.0					40 (13)			[Li and Armor, 1994]
Co-MFI	C_2H_6	2.0				50 (22)				[Burch and Scire, 1994]
H-MOR	C_3H_6	6.5			84 (66)					[Kim et al., 1995, 1997, 1998]
	C_2H_4	7.3		66 (17)[c]						[Kim et al., 1995, 1997, 1998]
Cu-MOR-48	C_3H_6	7.3			78 (28)					[Kim et al., 1995, 1997, 1998]
	C_2H_4	7.3		65 (21)[c]						[Kim et al., 1995, 1997, 1998]
Cu-NZA[d]-44	C_3H_6	7.3			91 (85)					[Kim et al., 1995, 1997, 1998]
	C_2H_4	7.3		58 (34)[c]						[Kim et al., 1995, 1997, 1998]
Ag/Al_2O_3	C_3H_6	1.5					43 (34)			[Bethke and Kung, 1997]
Cu-Pillared Clays	C_2H_4	5.0			55 (32)	71 (50)	81 (76)			[Li et al., 1997]
AuO_x/Al_2O_3	C_3H_6	9.8			30 (42)	57 (72)	45 (52)			[Ueda et al., 1997]
Cu-saponite	C_3H_6	8.0			41 (32)	35 (27)	27 (20)			[Sato et al., 1997]
Ag-saponite	C_3H_6	8.0			37 (51)	45 (45)	51 (37)			[Sato et al., 1997]
Mn_2O_3+Sn-MFI	C_3H_6	5.7	12 (65)	41 (74)	27 (45)		3 (10)			[Misono et al., 1997]
InO_x/Al_2O_3	C_3H_6	8.0		73 (26)	95 (55)	87 (57)	78 (42)	58 (25)		[Maunula et al., 1998]
$InO_x/Al_2O_3+Mn_3O_4$	C_3H_6	8.0		78 (72)	90 (83)	79 (73)	68 (58)	49 (46)		[Maunula et al., 1998]
Ga_2O_3/Al_2O_3	CH_4	2.5			6 (0)	13 (2)	28 (7)	70 (21)	62 (29)	[Shimizu et al., 1998]
Cu-aluminate	C_3H_6	10			37 (24)	25 (11)	14 (6)			[Shimizu et al., 1998]
Co-aluminate	C_3H_6	10			47 (28)	55 (47)	54 (44)			[Shimizu et al., 1998]
Ni-aluminate	C_3H_6	10			32 (22)	68 (52)	67 (51)			[Shimizu et al., 1998]
Pd-MOR	CH_4	9.0			87 (44)	91 (69)	76 (55)			[Ohtsuka and Tabata, 1999]
Pd-MFI	CH_4	9.0			62 (32)	69 (33)				[Ohtsuka and Tabata, 1999]
CoO_x/Al_2O_3	C_3H_6	8.0			88 (16)	81 (49)	62 (66)	23 (54)		[Maunula et al., 2000]
InO_x/Fe_2O_3+H-MFI	CH_4	3.3			84 (41)	100 (80)	100 (91)	100 (83)	100 (71)	[Wang et al., 2000]
In-FER	CH_4	2.0			60 (14)	58 (32)	56 (30)	41 (27)		[Ramallo-Lopez et al., 2001]
Co-FER-98	CH_4	5.0			83 (1)	88 (39)	70 (56)	47 (35)	27 (23)	[Lee et al., 2001]

[a] Numbers next to the zeolite structure designate the exchange percentage of each metal ion.

[b] Numbers in parentheses indicate NO_x conversion at wet condition.

[c] At 360 °C.

[d] Natural zeolite consisting mainly of a MOR structure.

ever, they are selective reductants with Co-MFI, Co-FER [Li and Armor, 1992; Li et al., 1993, 1994; Lee et al., 2001], Ga-MFI [Yogo et al., 1993; Tabata et al., 1994], H-zeolite [Yogo et al., 1993], Pt/ Al_2O_3 [Demicheli et al., 1993], Li-promoted MgO [Zhang et al., 1994], Pd-MOR [Ohtsuka and Tabata, 1999] and In-FER [Ramallo-Lopez et al., 2001]. Although the SCR activity is mainly related to the catalyst, the other variable may be the selectivity of the reductant for the present reaction system containing excess O_2 and water. The selectivity can be determined by the consumption of the reductant according to the reaction stoichiometry.

3. Catalyst Deactivation by Water

Although less than 1% of H_2O is commonly included in the exhaust stream of nitric acid plant [Adlhart et al., 1971], most of NO_x emission sources contain H_2O in the concentration ranges of 2 to 18% [Li et al., 1993]; therefore, the strong water tolerance of deNO$_x$ catalyst is essential for its practical use besides the sulfur tolerance of the catalyst in the presence of SO_x contained in the flue gas. There have been efforts not only to demonstrate the effect of H_2O on the NO_x SCR, but also to elucidate the reason why most SCR catalysts significantly lose catalytic activity under wet conditions [Iwamoto and Mizuno, 1993; Li et al., 1993; Kharas et al., 1993; Kim et al., 1995, 1997; Ohtsuka and Tabata, 1999; Lee et al., 2001]. A few of the representative investigations in this topic have focused on how to improve the water tolerance of zeolite catalysts for the reduction [Chung et al., 1999; Lee et al., 2001]. Based upon the earlier studies on the role of H_2O in reducing NO_x by HCs, the present review will focus on improving the water tolerance of zeolite catalysts for the present NO reduction technology intensively developed over the last decade. It is not intended to cover the application of the present technology, particularly to NO_x reduction under actual lean-burn and diesel engine conditions.

3-1. Effect of Water on NO Removal Activity

3-1-1. Metal Ion-Exchanged Zeolites

Up to now, the effect of H_2O on the catalytic activity for NO_x reduction by hydrocarbons and the cause of the activity loss in the presence of H_2O have been among the most important topics in this area of research, as extensively summarized in Table 3. Held and coworkers [Held and Konig, 1987; Held et al., 1988; 1990] *first* published illustrative results for the effect of H_2O on the selective reduction of NO_x by C_2H_4 over Cu ion-exchanged zeolite catalysts with excess oxygen. Using Cu-MOR, 37% of NO_x was removed at 350 °C when the feed gas stream contained 1,000 ppm of NO_x in the presence of 40 ppm of C_2H_4 and 1.5% O_2, but the NO_x conversion dropped down to 17% when 10% H_2O was subsequently included in the feed gas stream, as shown in Fig. 1. For Cu-MFI catalyst, the initial NO_x conversion of 50% decreased to 37% in the presence of 10% H_2O and further decrease was observed when the feed concentration of water increased to 16%. The degree of the loss of NO removal activity for Cu-MFI catalyst in the presence of H_2O is somewhat milder than that over Cu-MOR. This may be associated with the distinction of Si/Al ratio of both zeolites, although they were not specifically provided in the literature.

