

CHAPTER IV

RESULTS AND DISCUSSION

4.1 Catalyst Characterization

The specific surface area of the sol-gel silver supported on alumina catalysts and manganese oxide catalyst was determined by five-point BET method using surface area analyzer.

Table 4.1 lists the specific surface area, pore volume, and pore radius of all prepared catalysts. As seen from the table, the specific surface area of sol-gel Ag/Al₂O₃ catalysts was almost the same. No significance change was found. It appears that the specific surface area of these catalysts is independent of the effect of silver loading. The specific surface area of sol-gel Al₂O₃ catalyst is almost three times higher than that of the commercial alumina, which is around 100 m²/g. This is one of the advantages of the sol-gel method.

The XRD pattern for the manganese oxide catalyst is shown in Figure 4.1. This pattern identifies that the main composition of manganese oxide catalyst is Mn₂O₃. Other compositions, Mn₅O₈ and manganese silicates (Mn₆SiO₁₂), are also found. It was observed that the sodium ions were still present in this catalyst even the precipitate was washed by hot distilled water for several times. This indicates a disadvantage of the conventional precipitation method.

Table 4.1 Catalyst Characterization

| Catalyst | Method | Calcination Temperature (°C) | Surface Area* (m ² /g) | Pore Volume [†] (cm ³ /g) | Pore Radius [‡] (°A) |
|--|---------------|------------------------------|-----------------------------------|---|-------------------------------|
| Al ₂ O ₃ | Sol-gel | 700 | 271.8 | 0.10270 | 7.561 |
| 1 % Ag/Al ₂ O ₃ | Sol-gel | 700 | 252.9 | 0.09591 | 7.584 |
| 2 % Ag/Al ₂ O ₃ | Sol-gel | 700 | 254.5 | 0.09643 | 7.579 |
| 4 % Ag/Al ₂ O ₃ | Sol-gel | 700 | 257.4 | 0.09822 | 7.631 |
| 5 % Ag/Al ₂ O ₃ | Sol-gel | 700 | 247.1 | 0.09398 | 7.607 |
| 6 % Ag/Al ₂ O ₃ | Sol-gel | 700 | 229.3 | 0.08600 | 7.502 |
| 10 % Ag/Al ₂ O ₃ | Sol-gel | 700 | 254.4 | 0.09610 | 7.555 |
| Mn ₂ O ₃ | Precipitation | 500 | 21.4 | 0.00745 | 6.984 |

* : From 5 point BET

† : Total pore volume for pores with radius less than 8 °A at P/P₀ = 0.10841

‡ : Average pore radius

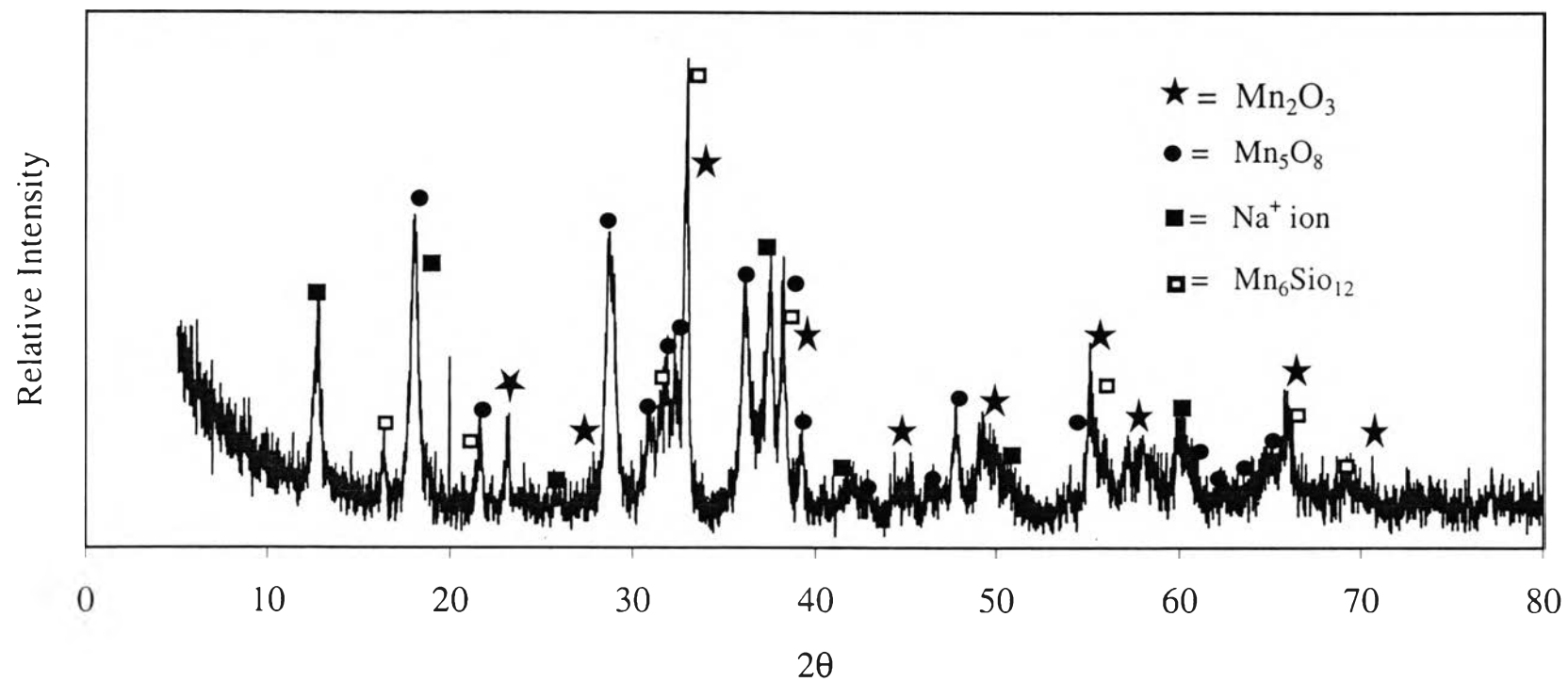


Figure 4.1 XRD Pattern for Manganese Oxide Catalyst

4.2 Catalyst Activity

4.2.1 Effect of Silver Loading

The silver loading was varied in the range of 0, 1.0, 2.0, 4.0, 5.0, 6.0, and 10.0 wt% in order to clarify the effect of metal (Ag) loading on the selective reduction of NO with C_3H_6 .

Figures 4.2-4.4 show the dependence of the catalyst activity on the silver loading at various reaction temperatures. Among the active catalysts for the lean NO_x reduction, Al_2O_3 would be a strong candidate for the practical catalyst since it is one of the widely used, cheap, and heat-stable catalysts (Iwamoto and Hamada, 1991). However, the active temperature is much higher than that of the emission gases released from a diesel engine which is around 300-500 °C and the activity is still low.

