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APPENDIX A

SAMPLE OF CALCULATIONS

A-1 Calculation of Si/Al Atomic Ratio for ZSM-5

The calculation is based on weight of Sodium Silicate ($\text{Na}_2\text{O} \cdot \text{SiO}_2 \cdot \text{H}_2\text{O}$) in B1 and B2 solutions. (Topic 4.1.1)

M.W. of Si	=	28.0855
M.W. of SiO_2	=	60.0843
Weight percent of SiO_2 in Sodium Silicate	=	28.5
M.W. of Al	=	26.9815
M.W. of AlCl_3	=	133.3405
Weight percent purity of AlCl_3	=	97

For example, to prepare ZSM-5 at Si/Al atomic ratio of 50.

Using Sodium Silicate 69 g with 45 g of water as B1 solution.

$$\begin{aligned} \text{mole of Si used} &= \frac{\text{wt. (\%)} \cdot (\text{M.W. of Si}) \cdot (1 \text{ mole})}{100 \cdot (\text{M.W. of SiO}_2) \cdot (\text{M.W. of Si})} \quad (\text{A-1.1}) \\ &= 69 \cdot (28.5/100) \cdot (1/60.0843) \\ &= 0.3273 \end{aligned}$$

Si/Al atomic ratio = 50

$$\begin{aligned} \text{mole of AlCl}_3 \text{ required} &= 0.3273/50 = 6.5458 \cdot 10^{-3} \text{ mole} \\ \text{amount of AlCl}_3 &= 6.5458 \cdot 10^{-3} \cdot 133.34 (100/97) \\ &= 0.8998 \text{ g} \end{aligned}$$

which used in A1 and A2 solutions

A-2 Calculation of the amount of metal ion-exchanged ZSM-5

For example: Determine the amount of Cu into catalyst = 0.2 wt.%

the catalyst use = x g

$$\text{so that } \text{Cu}/(\text{x}+\text{Cu}) = 0.2/100$$

$$100 \cdot \text{Cu} = 0.2 \cdot (\text{x}+\text{Cu})$$

$$(100-0.2) \cdot \text{Cu} = 0.2 \cdot \text{x}$$

$$\text{thus } \text{Cu} = 0.2 \cdot \text{x}/(100-0.2) \text{ g}$$

use $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ (M.W. 241.60, 26.30%Cu, purity 99.5%)

$$\begin{aligned} \text{weight of } \text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O} &= [0.2 \cdot \text{x}/(100-0.2)] \cdot [(100/26.30) \cdot \\ &(100/99.5)] \end{aligned}$$

A-3 Calculation of percent weight of copper in catalysts

Since the total copper content in catalysts used in this study were determined by AAS analysis, and the obtained results are always show as concentration of copper in prepared solution, it would better convert to the conventional value (% wt./ g. cat.)

$$\text{Weight of catalyst used for digestion} = w \text{ g.}$$

$$\text{Volume of solution obtained from digestion} = 50 \text{ ml.}$$

From the result of AAS analysis

$$\text{Concentration of copper in digested solution} = C \text{ ppm}$$

Thus,

Amount of copper in solution (50 ml.)

$$= \text{Amount of copper in digested solution}(w \text{ g.})$$

$$= (C * 50)/(1 \times 10^6) \text{ g.}$$

$$\text{Amount of copper in 1 g. catalyst} = (C * 50)/(1 \times 10^6 * w) \text{ g.}$$

Thus,

$$\text{Copper content in catalyst} = (C * 50 * 100)/(1 \times 10^6 * w) \text{ wt.}\% \quad (\text{A-3.1})$$

$$= 0.005 \cdot C/w \text{ wt.}\% \quad (\text{A-3.2})$$

A-4 Calculation of gas velocity

The catalyst used = 0.50 g

packed catalyst into quartz reactor (diameter = 0.6 cm)

determine the average high of catalyst bed = x cm

So that, volume of catalyst bed = $p \cdot (0.3)^2 \cdot x$ ml-catalyst

used GHSV (Gas Hourly Space Velocity) = $4,000 \text{ h}^{-1}$

$$\text{GHSV} = \frac{\text{Volumetric flow rate}}{\text{Volume of Catalyst}} = 4,000 \text{ h}^{-1}$$

$$\begin{aligned} \text{Volumetric flow rate} &= 4,000 \cdot \text{Volume of catalyst} \\ &= 4,000 \cdot p (0.3)^2 \cdot x \quad \text{ml/h} \\ &= 4,000 \cdot p (0.3)^2 \cdot x / 60 \quad \text{ml/ min} \end{aligned}$$

$$\text{at STP : Volumetric flow rate} = \frac{\text{Volume flow rate} \cdot (273.15+t)}{273.15} \quad (\text{A-4.1})$$

273.15

where : t = room temperature, °C

A-5 Calculation of NO and C₃H₈ conversion

The effluent gas was analyzed by gas chromatography, the NO reduction activity was evaluated in terms of the conversion of NO into N₂.

$$\text{NO Conversion (\%)} = (2[\text{N}_2]_{\text{out}} / [\text{NO}]_{\text{in}}) \cdot 100$$

The C₃H₈ oxidation activity was evaluated in terms of the conversion of C₃H₈ into CO and CO₂.

$$\text{C}_3\text{H}_8 \text{ Conversion (\%)} = \frac{([\text{C}_3\text{H}_8]_{\text{in}} - [\text{C}_3\text{H}_8]_{\text{out}})}{[\text{C}_3\text{H}_8]_{\text{in}}} \cdot 100 \quad (\text{A-5.1})$$

A-6 Calculation of gas specie adsorbed on catalyst

The weight of catalyst used	=	w	g.
Area of gas peak after adsorption	=	A	unit.
Average area of 30 μ l. standard gas peak	=	B	unit.
Amounts of gas adsorbed on catalyst	=	B-A	unit.
Volume of gas adsorbed on catalyst	=	$[(B-A)/B]*30$	μ l.
Volume of gas 1 mole at 30 °C	=	$24.86*10^6$	μ l.
Mole of gas adsorbed on catalyst	=	$[(B-A)/B]*[30/24.86*10^6]$	
	=	C	mol
Amount of gas adsorbed on catalyst per catalyst weight			
	=	$C*10^6/w$	μ mol/g