Significant effect of H_2O vapor on NO_x reduction activity by C_3H_6 was again examined for Cu-MFI-157 catalyst [Iwamoto et al., 1992]. Hereafter, the numbers next to zeolite structure codes will indicate an ion exchange rate. Introducing 3.9% of H_2O to the feed gas stream containing 250 ppm of SO_2, the catalytic activity at 500 °C suddenly decreased from 73% of NO conversion to 45%, as illustrated in Fig. 2. The wet activity remained unchanged even for 1.5 h under the identical reactor operating conditions and could be immediately restored to its initial conversion when H_2O was eliminated from the feed stream. This implies that the effect of H_2O is fully reversible and presumably suggests that the major active reaction sites on the catalyst surface, *i.e.*, Cu ions, may not be chemically altered by H_2O. Among a variety of zeolite structures including MFI, MOR and FAU (X and Y), significant NO removal ac-

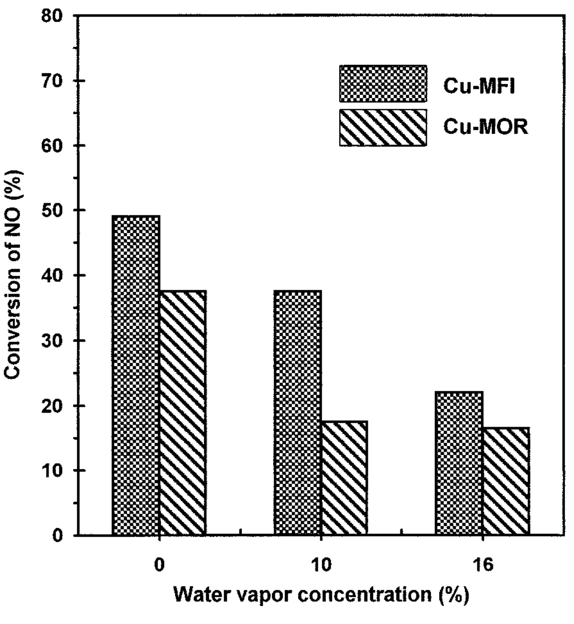

Fig. 1. Effect of water on NO_x conversion with zeolites. Reaction condition: NO_x 1,000 ppm, C_2H_4 40 ppm, O_2 1.5%, GHSV= 13,000 and T=350 °C [Held et al., 1990].

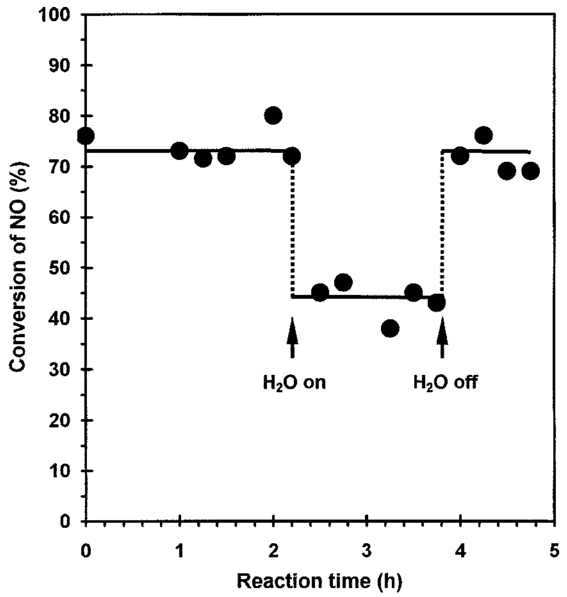

Fig. 2. Effect of H_2O on the catalytic activity of Cu-MFI-157 for the selective reduction of NO. [NO]=600 ppm; [O_2]=1.5%; [C_3H_6]=940 ppm; [SO_2]=250 ppm; [H_2O]=3.9%; W/F=0.1 g·s·cm^{-3}; T=500 °C [Iwamoto et al., 1992].

tivity by C_3H_8 was observed over Cu-exchanged MFI and MOR zeolites, but not over FAU type zeolite [Gopalakrishnan et al., 1993]. In a wet stream with 14% H_2O, the $deNO_x$ conversion of Cu-MFI-87 was reduced by 20% at both 350 and 500 °C and 40% at 400 °C, as listed in Table 3. The dry activity was not restored even after H_2O was fed into the reactor system off, implying an irreversible activity loss by water. This differs from the earlier result [Iwamoto et al., 1992] but is in good agreement with the irreversible catalyst deactivation of Cu-MFI-104 catalyst to remove NO from an actual diesel engine in the presence of 7% H_2O at 400 °C [Konno et al., 1992].

The water tolerance of transition metal ion-exchanged MFI, FER and MOR type zeolites for selectively reducing NO by CH_4 was examined by Armor and coworkers [Li and Armor, 1993; Li et al., 1993, 1994]. Both Co-MFI-98 and Co-FER-78 catalysts were highly active for NO removal reaction by CH_4, compared to Co-MOR-94, Mn-MFI-106, Ni-MFI-140 and H-MFI catalysts. However, the catalytic activity was severely suppressed in the presence of water vapor, regardless of metal ion exchanged on the catalyst surface (Table 3). As an example, Co-MFI-140 catalyst revealed 47% of NO conversion without H_2O, but the presence of 2% H_2O in a gas mixture resulted in the activity loss more than 30% at the reaction temperatures below 450 °C, as shown in Fig. 3. The effect of water on NO removal activity was reversible [Li and Armor, 1993], which was quite consistent with the earlier observation over Cu-MFI-157 catalyst by Iwamoto et al. [1992]. The alteration of cobalt state and zeolite structure might not be suspicious for the present catalytic system, since the activity in the wet condition was quite stable within the observation over 12 hours at the given reaction temperatures.

Based upon the comparison of Co-MFI-98 catalyst with Co-FER-78 for NO_x reduction by CH_4, Li and Armor [1993] observed that FER structure zeolite revealed the best NO removal activity even in a wet stream containing 2% of H_2O, as indicated in Table 3; however, this only occurs when CH_4 as a reducing agent is employed, since the $deNO_x$ activity of Co-BEA (β-zeolite)-80 catalyst under a wet stream with C_3H_8 was much greater than that of Co-FER catalyst [Tabata et al., 1998]. The overall conversion of CH_4 significantly decreased under the wet condition as well, regardless of zeolite structure. A complete reversible catalyst deactivation due to water was again observed for both Co-exchanged zeolites during a cyclic inclusion of water into the feed gas stream. Ga-zeolites have been highly active for the reduction of NO by CH_4 [Li and Armor, 1994; Tabata et al., 1994] and C_3H_8 [Yogo et al., 1993]. In a comparative study with Co-MFI catalyst for the reduction of NO by CH_4, Ga-MFI-162 with CH_4 revealed high performance of NO removal activity and was more selective than Co-MFI catalyst, but it showed a severer activity loss by H_2O; the respective $deNO_x$ conversions for Ga-MFI-162 and Co-MFI at 500 °C decreased from 40 to 13% and from 40 to 35% in the presence of 2% H_2O [Li and Armor, 1994].

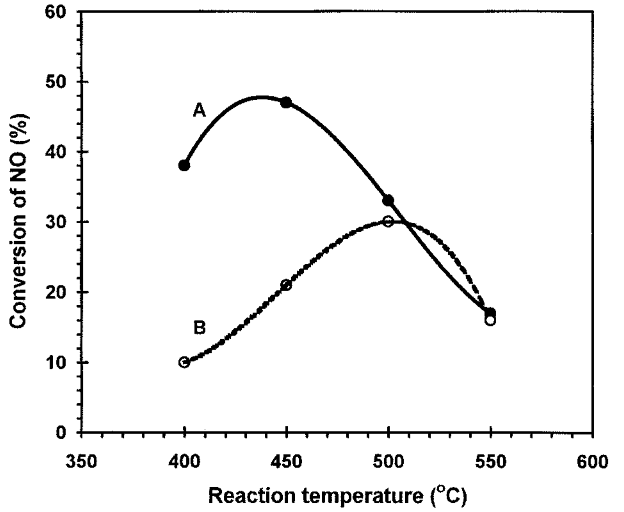

Fig. 3. Effect of water on the NO conversion over Co-MFI-140 as a function of reaction temperature. The reaction was run at GHSV=30,000, [NO]=820 ppm, [CH_4]=1,015 ppm, and [O_2]=2.5% ([H_2O]=2% for the wet feed). The reaction was run first with the dry feed with increasing temperature (line A), then 2% water vapor was added at 560 °C and the reaction was run with decreasing temperature (line B). Data were collected at each temperature for a period 1 to 2 h, and only stable, average data are shown [Li et al., 1993].