As seen from Figure 4.3, the 5 % Ag/ Al_2O_3 catalyst gives the highest NO conversion to N_2 among other silver loading catalysts and a maximum in NO conversion to N_2 which is 75% occurs at 450 °C.

From Figures 4.2-4.4, at a high temperature regime the NO conversion, conversion of NO to N_2 , and NO_x conversion decrease with increasing reaction temperature. This can be due to a lack of sufficient reductant (Misono, 1998). Normally, the reduction of NO to N_2 and the oxidation of hydrocarbon start at about the same temperature. The reductions reach a maximum and decrease at high temperature where the oxidation of hydrocarbon is dominant, the conversions of hydrocarbon approaches almost 100 % near the temperature at which the conversion of NO to N_2 is maximized. So there was not enough C_3H_6 to react with NO or NO_2 to form N_2 .

The catalysts for NO_x reduction are reasonably resistant to sintering at temperature up to about 550 °C. However, excursions in excess of

this temperature may result in a metal crystalline growth. Not only does sintering result in the loss of the exposed metal surface area but may also lead to changes in the catalytic properties of the supported metal (Gonzalez *et al.*, 1997). When the size of a crystallite is matched to the diameter of the pore, surface diffusion is inhibited and crystal growth will not occur.

The addition of a second oxide, for example BaO, to alumina catalyst appears to inhibit sintering (Ueno, 1992). It is thought that this inhibition to sintering occurs as a result of the formation of M_1-O-M_2 linkages between the supported metal and the modifying oxide. This phenomenon may be occurring with the sol-gel Ag/Al₂O₃ catalysts. The highly dispersed silver ions in the sol-gel catalysts react with alumina to form silver aluminate (AgAl₂O₄) by calcination at 700°C, and exhibited a high activity for SCR-NO. However, for the Ag catalyst, the XRD showed that the catalyst is in an amorphous structure (Lorpongpaiboon, 1998). Because of the limitation of XRD, the crystallite sizes of Ag which are less than 50 Å cannot be detected by XRD.



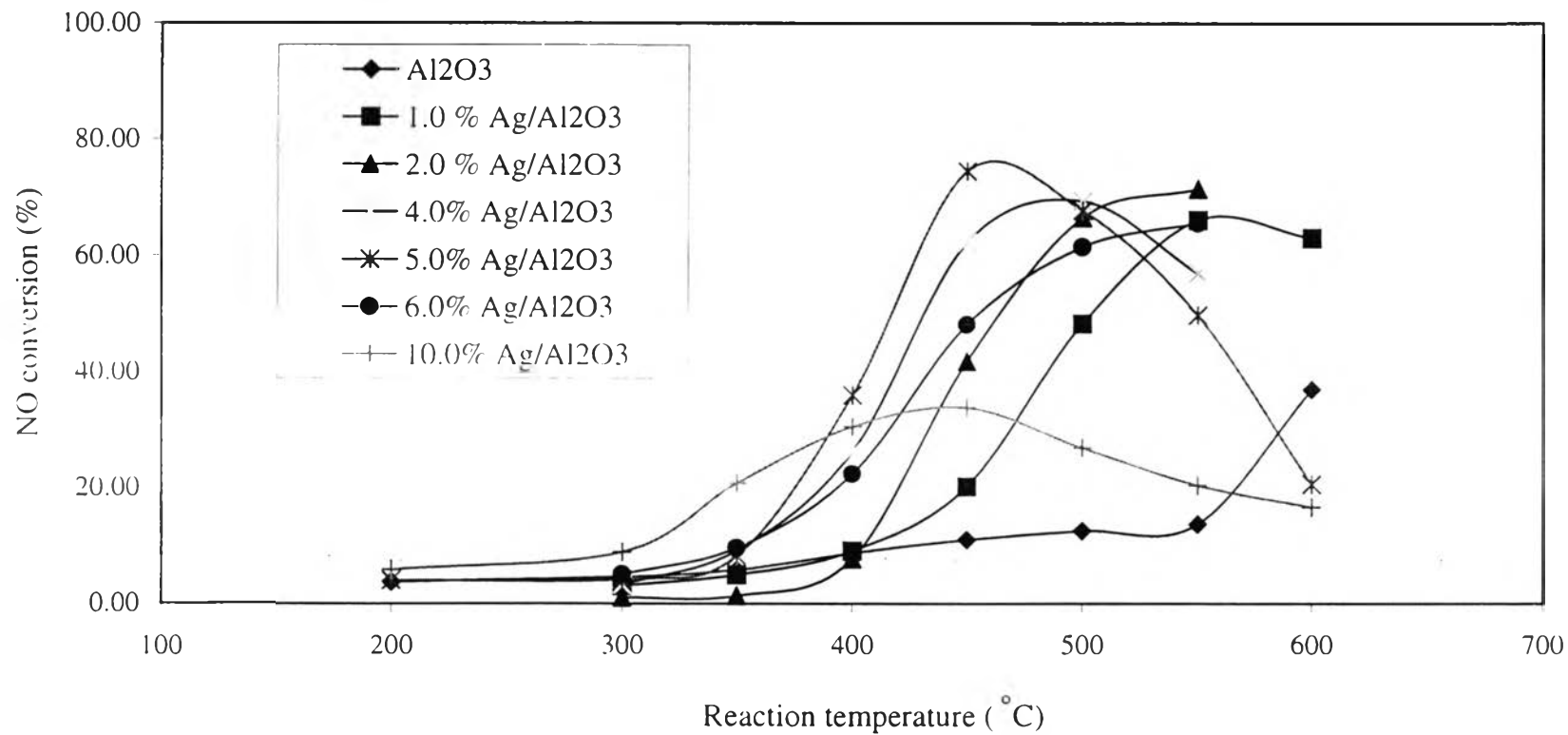


Figure 4.2 NO Conversion at Various Reaction Temperatures over Ag/Al₂O₃ Catalysts with Different Silver Loadings

