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CO Oxidation over Metal Oxide Catalyst Supported by Indonesian Natural Zeolite

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The objectives of this study are to attempt to develop catalysts and to find the operating conditions under which combustible waste gases concentrations in the exhaust gases can be eventually reduced to satisfy air pollution standards. The results shows that using impregnation method, nickel and vanadium metals, as active components of the catalyst, can be dispersed on the natural zeolite as catalyst support.

The reaction rate measurements of catalytic oxidation of CO was done in the temperature range between 300 and 550 °C using a differential micro-reactor. The catalysts used for this experiment were vanadium pentoxide and nickel oxide on activated natural zeolite. To avoid fluidization, the reactant gases were flowed downward. The results show that the reaction rate depends strongly on the bed temperature and feed concentration and is not controlled by bulk phase mass transfer and pore diffusion.

INTRODUCTION

Among the most complex problem to be faced by industries since industrial revolution are the problems of air pollution. The main pollutant coming from industries and automotive exhaust is carbon monoxide. This pollutant is very dangerous for human life. As little as 0.07 % of CO is capable, over a period time, of saturating 50 % of the blood hemoglobin, while a few breaths of 1.0 % CO may cause 60 to 80 % saturation and death. It should be noted that shortness of breath and possibility of slight headache may occur after 8 hours in a CO concentration of 0.01 % (Theodore and Buonicore, 1988; and Matros, 1989).

The rapid growth of industry in Indonesia has resulted in a progressive increase in atmospheric pollution. It is thus of practical importance to study CO oxidation, especially with respect to the control of CO pollution. Industrial waste gases can be oxidized further to be carbon dioxide and steam using catalyst made of metal or metal oxide supported by many materials. However, the existing catalysts were too expensive to be used in Indonesian industries. Hence, a new catalyst should be pursued to handle these kind of gases. The catalyst should be cheap, simple and efficient.

Natural zeolites are an economically and environmentally important classes of minerals that occur in significant abundance in Indonesia. Forty-seven zeolite deposits have been discovered mainly in Sumatra, Java and Nusa Tenggara (Husaini and Hardjatmo, 1996). Due to the special structure of zeolite, they have many important commercial properties such as high efficient adsorption and molecular sieve effect, cation exchange effect, property of catalyst, high activity, high strength and light mass. These properties make zeolite having a wide variety of purposes. Uses of natural zeolite from Indonesia deposit have been promoted proportionally, however the application is still limited. It is mainly due to the limitation basic research to match the specific zeolite with specific use. Therefore, this research will explore the use of natural zeolite as a fundamental data for deciding the alternative support for oxidative catalyst.

Although the oxidation of carbon monoxide on metal oxide catalyst is among the oldest known catalytic reactions, and has been studied by many researchers, the conclusions regarding the mechanisms and the rate equations are rather conflicting. Some researchers found that the reaction follows Langmuir-Hinschelwood (Voltz et al., 1973; and Nishiyama and Wise, 1974) and others believed that the CO oxidation on metal catalyst are an Eley-Rideal type reaction (Mc Charty et al., 1975). A part of the reason for the disagreements in the published work is the narrowness of the ranges of temperature and concentration of the reactants CO and oxygen. Also since the metal oxide catalyst is highly active for the oxidation of CO, the measured oxidation rate could be appreciably affected by mass transfer limitation.

The main objectives of this paper are to oxidize CO on metal catalyst supported by natural zeolite and to find model for kinetic of CO oxidation that will accurately predict oxidation rate under different temperatures and feed concentrations. This steady state kinetic studies can be used to support the mathematical modeling since a suitable reaction rate expression is essential for a successful reactor model. This paper consists of two parts, the first one concerns data analysis and results while the second one deals with modeling of the reaction kinetics.

EXPERIMENTAL

Catalyst development

For this step, nickel oxide and vanadium pentoxide catalyst supported on activated zeolite have been developed. Procedure of catalyst development includes several stages: activation of catalyst support, impregnation and calcinations. Several procedure and parameter conditions in the process of catalyst development have been made in order to get optimum result.

