

CHAPTER IV

RESULTS AND DISCUSSION

4.1 Characterization

All catalysts from impregnation and coprecipitation methods were prepared at 5% total metal loading. Catalysts containing 0%, 25%, 50%, 75%, and 100%Ag were prepared to study the effect of alloying. To study the effect of calcination temperature, the impregnation catalysts of 50%Ag were calcined at 200, 300, 400, 500, 600 and 700 °C.

The effects of the ratio of silver to gold and calcination temperature on the surface area, pore radius, and pore volume as well as crystallite size are shown in Table 4.1. For impregnation catalysts, the surface area decreases with increasing calcination temperature due to the sintering of Al_2O_3 . It is found that the amount of silver has no significant effect on the properties until 100%Ag is reached. The 100%Ag impregnation catalysts has about 25% less surface area. The table also gives the approximate crystallite sizes obtained from the X-ray line broadening measurements. Unfortunately there is too much variation in the measurements to get any conclusion out of it. The only conclusion obtained is that the average crystallite size for the metals is around 200-255 Å.

TEM pictures (Figures 4.1-4.3) taken from all of the samples show a wide distribution of crystallites ranging in size from 100 - 2000 Å. As expected, the impregnation catalysts have larger crystallites (Figure 4.1).

Figure 4.1 shows well faceted metallic crystallites ranging in size from 100 Å to 500 Å. Figure 4.2 shows the sintering of gold particles in the coprecipitation catalyst. Figure 4.3 shows small (50 Å) catalysts as well as clusters of larger silver crystallites.

Table 4.1 Catalyst characterization

| Catalyst | Method | Calcination temperature (°C) | BET surface area (m ² /g) | Pore Volume (ml/g) | Pore radius (Å) | Crystallite size (Å) |
|--------------------------------|--------|------------------------------|--------------------------------------|--------------------|-----------------|----------------------|
| Al ₂ O ₃ | - | - | 175.50 | 0.2636 | 30.04 | - |
| 50%Ag | A* | 200 | 168.40 | 0.2448 | 29.08 | 172.40 |
| 50%Ag | A | 300 | 159.90 | 0.2425 | 30.33 | 341.56 |
| 50%Ag | A | 400 | 166.40 | 0.2508 | 30.15 | 139.37 |
| 50%Ag | A | 500 | 156.70 | 0.2523 | 33.20 | 556.63 |
| 50%Ag | A | 600 | 148.60 | 0.2593 | 34.89 | 281.10 |
| 50%Ag | A | 700 | 125.60 | 0.2646 | 42.13 | 451.91 |
| 0%Ag | A | 300 | 155.80 | 0.2330 | 29.92 | 350.25 |
| 25%Ag | A | 300 | 159.00 | 0.2320 | 29.22 | 229.02 |
| 50%Ag | A | 300 | 162.70 | 0.2433 | 29.90 | 41.56 |
| 75%Ag | A | 300 | 171.60 | 0.2439 | 28.40 | 245.71 |
| 100%Ag | A | 300 | 127.00 | 0.1888 | 29.73 | 570.21 |
| 0%Ag | B* | 300 | 41.35 | 0.04683 | 175.0 | 145.25 |
| 25%Ag | B | 300 | 61.50 | 0.02581 | 130.4 | 257.83 |
| 50%Ag | B | 300 | 154.50 | 0.01839 | 154.3 | 162.19 |
| 75%Ag | B | 300 | 45.30 | 0.05403 | 212.8 | 241.91 |
| 100%Ag | B | 300 | 56.80 | .04684 | 110.9 | 195.48 |

* A : impregnation method

B : coprecipitation method



Figure 4.1 TEM of impregnation catalyst of 25%Ag calcined at 300 °C. (magnification = 80 K)

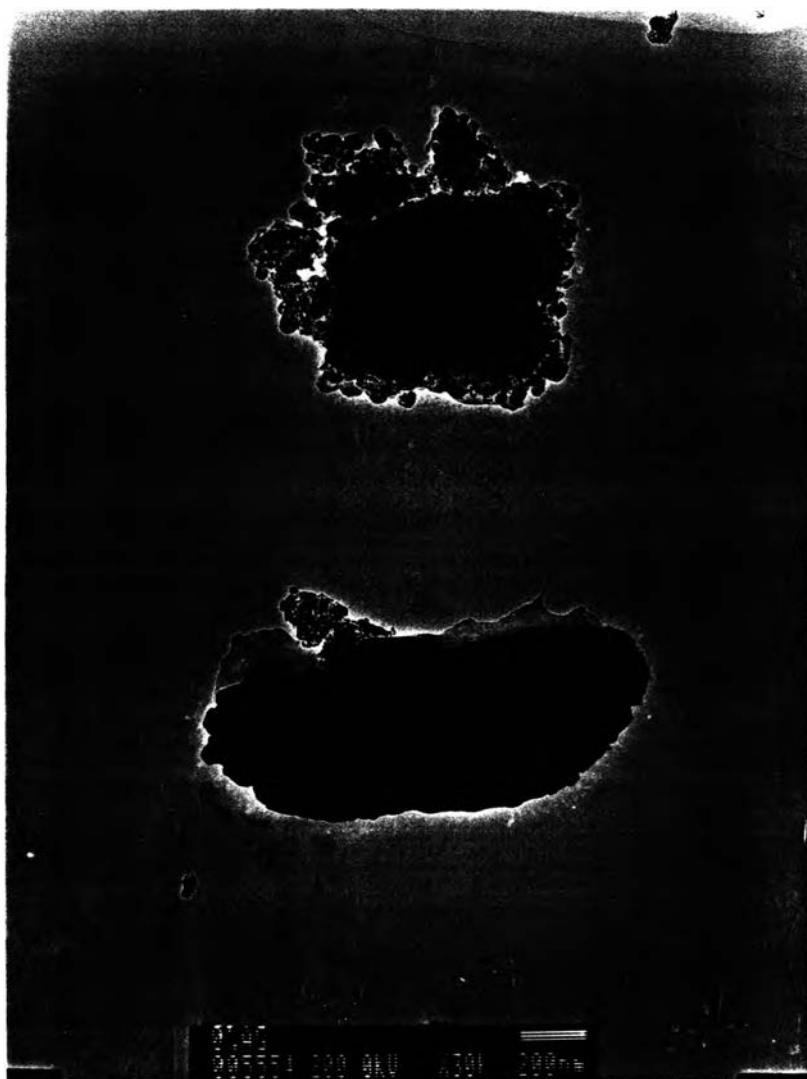


Figure 4.2 TEM of coprecipitation catalyst of 0%Ag calcined at 300 °C. (magnification = 30 K)



Figure 4.3 TEM of coprecipitation catalyst of 100%Ag calcined at 300 °C. (magnification = 120 K)

4.2 Catalyst activities

4.2.1 External film resistance

The external film resistance effect was estimated by measuring the reaction rate as a function of feed rate. The experiment was conducted in a differential flow reactor with 0.1 g of 25%Ag of total loading, impregnation method and 0.05 g of 100%Ag of total loading, coprecipitation method (both catalysts were calcined at 300 °C). Reactant gases with the composition of 2,000 ppm of NO and CO balanced in He were passed through the catalyst bed at 450 °C and 1 atm by varying the flow rate at constant reactant concentration.

Since external film resistance or the boundary layer thickness depends on the superficial velocity, the higher the velocity, the lower boundary layer thickness will be. The flow rate was varied at constant composition to find the flow rate without external film resistance. From Figures 4.4 and 4.5 the relationship between the rate of reaction and total flow rate shows that at flow rates greater than 200 ml/min the external resistance is negligible. From these results, a flow rate of 250 ml/min was chosen for all of the kinetic studies.

4.2.2 Effect of calcination temperature

The effect of the calcination temperature was studied with 0.1 g of 50%Ag, impregnation catalyst, which was calcined at 200, 300, 400, 500, 600, and 700 °C. The feed compositions at 100 ml/min flow rate were 1,000 ppm of NO and CO. The experiment was conducted at 450 °C under the atmospheric pressure.

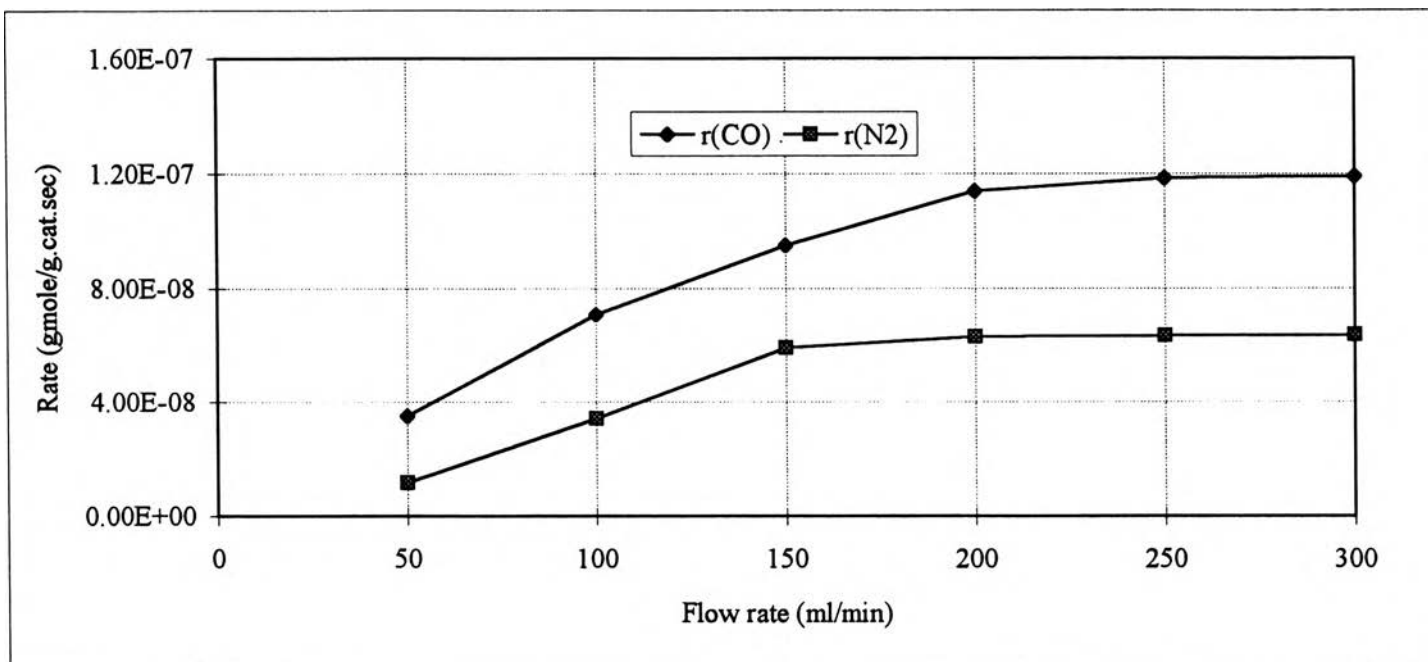


Figure 4.4 The external film resistance test (catalyst : 25%Ag, impregnation method).