A-7 Calculation of Equilibrium Conversion of Reaction

At an equilibrium of a reaction, the equilibrium constant, K, can be evaluated from the relation:

$$\Delta_r G = -RT \ln K \quad (\text{A-7.1})$$

where $\Delta_r G^\circ$ is the standard Gibbs energies of the reaction at temperature T, which is expressed in terms of the standard Gibbs energies of formation, $\Delta_f G^\circ$, of each reactant or product as:

$$\Delta_r G^\circ = \Delta_r H^\circ + T(S^\circ - \sum v_i S^\circ_i(\text{elem})) \quad (\text{A-7.2})$$

where $\Delta_r H^\circ$ is the standard enthalpy of formation of the substance which little change with temperature

S° is the standard entropy of the substance

and $\sum \nu_i S^\circ_i(\text{elem})$ is the sum of the standard entropies of the elements in the formation reaction of the desired substance.

The standard entropy at any temperature can be determined by :

$$S^\circ_T = S^\circ_{298} + \int_{298}^T \frac{C_p}{T} dT \quad (\text{A-7.3})$$

where S°_{298} is the standard entropy at the standard temperature (25 °C) and C_p is specific capacity of the substance which can be calculated the explicit correlation functional in term of temperature showed as:

$$C_p = A + BT + CT^2 + DT^3 \quad (\text{A-7.4})$$

where A, B, C, and D are constants specified for each substance.

If C_p in equation (A-7.3) was substituted by equation (A-7.4), the equation could be integrated and the result was showed as follows:

$$S^\circ_T = S^\circ_{298} + A \ln(T/298) + B(T-298) + C(T^2 - 298^2)/2 + D(T^3 - 298^3)/3 \quad (\text{A-7.5})$$

All above equations (A-7.1-4) are used to determine the equilibrium conversion of a reaction. For example, for the NO disproportionation which the reaction is showed as:



$$K_p = \frac{(P_{\text{N}_2\text{O}})^{1/2} (P_{\text{NO}_2})^{1/2}}{P_{\text{NO}}}$$

$$= \frac{(X_{\text{N}_2\text{O}})^{1/2} (X_{\text{NO}_2})^{1/2}}{X_{\text{NO}}} \quad (\text{A-7.6})$$

The composition of feed is 1.2 % NO and 98.8 % N₂ , so , at equilibrium, the composition of each gas would be

$$X_{N_2O} = 1/2(0.012 - X_{NO})$$

$$X_{NO_2} = 1/2(0.012 - X_{NO})$$

Substitute into equation (A-7.6), gives

$$K_p = \frac{(0.012 - X_{NO})}{2X_{NO}} \quad (A-7.7)$$

X_{NO} can be showed in term of K_p as

$$X_{NO} = 0.012/(1 + 2K_p) \quad (A-7.8)$$

K_p can be calculated by equation (A-7.1) which Gibbs energy of the NO disproportionation given from

$$\Delta_f G_{\text{reaction}} = 1/2 \Delta_f G_{N_2O} + 1/2 \Delta_f G_{NO_2} - \Delta_f G_{NO}$$

From equation (A-7.2), the Gibbs energy of each gas can be evaluated by following terms:

$$\Delta_f G_{NO} = \Delta_f H_{NO} - T(S^{\circ}_{NO} - 0.5S^{\circ}_{N_2} - 0.5S^{\circ}_{O_2})$$

$$\Delta_f G_{NO_2} = \Delta_f H_{NO_2} - T(S^{\circ}_{NO_2} - 0.5S^{\circ}_{N_2} - S^{\circ}_{O_2})$$

$$\Delta_f G_{N_2O} = \Delta_f H_{N_2O} - T(S^{\circ}_{N_2O} - S^{\circ}_{N_2} - 0.5S^{\circ}_{O_2})$$

Assume $\Delta_f H$ of each gas is constant independent with temperture and equal $\Delta_f H_{298}$

S° of each can be calculated by using equation (A-7.3,5) which A, B, C and D constants and the other values are showed as follow:

	NO	NO ₂	N ₂ O	N ₂	O ₂
A [J/mol.K]	29.35	24.23	21.62	31.15	28.11
B x 10 ⁴ [J/mol.K]	-9.378	483.6	728	-135.7	-0.037
C x 10 ⁶ [J/mol.K]	9.747	-20.81	-57.8	26.8	17.46
D x 10 ⁹ [J/mol.K]	-4.19	0.29	18.3	-11.68	-10.65
$\Delta_f H_{298}$ [J/mol]	90430	33870	81600	0	0
S°_{298} [J/mol.K]	210.76	240.03	220.05	191.61	205.14

The equilibrium constant and equilibrium conversion would then determined by equation(A-7.1) and (A-7.8). The results of the reaction of NO disproportionation are summeried below:

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APPENDIX B

PROPERTIES OF SUBSTANCES

B-1 Nitric oxides**Physical properties of NO**

Property	Value
mol. wt.	30.1
m.p., °C	-161
b.p., °C	-151.18
heat of fusion, kJ/mole	2.3023
heat of vaporization, kJ/mole	13.78
heat of formation, kJ/mole	90.00
density [0 °C, 1 atm], g/L	1.2536
sp. gr., gas, [0 °C, 1 atm], (air = 1)	-93
critical temperature, °C	1.018
critical pressure, atm at -94.8 °C	64
color	colorless gas, blue liquid and solid
odor	odorless
flash point	non - flammable
threshold limit value	25 ppm , 30 mg/m ³

Hazard and noxious effect.

Nitric oxide is converted in air to nitrogen dioxide, but at concentration below 50 ppm this conversion is slow

Animal experiments indicate Nitric oxide about 1/5 as toxic as nitrogen dioxide

Nitric oxide's chief toxic effect has been attributed to the formation of methemoglobin followed by central nervous system effects

In mixed exposure with either carbon monoxide or nitrogen dioxide, additive effects should be assumed.