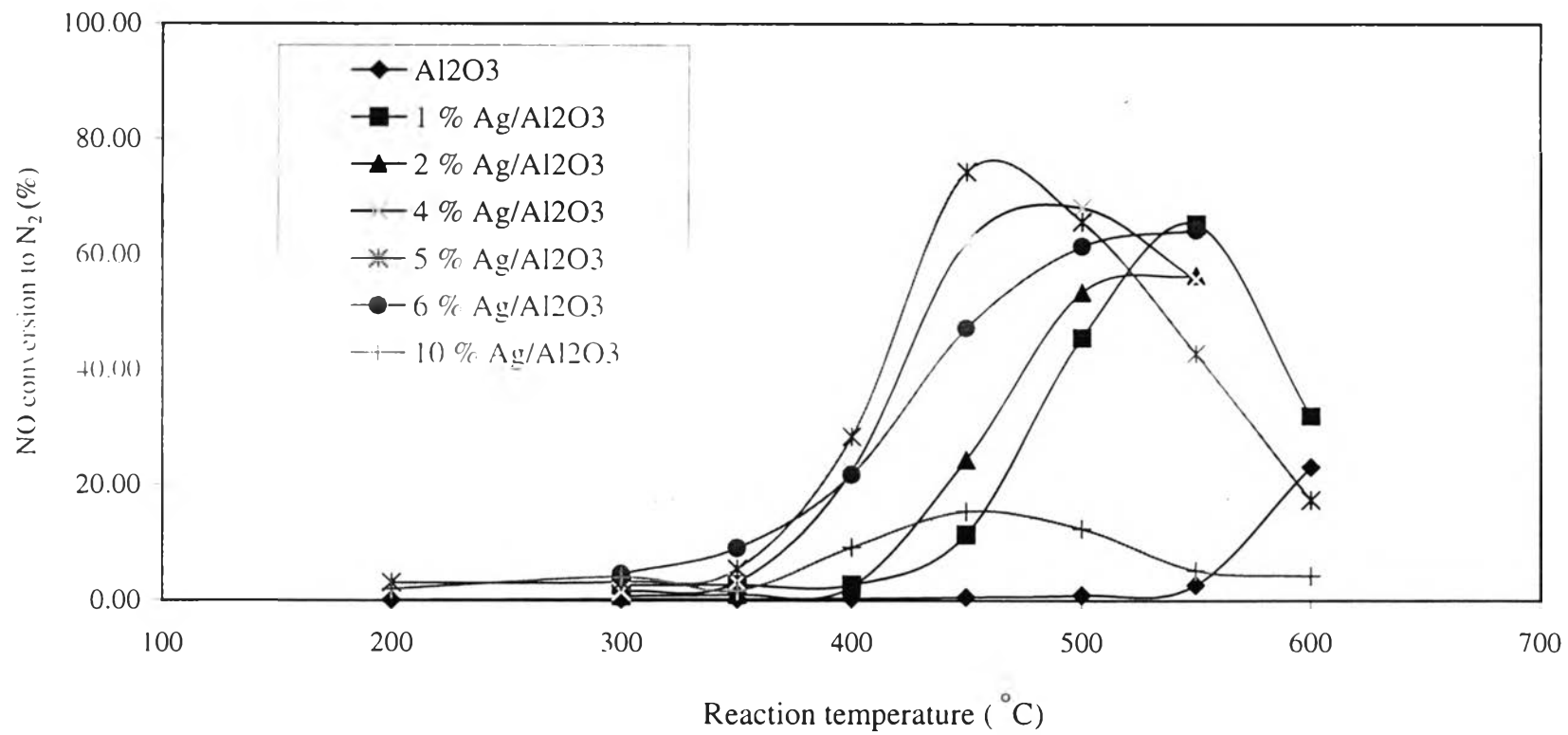


Figure 4.3 NO Conversion to N₂ at Various Reaction Temperatures over Ag/Al₂O₃ Catalysts with Different Silver Loadings

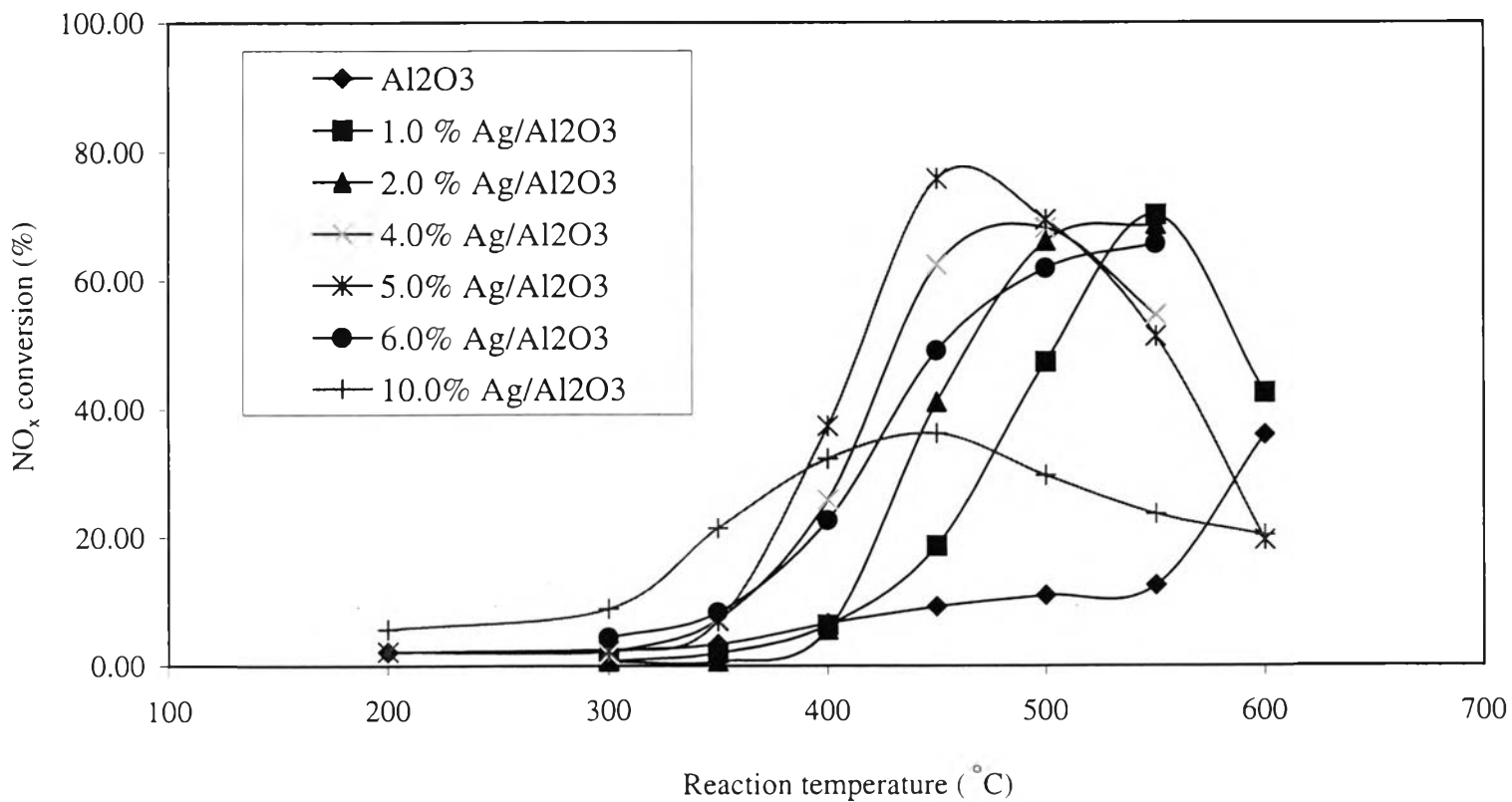


Figure 4.4 NO_x Conversion at Various Reaction Temperatures over Ag/Al₂O₃ Catalysts with Different Silver Loadings