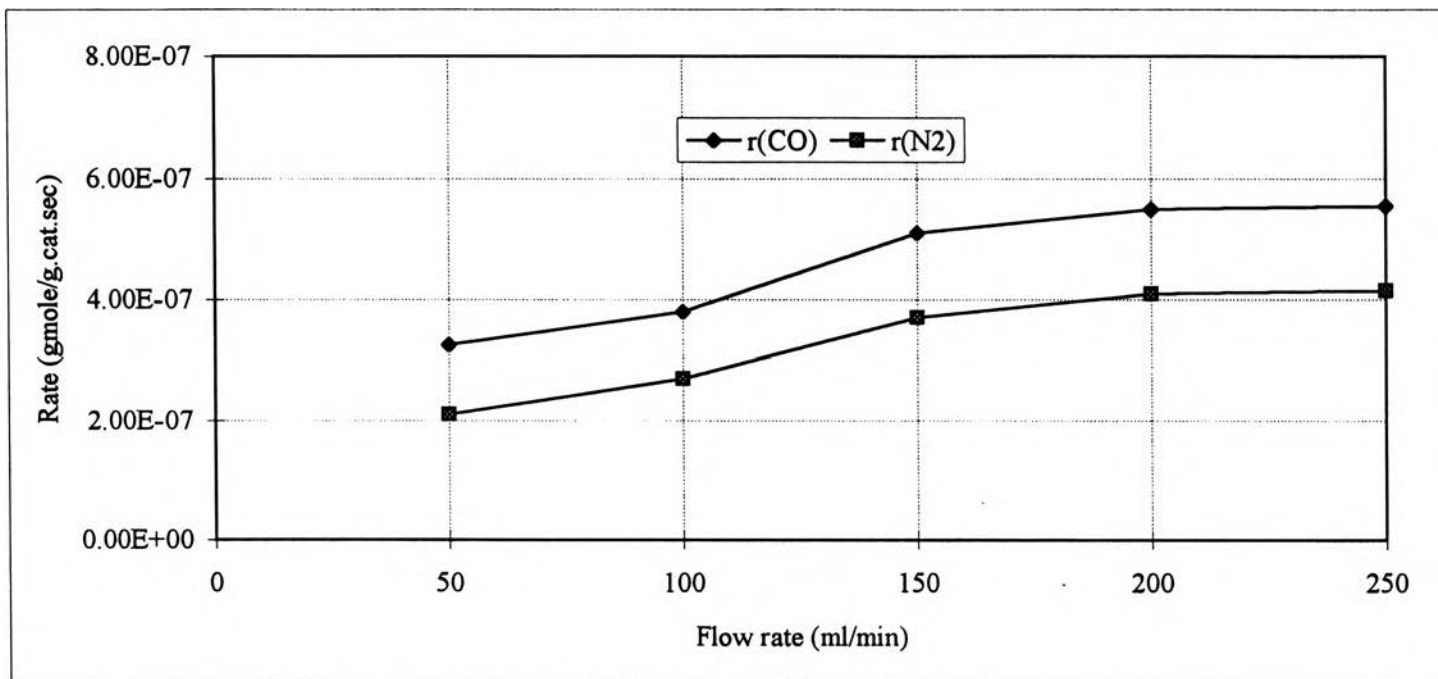


Figure 4.5 The external film resistance test (catalyst : 100%Ag, coprecipitation method).

The results given in Figures 4.6 to 4.11 show that the N_2 production rate initially increases with increasing calcination temperature and becomes slower when the temperature is above 500 °C.

In comparison, the CO oxidation activity is maximum when the catalyst is calcined at 200 °C and decreases with increasing calcination temperature. For the highest temperature catalysts (700 °C), CO oxidation is about 15-20% of N_2 production instead of 200% of N_2 .

4.2.3 Effect of Ag/Au ratio (in 5% loading)

All catalysts prepared by impregnation and coprecipitation methods were calcined at 300 °C under the atmospheric pressure. The conditions of the experiment were the same as the conditions used in studying the effect of calcination temperature.

Impregnation method

Figures 4.13-4.17 show the dependence of the catalyst activity on silver contents. The summary of the rates of reactions at steady-state conditions given in Figure 4.18 shows that the oxidation of CO is maximum when the catalyst contains 25%Ag. However, N_2 production activity shows slightly dependent on their Ag amount. The reaction with 25%Ag catalyst also shows almost a stoichiometric ratio of CO to N_2 amounts. However, when the amount of Ag increases, the decomposition activity also increases.

Coprecipitation method

The N_2 and CO activities of the coprecipitation catalysts calcined at 300 °C are shown in Figures 4.19-4.23. All catalysts are quite active

at the beginning but the reaction rate drops substantially after 100 minutes on stream for the catalysts containing gold. The 100%Ag catalyst does not show the same behavior as the others. Visual inspection of the deactivated catalysts containing gold revealed that there was extensive sintering. This caused the reduction in surface area was responsible for the decrease of its activity. The sintering was not observed in the case of 100%Ag catalyst. All of the catalysts initially have activity ratios of CO to N₂ formation close to two as shown in Figures 4.19-4.23 but after sintering the ratio is less than one for the catalyst containing gold as shown in Figure 4.24.

From Figure 4.2, the particle sizes of the catalyst containing gold are larger than that of catalyst containing silver. It implies that the catalyst containing gold is sintered and poisoned by the CO-NO reaction, causing the decrease of reaction rate after 100 minutes (Cant and Fredrickson, 1975).

4.2.4 The comparison of impregnation and coprecipitation methods

Figure 4.25 shows the effect of impregnation and coprecipitation methods. The catalysts prepared by impregnation and coprecipitation methods with the same Ag/Au ratio (0%Ag, 50%Ag, and 75%Ag), the CO oxidation rate and N₂ rate at steady-state were nearly the same. The 25%Ag catalyst prepared by impregnation was more active than the one prepared by coprecipitation. On the other hand, the 100%Ag catalyst prepared by impregnation was less active than the others. Before sintering, all of the coprecipitation catalysts had higher activities than that of the impregnation catalysts.

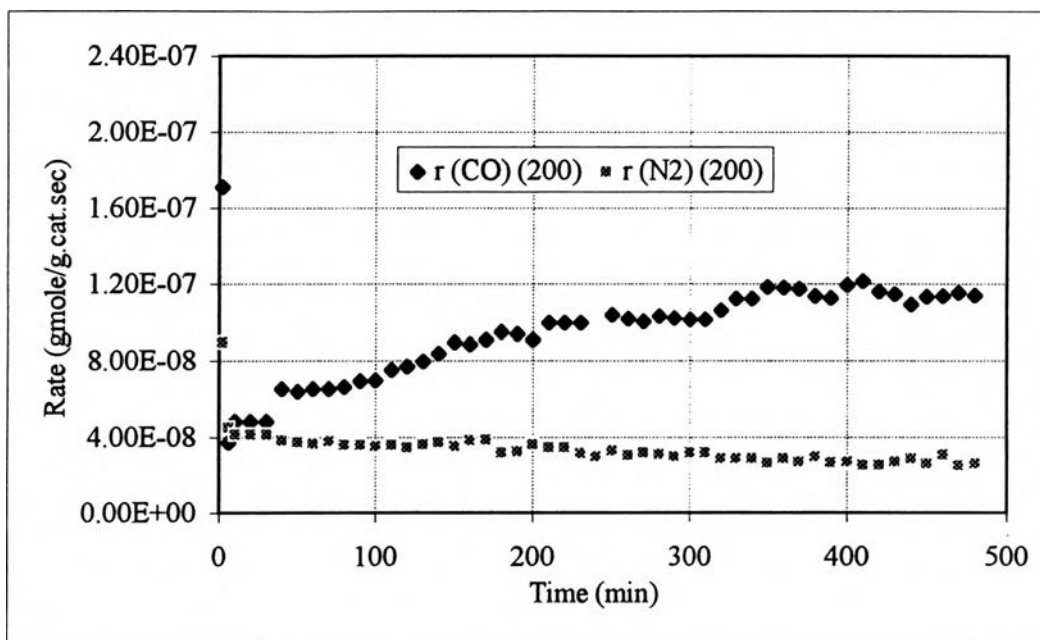


Figure 4.6 Variation of the rates of reactions for 50%Ag impregnation catalyst at calcination temperature of 200 °C.

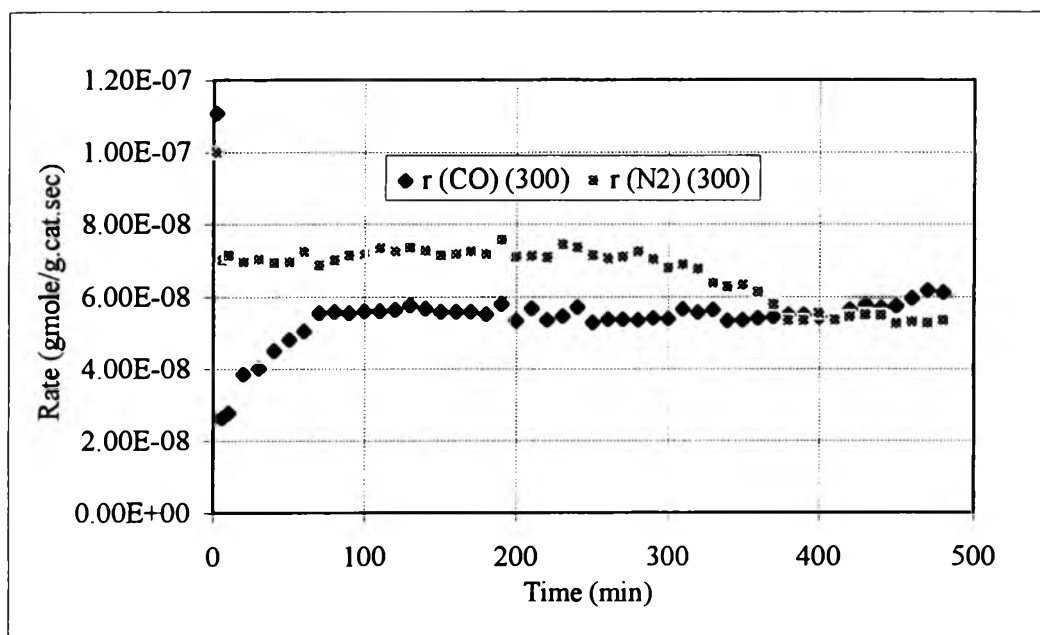


Figure 4.7 Variation of the rates of reactions for 50%Ag impregnation catalyst at calcination temperature of 300 °C.

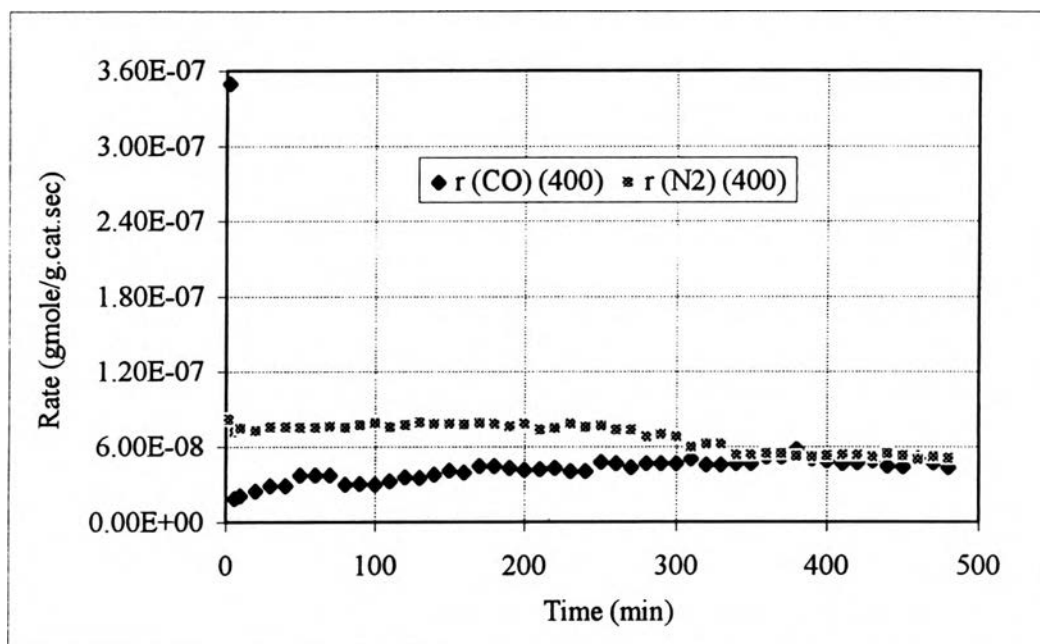


Figure 4.8 Variation of the rates of reactions for 50%Ag impregnation catalyst at calcination temperature of 400 °C.