An extensive study to elucidate the loss of NO removal activity by H_2O was conducted for Cu-exchanged MOR type zeolites by C_2H_4 and C_3H_6 [Kim et al., 1995, 1997, 1998]. Fig. 4 shows the water tolerance of Cu-exchanged synthetic MOR (H-MOR and Cu-MOR-48) and natural zeolite (Cu-NZA-44) by C_2H_4 as a function of the feed concentration of H_2O. The activity of the synthetic MOR without Cu ions decreased from 66 to 17% under the wet stream containing 7.3% of H_2O; however, the water tolerance could be appreciably improved as Cu ions were exchanged in the catalyst. Cu-NZA-44 reveals better water tolerance than the synthetic MOR containing copper ions. If C_3H_6 is employed as a reductant, the activity loss of Cu-NZA-44 catalyst is less than 5% even at 16% of H_2O in the feed gas stream, as illustrated in Fig. 5. The deactivation has been improved for the synthetic MOR catalysts when C_3H_6 is employed as a reductant instead of C_2H_4, regardless of the presence of Cu ions on the catalyst surface. It may imply that C_3H_6 is a better reductant than C_2H_4 in the presence of H_2O. The Cu-exchanged MOR type

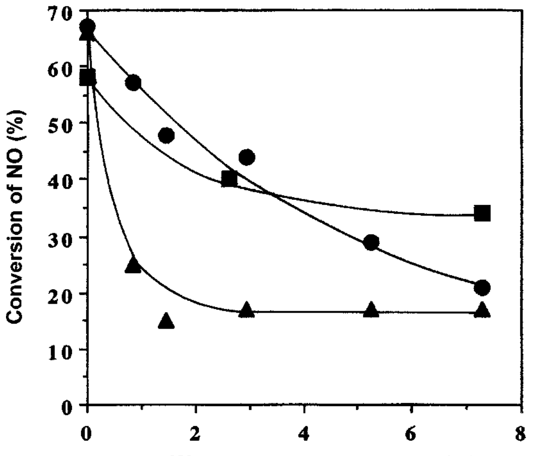

Fig. 4. Water tolerance of mordenite type zeolite catalysts for the reduction of NO by C_2H_4 : (●) Cu-MOR-48; (▲) H-MOR; (■) Cu-NZA-44. Reaction condition: NO 500 ppm, C_2H_4 1,000 ppm, O_2 4.2% and T=360 °C [Kim et al., 1997].

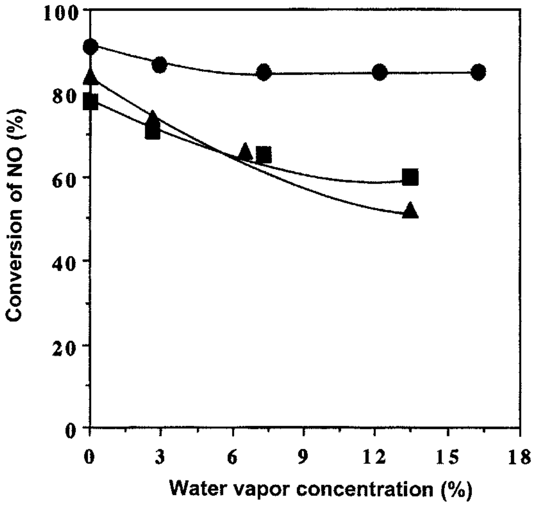

Fig. 5. Water tolerance of mordenite type zeolite catalysts for the reduction of NO by C_3H_6 : (■) Cu-MOR-48; (▲) H-MOR; (●) Cu-NZA-44. Reaction condition: NO 500 ppm, C_3H_6 2,000 ppm, O_2 4.2% and T=400 °C [Kim et al., 1997].

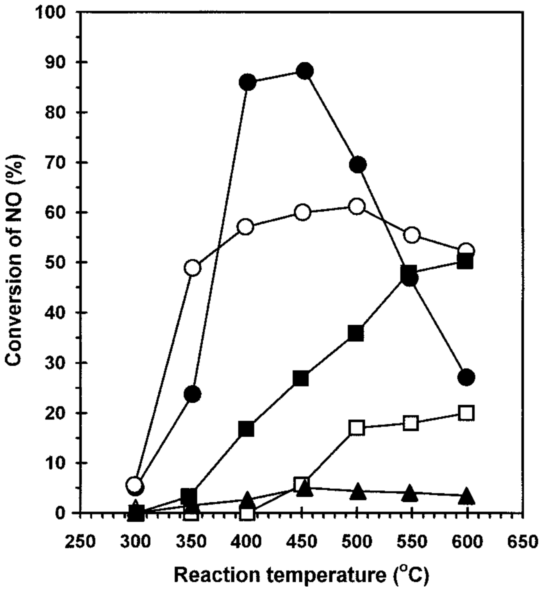

Fig. 6. Dry activity of metal-exchanged FER structure zeolite catalysts for NO reduction by CH_4 : (●) Co; (○) In; (■) Mn; (□) Ni; (▲) Cu. Reaction condition: NO 1,200 ppm, CH_4 1,600 ppm and O_2 3.2% [Lee et al., 2001].

zeolite shows milder catalyst deactivation by water than the copper-free catalyst, and the natural MOR type catalyst particularly contains stronger water tolerance than the synthetic MOR-based zeolites. It indicates that the zeolite structures and the existence of the copper ions are mainly associated with the distinctive water tolerance of the catalyst.

The NO removal activity of Cu-MOR-48 in the presence and absence of H_2O was completely reversible. The reversibility of NO conversion has been also observed for H-MOR and Cu-NZA-44 catalysts [Kim et al., 1996, 1997, 1998], regardless of reductant, which is consistent with the earlier studies for Cu-MFI-157 [Iwamoto et al., 1992] as well as for Co-FER-78 and Co-MFI-140 [Li and Armor, 1993; Li et al., 1993]. It is common for the oxidation of HCs into CO by the cyclic injection of water into the feed gas stream. It suggests that the deterioration of the catalytic activity is probably due to the adsorption characteristics of reactant and water, rather than due to the structural alteration of the catalyst by water.

Recently, NO removal activity by CH_4 has been examined over Co-exchanged FER, MOR, BEA and MFI type zeolites [Lee et al., 2001]. Co-FER-98 catalyst exhibited $deNO_x$ conversion of 88% at 450 °C under a dry condition but 50-60% for the other type of Co-zeolites, which is also consistent with the activity dependence on zeolite structure for the reduction by CH_4 [Li and Armor, 1993]. In a wet stream with 10% H_2O, only 30% of NO conversion has been achieved for Co-FER catalyst at 450 °C [Lee et al., 2001]. In addition, metal ions on the surface of FER structure may be another important catalyst variable for the high performance of NO removal, as revealed in Fig. 6. Although In-FER catalyst contains a wide operating temperature window with the maximum NO conversion of 60% at 400-500 °C, Co-FER is the most active catalyst from the view of the operating condition. The catalytic activity could be enhanced as the content of Co on the catalyst surface increases [Lee et al., 2001; Lamello-Lopez et al., 2001].

3-1-2. Supported Metal Oxides

A mixture of transition metal oxides and zirconium oxide catalyst prepared by co-precipitation method has been employed for NO reduction by either C_3H_6 or C_3H_8 [Bethke et al., 1994]. Cu-Zr-O was particularly active for the reaction, but the $deNO_x$ performance dramatically decreased mainly due to 2.4% of H_2O contained in the feed gas stream. Miyadera [1993] has reported high performance of AgO_x/Al_2O_3 for the reduction of NO with C_3H_6 in the absence of water. Although most of the metal oxide catalysts suffered from activity loss by H_2O, the supported AgO_x catalyst exhibited strong water tolerance (Table 3). This may be related to the weak adsorption of H_2O on the surface of silver. The water tolerance of alumina-supported InO_x and CoO_x catalysts for NO removal reaction with C_3H_6 was also examined by Maunula et al. [1998, 2000]. InO_x/Al_2O_3 catalyst in a dry stream revealed 95% of NO conversion at 400 °C [Maunula et al., 1998]. If 8% of H_2O was subsequently included in the feed gas stream, the catalytic performance notably dropped to 55% of NO conversion at the identical reaction temperature, as listed in Table 3. As Mn_3O_4 was physically added to the catalyst (unknown weight ratio), the water tolerance became stronger so as to be less than 10% of the decrease in NO conversion within the range of the reaction temperatures covered (Table 3). A similar enhanced water resistance was observed for NO reduction with CH_4 over a physical mixture of InO_x/Fe_2O_3 and H-MFI [Wang et al., 2000], as also included in Table 3.

