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NO_x REDUCTION BY ADSORPTION AND HYDROGEN-SELECTIVE CATALYTIC REDUCTION USING Pt-ZEOLITE : PART I. SPECTROSCOPIC STUDY AND EFFECT OF TEMPERATURE TO ACTIVITY

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ABSTRACT

In this paper, spectroscopic investigation on NO_x adsorption and Hydrogen-Selective Catalytic Reduction (H-SCR) by using Pt-zeolite and also study on the effect of temperature to the % activity of reduction are presented. FTIR and UV-Visible spectrophotometry reveal the chemisorption occure during NO_x adsorption by Pt-zeolite. Furthermore in the effect of temperature study, it concluded that both of processes significantly affected by temperature. Arrhenius model is used to predict this effect and the result show that activation energy of NO_x reduction in H-SCR system is 0.2640 Joule/mol and adsorption energy is 4.0617 Joule/mol.

Keywords: *NO_x, Adsorption, Selective Catalytic Reduction, Zeolite*

INTRODUCTION

Recently, global warming is a puler issue in the world. Several source of this problem are identified and one of these is exhaust gas from fuel combustion. Polutant gas such as CO_2, SO_2 and NO_x are accused as responsible component in environment so handling and expose prevention engineering are developed.

Several researchers (Guo et al., 1995) pay attention to several methods such adsorption and reduction reaction including catalytic reaction in exhaust gas vehicle. The last method is called as selective catalytic reduction (SCR) system. Among others, NO_x gas is main interest due to this highly toxicity to human and microorganism living at low concentration threshold.

Related to NO_x reduction by SCR process (designed as de-NO_x by SCR), physicochemical character and also activity of catalyst used play important role so there is currently worldwide interest in the development of an efficient catalyst for removal of NO_x. Several metal and metal oxide supported in inorganic materials are developed for this purpose. Among several metals, Platinum is a chosen metal related to this reduction capability and its stability in wide region of temperature (Guo et al., 1995). Dispersed Pt onto solid support is a good candidate catalyst reported in previous publication. As a method to improve activity and stability of catalyst in such critical condition in system, dispersion of platinum metal onto material support is developed. Supporting on several inorganic solid have been reported i.e on smectite minerals (Vicente, 2000, Kim, *et al.*, 2001), ZSM-5 (Guo *et al.*, 1995) zeolit and also MCM-41 (Jeon *et al.*, 2003).

In general, these minerals are silica-alumina materials which area naturally having high surface area and possible to improve activity through increase contact distribution of metal with reactant in mechanism. Due to the similarity and highly potency of natural zeolite in Indonesia, research on utilization of natural zeolite as a host for Pt dispersion and its application for de-NOx by SCR system is an interesting one.

Synthesis process, characterization and pre-activity test towards exhaust gas emission from motorcycle have been

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reported before (Hidayat *et al.*, 2007a, 2007b). In this paper, focus of study is on the basic process of adsorption and reduction by using spectroscopic method and investigation on the efect of temperature to catalyst activity. In order to evaluate the role of catalyst, hydrogen gas was used as reduction agent and NO_x gas was used as main model of exhaust gas. NO_x was in situ produced by reacting Cu powdered with nitric acid and then flowed by N_2 gas. Furthermore, according to such literature, the process is called as hydrogen selective catalytic reduction (H-SCR).

Main equipment used in this research consist of a unit reactor for activity test including automatic temperature controlling system and manual gas velocity controlling system (Fig.1).

Reagents. Sulphanilamide solution (A). Dissolve 0.5 g sulphanilamide in 100 mL of 20 peï cent v/v hydrochloric acid. N-(1-naphthyl) - ethylenediamine dihydrochloride solution/NEDA (B).

Spectroscopic study on NO_x adsorption by Pt-zeolite was performed by first weighing 0.5 gram of sample followed by evacuation at 105^oC for 1 h. Sample was placed in adsorption glass coloumn (1 cm in diameter, 20 cm in length) and then flowed by NOx gas in pressure of 1.1 atm for 30 minutes. Sample grounded with KBr and pelletized for FTIR analysis in the wave number range of 400- 4000 cm^{-1}. Similar procedure is enganged for spectrocopic study of CO_2 and CO_2-NO_x mixture in that the difference is due to the gas expossed in coloumn. For adsorption and reduction study, after adsorbed NO_x gas, sample expossed by H_2 gas at pressure of 1 atm for 5 minutes before analyzed by using FTIR spectrophotometer.