60 to 150 ppm, cause immediate nose & throat irritation with coughing and burning in the chest and throat.

100 to 150 ppm are dangerous for short exposures(30 to 60 minutes)

It is able to reach all parts of the respiratory system because of its low solubility in water. It diffuses through the Alveolar-cells and the adjacent capillary vessels of the lungs and damages the Alveolar-structures and their function throughout the lungs.

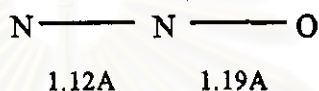
Chronic exposure may cause respiratory tract irritation, cough headache, appetite loss, teeth corrosion and dyspepsia.

It also play a major role in the photochemistry of the troposphere and the stratosphere. NO is rapidly oxidized by atmospheric oxidants such as ozone. NO₂ itself is a precursor for nitric acid, which contributes substantially to so-called acid rain. NO₂ is formed through oxidation of NO with ozone or through photochemically-generated peroxy radicals.

Species of oxides of nitrogen

N₂O. Nitrous oxide

Nitrous oxide is a colourless gas, Of the nitrogen oxides, it is the least reactive and moxious, being ralatively inert at room temperature and used as an anesthetic. A 500 C it decomposes to O₂, N₂ and NO and will be support the combustion of hydrogen and hydrocarbon. Nitrous oxide is is electroni with CO₂ and has the linear structure expected on this basis:



NO. Nitrogen oxide

NO is a colourless gas with a rather low condensation temperature of -152 °C. The electronic structure of NO is interesting because the molecules has an odd number of electrons. It has three pair pairs of bonding electrons and one antibonding electrons. The bond lengths and energies of NO and NO⁺ are compared as shown below:



Gaseous nitric oxide reacts directly with O₂ to form the red brown gas nitrogen dioxide, NO₂:



N₂O₃. Dinitrogen trioxide

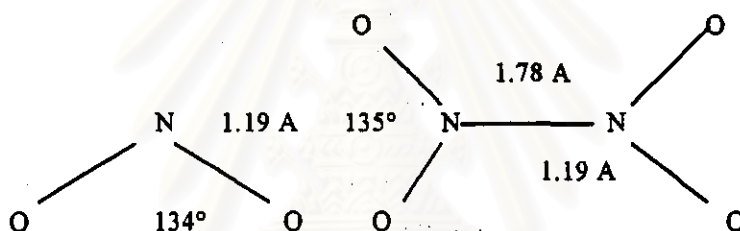
N₂O₃ exists as a blue solid at low temperatures, but in liquid and vapor state it largely dissociates to NO and NO₂.

NO₂ and N₂O₄. Nitrogen dioxide and dinitrogen tetroxide

NO_2 and N_2O_4 exist as gases in equilibrium with each other:

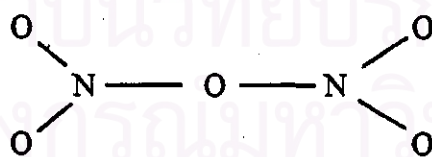


The dimer N_2O_4 has a planar structure, and the nitrogen-nitrogen bond is remarkably long and weak ($D^\circ(\text{N-N}) = 57.2 \text{ kJ/mol}$) compared to single bonds between nitrogen atoms in other molecules. At the 134° the bond angle in NO_2 is intermediate between the angles found in the related ions NO_2^+ (180°) and NO_2^- (116°). This is a specific sample of the general observation that among triatomic and ions:



N_2O_5 , Dinitrogen pentoxide

N_2O_5 is colorless gas which is the anhydride of nitric acid. Although the structure of N_2O_4 is not known in detail, the general arrangement of the atoms is given by



In addition, there are some important ions of oxides of nitrogen such as:

NO_2^+ : Nitronium ion

NO_3^- : Nitrate ion

NO_2^- : Nitrite ion

etc.

B-2 ZSM-5

Zeolite ZSM-5 can be constructed from five -member ring building units. These units link together to form chains leads to the formation of the channel system in the structure. The combination of these building units results in a framework containing two intersecting channel systems, one sinusoidal and the other straight. The pore openings are elliptical 10 - member rings. This structure is successfully described in the orthorhombic space group Pnma; however, it shows a reversible phase transition at about 330 K (though the temperature on the aluminum content to monoclinic symmetry). Below this temperature, the symmetry is monoclinic, and it is orthorhombic above the transition temperature. At room temperature this change in symmetry is observed upon absorption of molecules into the pores.

Properties of ZSM-5

Chemical Composition	$(\text{TPA,Na})_2\text{O} \cdot \text{Al}_2\text{O}_3 \cdot 5\text{-}100\text{SiO}_2 \cdot 4\text{H}_2\text{O}$
Symmetry	Orthorhombic
Space Group	Pnma
Unit Cell Constants (Å)	a = 20.1 b = 19.9 c = 13.4
Void Volume	0.10 g/cc
Pore Structure	Three-dimension intersecting 10 - member rings 5.3 x 5.6 Å and 5.1 x 5.5 Å

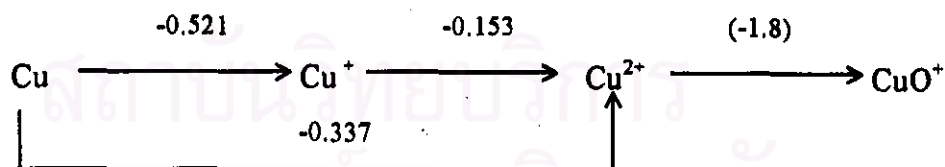
X-Ray Powder Diffraction Data of typical ZSM-5: (d(A°) (I/I₀))

11.10(s)	10.00(s)	7.40(w)	7.10(w)
6.30(w)	6.04(w)	5.97(w)	4.60(w)
4.25(w)	3.85(vs)	3.71(s)	3.04(w)
2.99(w)	2.94(w)		

*	w	=	weak
	s	=	strong
	vs	=	very strong

B-3 Copper

The copper family, following immediately after the transition metals, comprises the elements copper, silver and gold, with atomic numbers 29, 47 and 79 respectively. The atoms of all three members of this family possess ground state electronic configurations of the type $(n-1)d^{10}ns^1$. This thus is indicated by the fact that all three exhibit not only the monovalent oxidation state, which might be expected from the electron configuration, but the higher oxidation states +2 and +3 as well. However, in the most common compounds, copper is found in the +1 or the +2 oxidation states which are called cuprous and cupric ion respectively. The important oxidation potential relationships are summarized.

