CO Oxidation over Copper-Chromium Catalyst Supported by Indonesian Zeolite

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Abstract

The 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. The results shows that using impregnation method, copper and chromium 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 were done in the temperature range between 300 and 520 °C using a differential micro-reactor. 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.

Keywords: *catalytic oxidation, metal catalyst*

Introduction

The rapid growth of industry in Indonesia has resulted in a progressive in atmosphere 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. The idea of using copper–chromium (Cu – Cr) as active phase is because of the high activity of Cu – Cr for CO oxidation as was already reported by McCabe and Mitchell (1988) which showed that the activity of Cu-Cr for the CO oxidation is comparable with Pt-Rh systems. Chromium is thought to stabilize the Cu phase against sintering (Laine *et al.*, 1990) and to limit the extent of reduction by formation of $CuCr_2O_4$ phase. 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.

Fundamental

Any type of reactor with known contacting pattern may be used to explore the kinetics of catalytic reactions. Since only one fluid phase is present in these reactions, the rate can be found as with homogeneous reactions. The only special precaution to observe is to make sure that the performance equation used is dimensionally correct and that its terms are carefully and precisely defined. The reason for this precaution is the wide variety of bases (void or bulk or pellet volume, surface area, or mass of catalyst) that may be used to express rates of reaction.

The experimental strategy in studying catalytic kinetics usually involves measuring the extent of conversion of gas passing in steady flow through a batch of solids. Any flow pattern can be used, as long as the pattern selected is known; otherwise the kinetics cannot be found. A batch reactor can also be used. Several experimental devices can be used for finding the reaction rates such as differential (flow) reactor, integral (plug flow) reactor, mixed reactor and batch reactor. However, according to Levenspiel (1998), the differential flow reactor is the simplest and cheapest reactor for finding the rate. In this differential reactor the rate is assumed to be constant at all points within the reactor. Since the rates are concentration-dependent, this assumption is usually reasonable only for small conversions or for shallow small reactors.

The reaction rate can be derived from the mass balance around a volume element ΔV, in a fixed bed reactor for steady state condition. For the reaction rate calculation, the reactor was operated as differential reactor with the assumption that in the whole reactor, there is no heat and mass transfer; there is no concentration gradient; and there is no temperature gradient. Since the reaction rate can be assumed constant along the reactor, equation can be written as follows:

$$-r_A = F_{Ao}\frac{dX_A}{dW} \qquad (1)$$

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From the experimental work at several reaction temperatures, the conversion of reactant A, X_A, can be obtained. Thus each run gives directly a value for the rate at the average concentration in the reactor, and a series of runs gives a set of rate-concentration data which can then be analyzed for a rate reaction.

The suggested procedures are as follows: Make a series of kinetic runs using different $C_{A,in}$. Select the highest $C_{A,in}$ as the basis for calculating F_{Ao} and conversions, and call this concentration C_{Ao}. For each run determine W, $X_{A,in}$, $X_{A,out}$, and $C_{A,ave}$ From equation (1) calculate the rate for each run. We now have a series of rate-concentration data. Applying the differential method of analysis, a rate equation can be found from this information.

Experimental

Activation of Catalyst Support. The zeolite used in this experiment was from West Java. The samples composed of 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 depend upon in any factors such as the influence of fluid composition zeolite mineralogy, significance of associated clays, pressure and temperature, chemical stability relation among various zeolite and kinetic relation.

For activation of catalyst support, the zeolite granular were put in a reactor having 2 cm diameter and 40 cm length. For the activation, the zeolite granular were heated up to 400 °C while flowing nitrogen gas for 4 hours.

Catalyst Preparation. The catalyst was prepared by pore volume impregnation of zeolite with an aqueous of copper nitrate and chromium nitrate. After drying for 2 hours at 120 °C, the catalyst was calcined in air up to 500 °C (5 °C/min, 2 hours isothermal), resulting in 5 %wt Cu-Cr/zeolite catalyst with a Cu / Cr ratio 1.

The calcination, oxidation and reduction steps were done at temperature between 300 and 400 °C. Figure 1 is a schematic diagram for calcinations process.