Catalyst support

The zeolite used in this experiment was from West Java. The results of mineral identification is shown in Table 1. The samples composed of a mixture of mordernite and clinoptilolite. Some samples were also associated with other minerals such as montmorilonite and quartz. According to Bales (1988), the variation of zeolite composition in the samples was depend upon any factors such as the influence of fluid composition zeolite minerology, significance of associated clays, pressure and temperature, chemical stability relation among various zeolite and kinetic relation. The variation of mordernite and clinoptilolite distribution also are controlled by the volcanoclastic as parent material of zeolite as well as degree of zeolitisation. There are three variation of zeoilte activation : using temperature, acid solution and basic solution. According to Kharisun and Budiono (1999), acid activation tends to increase pH, EC, CEC and chemical and exchangeable bases. Therefore for this experiment, the zeolite was activated using acid treatment.

For activation of catalyst support, the 20 g of natural zeolite granular were put in 50 ml NH_4NO_3 solution and stirred for 12 hours. Then left it for another 12 hours. Then the sample were filtered using whatman paper and washed with deionised water. After that, the sample were then dried in oven with temperature of 110 °C for 4 hours. For the activation, the zeolite granular were heated up to 700 °C while flowing nitrogen gas for 4 hours in a reactor having 2 cm diameter and 40 cm length.

Catalyst preparation

The catalyst was prepared using dipping and vaporization methods. First of all, activated zeolite was sieved to get particles having diameter of 1 mm, 2.5 mm and 5 mm. Then nickel or vanadium solution was dissolved in the water stoichiometrically and the zeolite was put in the solution and stirred for 24 hours. The solution was dried and heated in an electrical stove and dried further in an oven. The calcinations was conducted in 1 ml/sec nitrogen stream for 4 hours at 600 °C. The amount of metal was varied in the range of 1 to 4 %.

Catalyst characterization

The solid catalyst obtained was characterized by using BET surface area analyzer utilizing liquid nitrogen as a probe molecule to find out surface area and pore size of the catalyst. The morphology (catalyst's surface texture) was observed using a Scanning Electron Microscope. The amount of metal in the catalyst surface was determined by Atomic Absorption Spectroscopy.

Table 1. Chemical composition of zeolite samples

No.	Chemical compound	
	Type of chemical	(%)
1.	SiO_2	69.81
2.	Al_2O_3	13.52
3.	Fe_2O_3	1.93
4.	TiO_2	0.21
5.	CaO	1.91
6.	MgO	0.89
7.	K_2O	1.93
8.	Na_2O	1.24
9.	Others	8.56

Source: Center of Mineral Research and development Technology, Directorate General of mines, Bandung, INDONESIA.

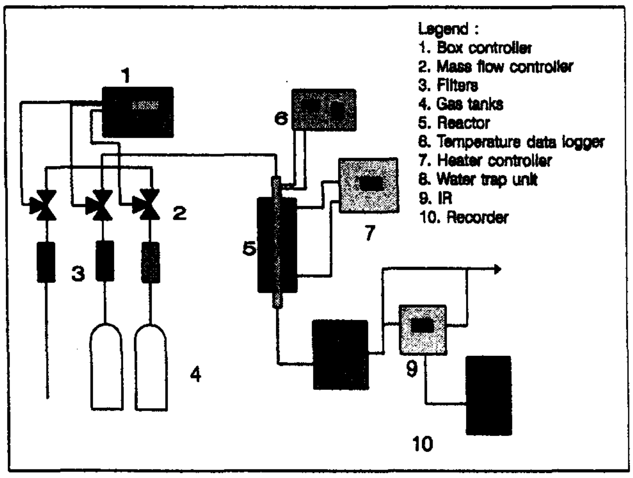

Figure1. Schematic diagram for CO and HC oxidation experiment.

Oxidation process

The oxidation process was done in a differential reactor equipped with an IR analyzer for detecting CO, CO_2 and light hydrocarbon. For this experiment, pure CO was used as source gas where the compressed air was used for oxygen supply.

Figure 1 is a schematic diagram of the experimental set-up. All gases flowing to the reactor were dried over filters containing 4A molecular sieves and anhydrous calcium sulphate to reduce traces of impurities. Omega flow transducer-controllers regulated the feed mass flow rate into the reactor. They permitted only uni-directional flow and therefore acted as check valves. The system operating pressure was measured by Omega pressure gauges. All the thermocouples in the system were connected to an Omega data logger. The reactor was 15 cm long and 0.635 cm ID stainless steel tubing. To prevent catalyst movement, stainless steel screens were installed at the inlet and outlet of the reactor.