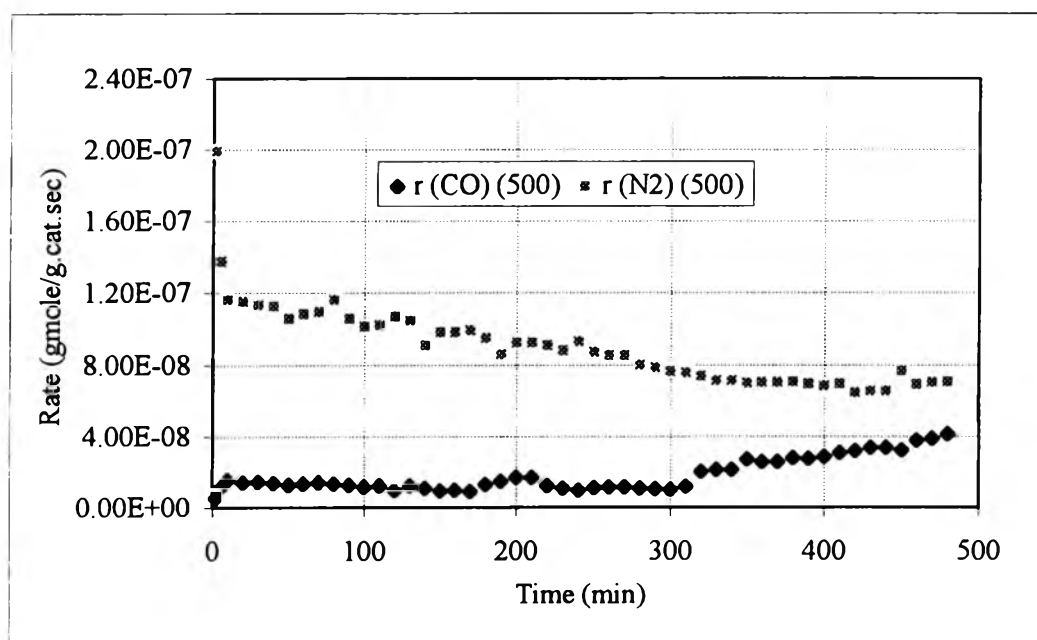


Figure 4.9 Variation of the rates of reactions for 50%Ag impregnation catalyst at calcination temperature of 500 °C.

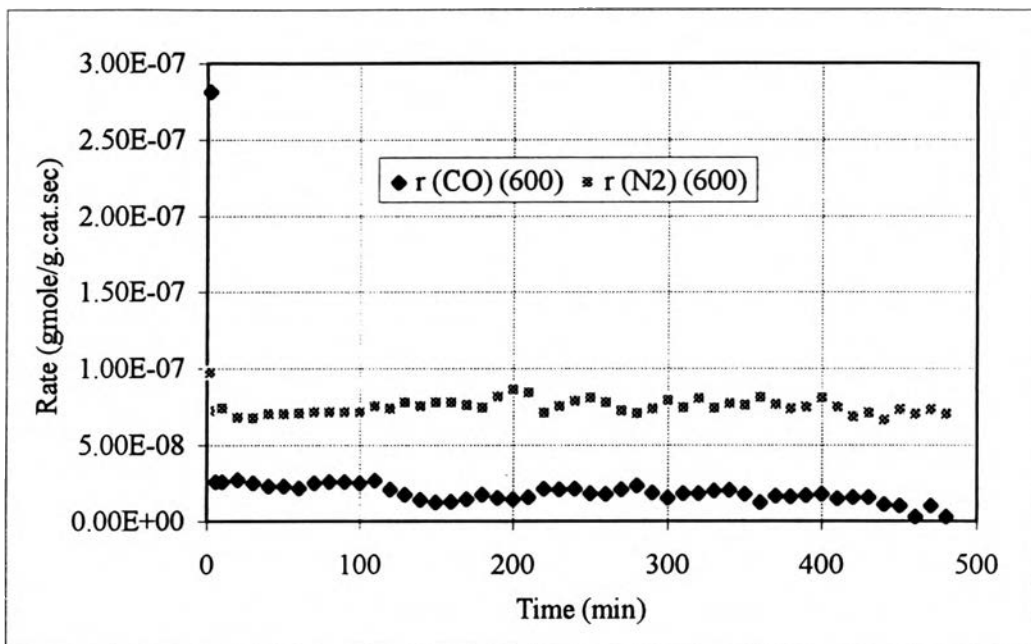


Figure 4.10 Variation of the rates of reactions for 50%Ag impregnation catalyst at calcination temperature of 600 °C.

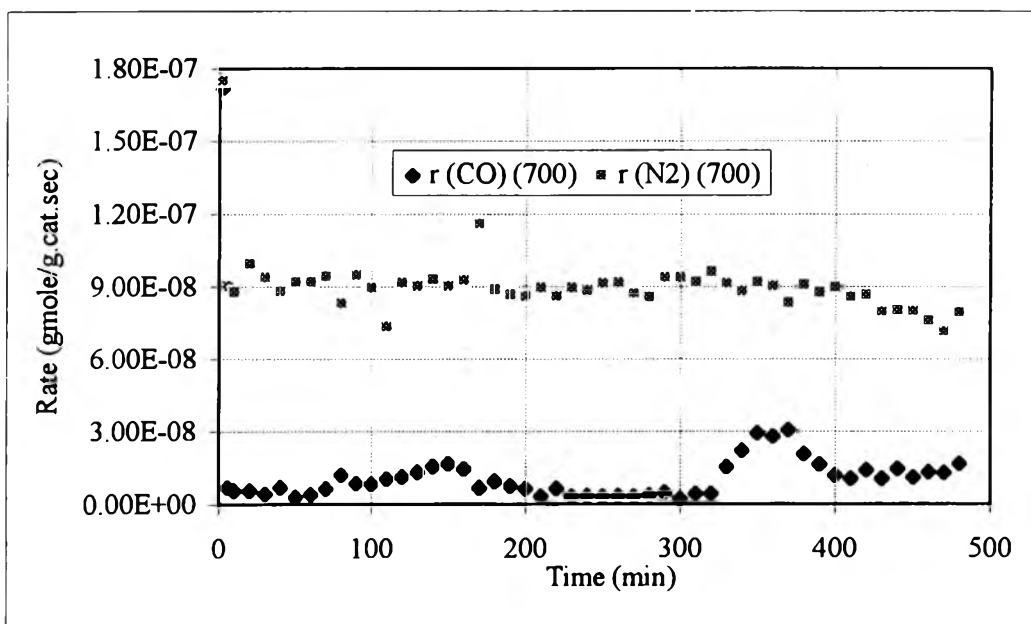


Figure 4.11 Variation of the rates of reactions for 50%Ag impregnation catalyst at calcination temperature of 700 °C.

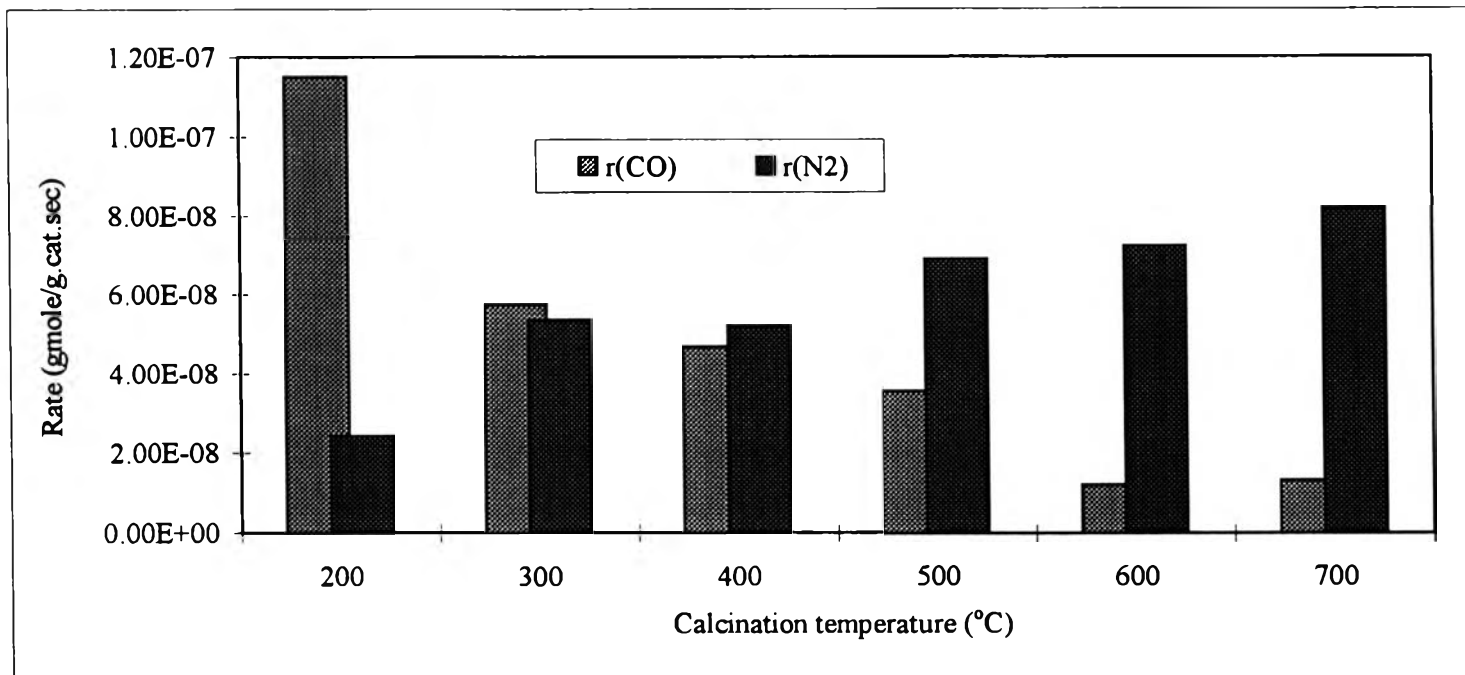


Figure 4.12 Comparison of the rates of reactions for 50%Ag impregnation catalyst at various calcination temperatures.

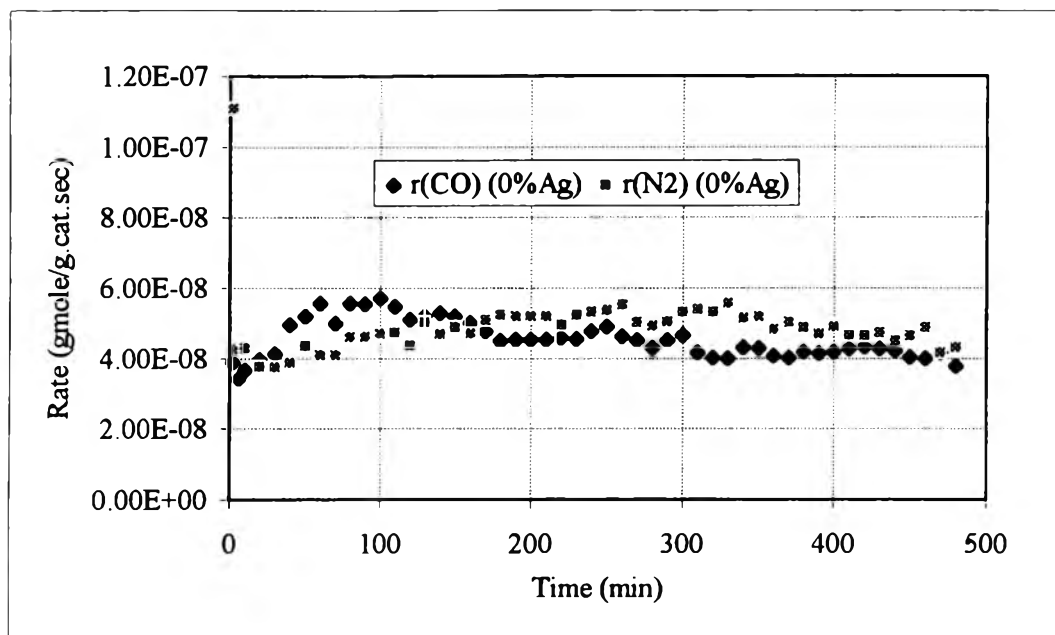


Figure 4.13 Variation of the rates of reactions for 0%Ag impregnation catalyst at calcination temperature of 300 °C.