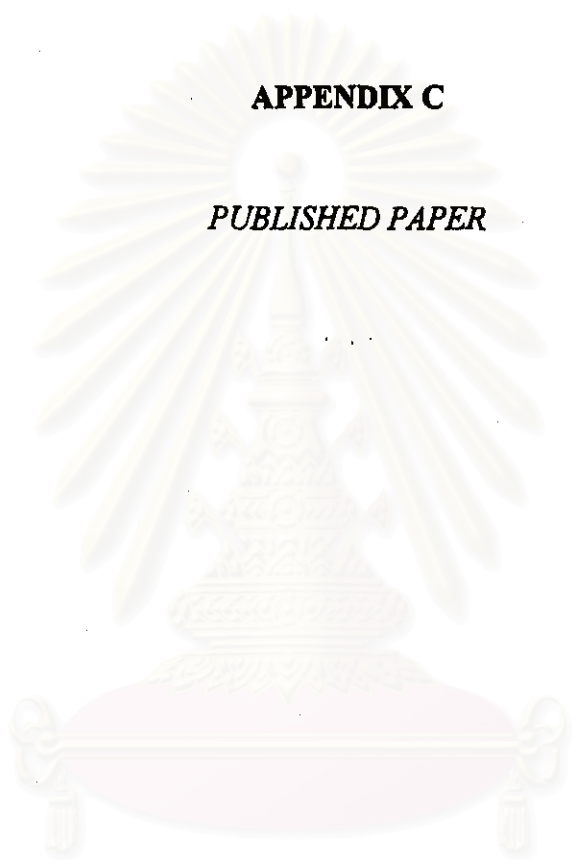


Some other properties of copper are given as follow:

properties	value
Colour	red
Natural isotopes	63, 65
Density, (g/cc)	8.94
Melting point (°C)	1083
Boiling point (°C)	2325
Crystal ionic radius, A	
Cu ¹⁺	0.93
Cu ²⁺	ca. 0.72
Tetrahedral covalent radius, A	1.35
Ionization potential, volts	
1 st electron	7.724
2 nd electron	20.287

List of some important copper compounds are also shown.

Name	formula	Colour&state	soluble
Copper acetate	$\text{Cu}(\text{C}_2\text{H}_3\text{O}_2)_2 \cdot \text{H}_2\text{O}$	Greenish-blue, fine powder	water, alcohol and ether
Copper benzoate	$(\text{C}_6\text{H}_5\text{COO})_2\text{Cu} \cdot 2\text{HOH}$	blue crystalline odorless powder	slightly in cold water
Copper chloride	$\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$	a) brownish-yellow powder b) green deliquescent crystal	a) hygroscopic b) water and alcohol
Copper nitrate	$\text{Cu}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$	Blue, desliquescent crystals	water and alcohol
Copper oxide black	CuO	Brownish-black powder	alcohol but hardly in water
Copper oxide red	Cu_2O	reddish-brown, octahedral crystal	acid and ammonium hydroxide but not in water

APPENDIX C*PUBLISHED PAPER*

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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 NO₂ 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 NO₂, 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 Cu¹⁺ had more than Cu/Na-ZSM-5. Cu¹⁺ plays an important role in NO decomposition to N₂ and O₂ which is likely to be the first step in NO reduction without oxygen.

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

1. Introduction

Cu/ZSM-5 was proposed as an active catalyst by Iwamoto et al.[1, 2] 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[3 - 8].

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 [6]. 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[3], 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[7, 9].

It was found that Na-ZSM-5 is not active in the SCR of NO [3, 10] while H-ZSM-5 is moderately active[10, 11]. 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 behavior of the reactions, the transient experiments would be carried out. Since proton on zeolite surfaces act as Brønsted 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[12]. The characteristics of Cu ion on both catalysts were examined. It has been known that CO could adsorb only on Cu^{1+} [13-16], CuO and Cu metal [16], however, no evidence of the existence of CuO and Cu metal in Cu/ZSM-5 thus was found[16]. O adsorption thus was applied to quantify the Cu^{1+} on the catalyst surface[13,14].

2. Experimental

2.1 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[17]. 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 exchanging Na-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.

Table 1 Composition and surface area of catalysts

Catalyst	Si/Al	BET surface 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

2.2 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, NO₂, N₂O, CO₂ and propane simultaneously. However, neither N₂ nor O₂ 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.

Table 2. IR Band of gases.

gas species	appearance peak (cm ⁻¹)
NO	1905(xl), 1850(l)
NO ₂	1630(xl), 1600(xl), 1750(l), 1263(l)
N ₂ O	2225(xl), 1290(l)
C ₃ H ₈	2970
CO ₂	2362

Note : xl = extra large, l = large

2.3 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% O₂ 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 CO₂ 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/cm² 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 Cu¹⁺ 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.

3. 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 (Fig. 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. [13], Li and Hall [18] and Pirone et al. [19].

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. [20] mentioned that O_2 from NO decomposition might further oxidize NO to produce NO_2 . Pirone et al. [21] 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 [19]. 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 .