4.2.2 Combination Study of Two Different Function Catalysts

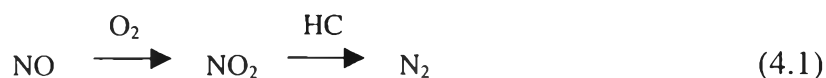
The study of two different function (reduction and oxidation) catalysts was performed to investigate the reaction mechanism which occur on the Ag catalysts by mixing Ag/Al₂O₃ and Mn₂O₃ physically. The NO oxidation catalyst, manganese oxide (Mn₂O₃), was obtained by thermal decomposition of manganese precipitate prepared from precipitation method.

The activities in terms of conversion of NO, NO conversion to N₂, and NO_x conversion were shown in Figures 4.5-4.7, respectively. The conversions were decreased with increasing the amount of added Mn₂O₃ from 0.2, 0.4, 0.8, 2.0, and 5.0 % by weight.

Before putting this mixed catalyst into the reactor, the Ag/Al₂O₃ and Mn₂O₃ were mixed mechanically in a mortar at least 30 minutes. Then calcined together in air flowing at 500 °C for 5 hours. During high temperature calcining, Mn₂O₃ diffuses into the pores of Al₂O₃ support as a thin layer. This results in increasing its proximity to silver aluminate and thus the higher reaction rate. The important issues are the dispersion of Mn₂O₃ catalyst in the mixed catalyst, which needed to be ground for a while. The high temperature calcination and grinding with Ag would accomplish the homogeneous dispersion of Mn₂O₃.

It is suggested that the lean NO_x reduction with hydrocarbon can proceed by a series or parallel reaction steps. The reaction mechanisms would be proposed by different kind of intermediates (Misono, 1998).

The first mechanism, where the oxidation of NO is dominant, NO is first oxidized to NO₂ which then (adsorbed or in the gas phase) reacts with hydrocarbon to form N₂.



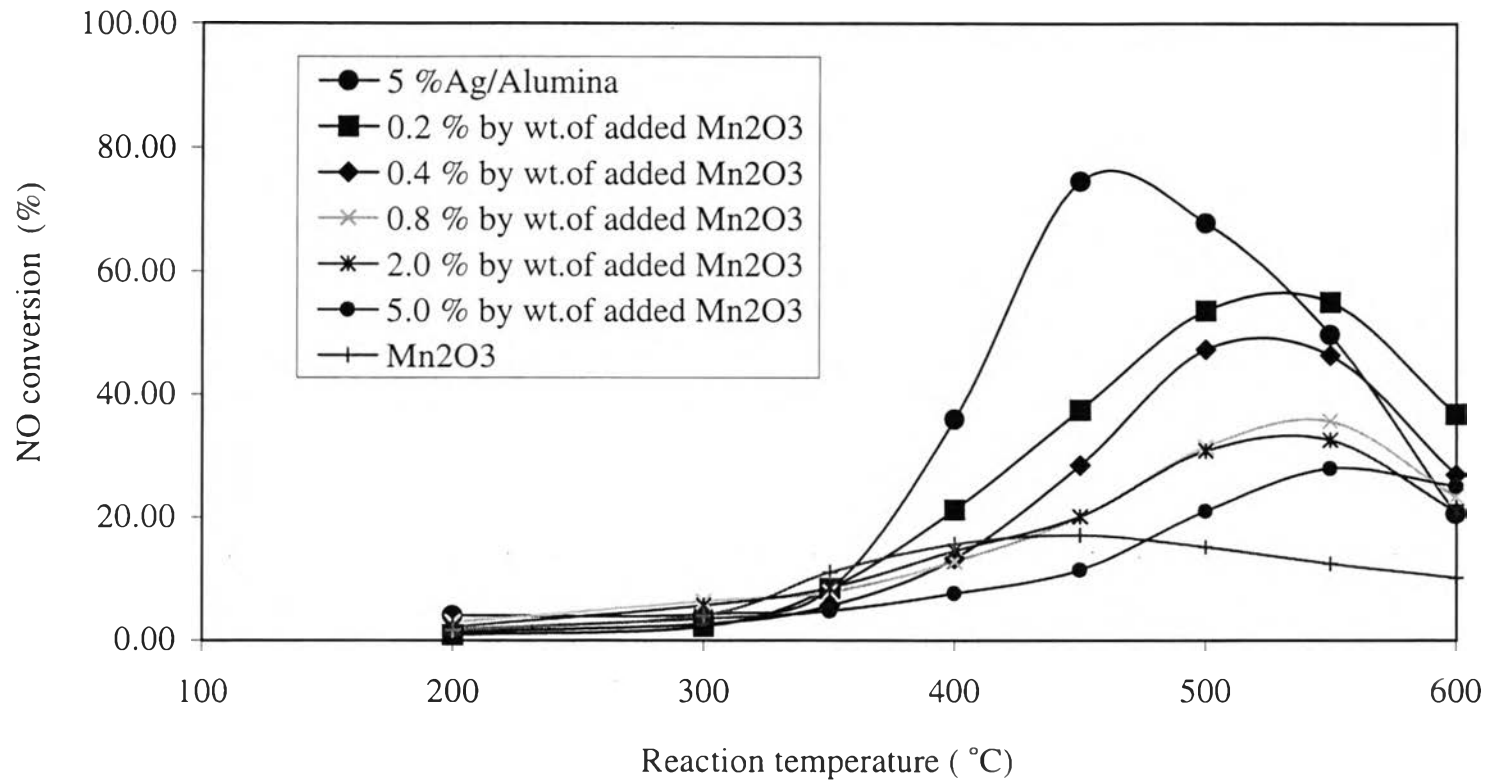


Figure 4.5 NO Conversion at Various Reaction Temperatures over the Combination of 5 % Ag/Al₂O₃ and Mn₂O₃ Catalysts

