

CHAPTER III

RESULTS AND DISCUSSION

3.1 Surface Area Measurement

The effect of Pd loading and calcination temperature on the surface area of catalyst were measured by BET, particle size analyzer and XRD. From Table 3.1, Figures 3.1, and 3.2, it can be seen that Pd loading and calcination temperature have no strong effect on surface area, pore volume, and pore radius under the variation range. When the calcination temperature was increased, the BET surface area slightly decreased. This was due to the sintering of alumina. At the higher calcination temperature, some of γ - Al_2O_3 changes to α - Al_2O_3 with collapsing of the structure and the formation of dense and low surface area material.

Table 3.1 Catalyst Characterization

| Catalyst | Calcined Temp.(°C) | BET Area m^2/gm | Particle Size (micron) | Pore Volume cc/gm | Pore Radius (Å) | Crystallite Size (Å) |
|----------|--------------------|---------------------------------|------------------------|-----------------------------------|-----------------|----------------------|
| Alumina | - | 102.20 | 101.93 | 0.2133 | 41.74 | - |
| 0.50 | 500 | 113.50 | 61.41 | 0.2209 | 38.92 | - |
| | 600 | 110.90 | 67.04 | 0.2209 | 39.83 | - |
| | 700 | 103.00 | 62.77 | 0.2280 | 44.28 | - |
| 1.00 | 500 | 114.10 | 64.04 | 0.2188 | 38.36 | - |
| | 600 | 107.70 | 73.42 | 0.2199 | 40.84 | - |
| | 700 | 98.54 | 70.79 | 0.2152 | 43.67 | - |
| 1.50 | 500 | 112.90 | 73.66 | 0.2180 | 38.63 | 145.87 |
| | 600 | 109.80 | 76.02 | 0.2141 | 38.99 | 168.27 |
| | 700 | 96.54 | 76.00 | 0.2157 | 44.68 | 185.76 |

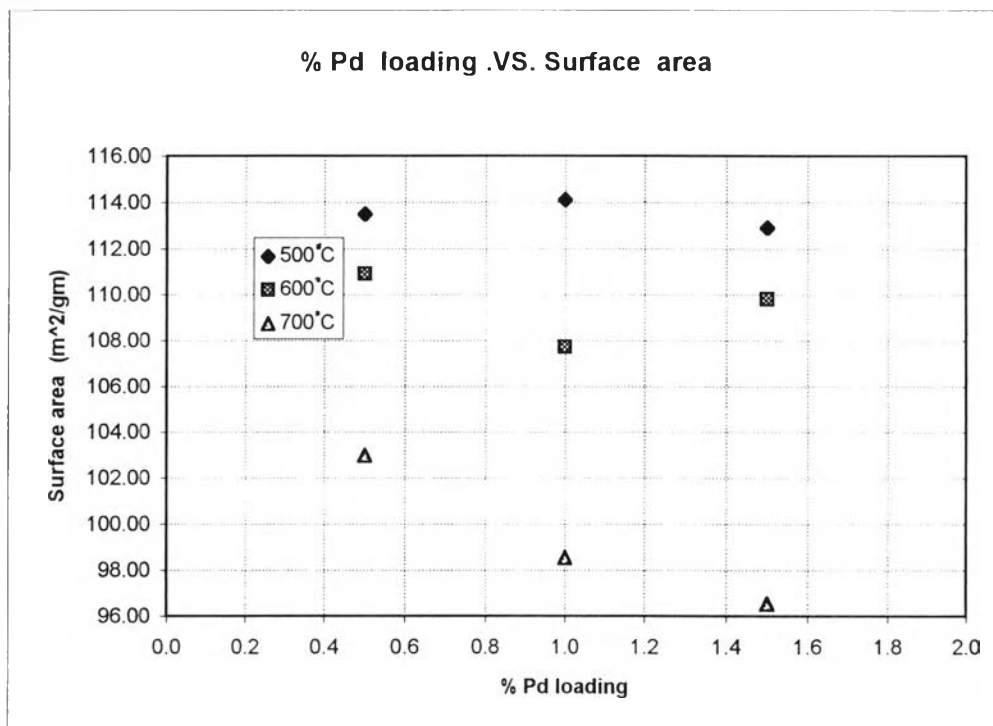


Figure 3.1 Effect of Pd loading and calcination temperature on BET surface area.

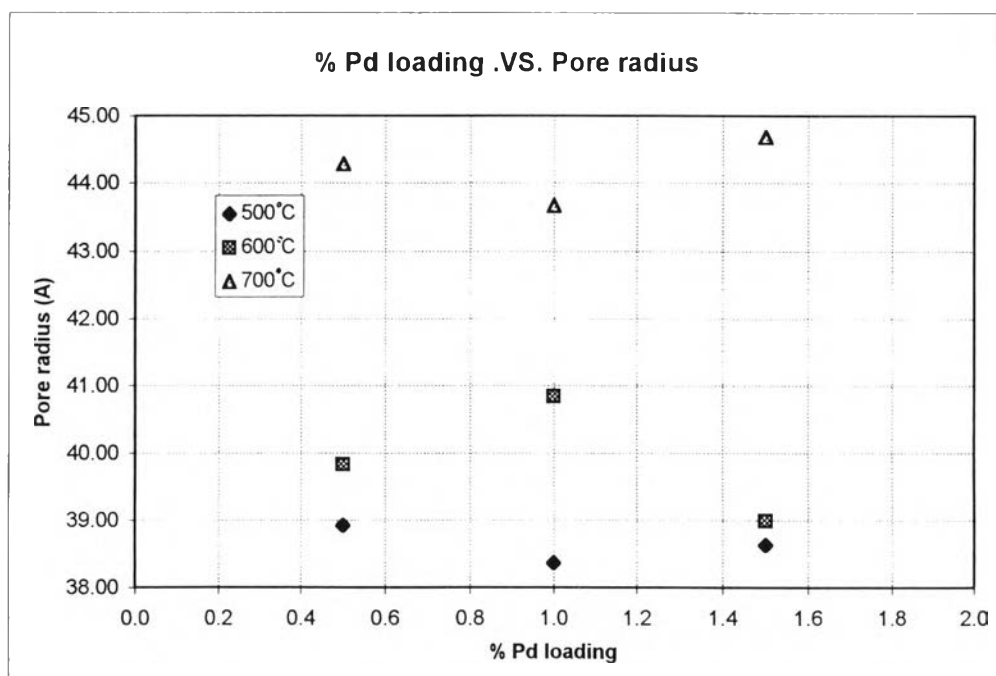


Figure 3.2 Effect of Pd loading and calcination temperature on pore radius.