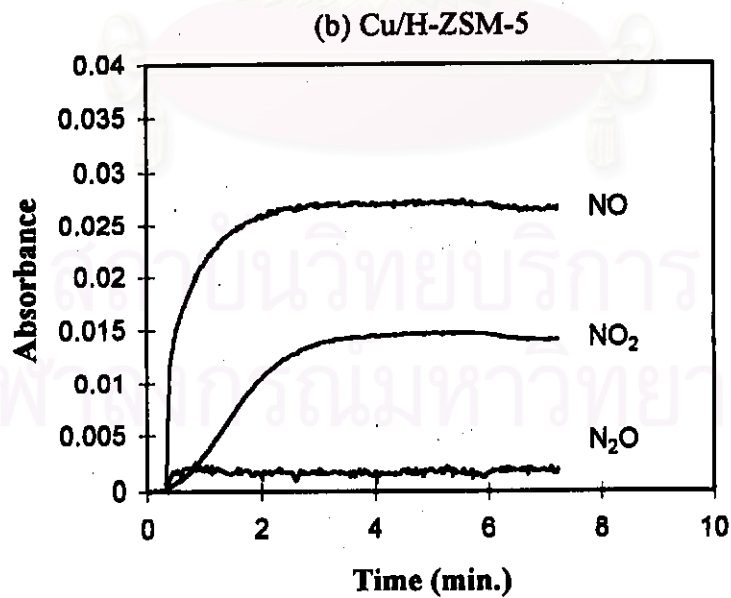
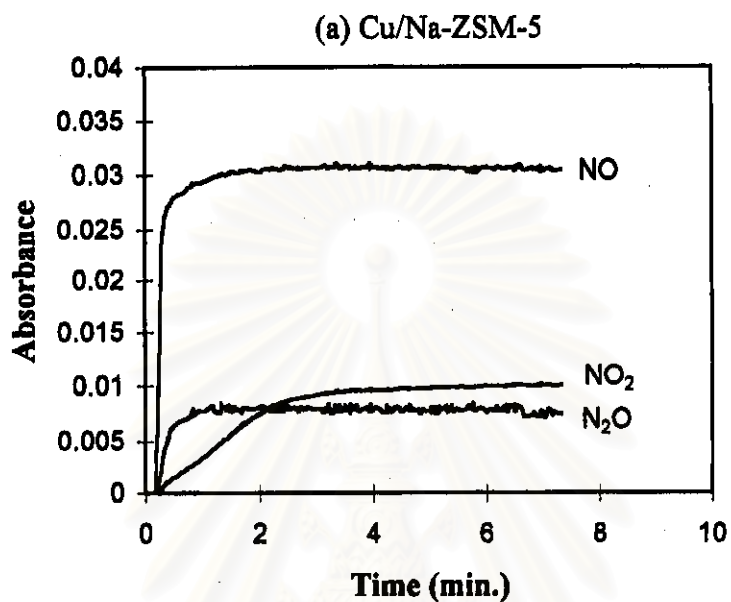


Fig. 1. Absorbance of gaseous species after switching from N₂ to 1.2%NO + N₂ at 400 °C over (a) Cu/Na-ZSM-5 and (b) Cu/H-ZSM-5.

From the result of the oxidation of NO experiment in Fig. 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(Fig.2) indicate the high NO₂ adsorption capacity of Cu/ZSM-5. However, the different retention time of NO appearance between the results in Fig. 1 and Fig. 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 Fig. 3 and 4, respectively. After inert gas(N₂) 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(Fig. 3). This clearly establishes strong C₃H₈ adsorption over the Cu/ZSM-5 catalysts. Burch et al.[22] and Cho[23] have observed a chromatographic effect when light hydrocarbon passes over these catalysts. The formation of CO₂ in the first few minutes after the step change to C₃H₈ 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[24, 25] and Larsen et al.[26] 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, CO₂ disappears from the reactor outlet. When NO is added to the gas feed, the reduction occurs. CO₂ emerged again. The appearance of CO₂ 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 CO₂ production over Cu/H-ZSM-5 was substantially higher than over Cu/Na-ZSM-5. In Fig. 4, when the gas stream was changed from N₂ to the gas mixture of C₃H₈ and O₂, only CO₂ was observed. Complete combustion took place over both Cu/Na-ZSM-5 and Cu/H-ZSM-5. When NO was added into the feed, CO₂ 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 CO₂ 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.