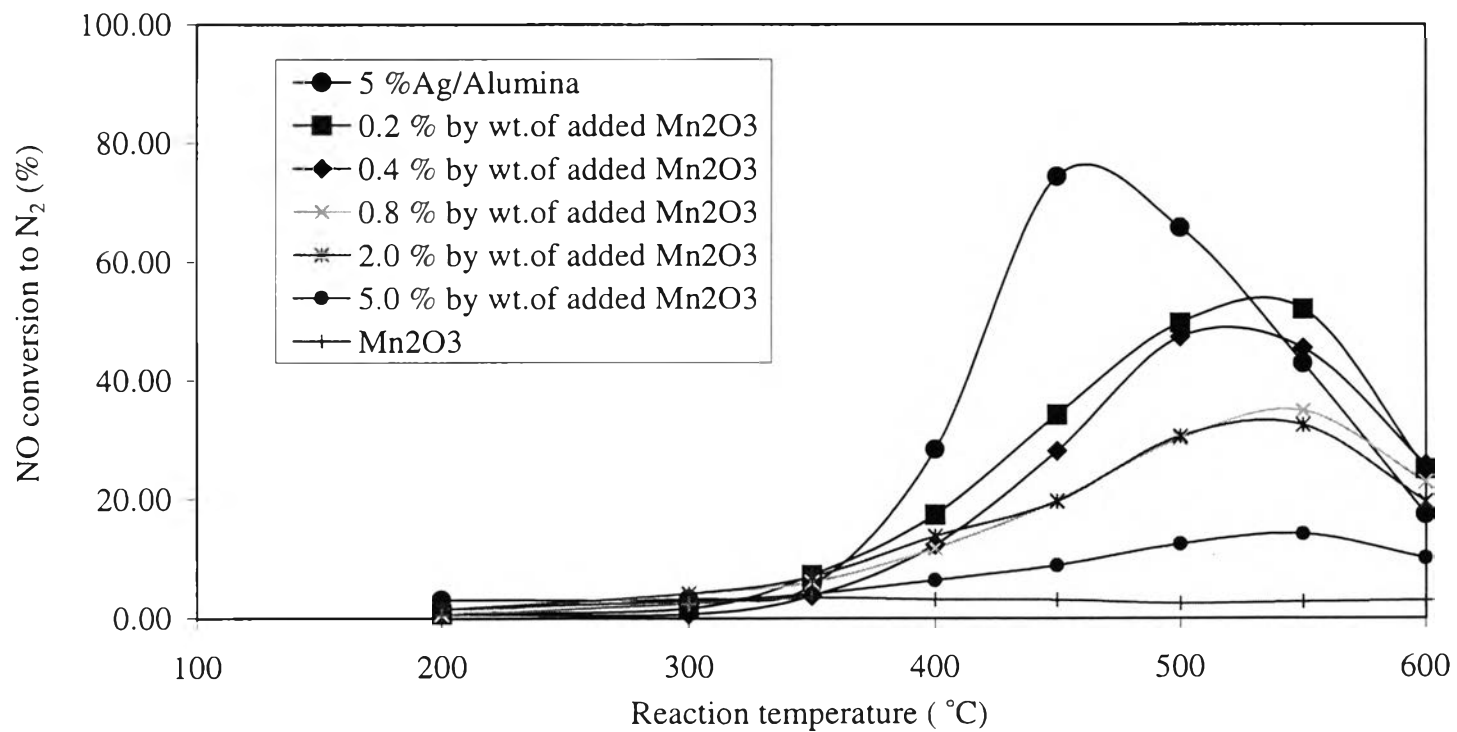


Figure 4.6 NO Conversion to N₂ at Various Reaction Temperatures over the Combination of 5 % Ag/Al₂O₃ and Mn₂O₃ Catalysts

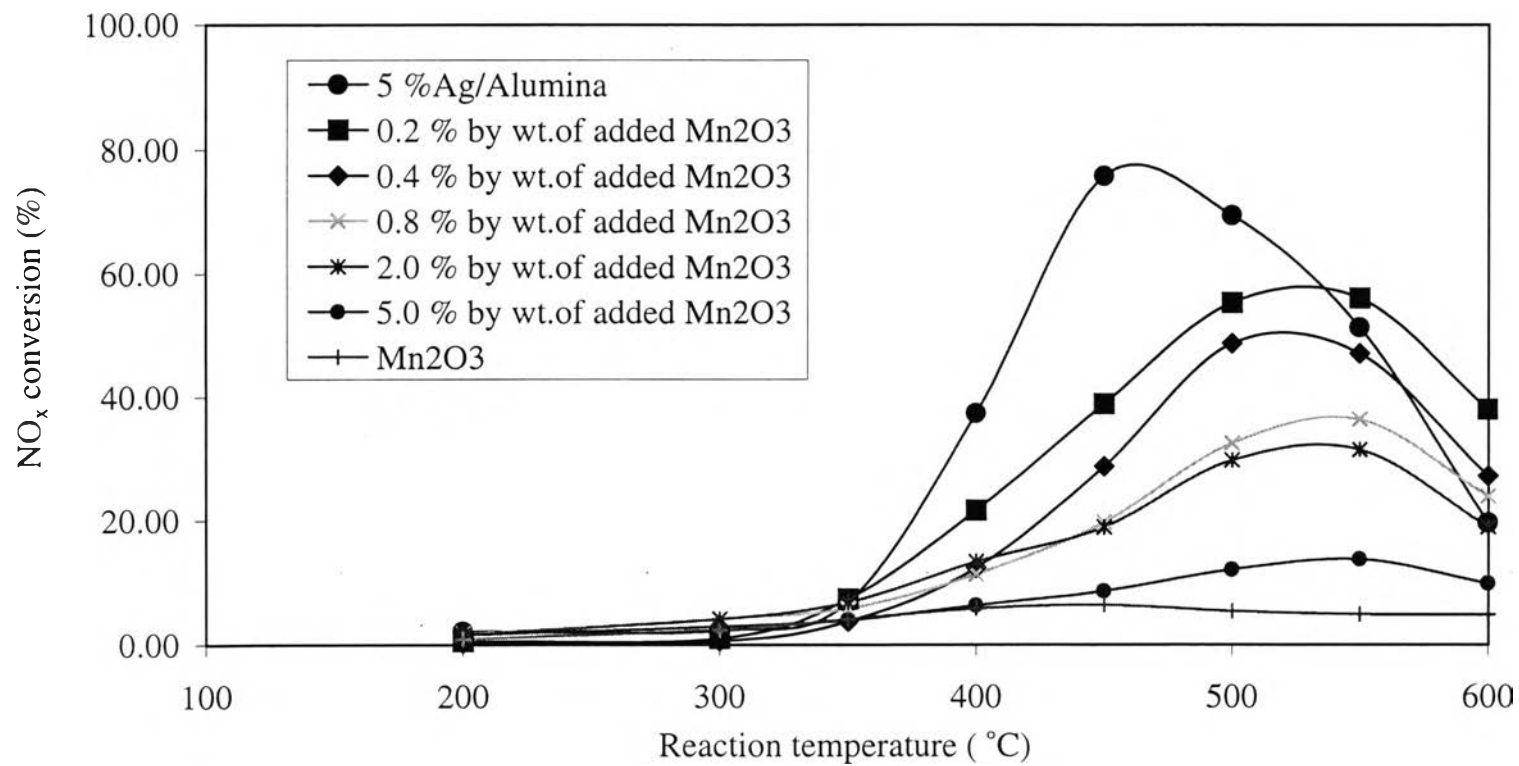
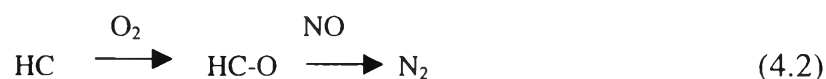


Figure 4.7 NO_x Conversion at Various Reaction Temperatures over the Combination of 5 % Ag/Al₂O₃ and Mn₂O₃ Catalysts

The second mechanism, where the partial oxidation of hydrocarbon is dominant, NO is reduced by reacting with intermediate generated from partial oxidation of hydrocarbon.