In addition, when the calcination temperature was increased, the Pd particle size increased and formed the higher thermodynamically stable of Pd particle size which formed more (111) plane of Pd crystallites.

3.2 Catalyst Activities

3.2.1 Effect of Pd Loading

Generally, the rate of reaction depends strongly on the amount of active site and the dispersion of palladium. When the percentage of Pd was increased, the rate of reaction increased. The dispersion of Pd depended on the method of impregnation, the strength of adsorption, the extent to which the metal compound was present as occluded solute (that is in the bulk liquid in the pores) in contrast to adsorbed species on pore walls, and the chemical reactions that occur upon heating and drying.

The dependence of the rate of reaction on Pd amount was investigated by varying the amount of Pd on alumina using 0.1 gm of three Pd loadings (0.5, 1.0, and 1.5 %) catalysts calcined at three different temperatures (500, 600, 700 °C). The reactant gases contained approximately 2,000 ppm of both CO and NO in helium. The total flowrate was 200 cc/min (SV= 120,000 cc/gm.cat/hr) at 450 °C and atmospheric pressure.

From Figures 3.3, 3.4, and 3.5, we see that the rate of reaction increased when the percentage Pd loading was increased. In contrast, for catalysts calcined at 700 °C, the rate of reaction decreased when the percentage Pd loading increased. This might be explained by the agglomeration of Pd and the phase change of alumina. At higher calcination temperature, the agglomeration of palladium in the catalyst probably occurs

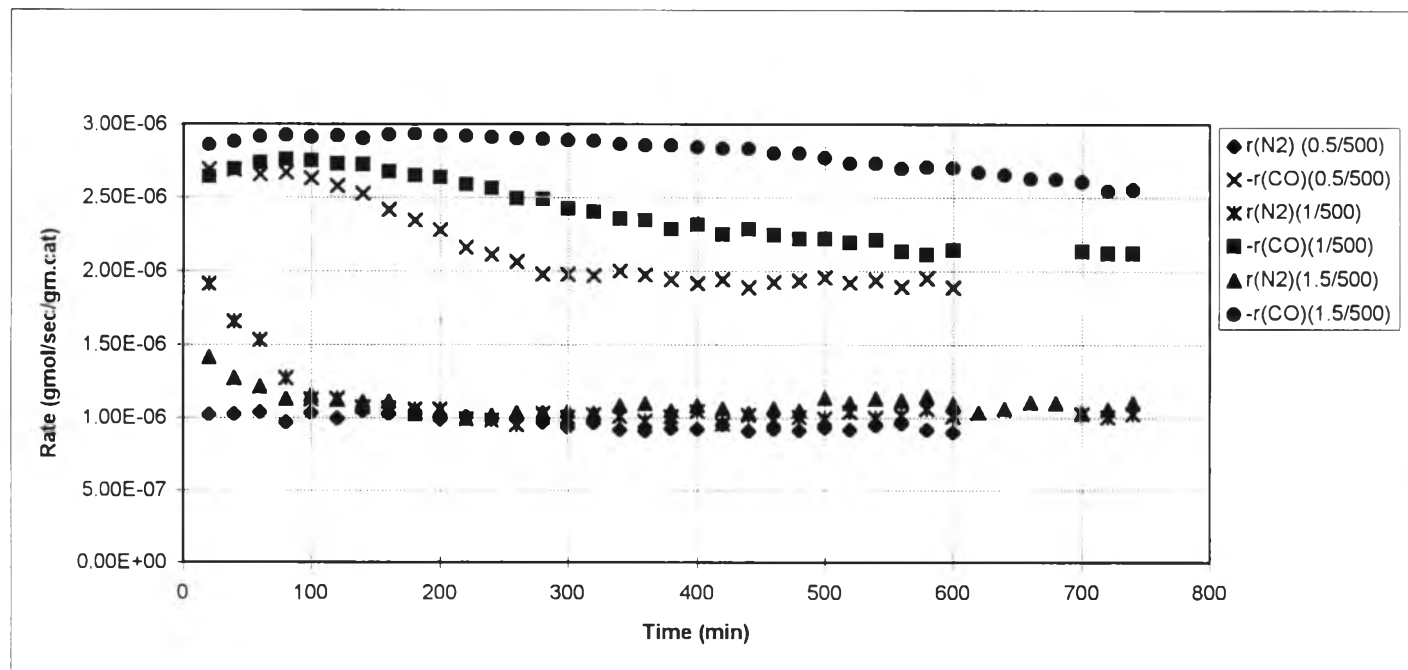


Figure 3.3 Effect of Pd loading at 500 °C of calcination temperature.