Experiments were conducted under varying reactant concentrations, bed temperatures and flow rates. All runs were isobaric and carried out just above one atmosphere pressure.

RESULTS AND DISCUSSION

Results of catalyst characterization

The results of characterization of the catalyst developed are shown in Table 2. The table shows the measurements of surface area, pore diameter and pore volume for nickel and vanadium catalysts supported on zeolite.

Catalyst development were done using two methods, vaporization and dipping. In the dipping method, the bonding between catalyst support and the metal was very weak, so that the metal was easily dissolved again into the washed water. Therefore, the amount of the metal impregnated was not the same as the metal added into the solution. The results of catalyst characterization show that, using the dipping method, the metal impregnated was only 70-80 %; whereas by using the vaporization method, the metal impregnated was almost 100 %. However, the distribution of metal in the catalyst support for dipping method was better than the vaporization method. It was also observed that increasing the concentration of metal ions will increase the metal content in catalyst. The increase of metal ions concentration in the solution will cause more collusion of the ions into support material so that adsorption of the ions into the solid become easier.

From the surface area measurement, it can be seen that the surface area increases when the diameter of the particle was decreased. On the other hand, when the concentration of the metal was increased, the total surface area decreased. Using the results of Scanning Electron Microscope (SEM), it can be seen that the area of the metal surface was bigger than the diameter of the pore on the catalyst support. Therefore, some of the metal blocked the pore, so that the surface area decreased as shown in Figure 2.

Catalytic oxidation

Several preliminary runs were made to test the catalytic activity of construction materials for the reactor (stainless steel), packing materials (pyrex beads) and thermocouple cement used in cementing thermocouples. This was done by passing the reactant stream through the heated reactor tube without catalyst. Conversion was not detectable. Thus, these materials are not active.

The data for the isothermal bed were gathered with the flow rate and reactant concentrations held constant while the varying temperature, ranging between 200 and 550 °C, depended on the feed gas. Experiments were repeated for reactant concentrations between 1.0 and 5.0 %. The flow rate was kept constant at 1200 or 1800 ml/min for all experiments. The catalyst used was 0.2 g for low feed concentrations and 0.1 g for high concentrations.

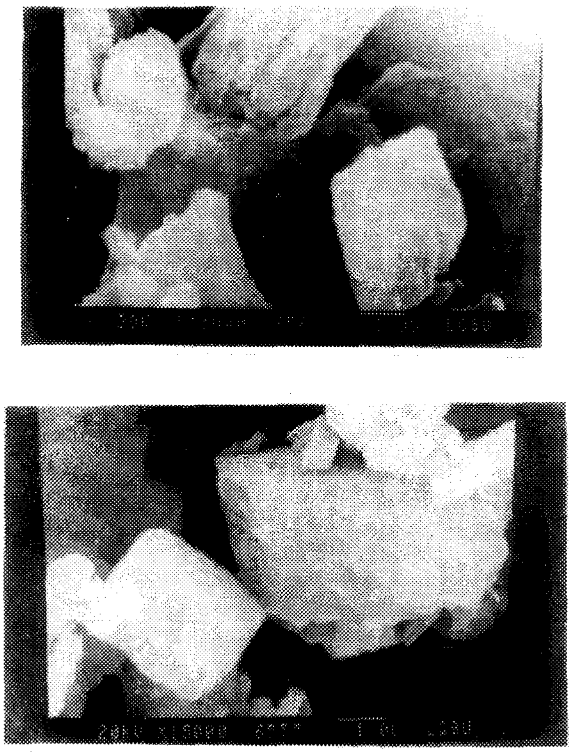

Figure 2. SEM image of Nickel catalyst supported by natural zeolite (2 and 4 % Ni)