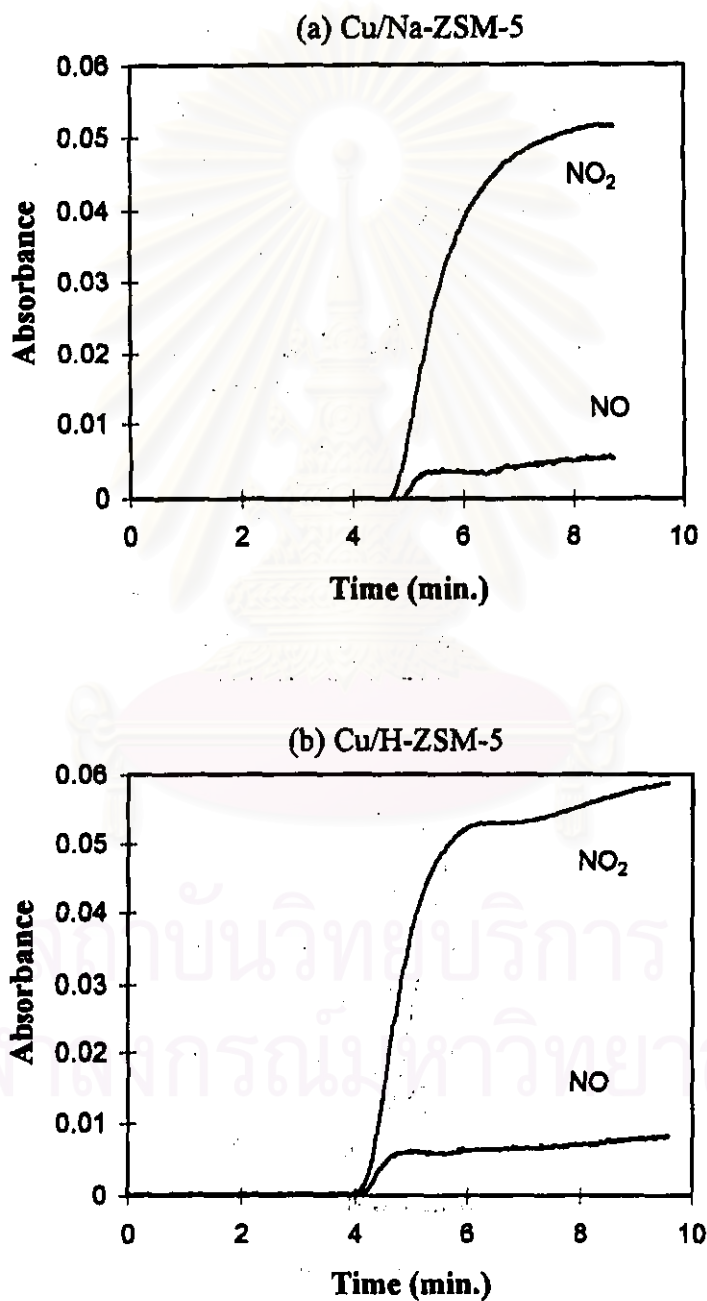


Fig. 2. Absorbance of gaseous species after switching from N₂ to 0.5%NO + 10%O₂ + N₂ at 350 °C over (a) Cu/Na-ZSM-5 and (b) Cu/H-ZSM-5.

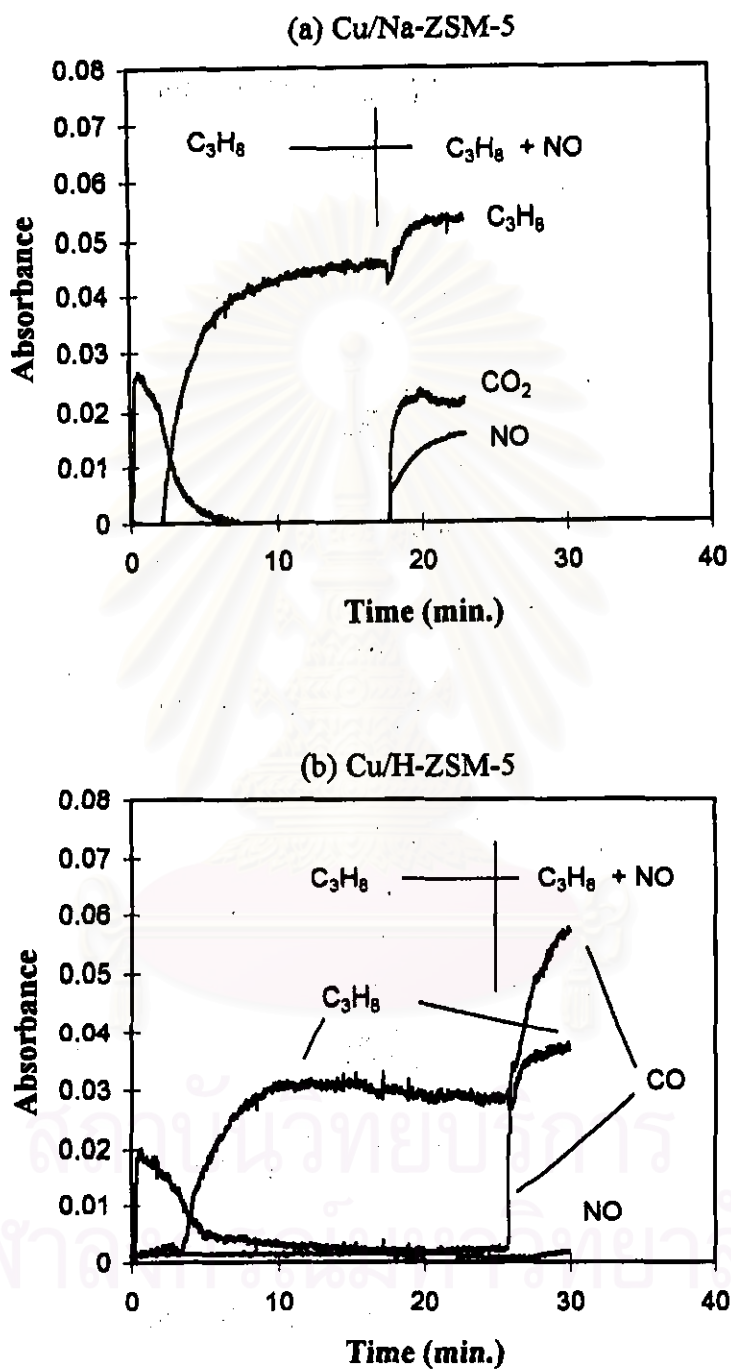


Fig. 3. Absorbance of gaseous species after switching from N_2 to $0.4\%C_3H_8 + N_2$ and to $0.4\%C_3H_8 + 0.5\%NO + N_2$ at $400^\circ C$ over (a) Cu/Na-ZSM-5 and (b) Cu/H-ZSM-5.