The $deNO_x$ activity of CoO_x catalysts in the dry condition significantly varied with respect to the phase of alumina employed as a catalyst support, the Co precursor and the calcination temperature. The catalyst calcined at 700 °C contained 90 to 60% of NO conversion without water at reaction temperatures ranging from 350 to 550 °C. With the addition of 8% H_2O to the dry gas mixture, the NO removal activity below 450 °C significantly decreased, while that above 500 °C increased, as shown in Table 3. This catalytic behavior of $deNO_x$ catalyst in the presence of water vapor is in good agreement with that of a mechanical mixture of Mn_2O_3 and Sn-MFI (weight ratio of 1 : 1) [Misono et al., 1997], Au/Al_2O_3 [Ueda et al., 1997] and Ag-saponite [Sato et al., 1997] on which their wet deNO$_x$ performance within either certain or wider temperature regions was higher than the dry activities. 3.2% GaO$_x$/Al$_2$O$_3$ catalyst exhibited poor activity less than 15% of NO conversion within the reaction temperatures covered [Li and Armor, 1994]. The catalytic activity was a strong function of the amount of GaO$_x$ dispersed on the surface of alumina support. NO conversion of 65% at 500 °C was obtained over 35% GaO$_x$/Al$_2$O$_3$ catalyst [Shimizu et al., 1998]; however, the catalyst contained weak water tolerance, as shown in Table 3. Besides the catalytic systems discussed in the present review, Cu-pillared clay [Bethke and Kung, 1997] and metal-incorporated aluminates [Shimizu et al., 1998] have been also suggested as a deNO$_x$ catalyst with HCs, as listed in Table 3.

3-2. Cause of the Activity Loss by H_2O

3-2-1. Chemical State of Metal Ions

Most HC-SCR DeNO$_x$ catalysts experience severe deactivation in their catalytic activity when H_2O exists in the feed gas stream, as summarized in Table 3; however, the extent of the catalyst deactivation under a wet stream seriously depends on catalyst, hydrocarbon, reaction temperature and water content employed for the reaction system. Few, if any, studies focusing on the reason why the performance of deNO$_x$ catalyst is too sensitive to water vapor in the feed gas stream could be found in the literature so far.

At the initial stage to understand the catalyst deactivation by H_2O, the earlier work by Kharas et al. [1993] should be cited. Using a simulated Air/Fuel feed ratio of 18 to the reactor system where 10% of H_2O is included, deNO$_x$ performance of Cu-MFI-387 was examined for 1 h at reaction temperatures from 600 to 800 °C. The primary cause of the catalyst deactivation is the alteration of Cu ions on the catalyst surface to CuO and Cu_2O based on the analysis of the catalyst surface before and after reaction by EXAFS and XRD. A substantial loss in initial micropore volume of the catalyst compared to fresh catalyst has been observed. The sintering of the copper ions could lead to the destruction of the zeolite structure along with the loss of catalytic activity during the course of reaction at the lean burn condition. A similar result has been also observed for Cu-MFI-106 and Cu-MFI-678 catalysts on which Cu ions are transferred to small CuO clusters through a durability test at 500°C for 500 h under a simulated lean burn exhaust containing 9% H_2O [Tabata et al., 1994]. The dealumination of the catalyst, the carbon deposition on the catalyst surface and the loss of the catalyst micropore volume have not been observed, as confirmed by the catalyst characterization including BET surface area, CO chemisorption, NMR and elemental carbon measurements.

Electronic and local structures of Cu-MOR-48 and Cu-NZA-44 catalysts after reaction at 400 °C for 1 h in the presence of 7.3% H_2O have been determined by XANES and EXAFS spectra along with those for the references including Cu foil, CuO, Cu_2O and $Cu(OH)_2$ [Kim et al., 1997]. Cu K-edge XANES spectra for both catalysts even after the reaction were basically similar to those of each fresh catalyst, indicating that no change in the electronic structure of the Cu ions occurs during the catalytic reaction with water. The spectra were quite distinctive compared with the reference samples even for the catalysts exposed to the wet stream, revealing that the copper species are neither Cu_2O, CuO nor $Cu(OH)_2$. A multiple scattering did not appear, therefore no formation of copper oxide clusters on the catalyst surface.

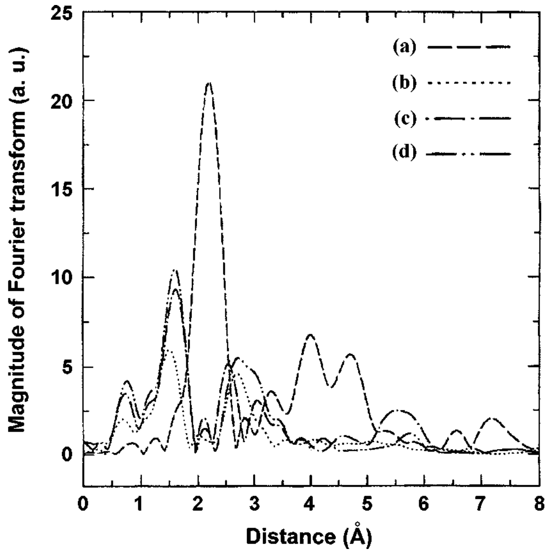

Fig. 7. Cu K-edge EXAFS spectra for (a) Cu foil, (b) Cu_2O, (c) CuO and (d) $Cu(OH)_2$ [Kim et al., 1997].

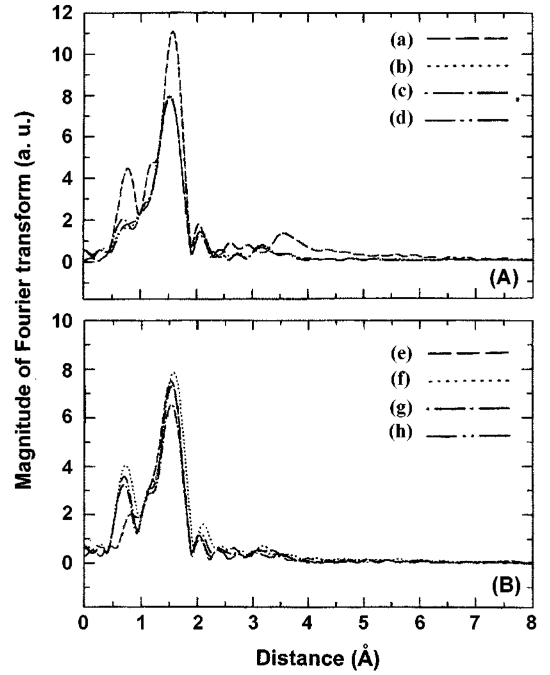

Fig. 8. Cu K-edge EXAFS spectra for (A) Cu-MOR-48 and (B) Cu-NZA-44 catalysts. (a) and (e) fresh; (b) and (f) after reaction with water at 400 °C for 1 h; (c) and (g) after reaction with water at 700 °C for 1 h; (d) and (h) after reaction with water at 400 °C for 1 h following reaction without water for 1 h. Reaction condition: NO 500 ppm, C_3H_6 2,000 ppm and O_2 4.2% [Kim et al., 1997].