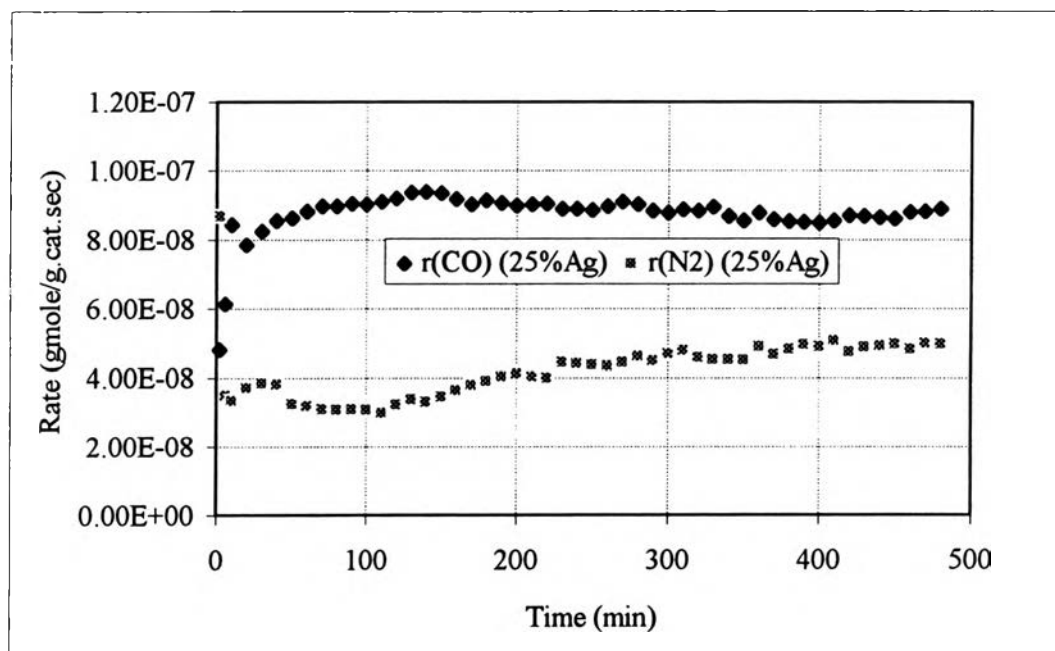


Figure 4.14 Variation of the rates of reactions for 25%Ag impregnation catalyst at calcination temperature of 300 °C.

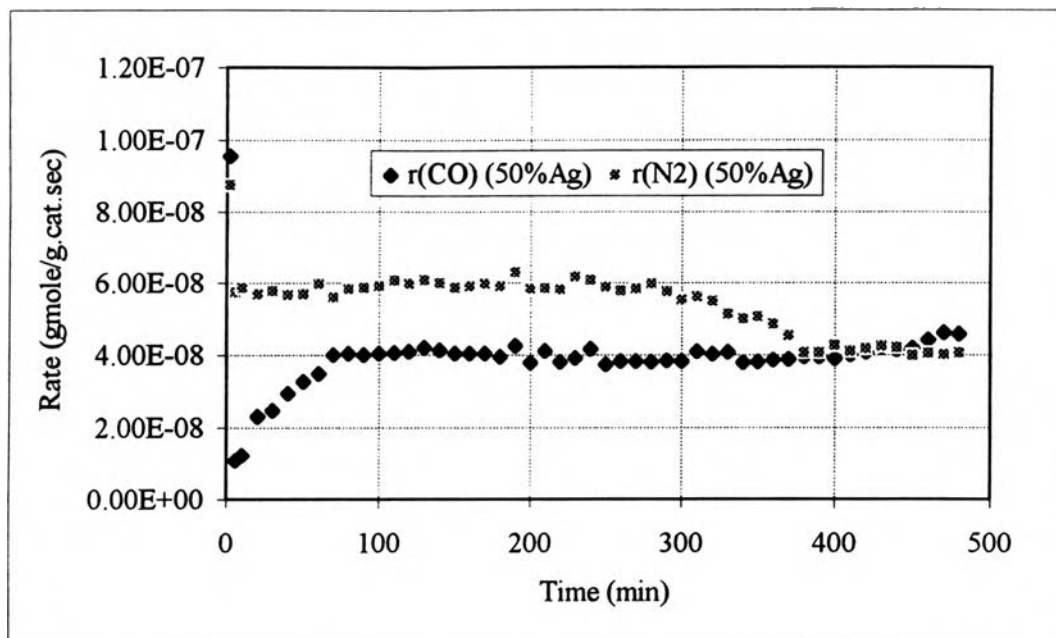


Figure 4.15 Variation of the rates of reactions for 50%Ag impregnation catalyst at calcination temperature of 300 °C.

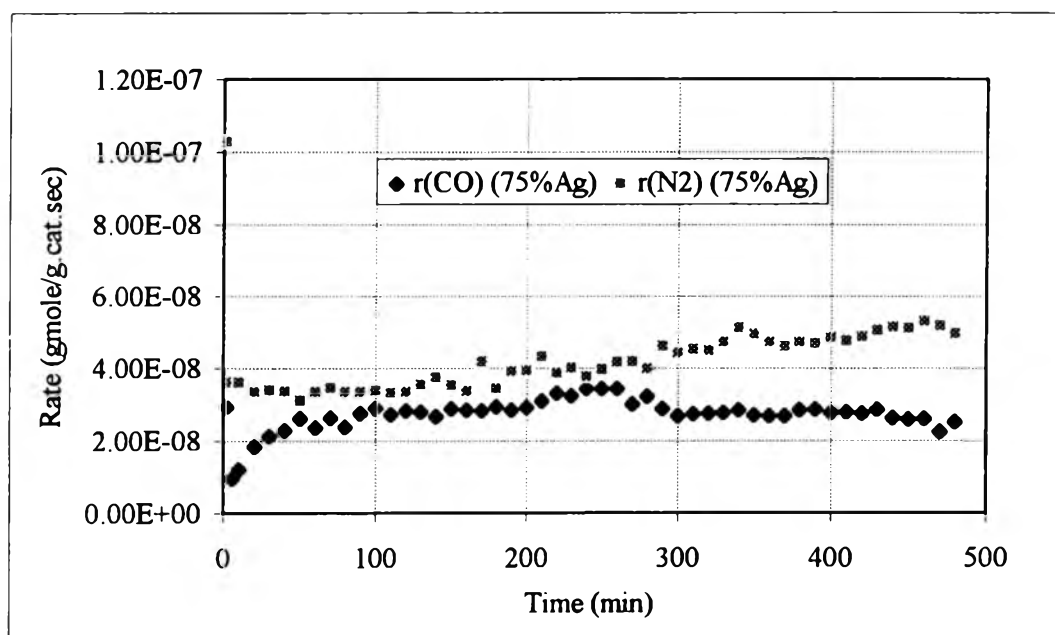


Figure 4.16 Variation of the rates of reactions for 75%Ag impregnation catalyst at calcination temperature of 300 °C.

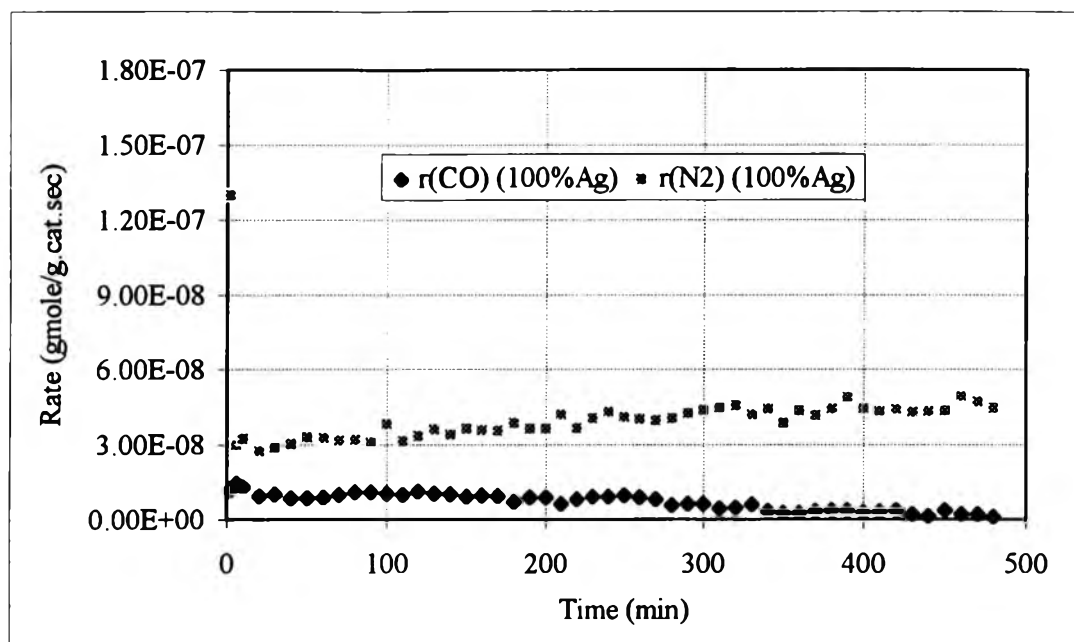


Figure 4.17 Variation of the rates of reactions for 100%Ag impregnation catalyst at calcination temperature of 300 °C.

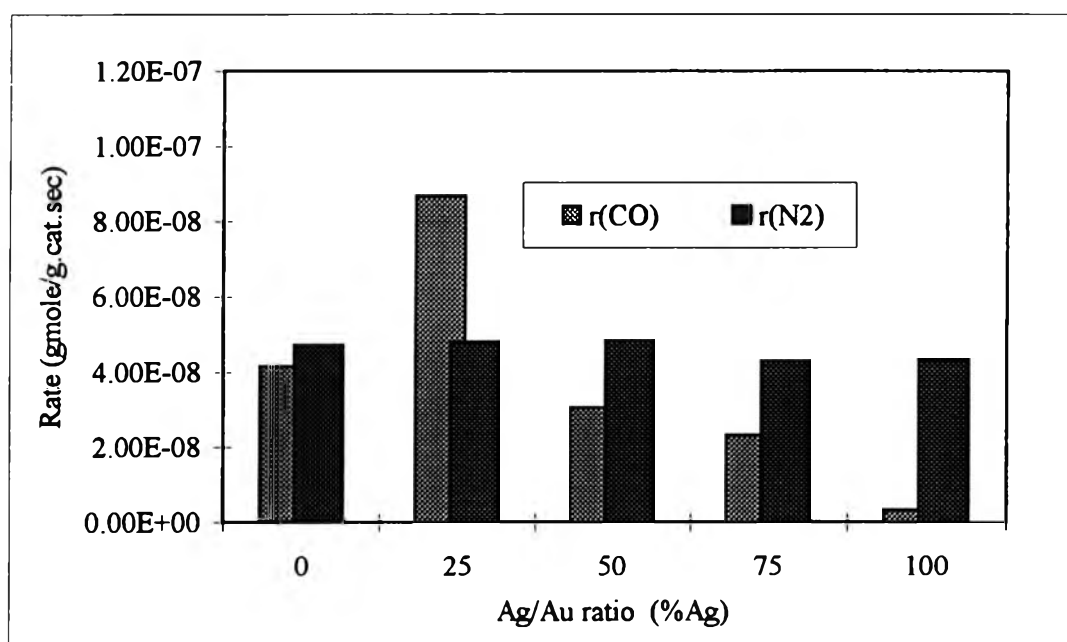


Figure 4.18 Steady-state rates of reactions at various Ag/Au ratios for impregnation catalyst calcined at 300 °C.