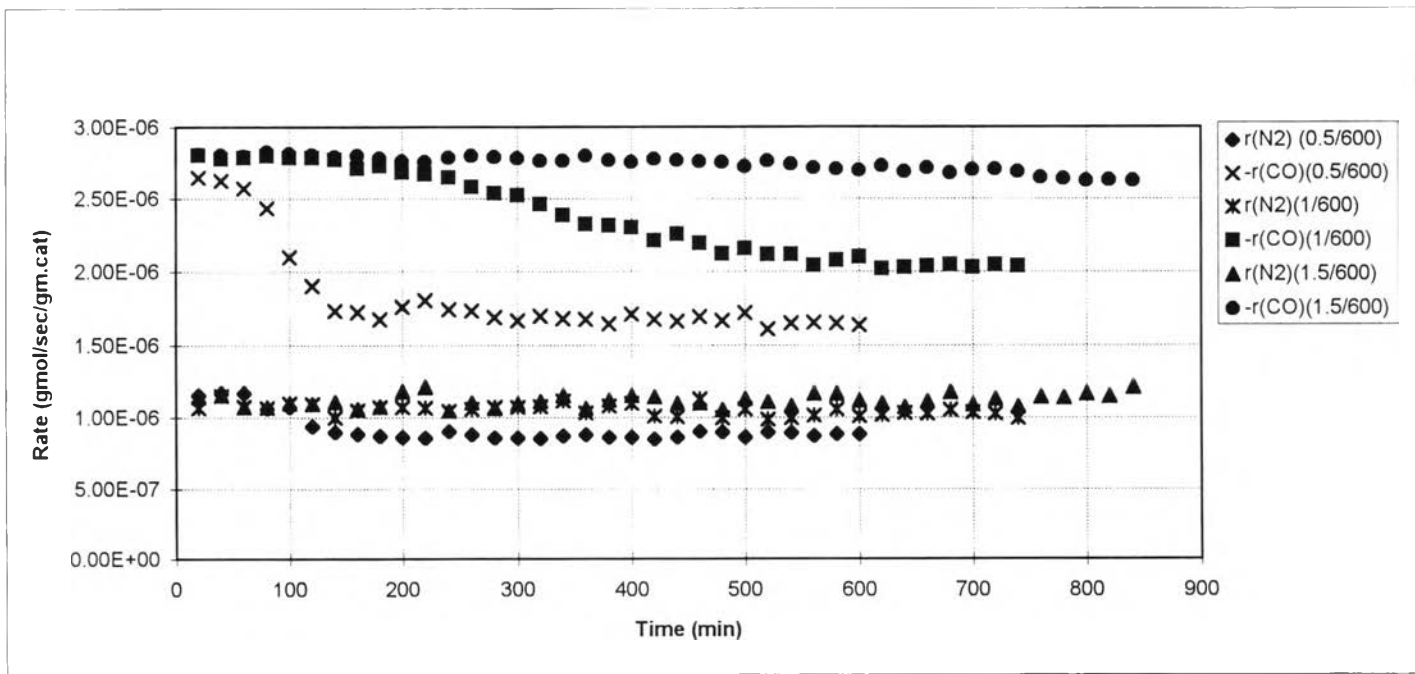


Figure 3.4 Effect of Pd loading at 600°C of calcination temperature.

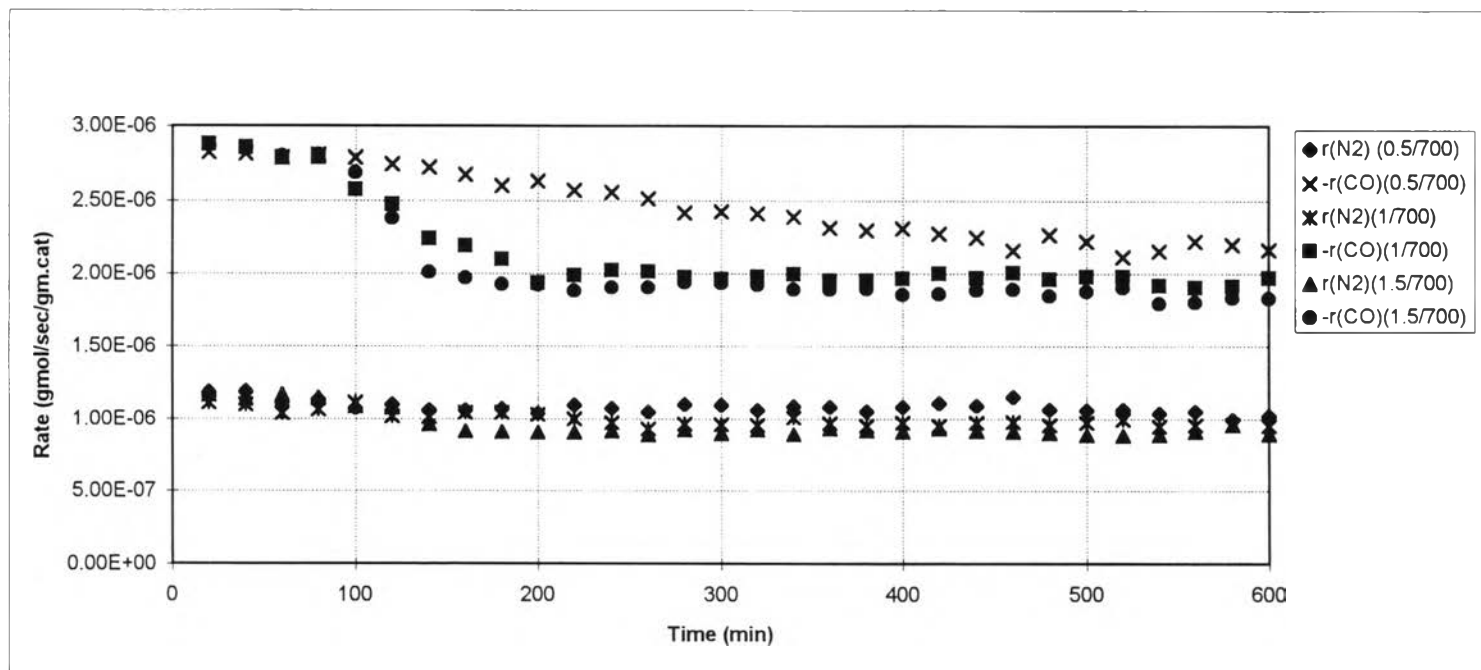


Figure 3.5 Effect of Pd loading at 700 °C of calcination temperature.

and decreases the ultimate degree of dispersion of Pd. The agglomeration of Pd resulted in the increasing of Pd particle size, decrease of active catalyst surface area and the decreasing of catalyst activity. The alumina phase may have changed from gamma to alpha phase which has a lower BET surface area.

3.2.2 Effect of Calcination Temperature

The rate of reaction was measured under the same operating conditions while varying the calcination temperature (600 and 700 °C).