Cu K-edge k^3-weighted EXAFS spectra could lead to the same conclusion for the two kinds of Cu-exchanged catalysts before and after the reaction compared to the references in Figs. 7 and 8. Cupric oxide shows the predominant peak at 1.62 Å due to the nearest Cu-O, as compared to 1.50 Å in Cu_2O (1.95 Å in CuO [Asbrink and Norrby, 1970] and 1.85 Å in Cu_2O [Wells, 1984]). Either one or two neighbor peaks appear at a longer distance: 2.73 Å for Cu_2O, and 2.55 and 3.08 Å for CuO. In the case of Cu(OH)$_2$, three prominent peaks are at 1.60 and 2.73, and 3.01 Å, corresponding to Cu-O and Cu-Cu distances. Both Cu-zeolite catalysts before and after the reaction exhibit only a single peak at 1.54 Å, as shown in Fig. 8, representing that the copper species are in the form neither of CuO and Cu$_2$O nor of Cu(OH)$_2$. The 1.54 Å peak is associated with the local structure between the Cu ions and the nearest zeolite framework oxygen, as well known for Cu-FAU [Matsumoto and Tanabe, 1990; Piffer et al., 1991] and Cu-MFI [Hamada et al., 1990; Kharas et al., 1993; Nakayama et al., 1993; Tabata et al., 1994]. These EXAFS spectra clearly indicate that the loss of the catalytic activity in the wet condition does not result from the transformation of copper ions to copper oxides, CuO and Cu$_2$O on the catalyst surface.

From an earlier work by Auger spectroscopy for the two catalysts hydrothermally aged at 800 °C during a few hours (>4 h) under flowing either 7.3 or 10% of H_2O in He [Kim, 1996], the formation of CuO had been observed as confirmed by a Cu L_3VV Auger line. This may be in good agreement with the earlier observations for Cu-MFI catalyst [Kharas et al., 1993; Tabata et al., 1994]; however, the sintering may not be directly related with the immediate decrease in catalytic activity at low temperatures with water and the complete restoration of the catalytic activity upon switching the feed of water to the reactor periodically.

3-2-2. Competitive Adsorption of NO, HCs and H_2O

Temperature programmed desorption of H_2O was conducted on H-MOR, Cu-MOR-48 and Cu-NZA-44 to provide the major reason for the catalyst deactivation under a wet stream [Kim et al., 1997]. Large amounts of H_2O were adsorbed on H-MOR and desorbed continuously up to 500 °C, as shown in Fig. 9, and on Cu-MOR-48 up to 380 °C. Much less hydrophobic surface is evident for the natural zeolite-based catalyst on which H_2O desorption peaks at 150, 210, 250 and 460 °C appear, but the total amount of water desorbed is significantly small. Based upon the present result from H_2O TPD, the adsorption capacity and strength of water on H-MOR is much higher than that on Cu-MOR-48 catalyst. The synthetic and natural zeolites contain the respective Si/Al ratios of 5.2 and 9.2; therefore, this distinction may bring Cu-NZA-44 to exhibit the greatest surface hydrophobicity. A similar result has also been observed for MFI type zeolite; the surface hydrophobicity of the catalyst is a strong function of Si/Al ratio of the zeolite [Flanigen et al., 1978]. The Kubelka-Munk spectra indicated that water molecules bounded on the Cu ions, depending on the adsorption temperature of water on the catalyst surface [Kim et al., 1997]. This was in good agreement with the relative hydrophobicity of both Cu-exchanged zeolites by H_2O TPD. Water coordinated to the copper ions may inhibit the adsorption of NO on the catalyst surface. It may well be correlated with the competitive adsorption of NO, HCs and H_2O on the catalytic reaction sites.

A close relationship of the catalyst hydrophobicity with the competitive adsorption has been confirmed by the simultaneous adsorption of NO and HC on the catalyst surface with and without H_2O [Kim et al., 1997]. For Cu-MOR-48 catalyst shown in Fig. 10, the desorption peaks of NO$_x$ at 110, 160, 210 and 280 °C have been observed, regardless of the presence of H_2O in the feed gas stream; however, the adsorption capacity considerably decreases upon the simultaneous adsorption of NO and H_2O on the catalyst surface. Since NO adsorption on H-MOR catalyst contains only the three desorption peaks at 110, 160, and 210 °C obtained for Cu-MOR, the last one shown for Cu-exchanged catalyst at 280 °C may be assigned to Cu^{2+}-NO$_x$ species, indicating that the copper sites could

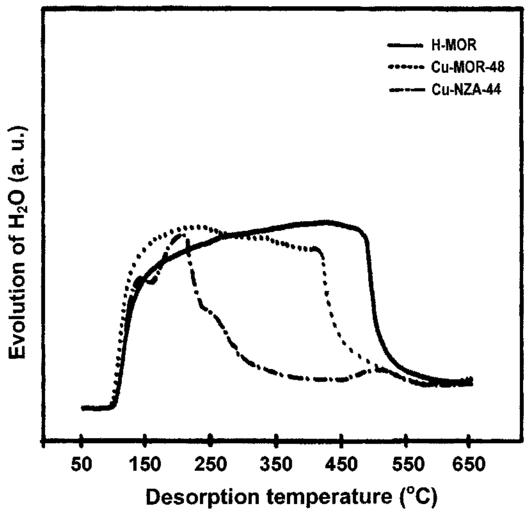

Fig. 9. Temperature-programmed desorption (TPD) of water for the catalysts. The ramping rate was 10 °C/min, and the carrier (He) flow rate was 40 cm^3/min [Kim et al., 1997].

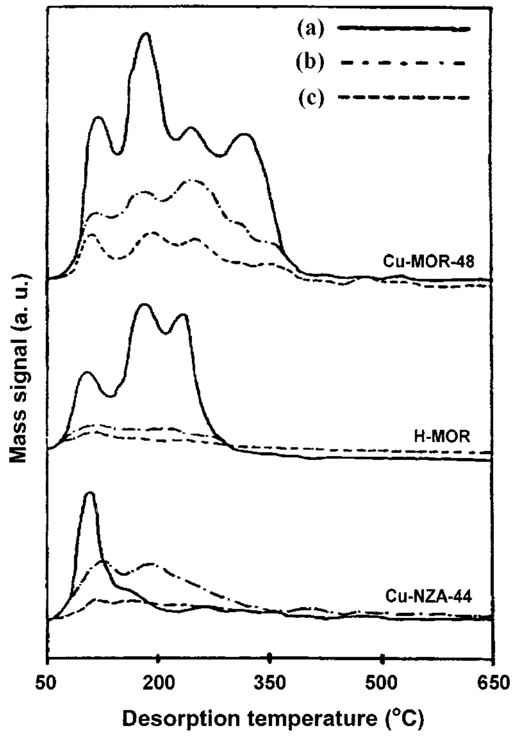

Fig. 10. Temperature-programmed desorption (TPD) of the catalysts adsorbing NO in the absence and presence of H_2O. (a) NO adsorption in the absence of H_2O; (b) summation of nitrogen compounds formed during NO adsorption in the presence of H_2O; (c) NO desorption after simultaneous adsorption of NO and H_2O. The ramping rate was 10 °C/min, and the carrier (He) flow rate was 40 cm^3/min [Kim et al., 1997].

be strongly inhibited by H_2O during NO adsorption with H_2O. The capability of H-MOR to adsorb NO in a wet stream is significantly low compared to that of Cu-MOR-48 catalyst.

Cu-NZA-44 catalyst contains three desorption peaks at 100, 146 and 230 °C when NO is only adsorbed on the catalyst surface, as also observed in Fig. 10. By the competitive adsorption of NO and H_2O, the amount of NO desorption from the catalyst surface severely decreases. However, the amount of total nitrogen compounds desorbed remains unchanged, implying that the adsorption sites on Cu-exchanged natural zeolite catalyst are still active even in the wet condition. The extent of the decrease of NO adsorption by H_2O well illustrates the water tolerance of the catalyst employed. It also agrees with the hydrophobicity of the catalyst surface. The complete reversibility of NO removal activity in dry and wet streams may be another evidence for the competitive adsorption of NO and water on the catalyst surface, which is consistent with the earlier results on Co-MFI-140, Co-MFI-98, Co-FER-78 and Co-MOR-94 [Li and Armor, 1993; Li et al., 1993], Cu-MFI-157 [Iwamoto et al., 1992], Pd-MOR [Uchida et al., 1996] and Co-FER-98 [Lee et al., 2001].