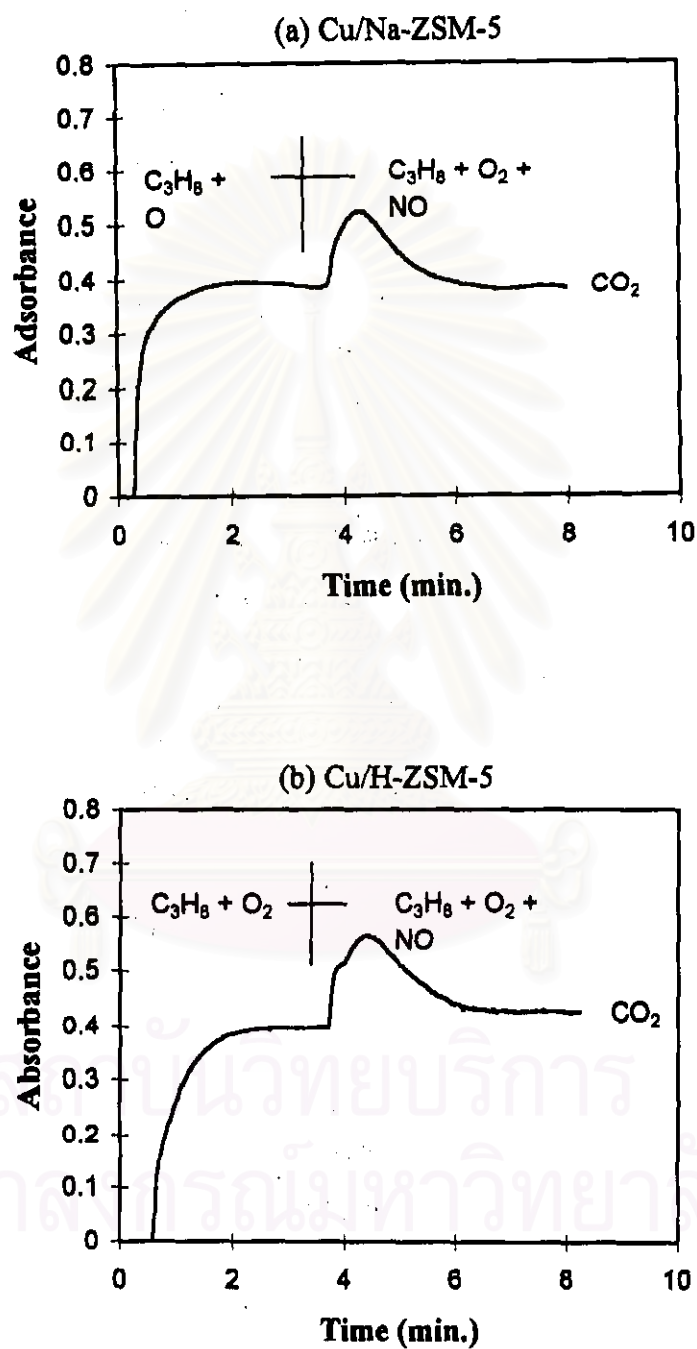


Fig. 4. Absorbance of gaseous species after switching from N_2 to $0.4\%C_3H_8 + 12\%O_2 + N_2$ and to $0.4\%C_3H_8 + 12\%O_2 + 0.5\%NO + N_2$ at $300^\circ C$ over (a) Cu/Na-ZSM-5 and (b) Cu/H-ZSM-5.

From the results of several transient reactions (Fig. 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 NO₂ 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 Brønsted acid which may involve a reaction mechanism [7]. 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 [12]. The spectra of adsorbed pyridine on Cu/Na-ZSM-5 and Cu/H-ZSM-5 are shown as a function of temperature in Fig. 5 and 6 respectively. The peaks at 1540 and 1640 cm⁻¹ are assigned to pyridinium ion at Brønsted acid sites [12, 27, 28]. Pyridine coordinately bonded to surface Lewis acid sites shows peaks at 1450 and 1600 cm⁻¹ [12, 27, 28]. The band at 1490 cm⁻¹ represents all adsorbed pyridine species [12, 29]. Both Brønsted 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 °C on both Cu/Na-ZSM-5 (Fig. 5) and Cu/H-ZSM-5 (Fig. 6). The amount and strength of pyridine adsorbed on both catalysts were almost the same. Connerton et. al. [30] 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.

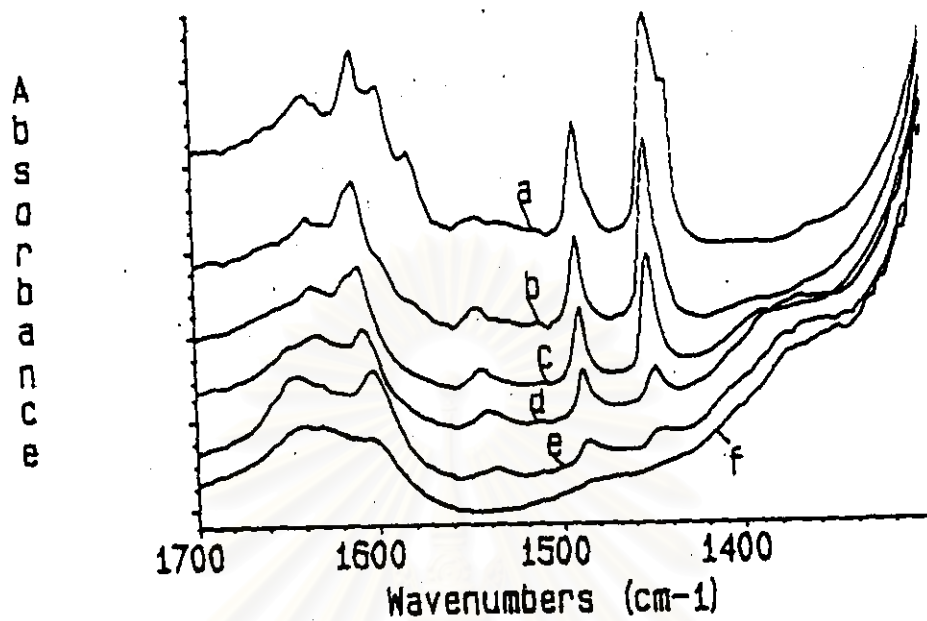


Fig. 5 Spectra of pyridine adsorption on Cu/Na-ZSM-5 at (a) rt. (b) 100 °C, (c) 200 °C, (d) 300 °C, (e) 400 °C and (f) 450 °C