From Figures 3.6, and 3.7, we observe that the rate of reaction decreased when calcination temperature increased. For the catalysts calcined at 500 and 600 °C, the rate of CO oxidation is double the rate of NO reduction selectivity to N₂ for 1% of Pd loading. For 1.5 % Pd loading, the rate of CO oxidation is approximately three times of the rate of NO reduction selectivity to N₂. We can conclude that the rate of NO reduction tends to increase the selectivity to N₂O with increased the Pd loading. However, for catalyst calcined at 700 °C, the rate of CO oxidation is double the rate of NO reduction selectivity to N₂ for both 1 and 1.5 % Pd loading. Thus the higher calcination temperatures tend to increase the selectivity to N₂. It means that the (111) plane is responsible for the selectivity of NO reduction to N₂.

3.3 Reaction Studies

3.3.1 External Film Resistance

The presence of external film resistance was tested by measuring the reaction rate with varying superficial velocity through the reactor. As the

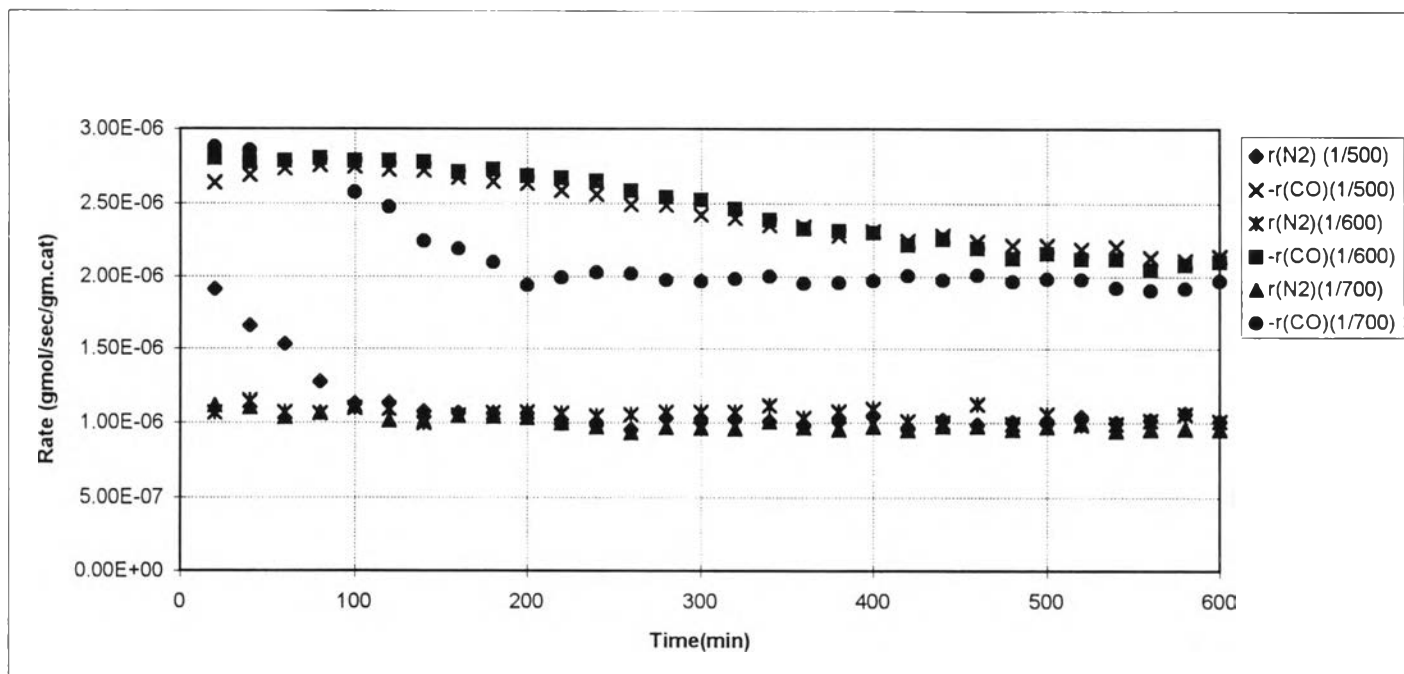


Figure 3.6 Effect of calcination temperature of 1.0 % Pd loading.