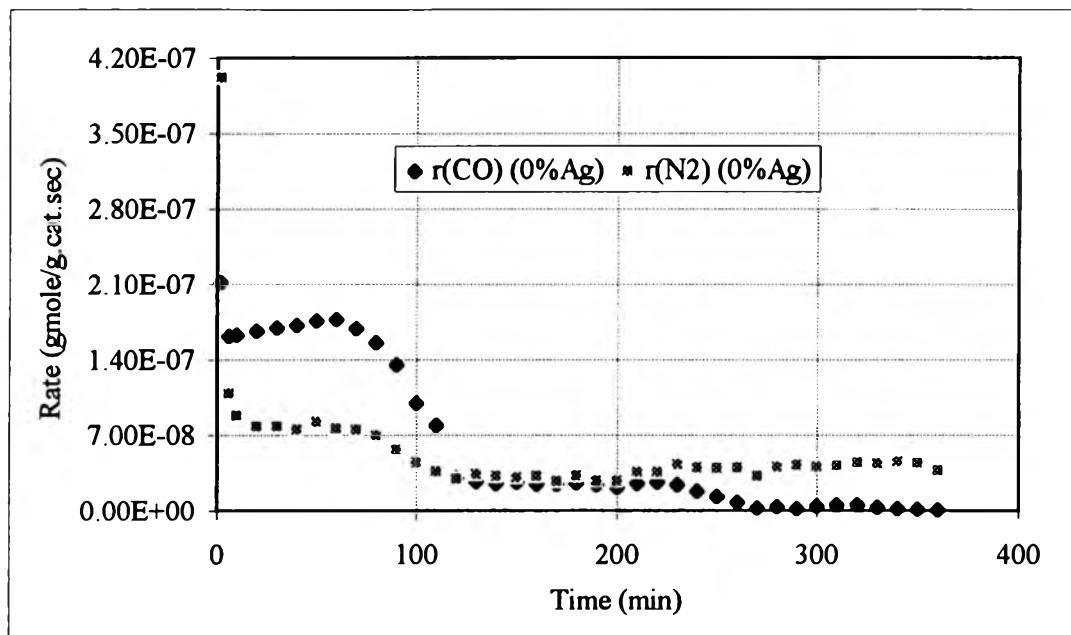


Figure 4.19 Variation of the rates of reactions for 0%Ag coprecipitation catalyst at calcination temperature of 300 °C.

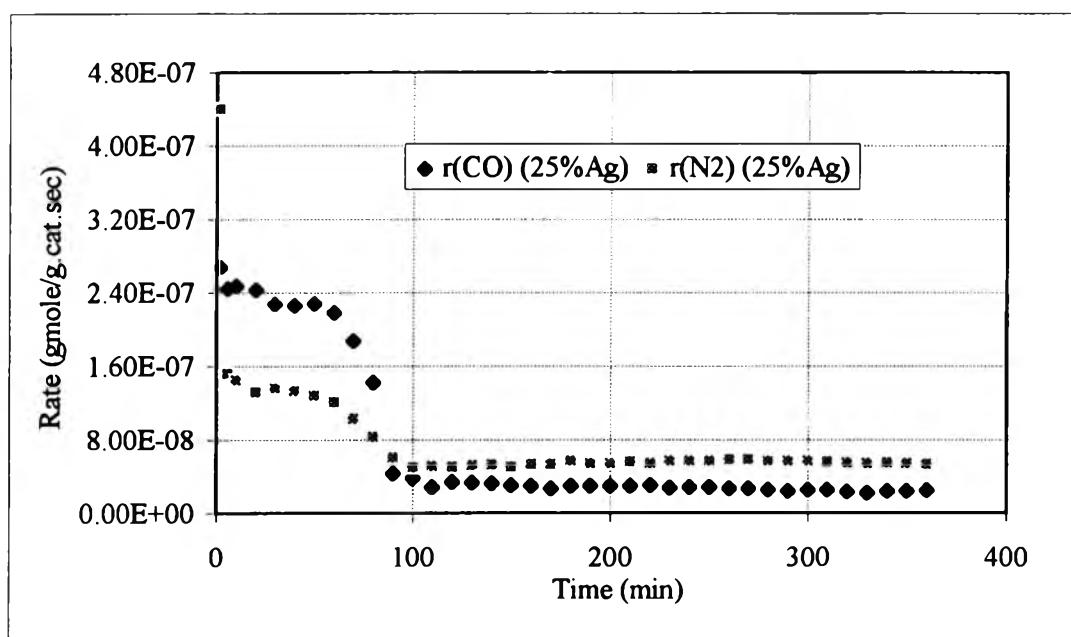


Figure 4.20 Variation of the rates of reactions for 25%Ag coprecipitation catalyst at calcination temperature of 300 °C.

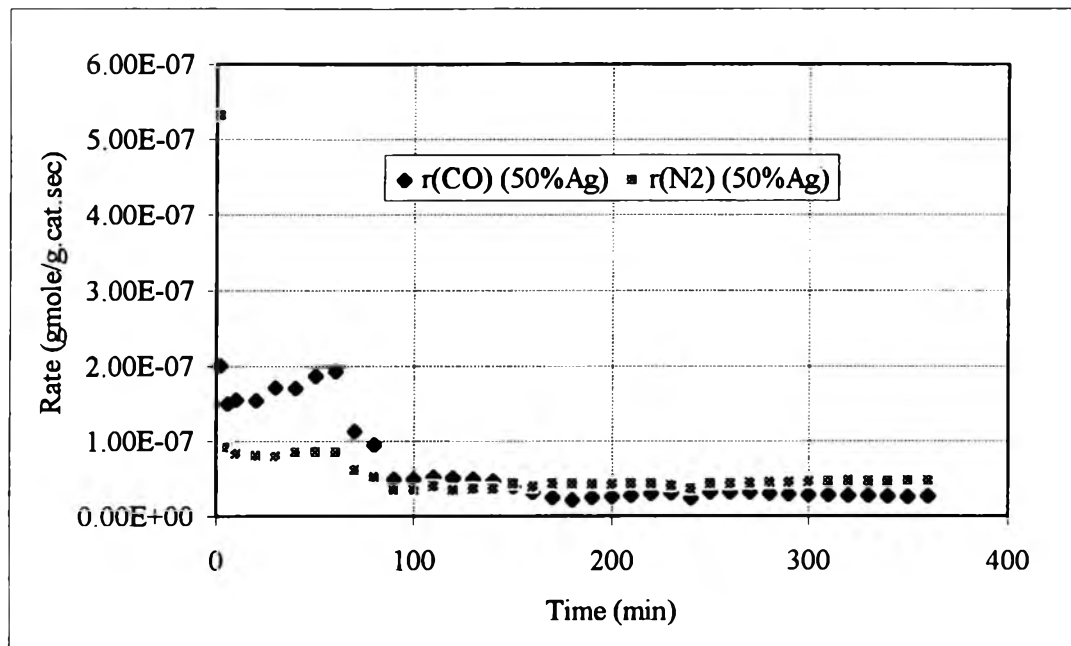


Figure 4.21 Variation of the rates of reactions for 50%Ag coprecipitation catalyst at calcination temperature of 300 °C.

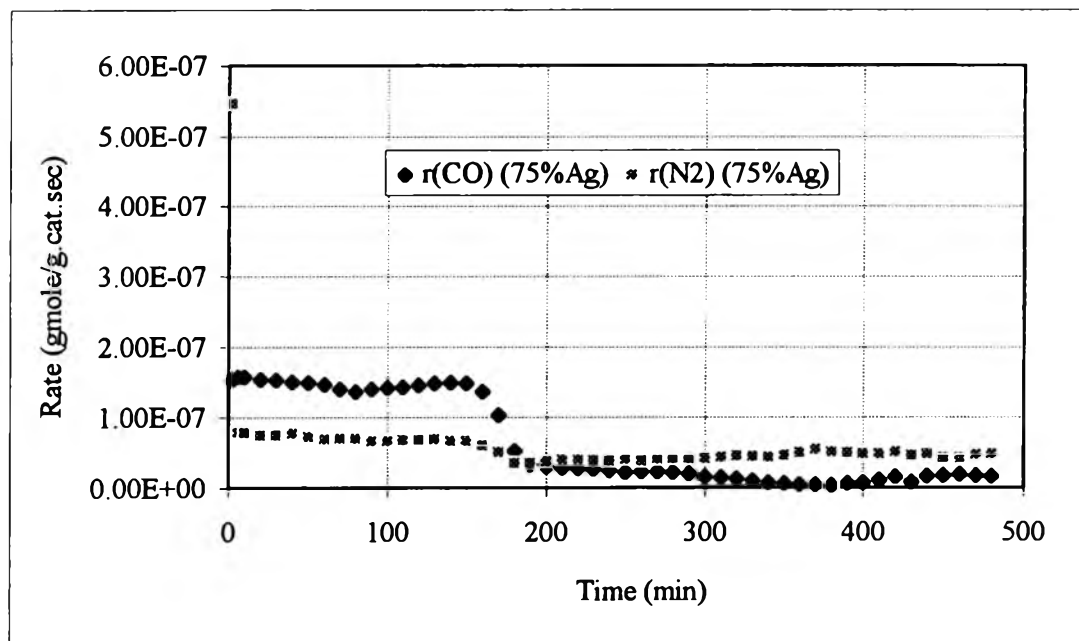


Figure 4.22 Variation of the rates of reactions for 75%Ag coprecipitation catalyst at calcination temperature of 300 °C.

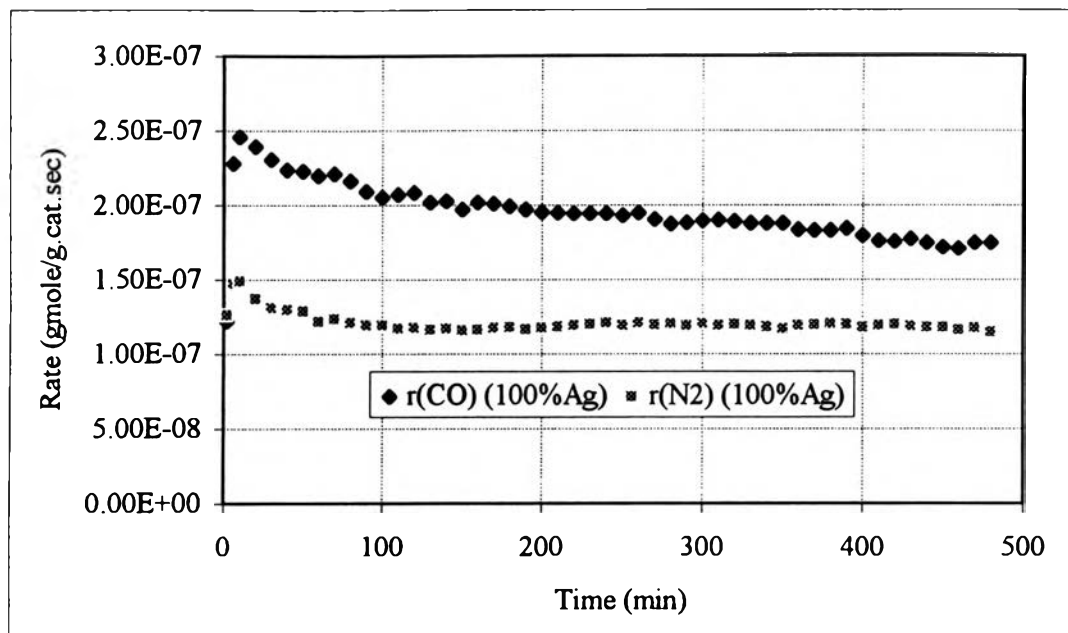


Figure 4.23 Variation of the rates of reactions for 100%Ag coprecipitation catalyst at calcination temperature of 300 °C.

