CHAPTER IV
RESULTS AND DISCUSSION

4.1 Catalyst Characterization

The specific surface area of the sol-gel silver supported on alumina (Ag/Al_2O_3), platinum supported on alumina (Pt/Al_2O_3), silver supported on titania (Ag/TiO_2), and platinum supported on titania (Pt/TiO_2) catalysts were determined by the five-point BET method using surface area analyzer. Table 4.1 lists the surface area of the prepared catalysts. The specific surface area of alumina catalysts is higher than titania catalysts. The specific surface area of these catalysts is independent of silver and platinum loadings.

The XRD pattern for Ag/Al_2O_3, Pt/Al_2O_3, Ag/TiO_2, and Pt/TiO_2 catalysts are shown in Figures 4.1-4.4. These patterns identify the kind of support structure and metal loading on support. Metal peaks are present and support peaks match those of alumina or titania exactly. Absence of any detectable metal crystallite peaks indicates that the average crystallite size in these catalysts is below the detection level by XRD.

The AAS or Atomic Adsorption Spectroscopy method (Varian Specter AA300) was used to analyze the concentration of metal in catalysts. The results are shown in Table 4.1.

4.2 Catalyst Activity

4.2.1 Effect of Metal Loading

4.2.1.1 Silver Supported on Alumina (Ag/Al_2O_3)

The silver loading was varied in the range of 4.0, 5.0, and 6.0 wt% in order to clarify the effect of silver loading on the selective reduction of NO with C_3H_6. Figure 4.5 shows the dependence of the catalyst

Table 4.1 Catalyst characterization.

Catalyst	Surface area (m^2/g)	Metal loading (%)
Al_2O_3	355.7	-
1.0% Ag/Al_2O_3	286.0	1.05
2.0% Ag/Al_2O_3	298.9	1.58
4.0% Ag/Al_2O_3	276.9	2.81
5.0% Ag/Al_2O_3	293.4	4.10
6.0% Ag/Al_2O_3	299.2	4.63
8.0% Ag/Al_2O_3	266.9	6.53
0.5% Pt/Al_2O_3	278.2	0.75
1.0% Pt/Al_2O_3	285.4	1.80
1.5% Pt/Al_2O_3	287.2	2.04
2.0% Pt/Al_2O_3	281.0	2.25
3.0% Pt/Al_2O_3	271.7	3.20
TiO_2	119.2	-
0.5% Ag/TiO_2	89.36	0.10
1.0% Ag/TiO_2	84.71	0.59
2.0% Ag/TiO_2	79.47	1.17
3.0% Ag/TiO_2	99.13	2.43
0.5% Pt/TiO_2	96.15	0.32
1.0% Pt/TiO_2	108.9	0.52
1.5% Pt/TiO_2	128.1	0.65
2.0% Pt/TiO_2	146.9	1.40
3.0% Pt/TiO_2	152.9	3.48
4.0% Pt/TiO_2	121.5	4.88