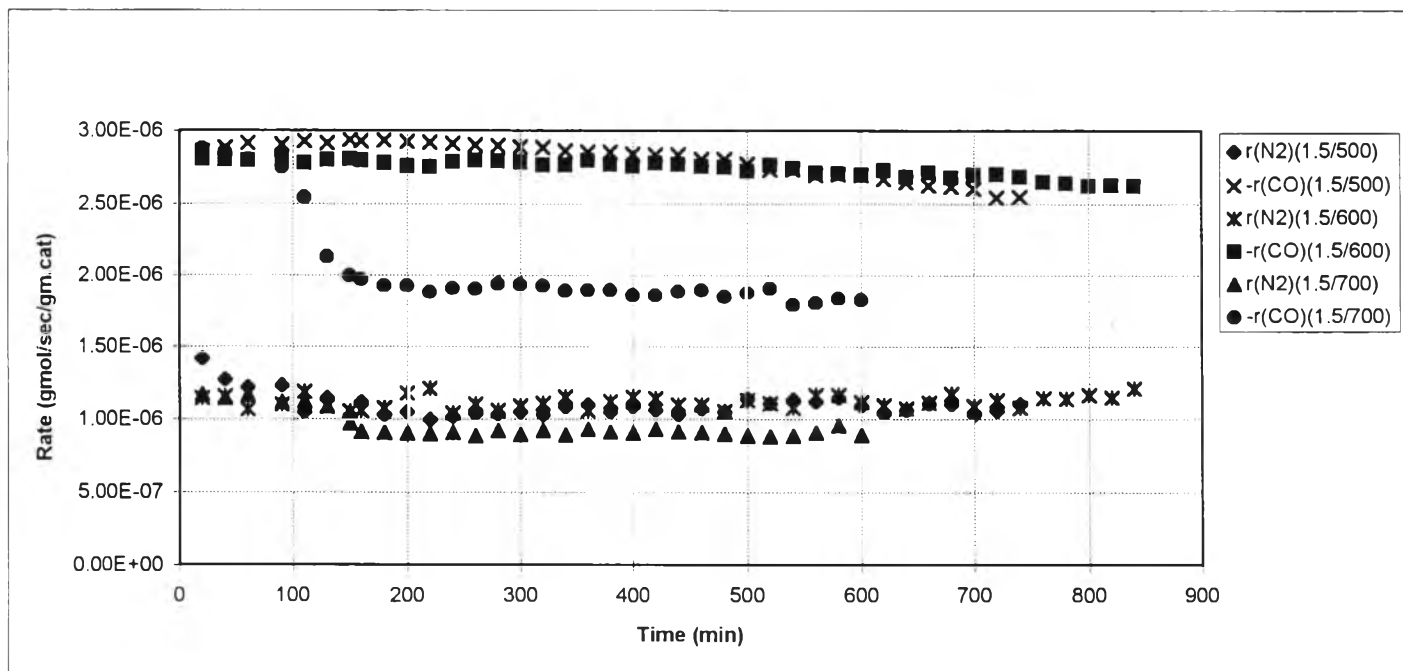


Figure 3.7 Effect of calcination temperature at 1.5 % Pd loading.

velocity through the reactor was increased, the boundary layer thickness decreased until the mass transfer across the boundary layer no longer limited the rate of reaction.

The measurements were carried out in a differential flow reactor with 0.1 gm of 0.5 % Pd/Al₂O₃ (calcined at 600 °C). Reactant gas consisted of 2,000 ppm of both CO and NO in helium. The reactants were passed through the catalyst bed at 450 °C under atmospheric pressure by varying the total flowrate and keeping the reactant concentration at 2,000 ppm. The results are shown in Figure 3.8. The plot between the rate of reaction versus total flowrate shows that the rate of reaction levels off at a total flowrate greater than 200 cc/min. Thus the external film resistance can be neglected when total flowrate is greater than 250 cc/min. All of the experiments were carried out at 250 cc/min of total flowrate.

In addition, the rate of CO oxidation double the rate of NO reduction selectivity to N₂. It may be concluded that most of reactions follow; $2\text{NO} + 2\text{CO} \rightleftharpoons \text{N}_2 + 2\text{CO}_2$ for this catalyst which produces N₂O in a very low level.

3.3.2 Kinetic Study

The steady-state kinetics of nitric oxide reduction with carbonmonoxide was studied. The objectives of this investigation were to establish the reactant orders with respect to NO and CO concentrations, and to examine the temperature dependence of the reaction rate.

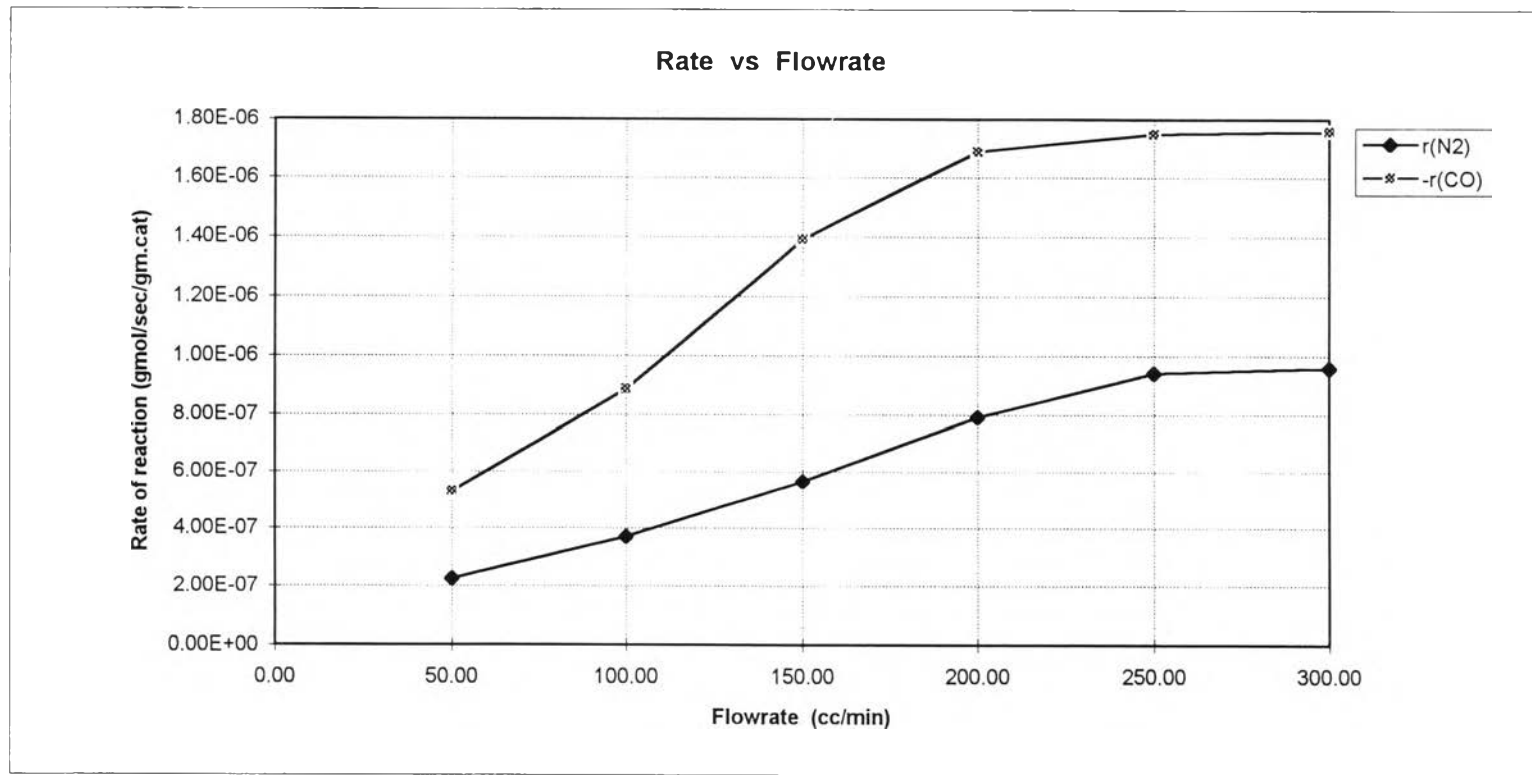


Figure 3.8 The external film resistance test.