Water could also affect the adsorption of hydrocarbon on the surface of the catalyst [Kim, 1996; Kim et al., 1997]. In a representative experiment for C_3H_6 TPD over Cu-NZA-44 catalyst, the adsorption of C_3H_6 without H_2O allowed two prominent desorption peaks at 100 and 350 °C [Kim et al., 1997]. Although the simultaneous adsorption of C_3H_6 and H_2O on the catalyst surface leads a significant decrease in the amounts of the desorption of C_3H_6 at the temperatures ranging from 130 to 250 °C, the amount of chemisorbed C_3H_6 on the catalyst surface at 350 °C maintains even in a wet stream. For the adsorption of C_2H_4 on the catalyst without H_2O, a doublet peak for its desorption below 200 °C has been observed with a broad one and centered at 370 °C. However, the intensity of the peaks decreases for the simultaneous adsorption of C_2H_4 and H_2O.

By a comparison of the desorption amounts of both HCs on the catalyst surface from 200 to 500 °C, it is evident that the adsorption capacity of C_3H_6 on the surface of Cu-NZA-44 is much greater than that of C_2H_4, irrespective of the presence of H_2O, and C_3H_6 is predominantly chemisorbed on the catalyst surface even under the wet condition, thereby providing an excellent activity maintenance in a catalytic system using Cu-NZA-44 with C_3H_6. This is quite consistent with the large amount of chemisorption and the high heat of adsorption of C_3H_6 compared to those of C_2H_4 [Kim, 1996; Kim et al., 1997]. The competitive adsorption of NO, HCs and H_2O leads to lower coverage on the catalyst surface for the chemisorption of NO and HCs, thus causing the loss of the catalytic activity in the presence of H_2O. This is also in good agreement with the observation in which smaller amounts of NO and HCs could be adsorbed on wet surfaces of Cu-MFI-111, Co-MFI-117 and Co-BEA-80 [Tabata et al., 1996] as well as of Pd-MFI catalyst [Ogura et al., 1999]. In addition, further reaction of HCs with H_2O could be a minor reason for the catalyst deactivation for SCR by HCs in a wet feed gas stream [Kim et al., 1997].

3-3. An Approach to Improve Water Tolerance

The water tolerance of zeolite-based deNO$_x$ catalysts for NO reduction by HCs strongly depends on the surface hydrophobicity of the catalyst which could be closely related to the competitive adsorption among NO, HCs and H_2O, as proposed by Kim et al. [1997].

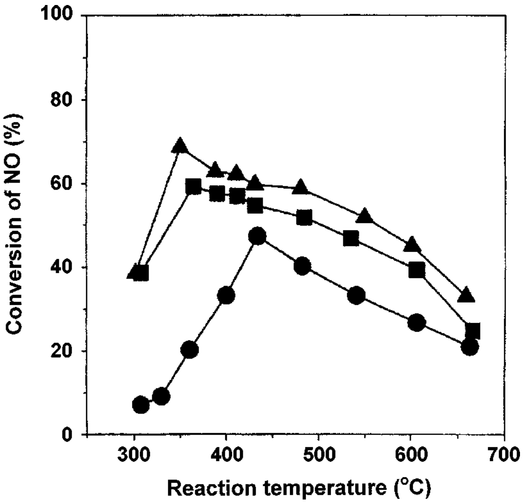

Fig. 11. NO removal activity of dealuminated Cu-MOR catalysts: (●) Cu-MOR-32 (6); (■) Cu-MOR-68 (12); (▲) Cu-MOR-90 (22). Reaction condition: NO 1,200 ppm, C_3H_6 1,600 ppm, O_2 3.2%, H_2O 10%, CO 3,000 ppm, H_2 1,000 ppm and CO_2 10% [Chung et al., 1999].

It is widely accepted that the hydrophobicity is associated with the ratio of silicon to aluminum in the structure of zeolite [Flanigen et al., 1978], anticipating that the surface of zeolite-based catalysts becomes hydrophobic as the Si/Al ratio of zeolite increases. Under a simulated lean NO$_x$ wet condition, the water tolerance of synthetic and natural MOR type zeolites containing a variety of Si/Al ratios, prepared by a common dealumination procedure, has been investigated, as shown in Fig. 11 [Chung et al., 1999]. Cu-MOR-32 (6) catalyst revealed 45% of NO conversion at 450 °C. Note that hereafter the Si/Al ratio of each catalyst is expressed in parenthesis followed by the exchanging ratio of the metal. Through the progressive dealumination of H-MOR from the Si/Al ratio of 5 to 22, the deNO$_x$ activity within the wide range of the reaction temperature significantly improves as the ratio increases.

The enhancement of the catalyst water tolerance is mainly attributed to the increase in the Si/Al ratio of zeolite, which has been also confirmed by the comparison of NO removal activity for Cu-MOR catalyst containing a variety of Cu/Al ratios at the given Si/Al ratio. NO removal activity of Cu-MOR-60 (5) catalyst is almost identical to that of Cu-MOR-32 (6) [Chung et al., 1999], although the maximum conversion of NO for the catalyst containing the low ratio of Cu/Al, shifts slightly to the high reaction temperature. A similar observation has also been made for the catalysts containing identical Si/Al ratio, such as Cu-MOR-28 (12) and Cu-MOR-68 (12) at the reaction temperature higher than 350 °C. However, the wet activity of Cu-MOR-28 (12) is much higher than that of Cu-MOR-32 (6) and this trend is also observed for Cu-MOR-60 (5) and the Cu-MOR-68 (12) [Chung et al., 1999].

The dependence of the water tolerance of zeolite catalyst on the Si/Al ratio was quite peculiar for Cu-MOR type catalyst as shown in Fig. 12. Three kinds of Cu-NZA catalyst in which the Cu/Al ratio of the catalysts is basically equal reveal the distinctive activity maintenances with respect to the Si/Al ratio of the catalysts. This clearly shows that the water tolerance is a strong function of the Si/Al ratio. It is also in good agreement with an earlier study on the deNO$_x$ ac-

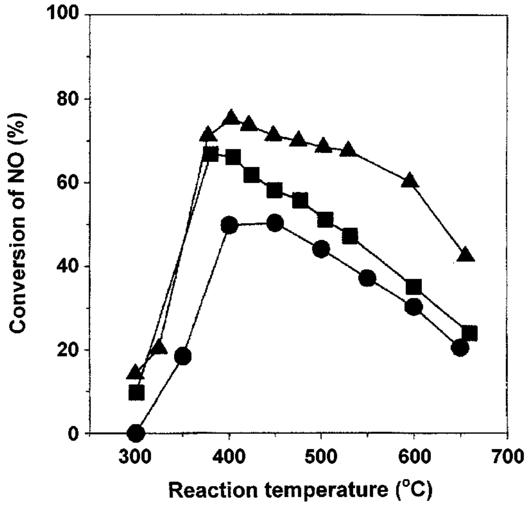

Fig. 12. NO removal activity of dealuminated Cu-NZA catalysts: (●) Cu-NZA-50 (4); (■) Cu-NZA-48 (10); (▲) Cu-NZA-56 (14). Reaction condition: NO 1,200 ppm, C_3H_6 1,600 ppm, O_2 3.2%, H_2O 10%, CO 3,000 ppm, H_2 1,000 ppm and CO_2 10% [Chung et al., 1999].