Table 2. Results of catalyst characterization

Metal Concentration (%)	Nickel catalyst			Vanadium catalyst		
	Surface area (m^2)	Pore radius (A^o)	Pore volume (cm^3/g)	Surface area (m^2)	Pore radius (A^o)	Pore volume (cm^3/g)
0	19.3200	29.2210	0.0271	19.2998	28.8115	0.0278
2	14.7720	23.4652	0.0173	22.7316	23.1730	0.0263
4	12.9222	25.2572	0.0163	12.5383	26.2018	0.0164

An example of the data employed for evaluation of model parameters are summarized in Tables 3 and 4. The tables show that the reaction rate increases with increasing bed temperature and reactant concentration. This phenomenon is caused by the adsorption process. At low temperature, the adsorbed reactant gas layer on the catalyst surface will resist the formation of CO_2. When the temperature is higher, the adsorbed reactant gas layer will decrease, so that the reactant layer on the catalyst will not resist the formation of CO_2. Meanwhile the oxygen remains thermally stable at temperature while the reactant gas on the catalyst surface decreases.

The results above also show that the higher the metal concentration on the catalyst surface, the higher conversion or reaction rate can be achieved. Catalyst with higher metal concentration

Table 3. Average isothermal bed results using vanadium catalyst

Temp. (°C)	Reaction rates (mol/h-kg cat)							
	(V_2O_5 = 2 %)				(V_2O_5 = 4 %)			
	2.05 %	2.40 %	3.13 %	3,89 %	2.05 %	2.40 %	3,13 %	3,89 %
300	1.682	1.831	3.774	9.024	2.340	4.679	7.325	14.216
320	1.688	3.662	5.661	9.224	4.679	6.891	9.767	17.059
340	3.363	5.493	7.547	13.836	7.018	9.023	12.208	22.745
360	5.045	7.324	9.434	18.448	11.697	13.535	17.092	28.431
380	6.726	9.155	16.981	25.088	16.376	18.047	24.417	36.960
400	10.088	12.816	22.642	29.979	23.395	24.815	31.742	45.489
420	13.452	16.478	30.188	36.897	30.423	31.583	39.067	54.019
450	18.496	21.971	37.735	49.631	37.432	38.351	51.276	65.392
500	30.267	31.125	54.716	64.569	46.789	47.374	58.601	82.449
550	40.356	43.941	75.471	78.406	53.807	58.654	70.809	93.882

Table 4. Average isothermal bed results using nickel catalyst

Temp. (°C)	Reaction rates (mol/h-kg cat)							
	(NiO = 2 %)				(NiO = 4 %)			
	2.05 %	2.40 %	3.13 %	3.89 %	2.05 %	2.40 %	3.13 %	3.89 %
300	0,827	1.373	2.747	4.023	2.856	5.237	5.837	5.932
320	1.838	1.673	3.868	7.332	6.736	7.436	8.628	8.994
340	1.963	2.491	4.552	10.629	8.348	10.113	11.452	11.847
360	3.245	4.382	6.431	14.729	11.293	12.365	14.382	14.493
380	4.525	6.183	11.189	20.629	15.392	15.638	17.389	20.682
400	8.934	10.452	14.628	24.446	17.226	17.493	22.916	26.671
420	11.428	13.472	20.881	31.862	22.639	22.674	30.964	35.629
450	15.824	18.939	27.537	39.340	29.532	30.335	42.458	44.842
500	23.956	26.521	44.617	54.291	38.347	40.639	56.283	65.327
550	33.518	37.492	65.471	71.628	47.846	55.827	70.527	83.024

has more active sites on the surface than the lower one. The reaction rate is affected by the amount of available active sites. Higher amount of active sites causes the increase of gases to be reacted and resulting on the higher reaction rate. Moreover, the results also show that vanadium pentoxide catalyst is better than nickel oxide. This can be explained using electron configuration. Vanadium has atom number 23 and the orbital can be written as $1s^2$ - $2s^2$ - $2p^6$ - $3s^2$ - $3p^6$ - $4s^2$ - $3d^3$. Nickel having atom number 28 has configuration $1s^2$ - $2s^2$ - $2p^6$ - $3s^2$ - $3p^6$ - $4s^2$ - $3d^8$. Both catalysts have unfilled 3d orbital. However, vanadium has more unpaired electron than nickel. This causes the ability of vanadium as a catalyst is better than nickel.