3.3.2.1 The Order of Reaction with Respect to CO

The rate of reaction was observed by varying the CO concentration and keeping the NO concentration constant at 10,000 ppm. The ratio of CO to NO was varied from 1/5 to 1/10. The amount of catalyst was 0.1 gm, obtained by mixing alumina with 0.5 % Pd/Al₂O₃ at ratio of 10:1 (calcined 600 °C).

The reaction rate as a function of carbonmonoxide concentration, at a constant nitric oxide concentration of 10,000 ppm and constant reaction temperatures of 310 and 315 °C is shown in Figure 3.9. The curve slope of natural logarithm of CO concentration versus natural logarithm of rate of CO oxidation was about -0.5 (-0.46) in concentration range from 1,000-2,000 ppm. The inverse 0.5 order dependence is probably the result of CO blocking the sites necessary for NO adsorption. Thus the rate of reaction decreases with increasing CO concentration. This result is consistent with that of Butler and Davis in 1976 and Taylor and Klimisch in 1973 who also observed that the reduction of NO by CO over palladium on alumina was inhibited by increasing CO concentration.

3.3.2.2 The Order of Reaction with Respect to NO

The rate of reaction was examined by varying the NO concentration and keeping CO concentration constant at 20,000 ppm. The ratio of NO to CO was varied from 1/5 to 1/10. The catalyst used in this study was 0.1 gm of 0.5 % Pd/Al₂O₃ (calcined 600 °C) without mixing with alumina. The total volumetric flowrate was 250 cc/min at atmospheric pressure. Reaction temperature was 310, 320, and 330 °C. The curve of natural logarithm of NO concentration versus natural logarithm of the rate of NO reduction selectivity

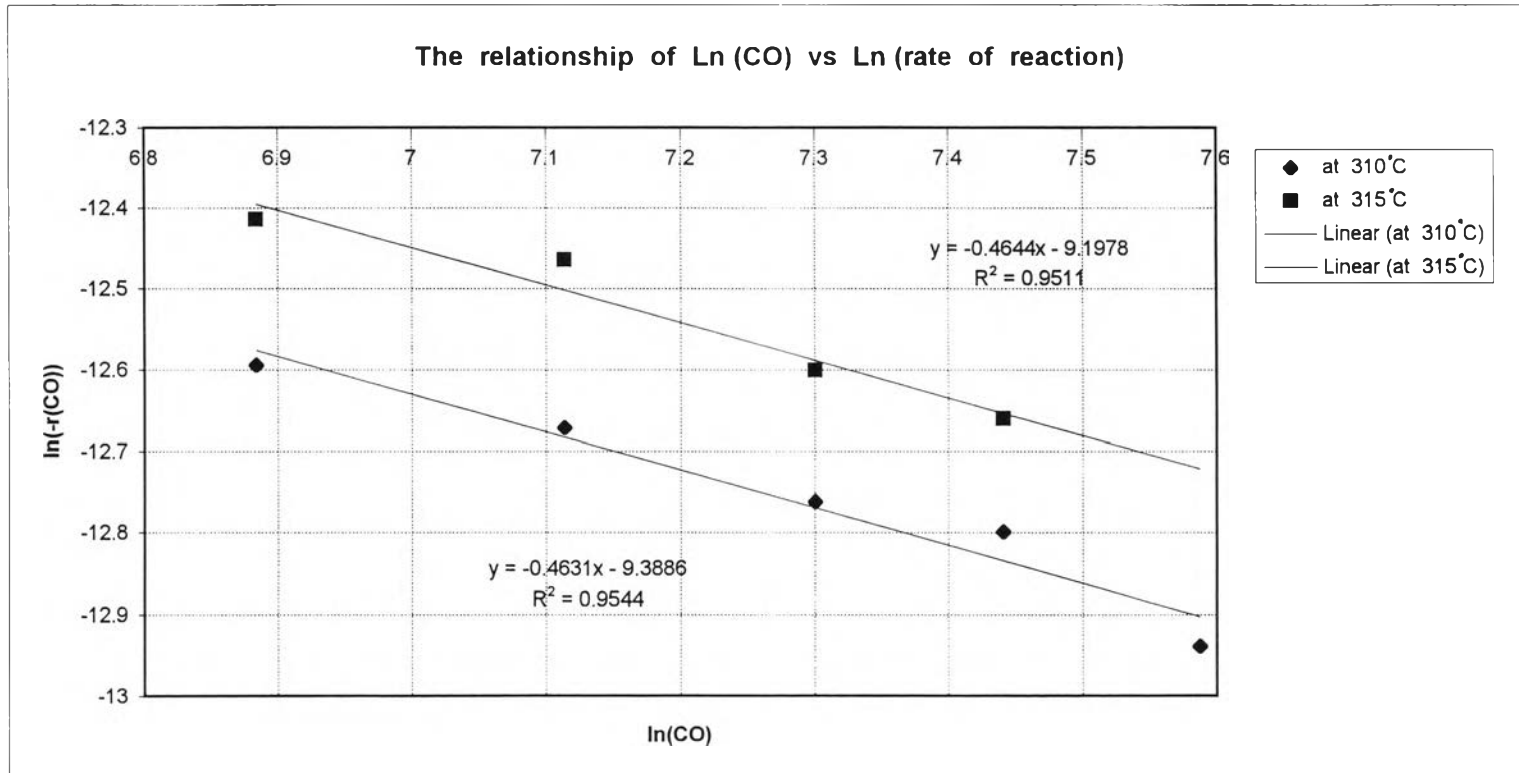


Figure 3.9 Carbonmonoxide order plot using a constant nitric oxide concentration of 10,000 ppm at 310 and 315°C.

to N_2 was plotted. In this study, the rate of NO reduction selectivity to N_2 was lower than 15 %.