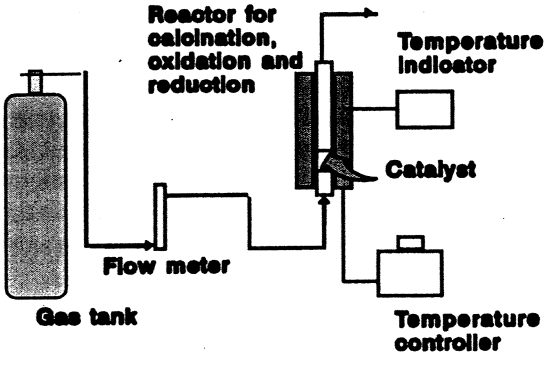

Figure 1. Schematic diagram for catalyst preparation

Catalyst Characterizations. The catalysts are characterized for surface area using nitrogen adsorption at the temperature of liquid nitrogen by the BET method. This method will also be used to determine the pore volume, average pore radius and pore size distribution. Crystalline phases are identified by x-ray diffraction using CuK_2 radiation. Surface acidity is determined by Temperature Programmed Desorption of Ammonia (NH_3-TPD). Dried samples are exposed to ammonia vapor for 1 h, about 2 mg of the ammonia bearing catalyst was loaded into a temperature programmed probe of a mass spectrometer and heated from room temperature to 500 °C at 10 °C/min at a pressure of 10^{-4} torr.

Desorption products are measured as a function of mass/charge ratio and time/temperature of desorption by the mass spectrometer. In order to know the most important variable deterring the activity of the used catalyst, Scanning Electron Microscope (SEM) was used for measuring topological surface and metal dispersion. Metal contents of the catalysts are measured by Atomic Adsorption Spectroscopy (AAS) or Neutron Activated Analysis (NAA).

Oxidation Process. The oxidation process was done in a differential reactor equipped with IR analyzer, capable for detecting CO, CO_2 and light hydrocarbon. 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.

In each run, the reactor system was heated to the desired temperature using a heating tape for about 2 to 3 hours in order to produce a stable bed temperature. Once a constant temperature was obtained, carbon monoxide and air were passed into the reactor. The gases were mixed before entering the reactor. The temperatures in the inlet and outlet catalyst bed were then monitored and recorded in an Instrulab 2000 data logger, and the concentrations of CO_2 was also monitored. To prevent fluidization of the catalyst particles, the gases from the preheater were passed downward through the reactor tube.

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

Using mass balance in the catalyst bed, the reaction rate can be calculated as follows:

$$-r_A = F_{Ao}\frac{dX_A}{dW} \qquad (2)$$

Since the conversion obtained more than 10%, the reaction rate cannot be assumed to be constant at each point in the reactor length. Therefore, the reaction rates are calculated from the following expression which is the integral of Equation 2.

$$W = \int_0^{X_A} \frac{F_{Ao}\, dX_A}{(-r_A)} \qquad (3)$$

where:

$(-r_A)$ = reaction rate (mol/h/kg-cat)
F_{Ao} = feed rate of reactant A (mol/h)
X_A = fractional conversion of A
W = amount of catalyst (kg)

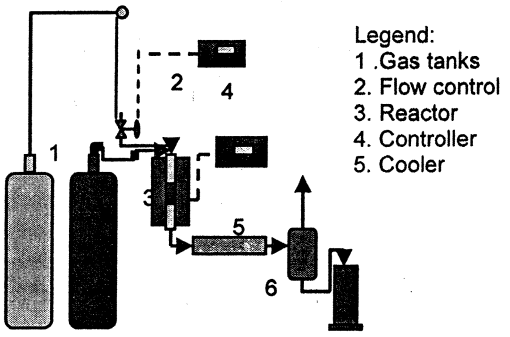

Figure 2. Schematic diagram for CO oxidation experiment

Results and Discussion

Results of Catalyst Characterization. The results of characterization of the catalyst developed are shown in Table 1. The table shows the measurements of surface area, pore diameter and pore volume for copper-chromate catalyst supported on zeolite and activated carbon.

Table 1. Results of Catalyst Characterization

Cu-Cr (%)	Supported by zeolite		
	Surface area (m^2)	Pore radius (Å)	Pore volume (cm^3/g)
0	31.489	21.323	0.035
0.5	39.540	21.679	0.042
1.0	37.489	21.930	0.039

Catalyst development was 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 dipping method, the metal impregnated was only 70–80%; whereas using 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 of 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 becomes easier.

Catalytic Oxidation. Several preliminary runs were made to test catalytic activity of materials of construction of the reactor (stainless steel), packing materials (pyrex beads) and thermocouple cement used for 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 results of CO oxidation 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 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. 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 CO oxidation.