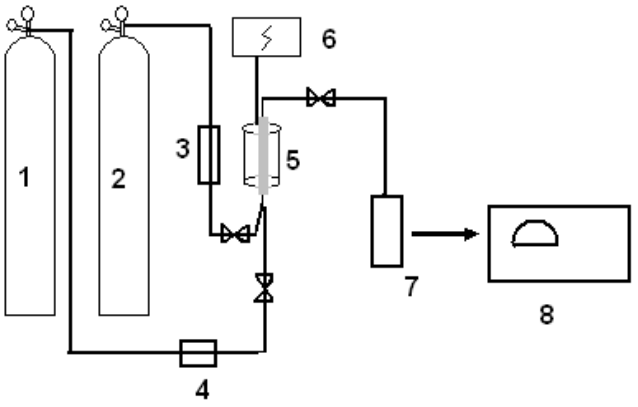

Fig. 1 Scheme of equipment used in activity test

Preparation of absorber solution, to 100 mL of the neutral sample solution (containing not more than 0.4 mg nitrite) 2.0 mL of solution A and, after 5 minutes, 2.0 mL of solution B are to be added. The pH at this point should be kept about 1.5.

General procedures for spectrophotometric determination of NO_x gas is absorbing gas into absorber solution and convert it into nitrites ion. Determination of nitrites are usually based upon some form of diazotisation reaction. In this case the nitrite ion, under acidic conditions, causes diazotisation of sulphanilamide (4-aminobenzenesulphonamide) to occur, and the product is coupled with N-(1-naphthyl) ethylenediamine dihydrochloride.

A half gram of sample was placed in reactor and condition was set to temperature variation (200, 300 and 400^oC) and gas concentration variation via gas flow rate setting. Under the condition chosed, NO_x gas was flowed in reactor and unreacted NO_s gas was trapped by Naphtyl ethylene diammine solution to form a pink complex solution.

Absorbance of the solution produced was analyzed by UV-Visible spectrophotometry in the wavelength of 543.5 nm. NO_x concentration before and after reaction were determined acording to the

quantitative analysis method related to NEDA-complex formation (Griess-Saltzman colorimetric procedure) (Schifftner, 2002).

To 10 mL of absorber solution 10 mL of aquadest was added and then the mixtured was placed into midget impinger. Gas from reactor flow into midget impinger connected with vacum pump for 5 sec. NO_x will produce a pink solution with absorber solution as indication of complex / coupling reaction. Absorbance of solution was analyzed after 10 minutes in the wavelength region of 543.5 nm (yellow-green filter), in UV-Visible HITACHI U-2080 spectrophotometer against a blank solution prepared in the same manner. concentration of NO_x was calculated as the nitrite from a calibration plot prepared from a senes of standard nitrite solutions.

Concentration of NO_x in air was evaluated based on NO_x data from spectrophotometer masurement, gas flow rate and time sampling for complex formation due to equation (2).

$$\text{Concentration in air volume} = \frac{[NO_X]_{spect} V_{sol}}{v.t} \quad \ldots (1)$$

$[NO_x]_{spect}$ = concentration measured by spectrophotometer (mg/L)
V_{sol} = volume of complex solution (L)
V = gas flow rate (mL/sec.)
T = time of sampleing (sec.)

DISCUSSION

Physicochemical character of catalyst Pt-zeolite material used is listed in Table 1.

Table 1. Physicochemical Character of pt-zeolite

Parameter	value
Specific surface area (m^2/g)	42,523
Pore volume (cc/g)	$30,813.10^{-3}$
Pore radius (Å)	14,492
Solid acidity (mmol pyridine/g)	$5,06.10^{-2}$
SiO_2 (% w/w)	33,60
Al_2O_3 (% w/w)	5,43
Pt (% w/w)	1.25

As shown in Table 1, main components of material are SiO_2 and Al_2O_3 and result of analysis, there are other minerals in material such as Ca, Mg and Na as minor components.

Activity test of catalyst in NO_x reduction and also adsorption was measured by NO_x conversion value whis is defined as equation (1).

$$\% \text{ activity} = \frac{[NOx]_{inlet} - [NOx]_{oultet}}{[NOx]_{inlet}} x100\% \quad \ldots (2)$$

Spectrum of material in spectroscopic study of NO_x adsorption and reduction by FTIR analysis after NO_x expose to the catalyst is shown in Fig. 2 and the important peak are listed in Table 2.

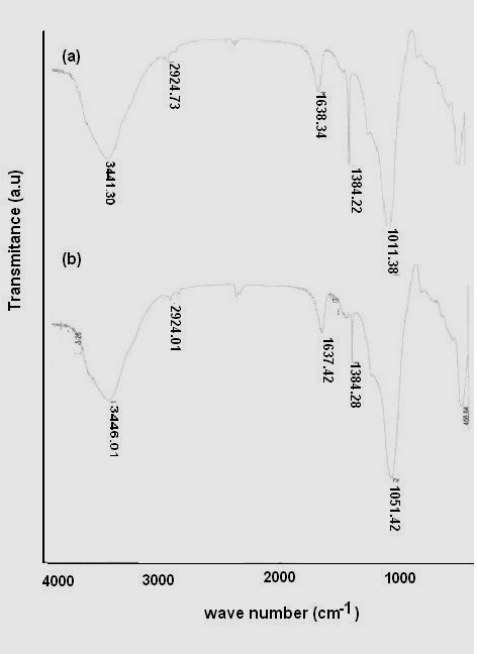

Fig. 2 Spectrum of Pt-zeolite (a) after NO_x adsorption, and (b) NO_x adsorption followed by reduction.