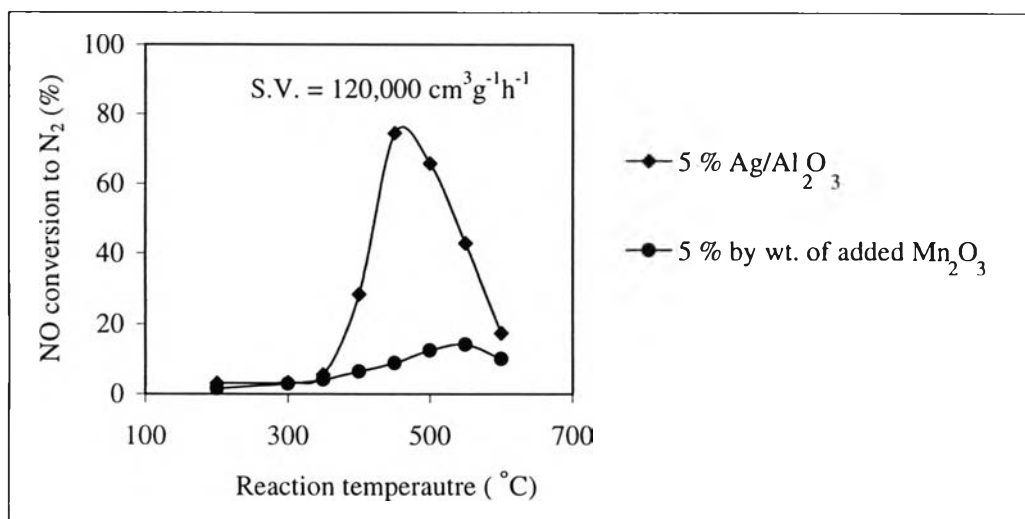
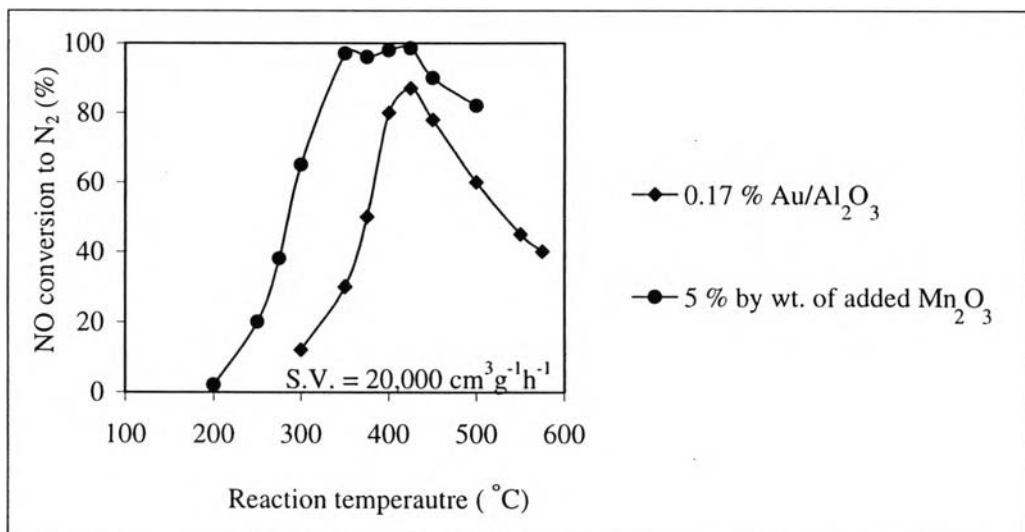


If the hydrocarbon oxidation activity on a catalyst is very high, the complete oxidation decreases the formation of intermediates from partial oxidation and results in low activity of lean NO_x reduction. On the other hand, if the oxidation activity is too low, the generation of the intermediates is slow and the rate of NO_x reduction becomes low (Jen, 1998).

In this study, the results verify the reaction mechanism that a partial oxidation of hydrocarbon initiates the lean NO_x reduction which occurs on the Ag catalysts. Although the NO oxidation was promoted by addition of the Mn₂O₃ catalyst, it can be seen that a drastic decrement is observed in conversions. The Mn₂O₃ catalyst exhibited the negative effect on the conversion of NO to N₂.

The Ag/Al₂O₃ gave the opposite result when compared with Au/Al₂O₃ catalyst (Ueda and Haruta, 1998). The comparison between the addition of Mn₂O₃ to Ag/Al₂O₃ and to Au/Al₂O₃ catalysts is shown in Figure 4.8. The 5.0 % by weight of Mn₂O₃ added mechanically to Au (0.17 wt%)/Al₂O₃ exhibits the highest activity among Au/Al₂O₃ catalysts (Ueda *et al.*, 1997).

The Au/Al₂O₃ was found to be more active if NO is oxidized first to form NO₂ by the promoting on NO oxidation from Mn₂O₃ catalyst. This results provide some evidence to support that the reduction of NO with C₃H₆ in the presence of oxygen over Au/Al₂O₃ catalysts proceeds through the preferential oxidation of NO with molecular oxygen to form NO₂, which then

(a) The Effect of Mn_2O_3 Catalyst Added to $\text{Ag}/\text{Al}_2\text{O}_3$ (b) The Effect of Mn_2O_3 Catalyst Added to $\text{Au}/\text{Al}_2\text{O}_3$ (From Ueda and Haruta, 1998)**Figure 4.8** Comparison of Addition of Mn_2O_3 Catalyst to $\text{Ag}/\text{Al}_2\text{O}_3$ and to $\text{Au}/\text{Al}_2\text{O}_3$

react with C_3H_6 to form N_2 . It is corresponding to the first mechanism, where the oxidation of NO is dominant, as described before.

4.2.3 Promoting Effect of Oxygen

The activities in terms of conversion of NO, NO conversion to N_2 , and NO_x conversion are shown in Figures 4.9-4.11, respectively. The activity of lean NO_x reduction increases as oxygen concentration increases from 5 % up to 20 % vol.