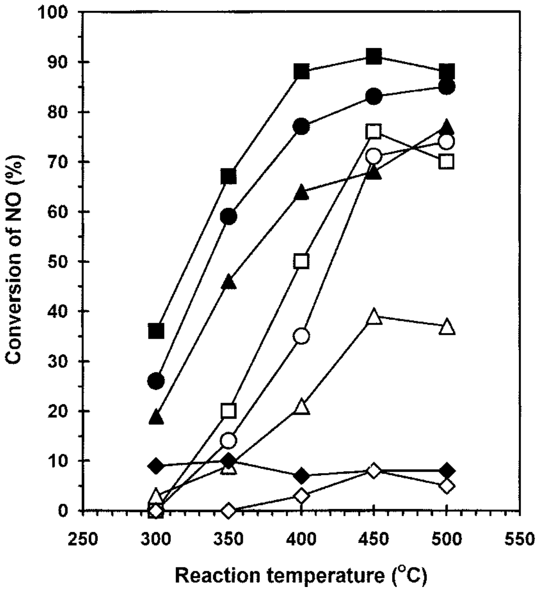

Fig. 13. Activity of Pd-MFI catalysts for the reduction of NO by CH_4 with and without H_2O: (●, ○) Pd-MFI-6 (15); (■, □) Pd-MFI-10 (15); (▲, △) Pd-MFI-10 (25); (◆, ◇) Pd-MFI-22 (75). Reaction condition: NO 150 ppm, CH_4 2,000 ppm, O_2 10% and H_2O 0 (closed symbols) or 9% (open symbols) [Ohtsuka and Tabata, 2000].

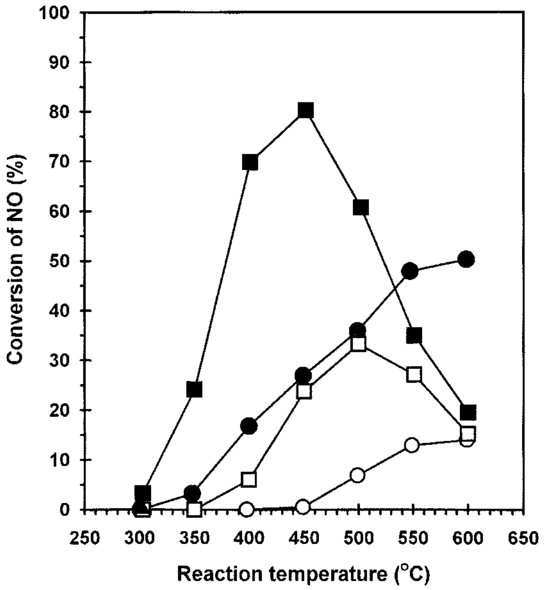

Fig. 14. NO removal activity of PdCo-FER catalyst for the reduction of NO by CH_4: (●, ○) Co-FER-44; (■, □) PdCo-FER-54. Reaction condition: NO 1,200 ppm, CH_4 1,600 ppm, O_2 3.2% and H_2O 0 (closed symbols) or 10% (open symbols) [Lee et al., 2001].

tivity of Cu-MFI-80 (27) and (11) by C_3H_6 with 2% of H_2O at temperatures below 400 °C [Torre-Abreu et al., 1997]. Recently, the influence of Si/Al ratio on the wet activity of Pd-MFI catalysts with respect to the ratio of Pd/Al has also been examined by Ohtsuka and Tabata [2000], as illustrated in Fig. 13. Pd-MFI-6 (15) catalyst reveals 78% of dry activity for NO reduction by CH_4 at 400 °C, while the presence of 9% H_2O decreases NO conversion to 34%, indicating that Pd ions are active reaction sites for the removal reaction but too sensitive to maintain its dry activity. When the Pd/Al ratio increases, the catalytic activity becomes higher in the absence of H_2O but the water tolerance is not improved. If parent MFI zeolite containing a high Si/Al ratio of 25 is employed for preparing Pd-MFI-10 catalyst, the dry performance is not improved at all. As the Si/Al ratio increases, the catalytic activity decreases and the higher Si/Al ratio cannot improve the water tolerance, either. It implies that the dealumination of zeolites, thereby increasing the Si/Al ratio, is a useful way for improving the water tolerance of the catalyst; however, optimal Si/Al and metal/Al ratio depending on zeolite structures should be selected to obtain the best performance of the catalyst in a wet stream.

Another approach for improving the water tolerance of zeolite catalysts is to introduce second metal ions into single metal-exchanged zeolite. In a such attempt with Co-FER-44 catalyst for reducing NO by CH_4 in the presence and absence of H_2O [Lee et al., 2001], the NO removal activity was about 27% in terms of NO conversion at 450 °C over the catalyst without H_2O but dropped to less than 1% under a wet condition with 10% of H_2O, as shown in Fig. 14. If a small amount of Pd (Pd/Al=0.04) is exchanged into H-FER after which Co ions at the ratio of Co/Al=0.23 are subsequently introduced into the Pd-FER sample, 80% of NO conversion at 450 °C is obtained with a dry feed gas stream and the presence of 10% H_2O allows the NO conversion of 24%. It is interesting to note that the degree of dry activity loss by H_2O is in the range of 27% of NO conversion for Co-FER-44 catalyst in which the Co/Al ratio is similar to the total metal to aluminum ratio, (Pd+Co)/Al=0.27. Not only could the pre-exchanged Pd ions play an important role in improving the water tolerance, but they can also enhance the dry performance of the catalyst. Other cocations, *i.e.*, In and La, are also useful in improving the water tolerance of Co-FER catalyst [Lee et al., 2001]. This result is also quite consistent with earlier and recent developments in this area of research.

Table 4. Physicochemical properties of MOR structure zeolite catalysts with and without a hydrothermal aging

Catalyst[a]	Cu content (wt%)[b]	Si/Al[b]	Cu/Al[b]	Surface area (m^2/g)	
				Fresh	Hydrothermally-aged[c]
H-MOR (5)		5		449	
H-MOR (10)		10			
H-MOR (20)		20		449	
Cu-MOR-32 (6)	2.02	6	0.16	368	22
Cu-MOR-60 (5)	4.20	5	0.30		
Cu-MOR-68 (12)	2.55	12	0.34	434	154
Cu-MOR-28 (12)	1.03	12	0.14		
Cu-MOR-90 (22)	1.73	22	0.45	450	330
Cu-NZA[d]-50 (4)	4.37	4	0.25	179	
Cu-NZA[d]-48 (10)	1.84	10	0.24	232	26
Cu-NZA[d]-56 (14)	1.75	14	0.28		
Cu-NZA[d]-62 (19)	1.64	19	0.31	128	
Cu-MFI-162 (26)	2.90	26	0.81	344	249
					27[e]

Note. This table was prepared using data published by Chung et al. [1999].

[a] Numbers next to the zeolite structure designate the exchange percentage of each metal ion.

[b] Based on fresh samples.

[c] Under flowing 10% H_2O in He 800 °C for 24 h.

[d] Natural zeolite consisting mainly of a MOR structure.

[e] At 900 °C.

By adding small amounts of Na and Ba to Cu-based MOR catalyst at the given ratio of Cu/Al (0.10), improved performance of the catalyst for NO reduction by C_3H_6 in the presence of 2% H_2O was obtained compared to Cu-MOR-20, but all the catalysts in the presence of H_2O were deactivated in the range of NO conversion less than 20% [Torre-Abreu et al., 1997]. For Pd (0.4 wt%)-MFI catalyst without Co ions, the conversion of NO at 500 °C was in the range of 5% when 10% of H_2O existed in the feed gas stream, while 64% of NO conversion was attained for Pd-MFI catalyst containing 3.3 wt% of Co ions. A similar role of second metals in improving the water tolerance of $deNO_x$ catalysts has also been observed for Pd/Ag/H-MOR [Masuda et al., 1998], Ce-Ag-MFI [Li and Flytzani-Stephanopoulos, 1999], Pt-In-FER [Ramallo-Lopez et al., 2001], Pt-Co-MOR [Gutierrez et al., 2001] and Pt-Co-MFI [Maisuls et al., 2001] for NO reduction by HCs in a wet condition.