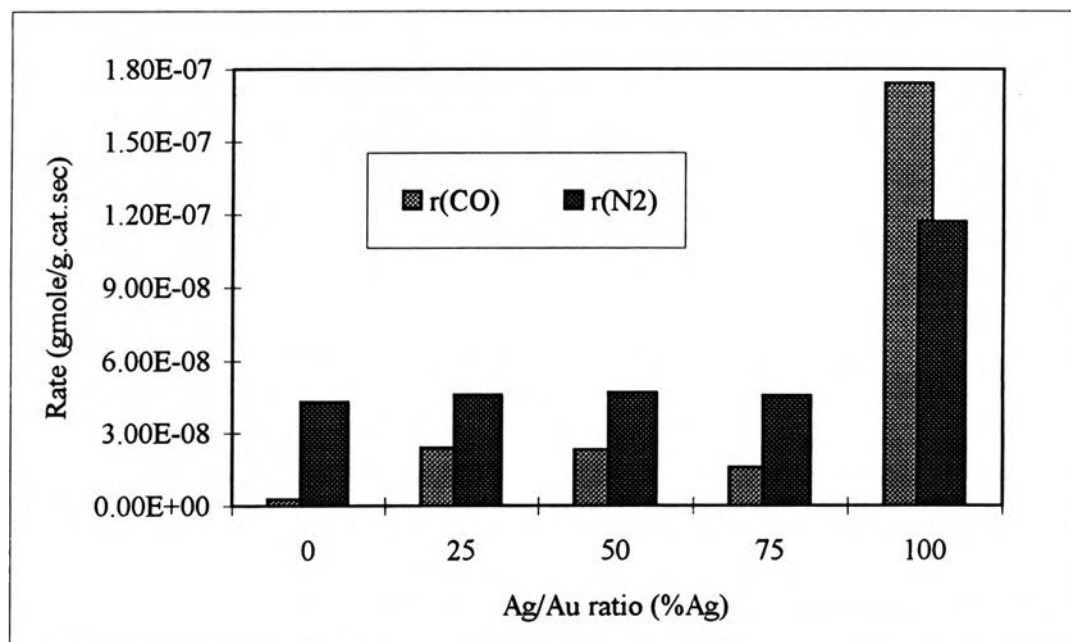


Figure 4.24 Steady-state rates of reactions at various Ag/Au ratios for coprecipitation catalyst calcined at 300 °C.

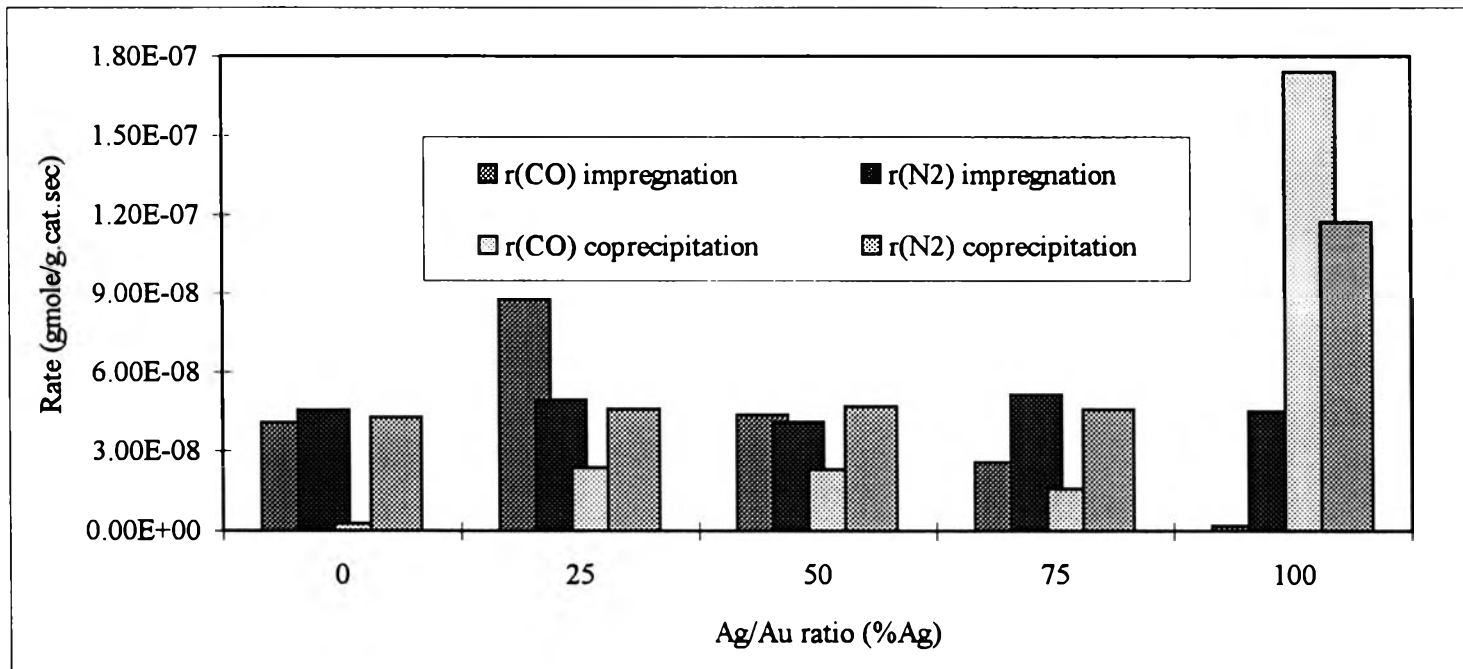


Figure 4.25 The comparison of impregnation and coprecipitation methods at various Ag/Au ratios.

4.3 Kinetic studies

4.3.1 The order of reaction with respect to CO and NO

The order of reaction with respect to CO was determined by varying the CO concentration and keeping the NO concentration at 10,000 ppm. The ratio of CO to NO was varied from 1/5 to 1/20 at a total flow rate of 250 ml/min. 0.1 g of the 25%Ag impregnation catalyst and 0.05 g of the 100%Ag, coprecipitation catalyst (both catalysts were calcined at 300 °C) were used. In the kinetics measurements, the conversion was kept below 20 %.

The order of reaction with respect to NO was observed by keeping the CO concentration constant at 20,000 ppm and varying the ratio of NO to CO from 1/5 to 1/10. The conditions of the experiment were the same as above.

Figures 4.26 and 4.27 show the rate of CO oxidation as a function of CO concentration in excess of NO. The order with respect to CO is around 0.56 and 0.33 for the 25% Ag impregnation catalyst and 100% Ag coprecipitation catalyst respectively.

Figures 4.28 and 4.29 show the dependence of N₂ formation rate on NO concentration in the feed. The orders of reaction with respect to NO for the 25% Ag impregnation catalyst and the 100% Ag coprecipitation catalyst are 0.55 and 0.04 respectively.

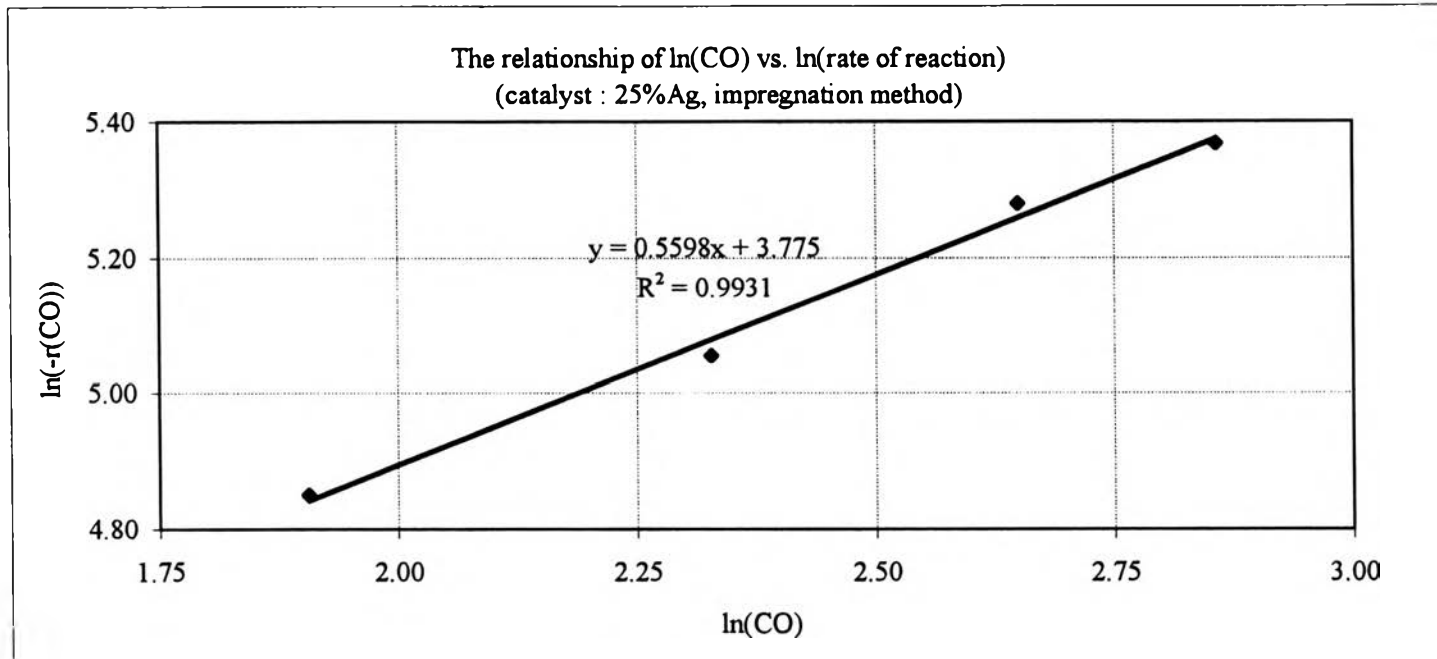


Figure 4.26 Carbon monoxide order plot using a constant nitric oxide concentration of 10,000 ppm (catalyst : 25%Ag, impregnation method).

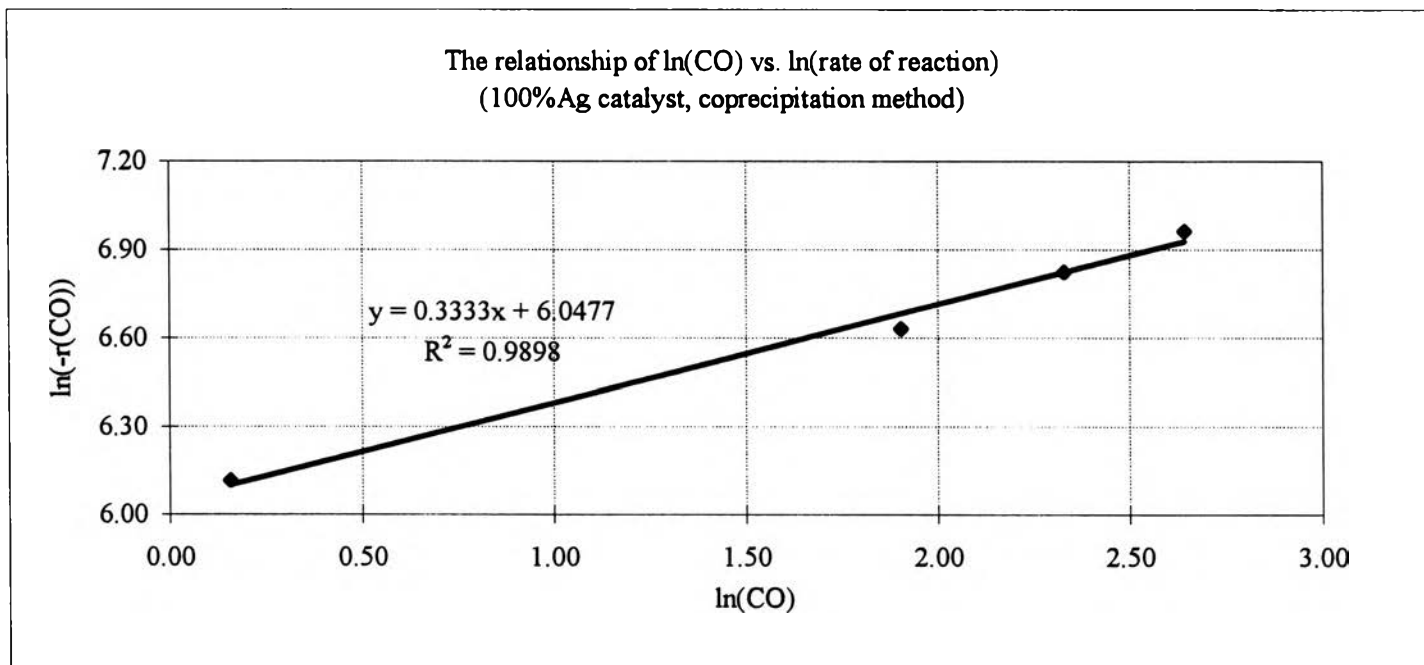


Figure 4.27 Carbon monoxide order plot using a constant nitric oxide concentration of 10,000 ppm (catalyst : 100%Ag, coprecipitation method).