The results are shown in Figure 3.10. The nitric oxide order plot illustrates a behavior inverse of the carbonmonoxide order plot. The rate increases with NO concentration. The order with respect to nitric oxide is about 1.0 (0.96) in NO concentration range of 2,000 - 4,000 ppm. This result also is consistent with that of Butler and Davis in 1976 who found that rate of reaction increased with increasing NO concentration. In contrast, Taylor and Klimisch in 1973 found that the increasing of NO concentration tended to decrease both the rate of NO removal and the extent of ammonia formation on ruthenium catalyst.

3.3.2.3 The Specific Rate Constant of NO-CO Reaction

The activation energy was obtained from a plot of natural logarithm of reaction rate constant versus $1/T$. The plot should be a straight line whose slope is proportional to the activation energy. The specific rate constant was calculated from the equation of $r = k(CO)^a(NO)^b$ which a and b are the order of reaction with respect to CO and NO concentrations, respectively, and r is the rate of NO reduction selectivity to N_2 .

The rate of reaction was investigated by using 0.1 gm of 0.5 % Pd/ Al_2O_3 (calcined 600 °C). The temperature of the reactor was varied from 300 to 350 °C. The feed consisted of 4,000 ppm of both NO and CO concentrations.

The temperature dependence of the reaction rate is shown in Figure 3.11, in the form of a standard Arrhenius plot. From figure 3.11, we calculated

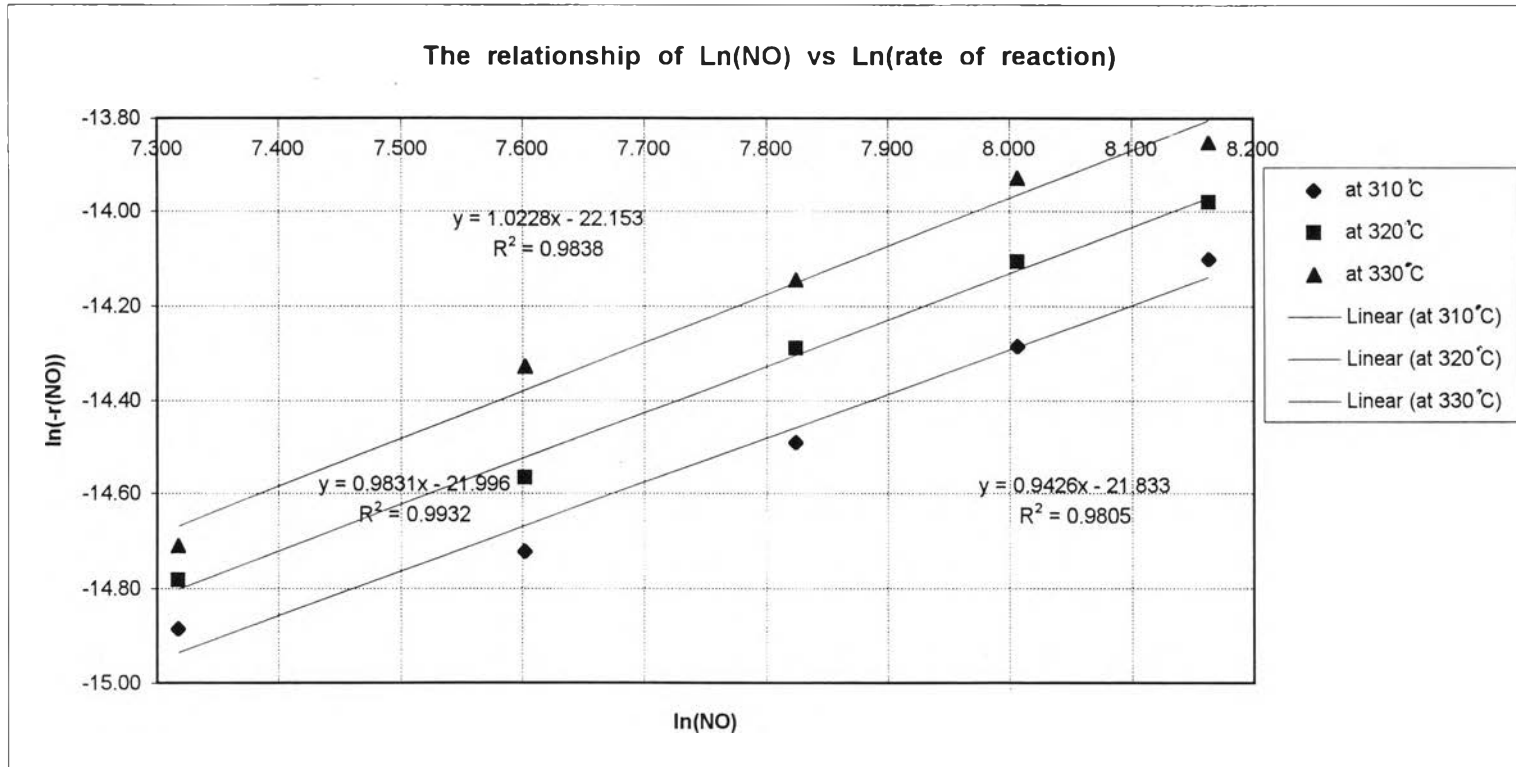


Figure 3.10 Nitric oxide order plot using a constant carbonmonoxide concentration of 20,000 ppm at 310, 320, and 330°C.