Table 5. Parameters for power law reaction rates model

Catalyst	CO oxidation			
	A	E	Power law	
			CO	O_2
V_2O_5 (2%)	3.3×10^5	14877	- 0. 6209	0.4116
V_2O_5 (4 %)	3.7×10^5	13667	- 0. 6156	0.3531
NiO (2 %)	3.2×10^5	11732	- 0.6163	0.4114
NiO (4 %)	3.6×10^5	12191	- 0.5951	0.3755

Kinetic model

The reaction rate expressions, which correlate rate data obtained from the experiments, can either be empirical or be developed on the basis that one of chemical steps is rate controlling. The latter is often called Langmuir-Hinschelwood-Yang-Hougen-Watson (LHYHW) models.

Power law model

The power law model for the reaction rate of carbon monoxide oxidation in excess air is:

$$(-r_c) = A e^{(-E/RT)} P_{CO}^{a} P_{O_2}^{b} \tag{1}$$

Fitting this model to the experimental data, using simple linear regression method, the parameters A, E, a and b were established assuming the Arrhenius expression applied. The results can be seen in Table 5. From the power law model, the reaction rate has been found to be proportional to the negative power of partial pressure of CO or CO inhibition in the range of concentrations and temperature studied. This predicts an infinite reaction rate as the partial pressure of CO approaches zero. Intuitively, one would expect that the reaction rate becomes zero as the partial pressure approaches zero. This contradiction illustrates a limitation of empirical models. They cannot be extrapolated beyond the experimental range. Therefore, a theoretical reaction rate model which has a CO partial pressure in the denominator should be used.

Mechanistic model

If both gases (CO and O_2) are adsorbed on the catalyst surface, the reaction mechanism follows the Langmuir-Hinschelwood model. However, if one of the reactant is in the gas phase and the other is adsorbed on the catalyst surface, the reactor mechanism follows Elley-Rideal model.

In the Langmuir-Hinschelwood mechanism, there are two models:

Model 1: CO and O_2 are adsorbed on the catalyst surface, then the rate expression is:

$$(-r_c) = \frac{k K_{CO} P_{CO} \left(K_{O_2} P_{O_2}\right)^{0.5}}{\left(1 + K_{CO} P_{CO} + \left(K_{O_2} P_{O_2}\right)^{0.5}\right)^2} \tag{2}$$

Model 2 : If adsorption of O in the form of O2s, the reaction rate expression is:

$$(-r_c) = \frac{k K_{CO} K_{O_2} P_{CO} P_{O_2}}{\left(1 + K_{CO} P_{CO} + K_{O_2} P_{O_2}\right)^2} \tag{3}$$

There are three models in the Eley-Rideal mechanism

Model 3 : Reaction between CO in the gas phase and Adsorbed O_2

$$(-r_c) = \frac{k P_{CO} \left(K_{O_2} P_{O_2}\right)^{0.5}}{1 + \left(K_{O_2} P_{O_2}\right)^{0.5}} \tag{4}$$

Model 4 : Reaction between CO in the gas phase and adsorbed O_2 in the form of O_2s

$$(-r_c) = \frac{k K_{O_2} P_{CO} P_{O_2}}{1 + K_{O_2} P_{O_2}} \tag{5}$$

Model 5 : Reaction between O_2 in the gas phase and adsorbed CO

$$(-r_c) = \frac{k K_{CO} P_{CO} P_{O_2}^{0.5}}{1 + K_{CO} P_{CO}} \tag{6}$$

Fitting the kinetic model to the experimental data, the parameter k, K_{CO} and K_{O2} were established assuming the Arrhenius expression for k as shown below.

$k = A \exp(-E/RT)$ (7)

$K_{CO} = a \exp(b/RT)$ (8)

$K_{O2} = c \exp(d/RT)$ (9)

A Hooke-Jeeves method was used to optimize the all parameters.

From five models above, model 2 is the best model for this reaction since it gives the minimum of Sums of Square of Errors (SSE). The rate expressions is as follows and the parameters are presented in Table 6 :

$$(-r_c) = \frac{k K_{CO} K_{O_2} P_{CO} P_{O_2}}{\left(1 + K_{CO} P_{CO} + K_{O_2} P_{O_2}\right)^2} \tag{10}$$

This rate expression can predict the reaction rate from zero to several percent of CO and does not go to infinity as the partial pressure of CO approaches zero. The kinetic model and the comparison between calculated and observed values show that kinetic rate model fits the experimental data very well as shown in Figures 3 and 4. Statistical calculations also show that the model is an appropriate representation of the data since the coefficient of determination, R^2, for all experiments is close to one.