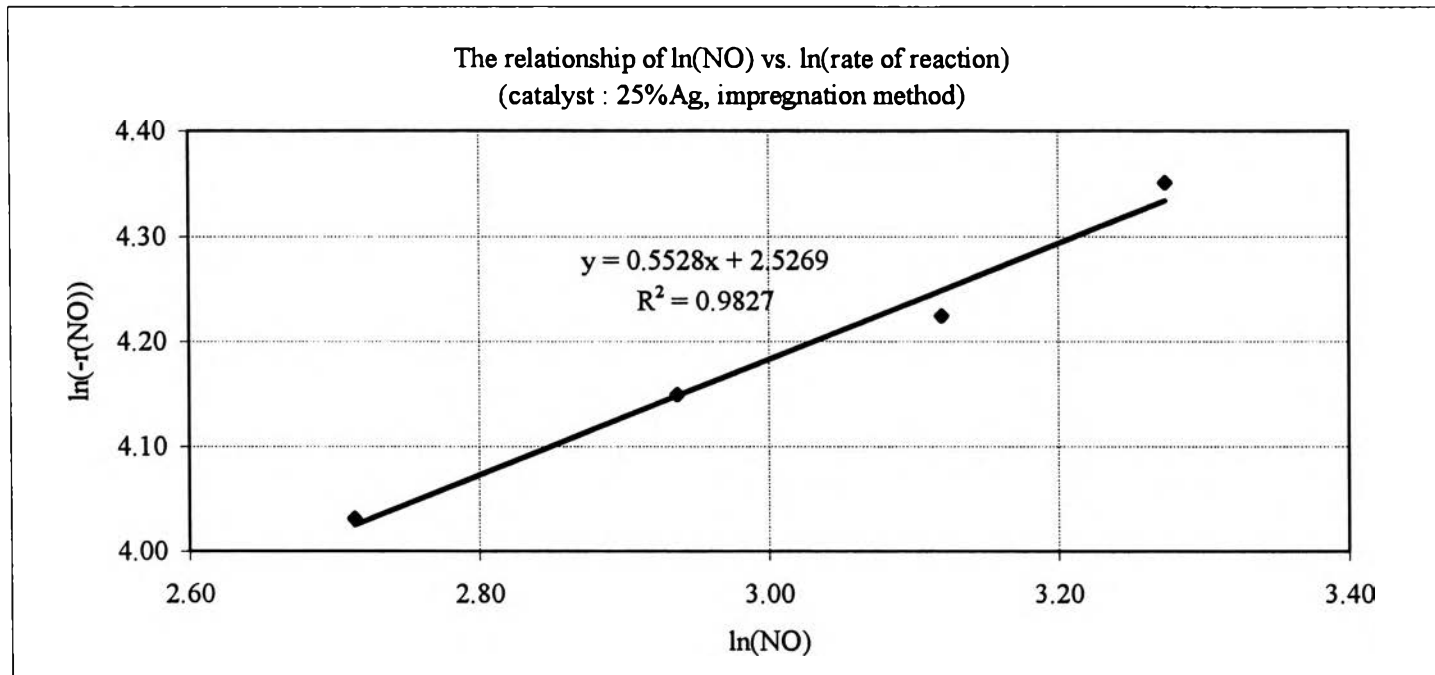


Figure 4.28 Nitric oxide order plot using a constant carbon monoxide concentration of 20,000 ppm (catalyst : 25%Ag, impregnation method).

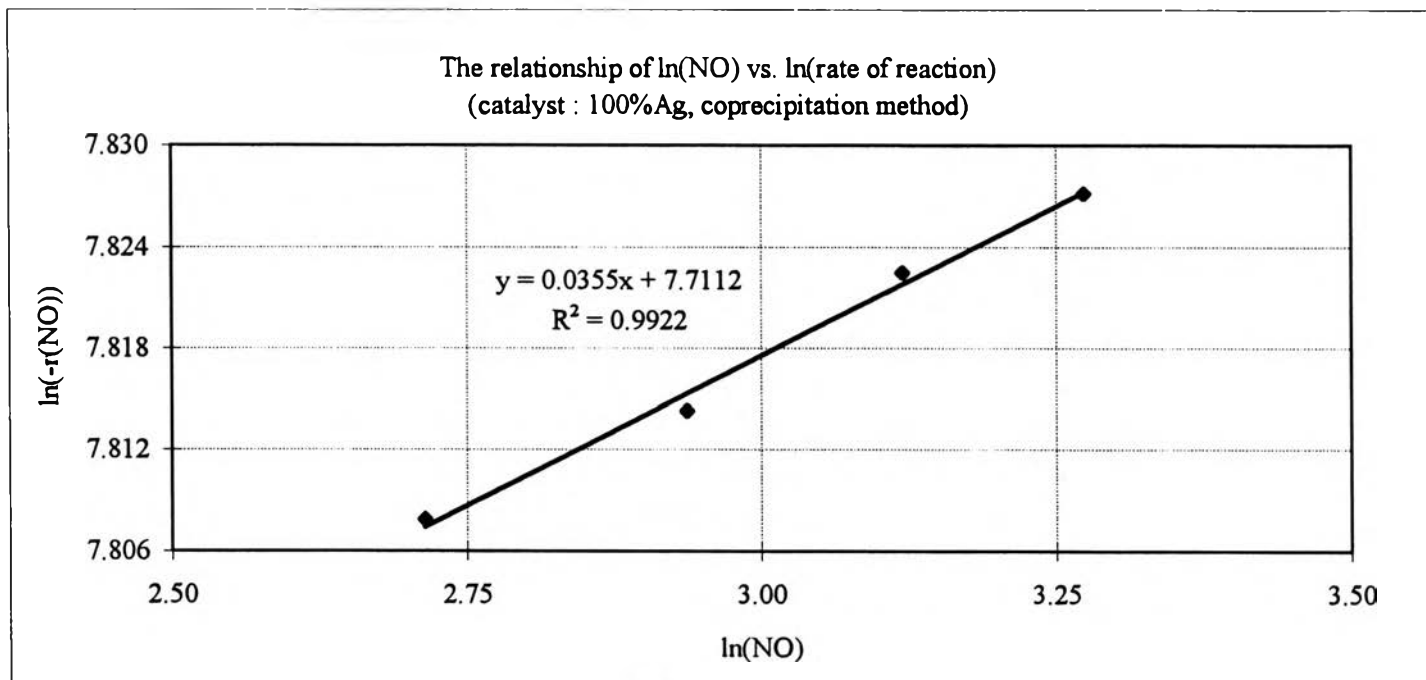


Figure 4.29 Nitric oxide order plot using a constant carbon monoxide concentration of 20,000 ppm (catalyst : 100%Ag, coprecipitation method).

The impregnation catalyst give the values of CO order and NO order nearly the same. As a result, the effect of CO concentration and NO concentration are the same.

4.3.2 The activation energy (Ea)

0.1 g of 25%Ag impregnation catalyst and 0.05 g of 100%Ag coprecipitation catalyst were used to find the activation energy (Ea) for the flow of 250 ml/min which composed of 4,000 ppm of NO and CO balanced in He for impregnation catalyst and 2,000 ppm of NO and CO balanced in He for coprecipitation catalyst.

Arrhenius plot was used to find the activation energies are shown in Figures 4.30 and 4.31. To calculate the specific rate constant of the catalyst prepared by impregnation method and coprecipitation method, the equation $r=k[\text{CO}]^a[\text{NO}]^b$ was used. a and b were the orders with respect to CO and NO respectively and r was the CO oxidation rate. Therefore, the overall rate of NO reduction and CO oxidation of the catalyst prepared by impregnation method (25%Ag) and coprecipitation method (100%Ag) can be calculated which is shown in Table 4.2.

$$\text{rate of reaction} = A \cdot \exp\left(\frac{-E_a}{RT}\right) [\text{CO}]^a [\text{NO}]^b$$

where

| | | |
|----|---|--|
| A | = | Frequency factor |
| Ea | = | Activation energy, kcal/mole |
| R | = | 1.987 kcal/mole/K |
| a | = | the order with respect to CO concentration |
| b | = | the order with respect to NO concentration |

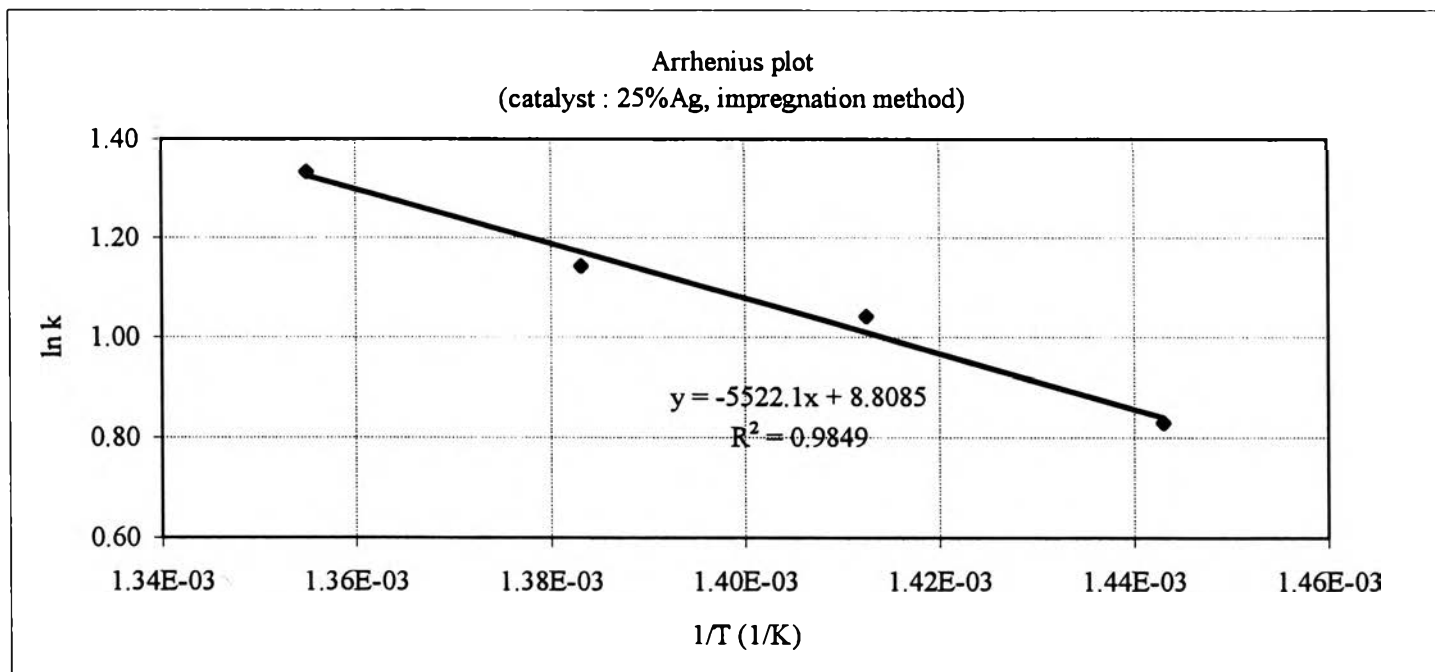


Figure 4.30 Temperature dependence of reaction rate (catalyst : 25%Ag, impregnation method).