Table 2. Effect of Temperature on the Average Isothermal Bed Results for 2.5% and 5% Catalyst

T (°C)	Reaction rate (mol/h/kg-cat)		
	3.8%	4.3%	6.7%
300	2.59	5.30	10.60
320	5.18	7.95	13.25
360	10.36	13.25	21.20
380	12.95	23.85	29.15
400	18.13	29.15	34.45
440	31.08	45.05	42.40
480	44.03	58.30	68.90
520	59.57	74.20	79.51

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	3.8%	4.3%	6.7%
300	5.30	7.95	13.25
320	7.95	10.60	15.90
360	15.90	18.55	26.50
380	21.20	26.50	34.45
400	29.15	34.45	42.40
440	45.05	42.40	50.35
480	55.65	63.60	76.86
520	68.90	76.86	87.46

The results of oxidation processes show that the higher the metal concentration on the catalyst surface, the higher conversion or reaction rate can be achieved resulting in higher reaction rate, as shown in Table 2. Catalyst with higher metal concentration 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.

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.

The CO oxidation over platinum catalysts proceeds by a Langmuir-Hinshelwood model. Typically, at low CO concentrations the reaction rate increases with the CO concentration, while at high concentration it passes through a maximum due to the strong CO adsorption at the Pt surface (Purwono, 2000). For this Cu-Cr catalyst at equal condition, the reaction rate still increase even up to 6.7% CO, indicating a weak adsorption of CO or reaction of CO from the gas phase. This strongly suggests that CO does not have to adsorb before reacting.

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

$$(-r_c) = Ae^{(-E/RT)}P_A^a P_B^b \qquad (4)$$

Fitting this model to the experimental data, using simple linear regression method (Box *et al.*, 1978), the parameters A, E, a and b were established assuming the Arhenius expression applied.

Mechanistic model. If both gases (CO and O_2) are adsorbed on the catalyst surface, the reaction mechanism follows 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:

$$(-r_c) = \frac{kK_A P_A (K_B P_B)^{0.5}}{\left(1 + K_A P_A + (K_B P_B)^{0.5}\right)^2} \qquad (5)$$

Model 2: If adsorption of O in the form of O_2s, the reaction rate expression is:

$$(-r_c) = \frac{kK_A K_B P_A P_B}{(1 + K_A P_A + K_B P_B)^2} \qquad (6)$$

There are three models in the Eley-Rideal mechanism:

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

$$(-r_c) = \frac{kP_A (K_B P_B)^{0.5}}{1 + (K_B P_B)^{0.5}} \qquad (7)$$

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

$$(-r_c) = \frac{kK_B P_A P_B}{1 + K_B P_B} \qquad (8)$$

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

$$(-r_c) = \frac{kK_A P_A P_B^{0.5}}{1 + K_A P_A} \qquad (9)$$

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

$$k = A\exp(-E/RT) \qquad (10)$$

A Hooke-Jeeves method was used to optimize the all parameters and the parameters are presented in Table 3. From five models above, model 5 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:

$$(-r_c) = \frac{kK_A P_A P_B^{0.5}}{1 + K_A P_A} \qquad (11)$$

Table 3. Parameters for Reaction Rates Model

Catalyst	$A \times 10^8$	E	K_A
Cu-Cr	2.142	13482	334

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. 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. The influence of mass transfer within a porous structure on observed rates for CO oxidation has also been checked from effectiveness calculation 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 oxidation.

Check for Transport Limitations. According to McCarthy (1973) 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 detectability of CO and CO_2 by the IR.

External mass transfer interference in a microreactor can be identified by varying the volumetric flow rate. As the total volumetric flow rate is increased, the F_{A0} in Equation 5 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 the combination of low conversion and high volumetric flow rate has made gas and particle temperatures equal.

Conclusions

The results of this investigation lead to the following conclusions: the catalyst developed in the laboratory can be used for oxidizing CO. For the conditions of the experiments and type of catalyst 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 and light hydrocarbon. 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 as $(-r_c) = Ae^{(-E/RT)}P_A^a P_B^b$ and mechanistic model as $(-r_c) = \frac{kK_A P_A P_B^{0.5}}{1+K_A P_A}$. The results of this investigation shows that the catalyst developed in the laboratory can be used for oxidizing CO. For the conditions of the experiments and type of catalyst 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.

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