An intense band in the region of 1384.22-1384.28 cm^{-1} for both of samples show the efect of interaction between NO_2 in surface produce nitric ion due to the solid properties of Pt-zeolite surface. Interaction also reveal from the band at region of 1638 cm^{-1} which is indicate bidentate nitrate formation (Valverde *et al*., 2005). However, by these intensity, there is reamarkably difference intensity in which after reduction intensity is reduced. The shift of band to higher region: from 1384.22 cm^{-1} after adsorption to 1384.32 cm^{-1} after adsorption-reduction

is probably related to decreasing interaction of NO_x-Pt caused by reduction. Bands at 2900–2700 cm^{-1} may be originated by bridged nitrate (ν(N= O) + $\nu_{asymmetric}$ (NO_2)). Similar result also reported by Despres *et al*. (2003), Chmielarz *et al.* (2004) and Kikuyama *et al.* (2002). By using FTIR spectroscopic analysis, nitro gruop and bidentate nitrate are produced in NOx adsorption by Pt-ZrO_2/Al_2O_3 and Cu/ZSM-5. This conversion indicate the strong interaction of surface and gas during adsorption step.

Table 2. Important peak in FTIR analysis toward Pt-zeolite after NOx adsorption and adsorption-reduction

Spectra band (cm^{-1})		Identification
After adsorption	After adsorption and reduction	
1384.22	1384.32	Symetric vibration of nitric
1430.34	1430.34	Asymetric vibration of nitric
1560.17		Nitro group
1638.34	1637.42	Bidentate nitrate
2924.73	2924.01	N=O and NO2

In agreement with these analysis, UV-Visible spectrum of leached NO_x by solid are also suggest this assumption. After adsorption and adsorption-reduction process, samples were contacted with NEDA solution. This process called as NO_x leaching. A pink solution produced (NO_x leaching solution) is indication of NEDA-NO_2 coupling reaction.

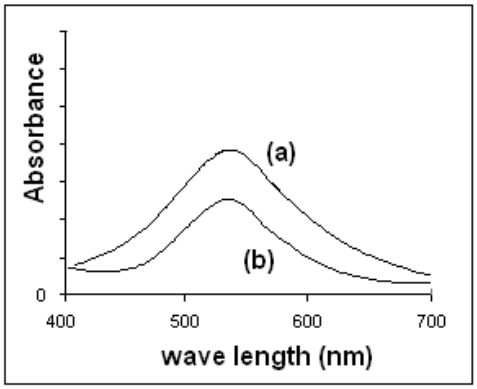

Fig. 3 Spectrum of NO_x leaching solution from dillution of Pt-zeolite (a) after NO_x adsorption (b) after NOx adsorption-reduction

From Fig.3, It is shown that both of leaching solution give maximum wavelength of 543.5 nm appropriate with standard solution produced by interact NO_2^- with NEDA solution. Absorbance of adsorption-reduction sample is lower than do adsorption sample one. It indicate that reduction make a conversion toward NO_x in surface as concentration decrease.

An important conclusion of these spectroscopic study is that there is a strong chemisorption and also reduction of NO_x over Pt-zeolite. To make an intensive study for the reduction mechanism, the effect of NO_x concentration to NO_x adsorption is also studied. As an equillibrium interaction, distribution constant or also called as adsorption constant is a parameter determine value of gas concentration before and after adsorption.

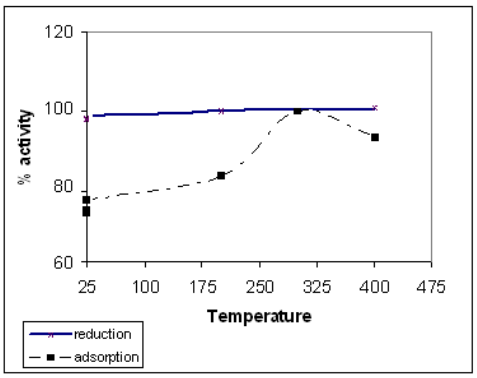

Fig 4. Activity of NO_x Adsorption and SCR by Pt-zeolite in Varied temperature

Activity test of NO_x reduction was performed at different temperature with initial NO_x concentration of 72.11 mg/L. Concentration of NO_x control was examined by fixing gas flow rate. Hydrogen flow rate in this set up is 1000/h. NO_x conversion profile is depicted in Fig.4. Fi-

gure 4 shows NO_x conversion as a function of temperature determined by % activity.