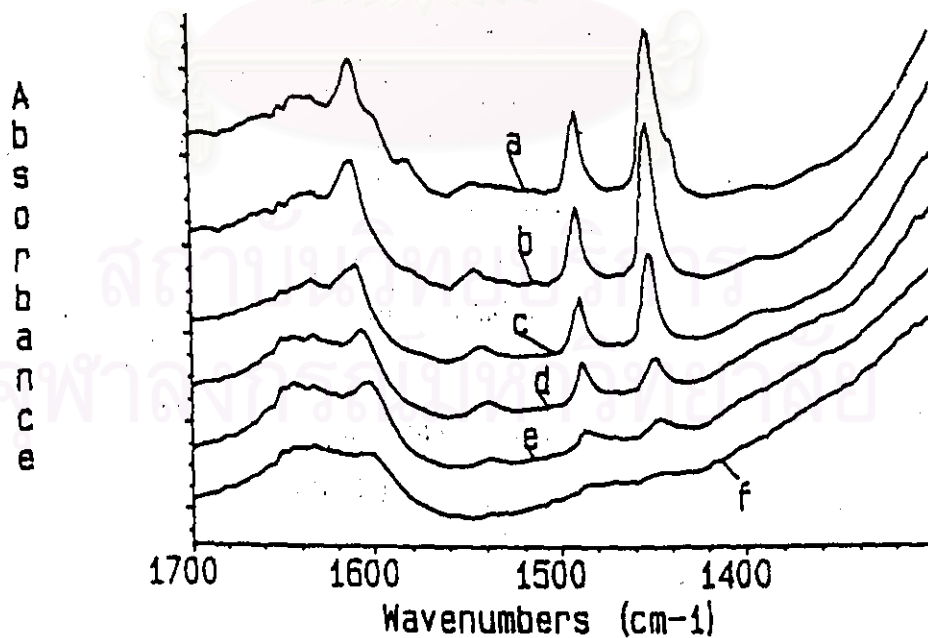


Fig. 6 Spectra of pyridine adsorption on Cu/H-ZSM-5 at (a) rt. (b) 100 °C, (c) 200 °C, (d) 300 °C, (e) 400 °C and (f) 450 °C

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 Fig. 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.

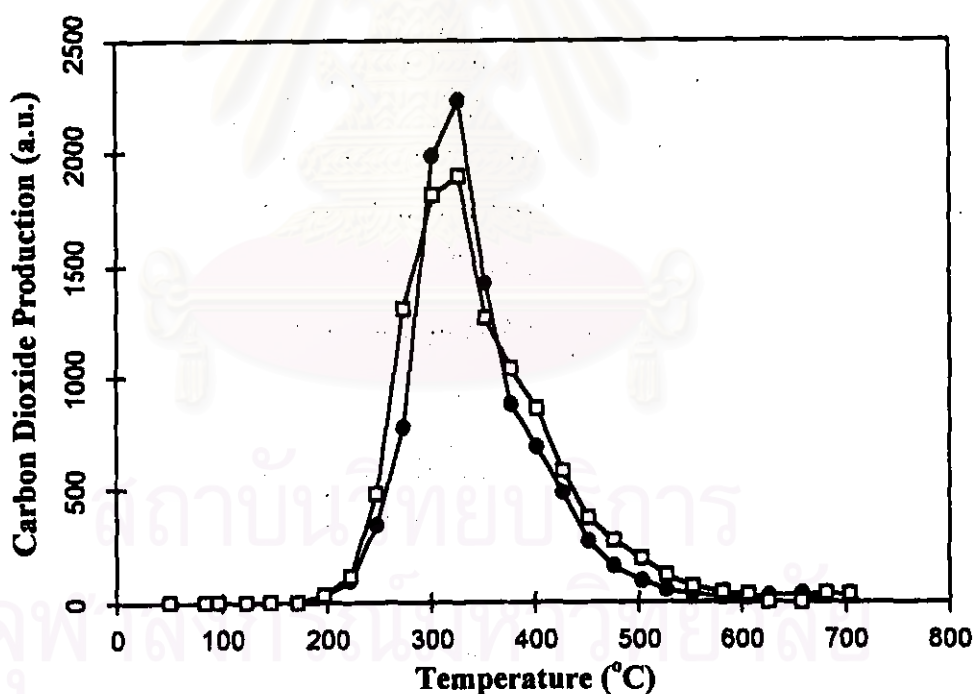


Fig. 7. Temperature Programmed Oxidation of (●) Cu/Na-ZSM-5 and (□) Cu/H-ZSM-5 after used in the transient experiment of switching from 0.4% C₃H₈ to 0.4% C₃H₈ + 0.5% NO

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 [31] studied the acidity of copper on ZSM-5 and suggested that the copper site exhibited Lewis acid properties rather than Brønsted acid ones. Moreover, Satsuma et al. [32] 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 [3 - 8]. 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 be due to the difference in the characteristics of the copper site. There have been many reports concerning types of copper on ZSM-5 surface [5, 24-26]. Forms of copper on zeolite generally are cuprous ($1+$) ions and cupric ($2+$) ions [7, 13-16, 24-26]. However, many authors [13-16, 33-35] accepted that Cu^{2+} can be reduced to Cu^{1+} or even Cu^0 in suitable conditions [33]. Copper in different states has the different properties and activities. CO adsorption is an easy method to investigate the quantity of Cu^{1+} [13, 14]. The amount of CO adsorption on Cu/Na-ZSM-5 and Cu/H-ZSM-5 is shown in Table 3. The amount of CO adsorption 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 $\text{Cu}^{1+}/\text{Cu}^{2+}$ ratio. The difference in $\text{Cu}^{1+}/\text{Cu}^{2+}$ might have had an effect on the activity in both catalysts.

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

Catalyst	Amount of CO adsorbed($\mu\text{mol/g. cat}$)	Number of Cu^{1+} ($\times 10^{19}$ site/g. cat.)
Cu/Na-ZSM-5	1.121	1.35
Cu/H-ZSM-5	2.247	2.71

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 [36] and it is also suggested that it is the intermediate of the NO reduction by hydrocarbon[37 - 40]. 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[13, 20, 41, 42] whereas Cu^{2+} has been proposed as an active site for NO reduction by hydrocarbon[7, 43, 44]. 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[2, 3, 10]. However, further study for confirmation should be conducted.

4. Conclusion

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 $\text{Cu}^{1+}/\text{Cu}^{2+}$ 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, $\text{Cu}^{1+}/\text{Cu}^{2+}$ ratio, rather than to the difference of residual cations, Na^+ and H^+ .

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