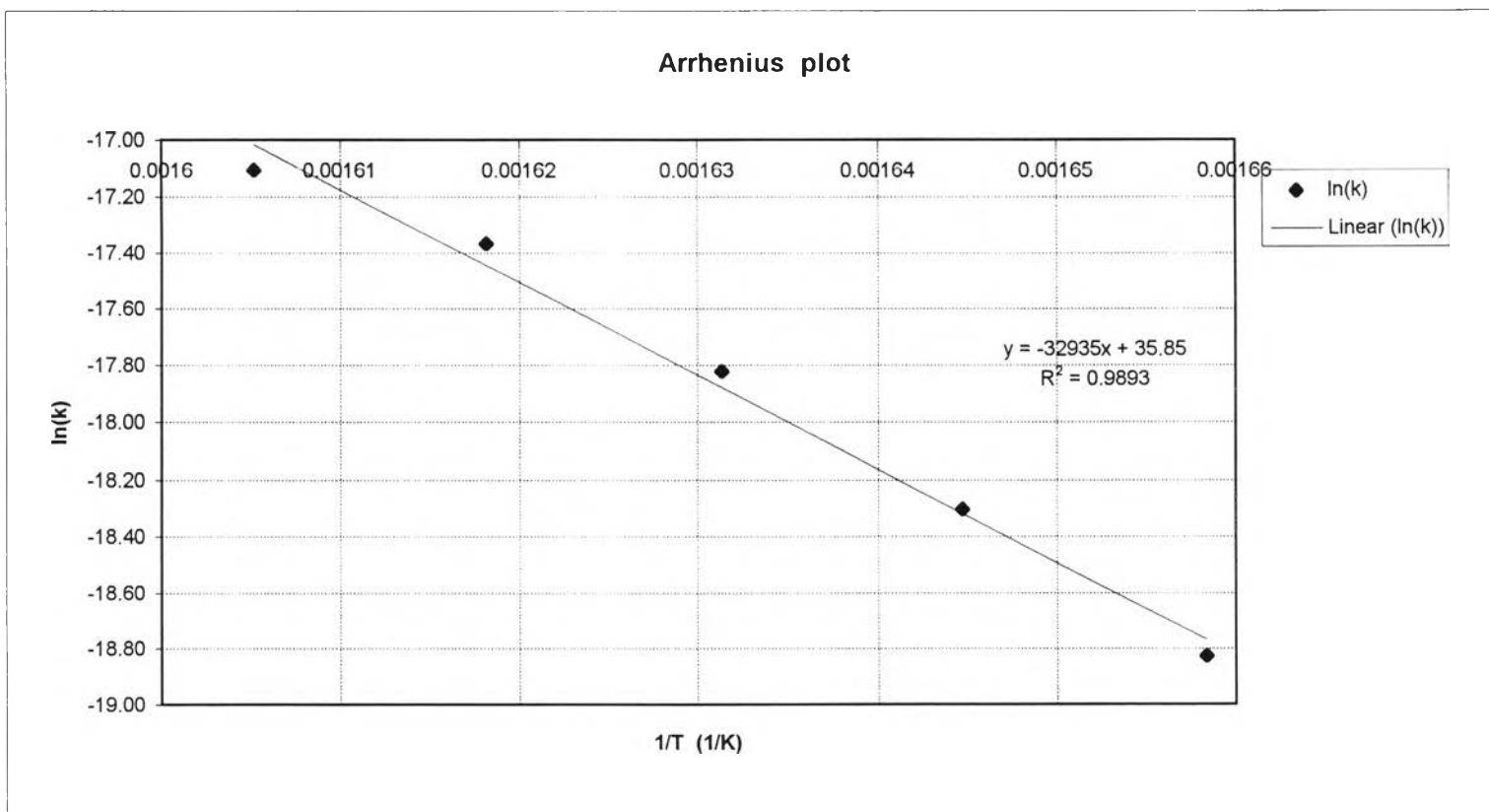


Figure 3.11 Temperature dependence of reaction rate using a constant carbonmonoxide concentration and nitric oxide concentration of 4,000 ppm.

an activation energy equal to 65.44 Kcal/mole at 4,000 ppm of both CO and NO concentrations. This activation energy is approximately triple that of the activation energy of CO oxidation by oxygen on Pd(100) (Logan and Paffett in 1992) and double of the activation energy of the NO and CO reaction on (111) Rh (Peden, et al. in 1995).

Thus the overall rate of reaction is given by :

$$\text{rate of reaction} = A * \exp(-E/RT) * [\text{CO}]^a * [\text{NO}]^b \quad (3.1)$$

where

$$A = 3.70999\text{E}+15$$

$$E = 65441.554 \quad \text{cal/mole}$$

$$R = 1.987 \quad \text{cal/mole/ K}$$

$$a = -0.4637$$

$$b = 0.9829$$

T = temperature of reaction in unit of K

NO and CO in unit of ppm,

and rate of reaction in unit of gmmole/sec/gm of catalyst.

From equation 3.1, it can be seen that 4.167×10^{-6} gmmole of NO will be reacted to N_2 per second per gram of catalyst, or 8.335×10^{-4} gmmole of NO will be reacted to N_2 per second per gram of palladium at 2,000 ppm of CO, 4,000 ppm of NO and 350 °C of reaction temperature.

This rate of NO reaction selectivity to N_2 can be compared to other reported results shown in Table 3.2 below:

Table 3.2 Comparison of activities for NO reduction

| Catalyst | Conditions | Reducing Agent | Activity(gmmol/gm.cat/sec) | Ref. |
|--|--|----------------|-----------------------------------|------------------------------|
| Cr ₂ O ₃ | 350 °C, 1400 cc/min | CO | 3.7138 x 10 ⁻⁷ (*) | Shelef.et al.,(1968) |
| 0.5 % Pd on Al ₂ O ₃ | 350 °C, GHSV 24,000 | H ₂ | 6.0610 x 10 ⁻⁴ (*) | Kobylinski and Taylor |
| 0.5 % Pd on Al ₂ O ₃ | 400 °C, GHSV 24,000 | CO | 1.2121 x 10 ⁻⁴ (*) | Kobylinski and Taylor (1974) |
| 0.05Ag on Cr ₃ O ₄ | 400 °C, contact time 2 gm of cat.*sec/cc | - | 4.5455 x 10 ⁻⁶ (**) | Iwamoto and Hamada (1991) |
| 0.5 % Pd on Al ₂ O ₃ | 350 °C, 250 cc/min, | CO | 4.1670 x 10 ⁻⁶ (**) | This work |

(*) is the rate of NO reduction

(**) is the rate of NO reduction selectivity to N₂