Activity of adsorption and reduction toward NO_x are lower than 80% achieved for all temperature and treatment. From the pattern in reduction process, the % activity was increase as temperature elevation as also shown by the effect of temperature in adsorption process at lower thn 300°C. This pattern indicate the thermodynamic control in both of process in which Gibs fuction (ΔG) decrease as temperature increase. However, a point showed a deviation at temperature of 400°C by adsorption process in that the % activity is lower than do obtained at 300°C. Theoritical explanation will be clear if discussion also involve physicochemical character of catalyst in this condition. The discusion will be apart in part two: physicochemical character effectof Pt-zeolite to NO_x reduction.

In order to ensure that adsorption and reduction process give different effect to reduce NO_x concentration and also to determine thermal effect for both of processes, statistical analysis to the data was measured by using two way analysis of variance (two way ANOVA) with the % activity as response and temperature and also treatment (adsrption and SCR) as factor. Analysis was performed by using SPSS 11.0 for windows and result of analysis is presented in Table 3.

Table 3. Out put of two way ANOVA to the effect of temperature and treatment to % activity

Analysis of factor	F	Sig.
Treatment (adsorption and SCR)	18.731	0.000
Effect of Temperature in Reduction Process	58.968	0.000
Effect of Temperature in Adsorption Process	154.471	0.000

As shown in Table 3, according to F and significance value, temperature variation give effect to reduction and adsorption process significantly as well as effect of treatments to the % activity. By comparing F value of analysis, we can assume that effect of temperature in adsorption process is greather than do in reduction process. However, in this range it is concluded that all variation in process is significant.

Arrhenius plot from ln k versus 1/T due to due to equation (3) depicted in Fig. 5.

$$\ln k = \ln A - \frac{Ea}{RT} \quad \ldots (3)$$

k = rate constant
A = pre exponential factor
T = temperature (K)
Ea= activation energy (Joule/mol)

The model was examined by the assumption that hydrogen concentration as reactant is a constant so the reduction reaction is unimolecular reaction. As reaction in first order.

$$\frac{d[NOx]}{dt} = k[NO_x] \quad \text{or} \quad \ln\frac{[NO_x]}{[NO_x]_o} = -k.t \quad \ldots (4)$$

By consideration equation (2), activity also represented as =

$$activity = \frac{[NO_x]_0 - [NO_x]}{[NO_x]_0} = 1 - \frac{[NO_x]}{[NO_x]_0}$$

so

$$\ln[1 - activity] = -kt \text{ or}$$

$$k = -\frac{\ln[1 - activity]}{t} \quad \ldots\ldots\ldots (5)$$

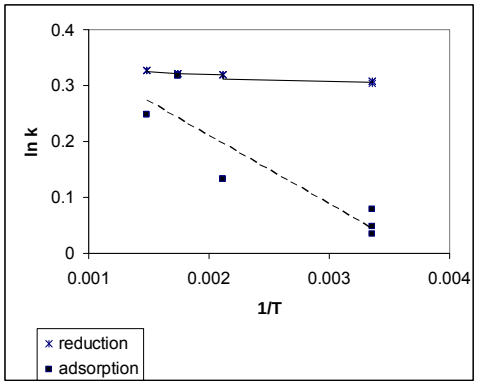

Fig. 5 Arrhenis plot of NOx reduction activity by (a) adsorption (b) SCR

Statistical evaluation on the liner model and activation energy (Ea) from both of process are listed in Table 4. Low correlation parameter from Arrhenius model in adsorption process is related to outlier data derived at the temperature of 400°C. By H-SCR process, it is showed that linear correlation occure as indica-

tion that there is a theoritically reason of temperature effect to the activity.

Table 4. Statistical parameter on Arrhenius equation linear model toward adsorption and SCR activity

Parameter	Adsorption	SCR
Correlation factor of Equation (3)	-0.8596	-0.9874
Slope	-131.945	-10.4876
Intercept	0.4885	0.0318
Ea (Joule/mol)	4.0617	0.2640

It is also determined that activation energy of H-SCR process is lower (0.2640 Joule/mol) than do adsorption energy (4.0617 Joule/mol) as a conclusion that Pt-zeolite is well proven active for reduce NO_x in selective catalytic reduction system.

CONCLUSIONS

Pt-zeolite synthesized from natural zeolite was examined as an adsorben and also catalyst for NO_x removal by hydrogen. Spectroscopic studies on NO_x adsorption and reduction reveal that there is a chemical interaction during process. Effect of temperature to the activity was also evaluated to both of process and indicate that temperature significantly influence the % activity in NO_x reduction in that the higher temperature the higher activity gained in reduction. Activation energy of H-SCR is 0.2640 Joule/mol and adsorption energy is 4.0617 Joule/mol.

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