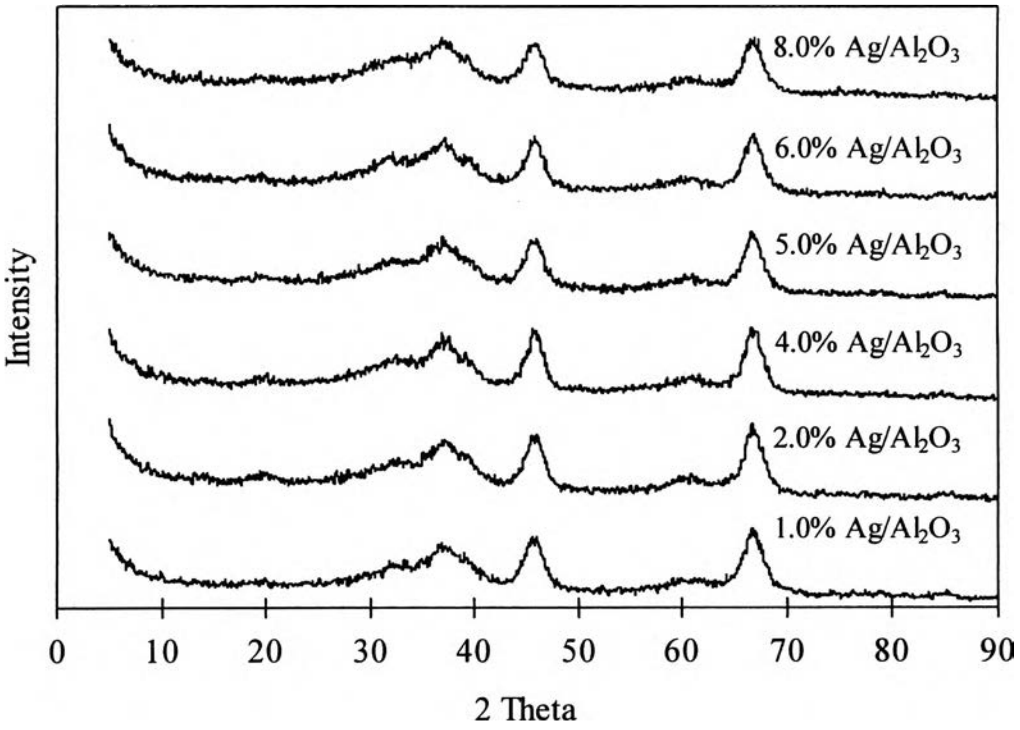

Figure 4.1 XRD pattern for Ag/Al_2O_3 catalysts.

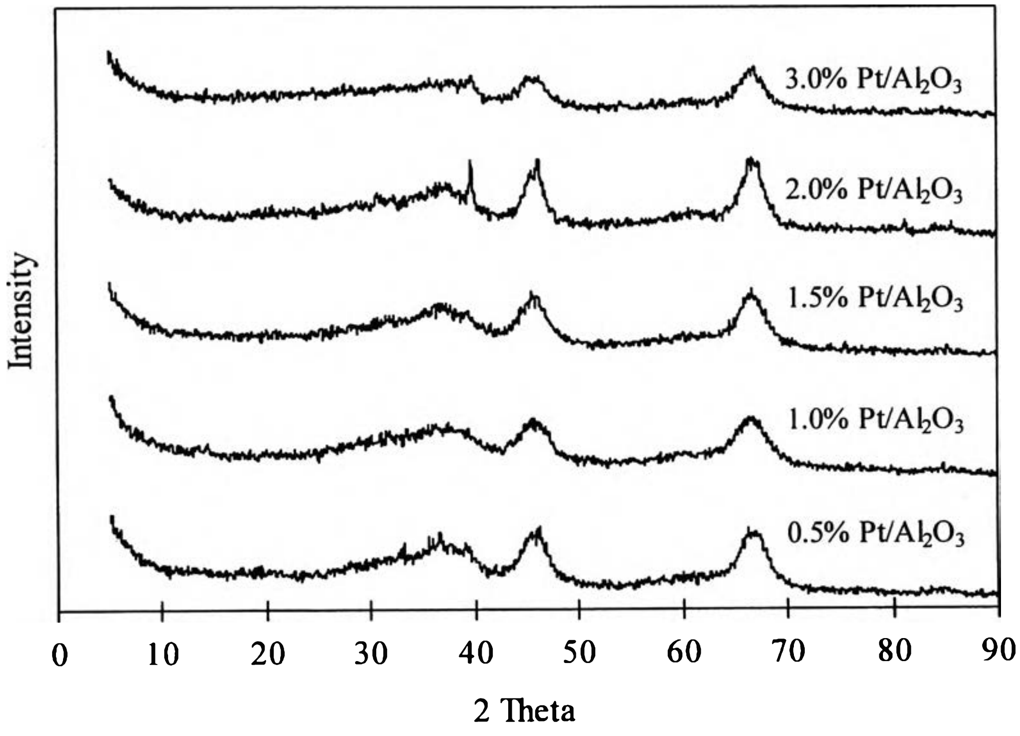

Figure 4.2 XRD pattern for Pt/Al_2O_3 catalysts.