Check for transport limitations

According to Aris and Somorjai (1987) the importance of the transport processes in a catalytic reactor can be written as follows (in decreasing order): external film heat transfer > intraparticle mass transport > external film mass transfer > intraparticle heat transfer. To make sure that the reaction kinetics are not masked by inter and intraparticle heat and mass transfer, the following measures were undertaken. By using small particles, the effect of intraparticle transport can be eliminated. In this study, catalyst particles used were 40/50 mesh size with average diameter 3.58×10^{-4} m. External heat and mass transfer resistances can be reduced or eliminated by employing high volumetric flow rates. For a given amount of catalyst, the upper limit of flow rate, however, is limited by the detect ability of CO and CO_2 by the IR. External mass transfer interference in a micro reactor can be identified by varying the volumetric flow rate. As the total volumetric flow rate is increased, the F_{A0} will increase and decrease in the fractional conversion of reactant in the outlet by the same factor. The reaction rate should remain constant. However, if the reaction rate does change with the flow rate, it means that the mass transfer interference is present. The results show that the reaction rate is not affected by the volumetric flow rate suggesting that no important external mass transfer resistance is present. It also suggests that

Table 6. Parameters for mechanistic reaction rates model

Catalyst	CO oxidation					
	A	E	Power for mechanistic model			
			a	b	c	d
V_2O_5 (2%)	3.3×10^5	14877	2.09	5459	2.16×10^{-5}	12334
V_2O_5 (4 %)	3.7×10^5	13667	1.56	5433	2.31×10^{-5}	12454
NiO (2 %)	4.2×10^5	11732	1.63	4845	2.14×10^{-5}	11427
NiO (4 %)	4.6×10^5	12191	0.95	4926	2.55×10^{-5}	11332