From the practical point of views, namely, to exhaust gases from lean burn gasoline engines and diesel engines, a catalyst should operate under a large excess of oxygen in the range of 2 to 10 % vol., at a large hourly space velocities over $1 \times 10^5 \text{ h}^{-1}$ (Ueda *et al.*, 1997). Therefore the effect of various concentrations of oxygen on the sol-gel silver supported on alumina catalyst was investigated.

The promoting effect of oxygen on the rate of NO reduction by hydrocarbons was first reported by Iwamoto and Hamada (1991). Over Cu-ZSM-5, the rate of NO reduction by propene at temperatures below 400 °C was found to increase with the addition of oxygen concentrations of 1-2 % while at higher oxygen concentrations the activity decreased slightly.

From the results, it appears that the combustion of hydrocarbon was being shifted to a lower temperature and therefore the reduction peak temperature was shifted as the oxygen content was increased. Oxygen has an inhibiting effect at higher temperatures, since under these conditions the complete hydrocarbon combustion process was accelerated.

The difference in the effect of oxygen concentration can be attributed to the difference in the activities of hydrocarbon oxidation (Jen, 1998). It was found by Jen that for the Cu/Al_2O_3 catalyst, only a small amount of oxygen is required to initiate the partial oxidation of hydrocarbon for the

reduction of NO_x . Thus high levels of oxygen may result in enhancing the complete oxidation of hydrocarbon, thereby decreasing the concentration of reactive intermediates and the rate of NO_x reduction. On the other hand, for $\text{Ag}/\text{Al}_2\text{O}_3$ catalyst, it has lower hydrocarbon oxidation activity than a Cu catalyst, therefore increasing the oxygen concentration may promote the partial oxidation of hydrocarbon rather than the total oxidation.

It was observed that the sol-gel catalyst used in this study can be operated over a wide range of oxygen concentrations without losing its activity on the selective reduction of NO with C_3H_6 .

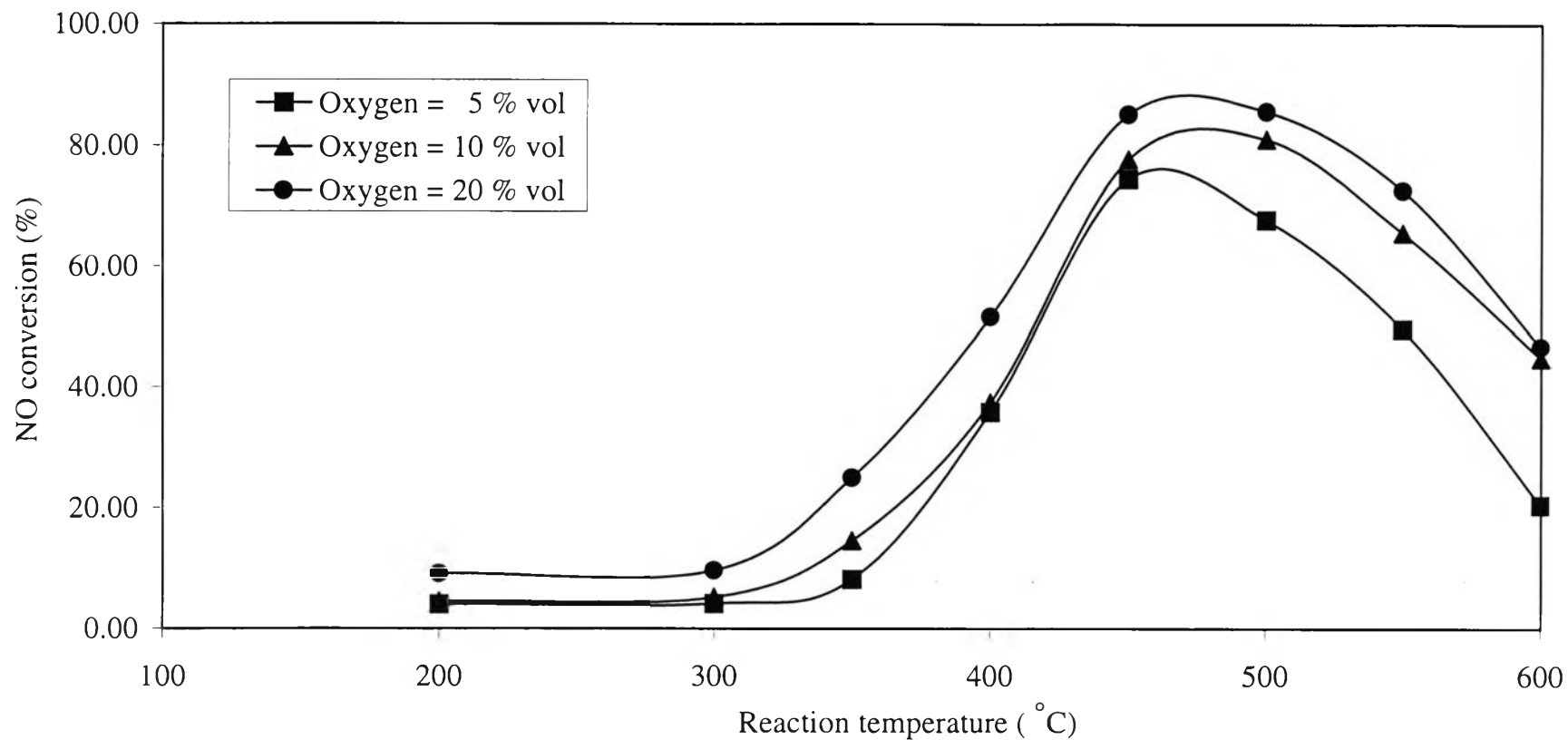


Figure 4.9 NO Conversion at Various Reaction Temperatures over 5 % Ag/Al₂O₃ Catalyst with Different O₂ Concentrations