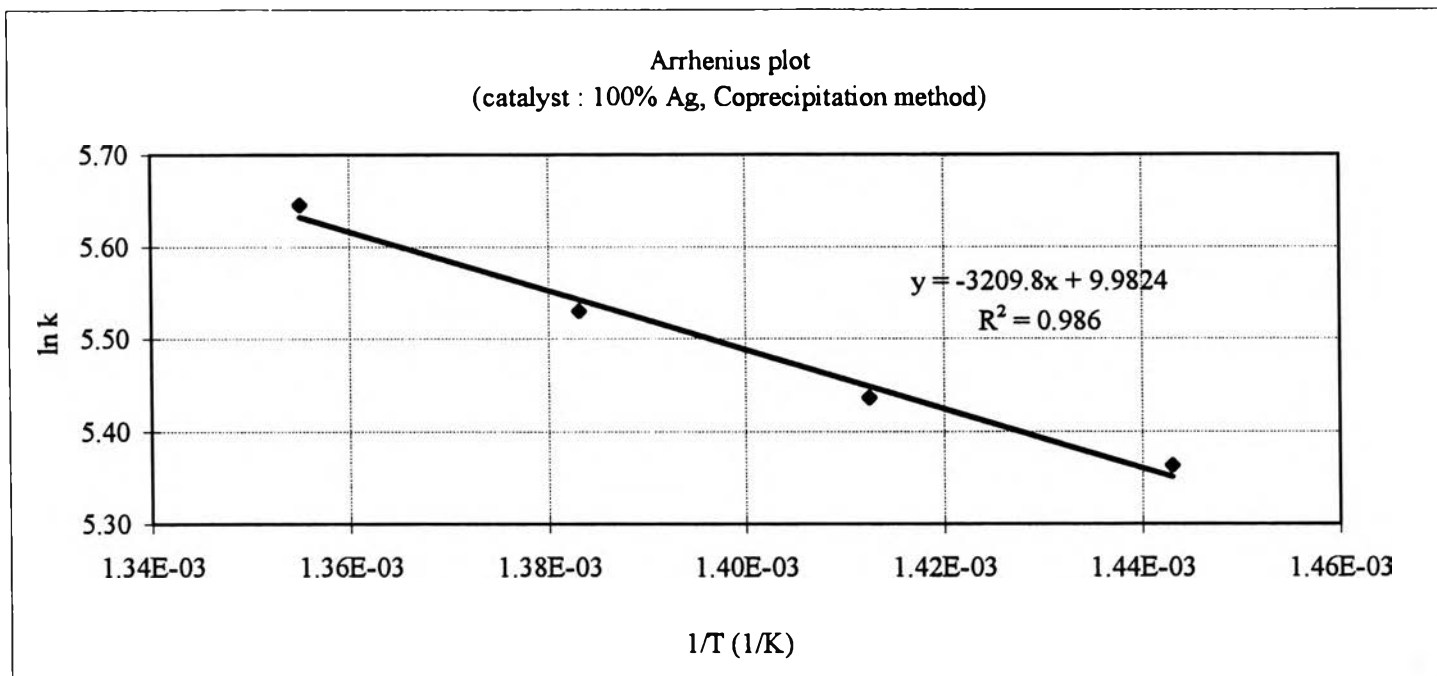


Figure 4.31 Temperature dependence of reaction rate (catalyst : 100%Ag, coprecipitation method).

Table 4.2 The order and activation energy

| Catalyst | A | Ea (kcal/mole) | a | b |
|--------------------------------------|-----------|-------------------|--------|--------|
| 25%Ag impregnation method | 6690.8754 | 10.9724 | 0.5598 | 0.5528 |
| 100%Ag coprecipitati on method | 26142.19 | 6.3779 | 0.3333 | 0.0355 |

From Table 4.2, it is seen that, the activation energy is around 11 kcal/mole for the impregnation catalyst and around 6.4 kcal/mole for the coprecipitation catalyst indicating that for lower temperature applications the coprecipitation catalyst is better.

From Table 4.2, the NO order (0.0355) is less than the CO order (0.3333) for 100%Ag coprecipitation catalyst. So it can be assumed that the step of NO adsorption is the rate-determining step. For the impregnation catalyst of 25%Ag, the NO order (0.5528) and CO order (0.5598) are close. Therefore, the rate-determining step can not be determined.

From Table 4.3, the impregnation catalyst of 25%Ag and the coprecipitation catalyst of 100%Ag show a low activation energy compared to the other catalysts such as 4% Sr/La₂O₃, La₂O₃, Mn₂O₃, Cu/ZSM-5 etc. in the literature. However, those still have a low activity of N₂ formation when compared to Rh. The silver catalysts from Cant and Fredrickson (1975) have an activation energy lower than the silver and gold catalysts used in this study.

From Table 4.4, all of silver and gold catalysts prepared by impregnation and coprecipitation methods are good for NO reduction and NO decomposition. The coprecipitation catalysts have a higher dispersion of Au than the impregnation catalysts, which results in higher reaction rate.

Table 4.3 The comparison of NO reduction and NO decomposition catalysts

| Catalyst | Conditions | Reaction | Order | Activation energy (Ea) (kcal/mole) | Activity (gmole N ₂ / g.cat.sec) | Reference |
|--------------------------------------|--|--|-------------------------------------|---------------------------------------|---|---|
| 4% Sr/La ₂ O ₃ | GHSV=34,800 h ⁻¹ , 773-793 K | 2NO → N ₂ +O ₂ | NO = 1.08 | 28.0 | 1.4 × 10 ⁻⁹ | Zhang et al. (1996) |
| La ₂ O ₃ | 773-793 K | 2NO → N ₂ +O ₂ | - | - | 8.4 × 10 ⁻¹⁰ | Zhang and Walters (1994) |
| Mn ₂ O ₃ | 773-793 K | 2NO → N ₂ +O ₂ | - | - | 1.4 × 10 ⁻⁹ | Yamashitan et al. (1994) |
| 4% Sr/La ₂ O ₃ | GHSV=34,800 h ⁻¹ , 773-793 K | 4NO+CH ₄ → 2N ₂ +CO ₂ + 2H ₂ O | NO = 0.73 CH ₄ = 0.19 | 26.2 | 7.8 × 10 ⁻⁹ | Zhang, Walters and Vannice (1994) |
| 4%Rh/SiO ₂ | 478-498 K | 4NO+2CO → N ₂ +2CO ₂ | CO = 0.07 NO = 0.05 | 33.5 | 6.1 × 10 ⁻⁵ | Hecker and Bell (1983) |

Table 4.3 The comparison of NO reduction and NO decomposition catalysts (continued)

| Catalyst | Conditions | Reaction | Order | Activation energy (E _a) (kcal/mole) | Activity (gmoleN ₂ /g.cat.sec) | Reference |
|--------------------------------|---|---|-------------------------------------|---|---|------------------------------------|
| Ag | 87-156 °C CO and NO = 12.5 Torr | 4NO+2CO→ N ₂ O+2CO ₂ | CO = 1 NO = -1 | 14 (<120°C) 4 (>120 °C) | - | Cant and Freddrickson (1975) |
| Au | 30 - 100 °C | 4NO+2CO→ N ₂ O+2CO ₂ | - | - | - | Cant and Freddrickson (1975) |
| La ₂ O ₃ | GHSV = 8,700 h ⁻¹ , 773-973 | 4NO+CH ₄ → 2N ₂ +2CO ₂ + 2H ₂ O | CH ₄ = 0.26 NO = 0.98 | 24.4 | - | Zhang et al. (1994) |
| Rh(111) | 575 K, 8 Torr of CO and NO | 4NO+2CO→ N ₂ O+2CO ₂ | NO = 0 CO = 0.06 | 33.5 | - | Belton and Schmiege (1993) |
| 4%Li/MgO | 773-973 K | 4NO+CH ₄ → 2N ₂ +2CO ₂ + 2H ₂ O | CH ₄ = 0.70 NO = 0.35 | 30.5 | - | Zhang et al. (1994) |

Table 4.4 The conclusion of N₂ decomposition and N₂ reduction
(Temperature 450 °C, flow rate 100 ml/min)

| Catalyst | Calcination temperature (°C) | Method | N ₂ decomposition (gmole/g.metal sec.) | N ₂ reduction (gmole/g.metal sec.) |
|----------|------------------------------|--------------|---|---|
| 50%Ag | 200 | impregnation | - | 4.83×10^{-7} |
| 50%Ag | 300 | impregnation | 4.98×10^{-7} | 5.75×10^{-7} |
| 50%Ag | 400 | impregnation | 5.70×10^{-7} | 4.67×10^{-7} |
| 50%Ag | 500 | impregnation | 1.02×10^{-6} | 3.55×10^{-7} |
| 50%Ag | 600 | impregnation | 1.32×10^{-6} | 1.19×10^{-7} |
| 50%Ag | 700 | impregnation | 1.50×10^{-6} | 1.31×10^{-7} |
| 0%Ag | 300 | impregnation | 4.98×10^{-7} | 4.07×10^{-7} |
| 25%Ag | 300 | impregnation | 1.12×10^{-7} | 8.73×10^{-7} |
| 50%Ag | 300 | impregnation | 3.81×10^{-7} | 4.36×10^{-7} |
| 75%Ag | 300 | impregnation | 7.66×10^{-7} | 2.57×10^{-7} |
| 100%Ag | 300 | impregnation | 8.79×10^{-7} | 2.06×10^{-8} |

Table 4.4 The conclusion of N₂ decomposition and N₂ reduction
(Temperature 450 °C, flow rate 100 ml/min)

| Catalyst | Calcination temperature (°C) | Method | N ₂ decomposition (gmole/g.metal sec.) | N ₂ reduction (gmole/g.metal sec.) |
|----------|------------------------------|--------------|---|---|
| 50%Ag | 200 | impregnation | - | 4.83×10^{-7} |
| 50%Ag | 300 | impregnation | 4.98×10^{-7} | 5.75×10^{-7} |
| 50%Ag | 400 | impregnation | 5.70×10^{-7} | 4.67×10^{-7} |
| 50%Ag | 500 | impregnation | 1.02×10^{-6} | 3.55×10^{-7} |
| 50%Ag | 600 | impregnation | 1.32×10^{-6} | 1.19×10^{-7} |
| 50%Ag | 700 | impregnation | 1.50×10^{-6} | 1.31×10^{-7} |
| 0%Ag | 300 | impregnation | 4.98×10^{-7} | 4.07×10^{-7} |
| 25%Ag | 300 | impregnation | 1.12×10^{-7} | 8.73×10^{-7} |
| 50%Ag | 300 | impregnation | 3.81×10^{-7} | 4.36×10^{-7} |
| 75%Ag | 300 | impregnation | 7.66×10^{-7} | 2.57×10^{-7} |
| 100%Ag | 300 | impregnation | 8.79×10^{-7} | 2.06×10^{-8} |

Table 4.4 The conclusion of N₂ decomposition and N₂ reduction (continued)
 (Temperature 450 °C, flow rate 100 ml/min)

| Catalyst | Calcination temperature (°C) | Method | N ₂ decomposition (gmole/g.metal sec.) | N ₂ reduction (gmole/g.metal sec.) |
|----------|------------------------------|-----------------|---|---|
| 0%Ag | 300 | coprecipitation | 8.26×10^{-7} | 2.75×10^{-8} |
| 25%Ag | 300 | coprecipitation | 6.79×10^{-7} | 2.38×10^{-7} |
| 50%Ag | 300 | coprecipitation | 7.09×10^{-7} | 2.30×10^{-7} |
| 75%Ag | 300 | coprecipitation | 7.54×10^{-7} | 1.58×10^{-7} |
| 100%Ag | 300 | coprecipitation | 6.01×10^{-7} | 1.74×10^{-6} |