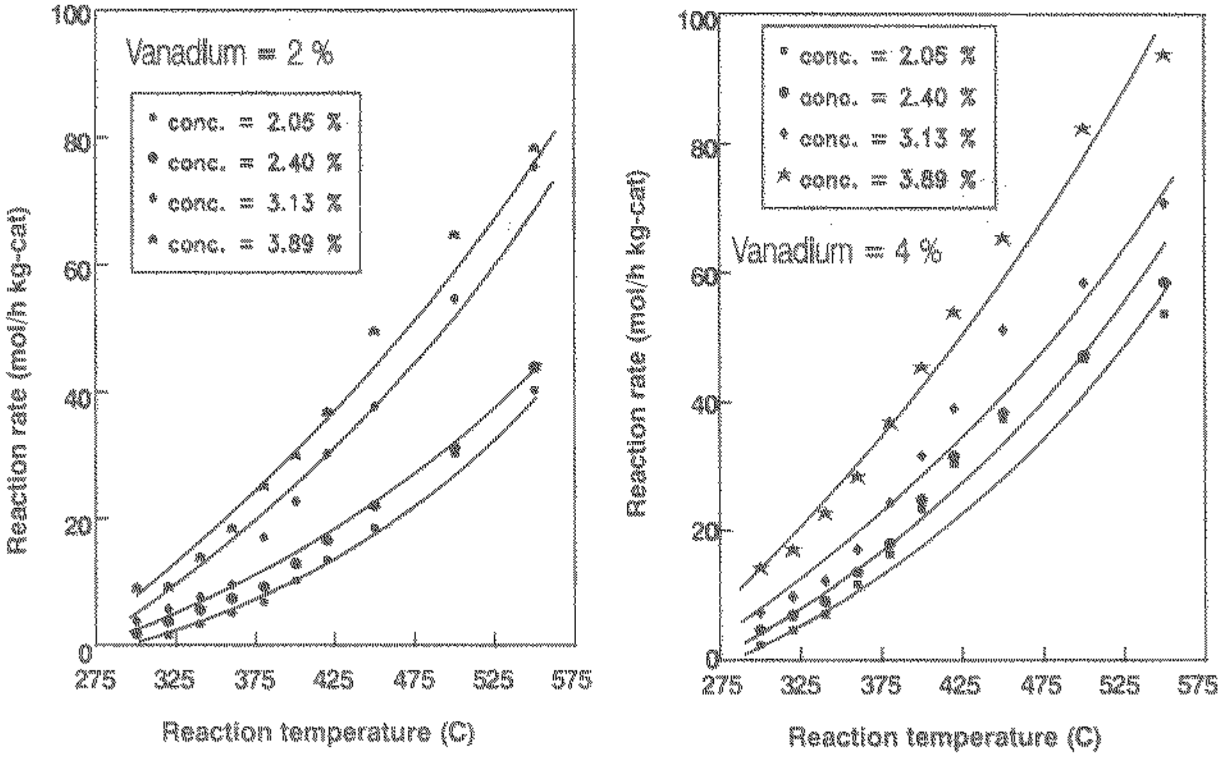

Figure 3. Temperature effect on the reaction rate using vanadium catalyst

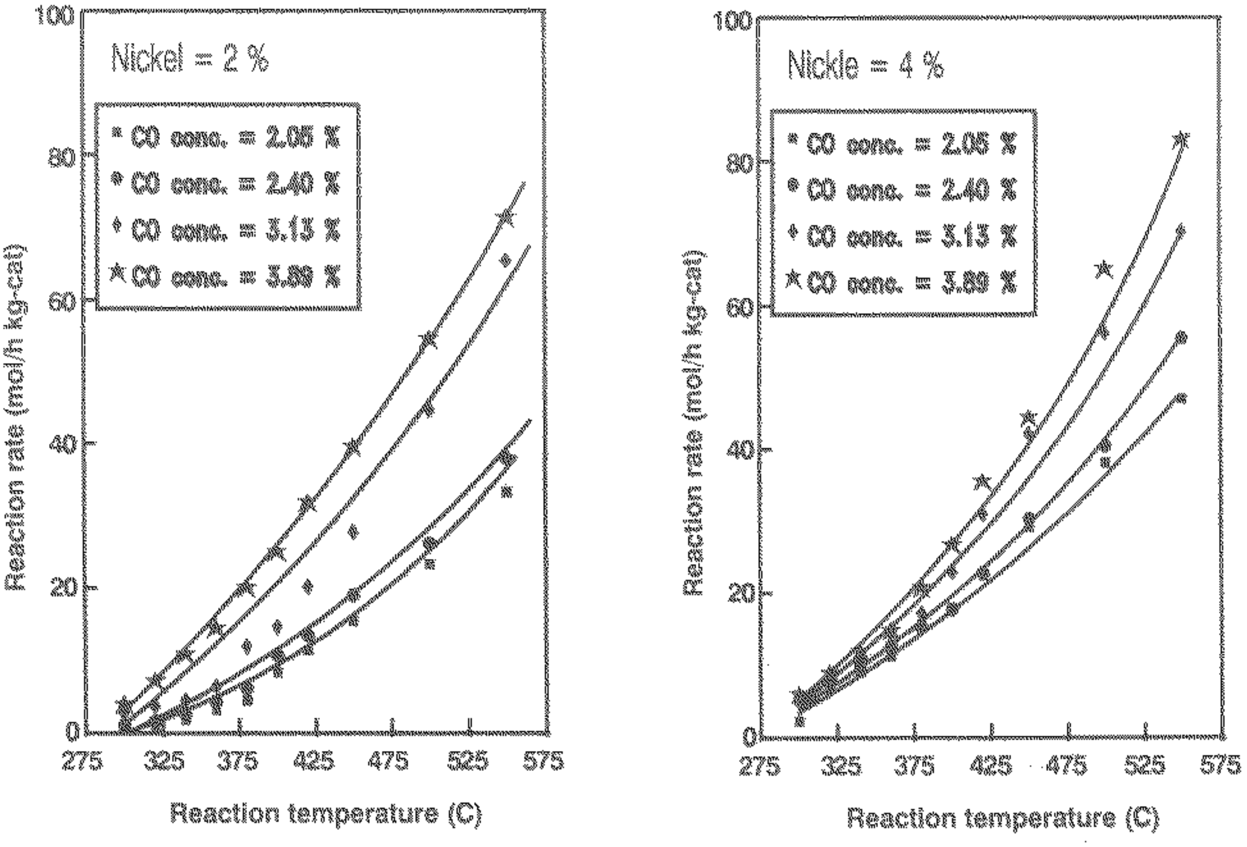

Figure 4. Temperature effect on the reaction rate using nickel catalyst

the combination of low conversion and high volumetric flow rate has made gas and particle temperatures equal.