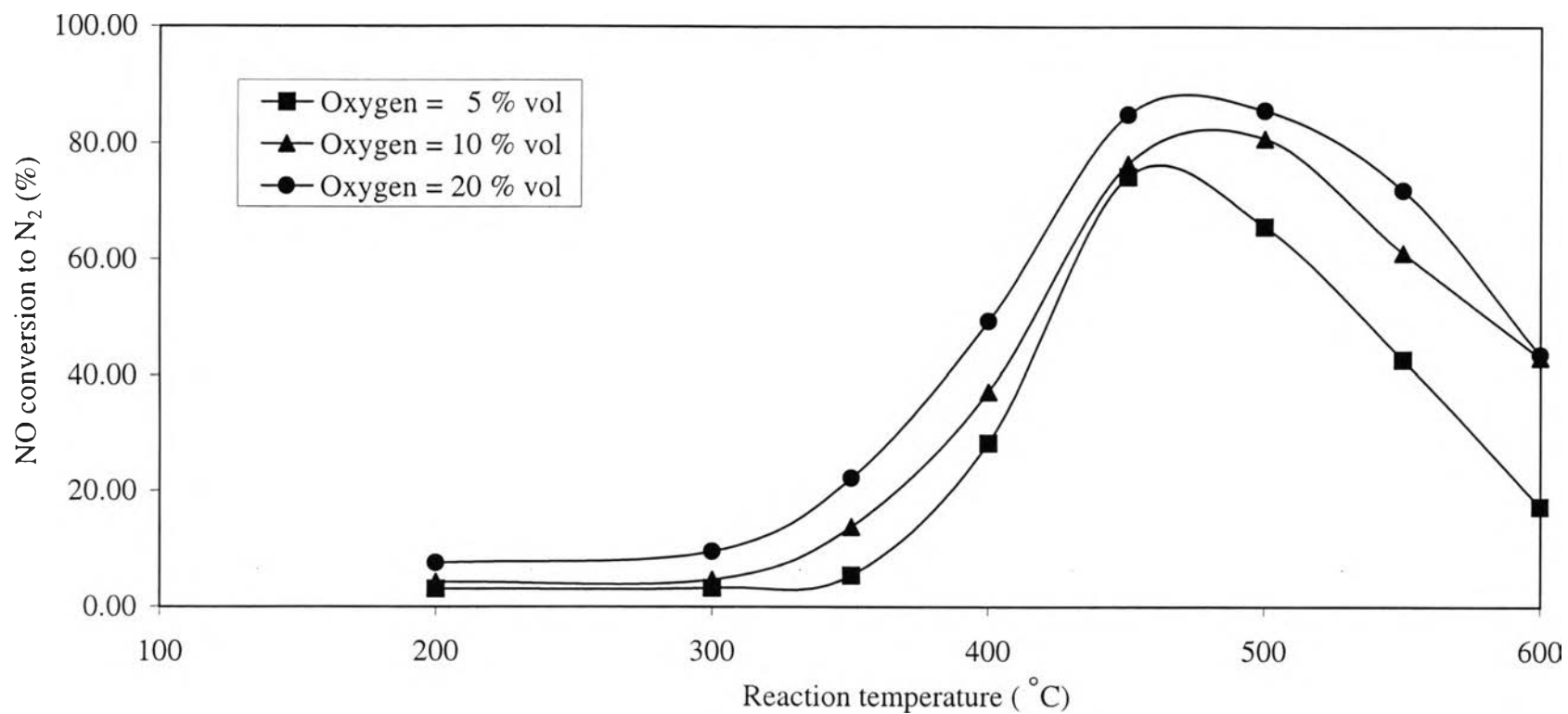


Figure 4.10 NO Conversion to N₂ at Various Reaction Temperatures over 5 % Ag/Al₂O₃ Catalyst with Different O₂ Concentrations

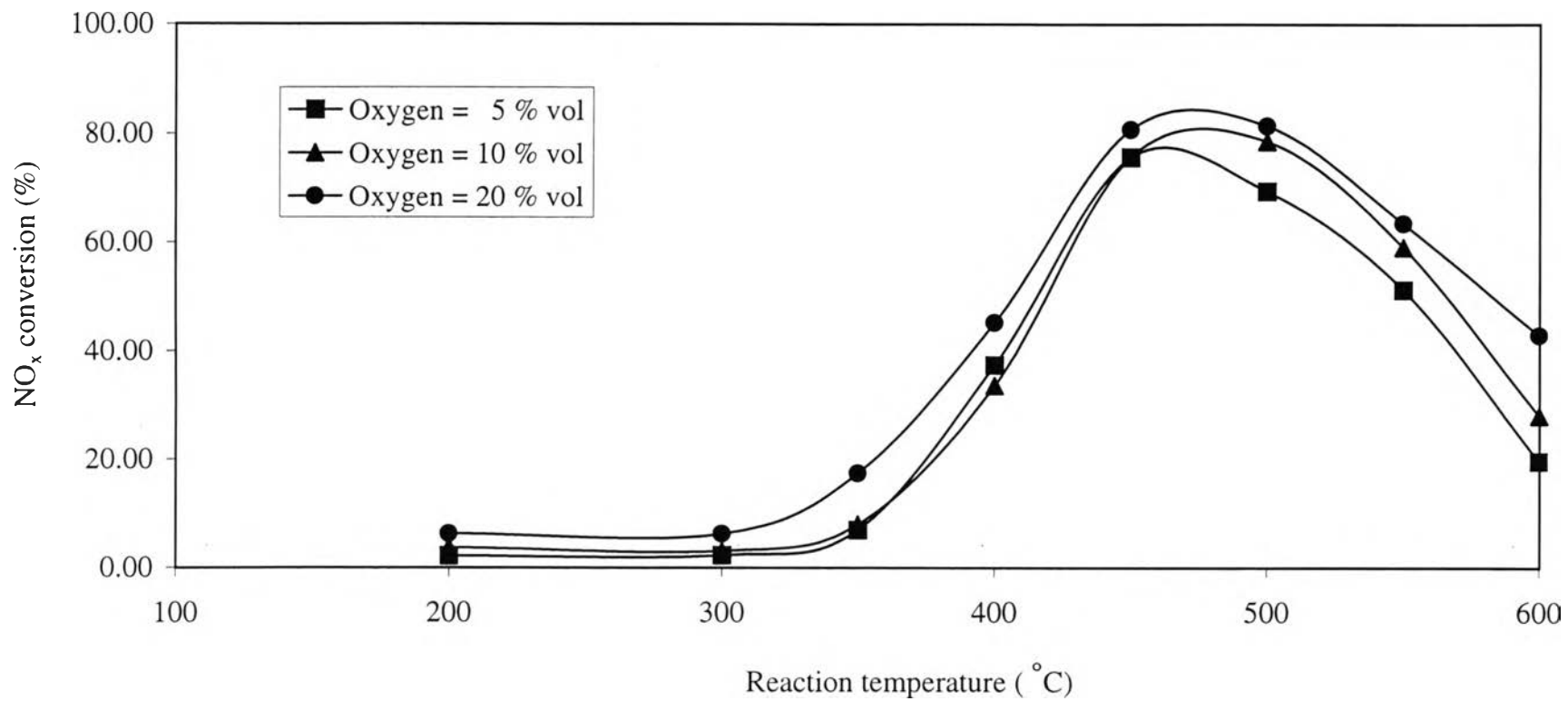


Figure 4.11 NO_x Conversion at Various Reaction Temperatures over 5 % Ag/Al₂O₃ Catalyst with Different O₂ Concentrations