4. Hydrothermal Stability of HC-SCR $DeNO_x$ Catalysts

Few investigations concerning the hydrothermal stability of $deNO_x$ catalyst for NO removal reaction with HCs could be found in the literature. Hydrothermal stability has been examined for Cu-SAPO-75 and Cu-MFI (unknown Cu content) [Ishihara et al., 1997]. The catalyst samples have been aged under flowing of 3% H_2O in air for 2 h at the temperatures 500, 700 and 800 °C to examine the hydrothermal stability of the catalyst. Although Cu-SAPO catalyst revealed strong hydrothermal stability, both catalysts after the aging at 800 °C showed the catalyst deactivation within the reaction temperatures covered. The dependence of the stability on the aging temperature has been also observed for Ce-Ag-MFI catalyst aged in He containing 14% of water for 24 h with respect to the temperatures [Li and Flytzani-Stephanopoulos, 1999]. In an earlier attempt to investigate the effect of Si/Al ratio of zeolite on the stability of Cu-MFI [Torre-Abreu et al., 1997], the activity maintenance of the catalyst containing high Si/Al ratio was stable according to the comparison of the catalyst deactivation of Cu-MFI-40 (11) and Cu-MFI-80 (27) catalysts, indicating that hydrothermal stability can be improved by an increase of the Si/Al ratio of the catalyst.

A systematic study to provide the dominant parameter in determining the hydrothermal stability of zeolites has been postulated for MOR type zeolites. Chung et al. [1999] have attempted to illustrate the main role of Si/Al ratio in improving the hydrothermal

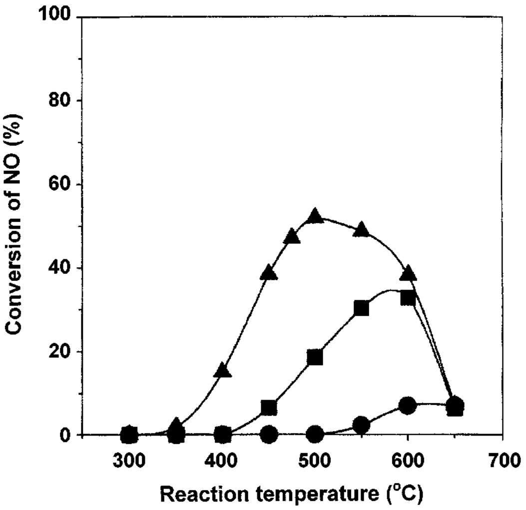

Fig. 15. Hydrothermal stability of dealuminated Cu-MOR catalysts: (●) Cu-MOR-32 (6); (■) Cu-MOR-68 (12); (▲) Cu-MOR-90 (22). Reaction condition: NO 1,200 ppm, C_3H_6 1,600 ppm, O_2 3.2%, H_2O 10%, CO 3,000 ppm, H_2 1,000 ppm and CO_2 10% [Chung et al., 1999].

stability of synthetic Cu-MOR catalysts containing the variety of the Si/Al ratios, as listed in Table 4. The catalyst was prepared by using a typical dealumination technique of zeolite with hydrochloric acid. As shown in Fig. 15, zero activity at the temperatures below 550 °C under a simulated lean NO$_x$ condition has been observed for Cu-MOR-32 (6) catalyst hydrothermally aged at 800 °C in a flowing mixture of 10% H_2O/90% He for 24 h. The dealuminated Cu-MOR catalysts exhibit strong activity maintenance with respect to the Si/Al ratio of the catalysts: the NO conversions after aging are 50, 20 and 0% for Cu-MOR-90 (22), Cu-MOR-68 (12) and Cu-MOR-32 (6) at 500 °C, respectively. It clearly presents that hydrothermal stability could be improved by dealumination, thereby increasing the Si/Al ratio of the catalyst.

The dependence of hydrothermal stability on the Si/Al ratio for MOR type Cu-NZA catalyst has been also examined [Chung et al., 1999]. Essentially, the same trend in the hydrothermal stability has been observed as the Si/Al ratio increases. It may be a typical example presenting the close relationship of the Si/Al ratio of zeolites with the hydrothermal durability of the catalyst in the present reaction system. Although the catalyst deactivation by sintering can be improved by the modification of the Si/Al ratio of zeolite, the catalyst still reveals the loss of NO removal activity compared to that of the fresh catalyst. This could be mainly due to the destruction of zeolite structure during the hydrothermal aging, thus resulting in the sintering of active reaction site, Cu^{2+} ions on the catalyst surface to CuO species, as extensively observed by BET, XRD and ESR studies [Chung et al., 1999]. A typical evidence for the zeolite structure destruction upon the hydrothermal aging could be provided by BET surface area measurements, as listed in Table 4. It is also in good agreement with the formation of CuO on the surface of Cu-MOR-48 catalyst when hydrothermally aged under the similar sintering condition, as illustrated by AES [Kim, 1996].

In addition, the hydrothermal stability of Pd-MFI-14 (25) and Pd-silicallite-40 (131) aged at 800 °C for 6 h under N_2 flow with 10% H_2O has been also examined, and they are seriously deactivated even in dry stream probably due to the agglomeration of active Pd ions and their transformation to PdO species, as confirmed from XRD, TEM and NMR studies [Descorme et al., 1997]. It has been observed that the hydrothermal durability of zeolite mainly depends on both exchanged metal and its type [Ohtsuka and Tabata, 1999].

5. General Remarks

Inhibiting NO and HC adsorption sites on the catalyst surface by water is one of the main reasons for the loss of catalytic activity for the reduction of NO by HCs over zeolite catalyst. It well elucidates the cause of the catalyst deactivation by water, regardless of the degree of the activity loss. Surface hydrophobicity of zeolite catalyst may play a critical role in determining the extent of the catalyst deactivation in a wet stream. The reversibility of the catalyst deactivation by the existence of water in the feed gas stream may be an experimental evidence for the competitive adsorption of the reactants including water during the course of the reaction. It has also been observed for the decomposition of NO over excessively ion-exchanged Cu-zeolite. However, it becomes complicated due to the chemical alteration of metal ions to metal oxides after aging in a wet stream, as extensively discussed. This implies that no single cause can elucidate the catalyst deactivation by water for the reduction of NO by HCs. It varies with the catalyst, the reductant and the operating condition employed for the reduction.

No HC-SCR catalyst without the catalyst deactivation by water has been proposed so far. The extent of the activity loss for the reduction of NO$_x$ by NH_3 in a wet stream strongly depends on the catalyst employed. In general, negligible activity decrease in the reduction even with H_2O has been observed for V_2O_5/TiO_2 catalyst, a commercial deNO$_x$ catalyst by NH_3; NO removal activity simply shifts to the region of the high reaction temperature where the effect of water becomes negligible. This may be due to the distinction of the reaction mechanism depending upon the catalyst. Earlier studies indicate that NO removal reaction of V_2O_5/TiO_2 proceeds on the basis of Eley-Rideal (ER) kinetic mechanism, while that for Cu-MOR catalyst occurs by Langmuir-Hinshelwood Hougen Watson (LHHW) mechanism. This leads to the fact that the reaction mechanism can vary with the catalysts employed. If the catalytic deNO$_x$ reaction with NH_3 over V_2O_5/TiO_2 catalyst was governed by the latter mechanism, significant activity loss at low reaction temperatures in the presence of H_2O should be unavoidable. The major distinction of the reaction mechanisms described may be the adsorption of NO on the catalyst surface along with NH_3 and water. No adsorption of NO is generally known for SCR of NO by NH_3 based upon ER mechanism. Since the catalytic reduction of NO$_x$ by HCs takes place by LHHW mechanism, a future approach for developing the catalyst containing strong water tolerance may be first directed to understand the reaction mechanism of the reduction of NO by HCs.

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