The influence of mass transfer within a porous structure on observed rates for CO oxidation has also been checked from effectiveness calculation (Froment and Bischoff, 1990) and from Hudgins Criterion (1972). The results of these calculations show that the effectiveness factor for all experiments is equal to 1. This means that there is no internal diffusion limitation in the propylene oxidation. The Hudgins criterion supported this conclusion. The values of Hudgins criterion are less than 3.0.

CONCLUSIONS

Metal oxide catalyst supported by Indonesian natural zeolite developed in the laboratory was capable for oxidizing CO. The oxidation kinetics of CO has been studied and the rate equation and apparent activation energy have been determined. The results presented show the applicability of kinetic modeling based on elementary processes, selected on the basis of mechanistic studies, pertaining to the overall process of the CO oxidation by O_2 over metal oxide/natural zeolite catalyst. This standard Langmuir-Hinschelwood model predicts excellently the steady state behavior of the catalyst over a wide range of operating condition. For the conditions of the esperiments and type of cdatalyst used in this work, it was established that bulk phase mass transfer and pore diffusion resistance do not control the rate of catalytic oxidation of CO. Therefore, the observed kinetics represent the true surface reactions rate. The differential isothermal bed data can be correlated equally well by simple power law model and mechanistic model.

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Notation and units

A = Arrhenius constant, (mol/h kg-cat)
E = Activation energy, cal/mol
k = Reaction rate constant, (mol/h kg-cat)
K = Adsorption coefficient
r = Reaction rate (mol/h kg-cat)
R = Gas constant, cal / mol K
P = Partial pressure
T = Temperature, K

REFERENCES

Aris, R. and Somorjai, G.A., 1987, "Catalyst Design", John Wiley and Sons. New York.

Bales, J.R., 1988, "Occurence of Natural Zeolites Present Status and Future Research", Akademia Kiado, Budapest.

Barshad, Y. and Gulary, E., 1985, "A Dynamic Study of CO Oxidation on Supported Platinum", A.I.Ch.E Journal, 31, 649-657.

Foger, K., 1984, "Dispersed Metal Catalyst and Surface Lab", University of Melbourne, Melbourne.

Froment, G. F. and Bischoff, K. B., 1990, "Chemical Reactor Analysis and Design", 2nd ed., John Wiley and Sons, New York.

Hudgins, R.R., 1972, "Criteria for Transport Limitation", Can. J. Chem., 50, 427-428.

Husaini and Hardjatmo, 1996, "Natural Zeolite Occurrences in Indonesia", Proc. Int. Sem. on Novel Uses of Inorganic Natural Resources, UGM, Yogyakarta.

Kharisun and Budiono, 1999, "An Alternative Activation Method for Natural Zeolite from Indonesian Deposits Based on Its Chemical Properties", Proc. Int. Workshop and Sem. On Catalyst Chemistry, UGM, Yogyakarta.

Matros, Y.S., 1989, "Catalytic Processes under Unsteady-state Conditions", Elsevier, New York.

Mc Charty, D.E., 1975, "Mechanism of CO Oxidation", Ind. Eng. Chem. Proc. Des. Dev., 10, 541-545.

Nishiyama, Y and Wise, H, 1977, "Kinetic Oxidation of Carbon Monoxide", Chem. Eng. Sci., 32, 50.

Theodore, L and Bounicore, A.J., 1988, "Air Polution Control Equipment", CRC Press Inc, Florida.

Voltz, S.E., Morgan, C.R., Liederman, D. and Jacob, S.M., 1973, "Kinetic Study of Carbon Monoxide and Propylene Oxidation on Platinum Catalysts", Ind. Eng. Chem. Prod. Res. Dev., 12, 294-301.