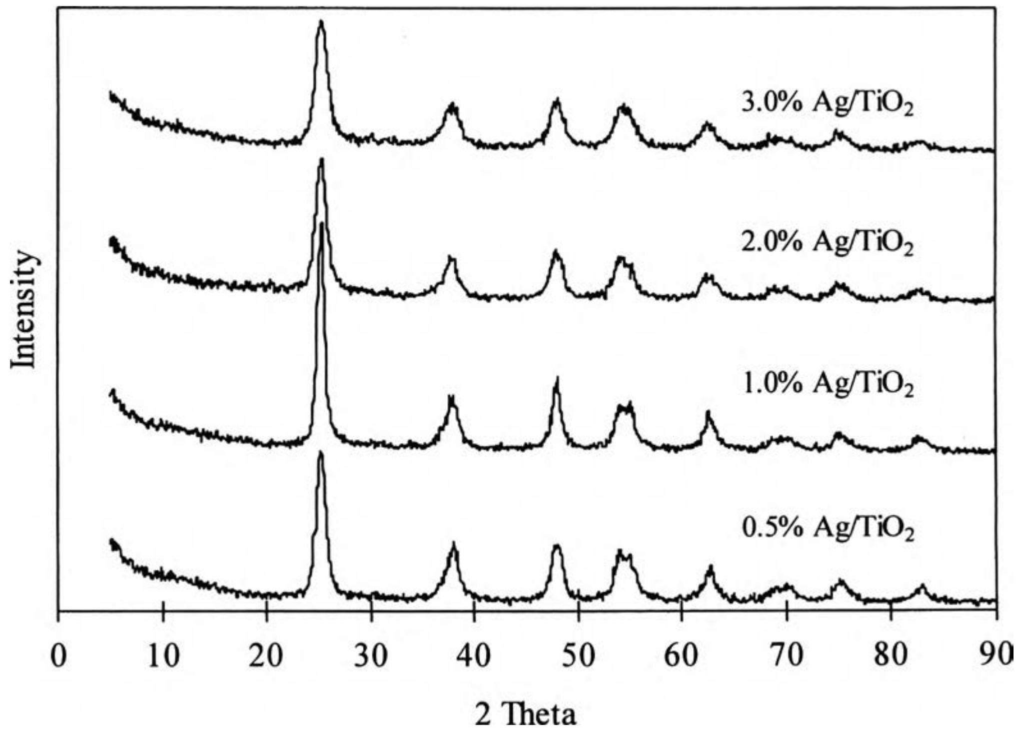

Figure 4.3 XRD pattern for Ag/TiO$_2$ catalysts.

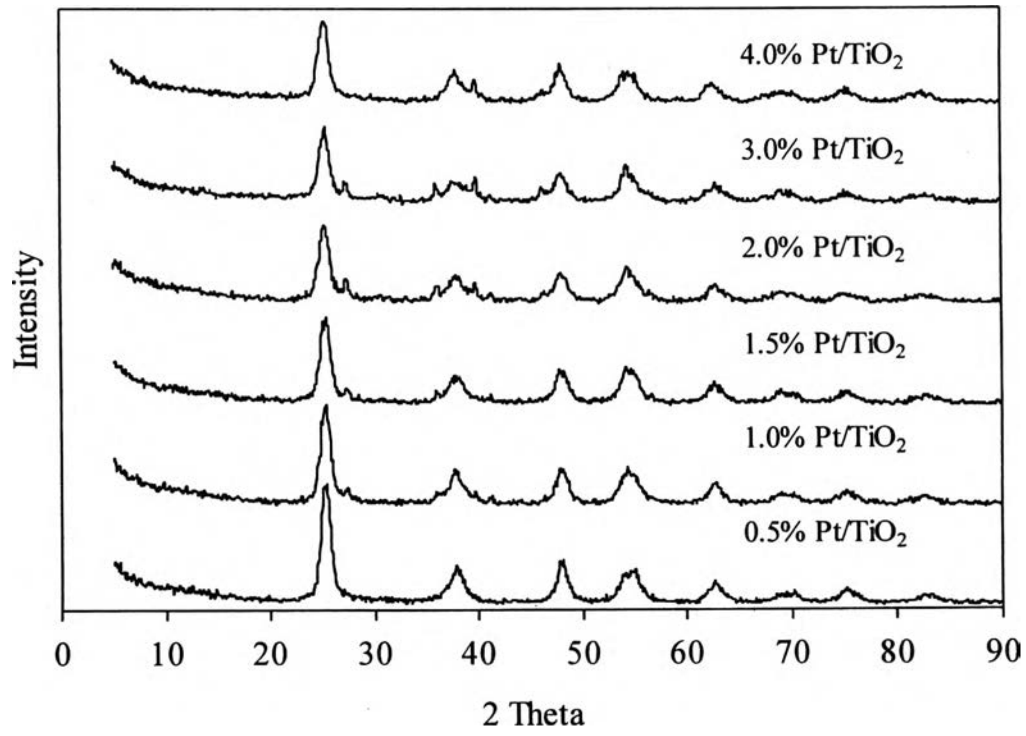

Figure 4.4 XRD pattern for Pt/TiO$_2$ catalysts.

activity on the silver loading at various reaction temperatures. It shows that the 6% Ag/Al_2O_3 catalyst gives the highest NO_x conversion among other silver loading catalysts and a maximum NO_x conversion of 89% occurs at 450°C. It appears that the sol-gel technique stabilize the small crystals of silver in the pore so that sintering is prevented even at the high temperatures. In this case, increasing the loading just increased the number of crystallines, which gave rise to higher activity.

4.2.1.2 Platinum Supported on Alumina (Pt/Al_2O_3)

The platinum loading was varied in the range of 1.0, 1.5, and 2.0 wt%. Figure 4.6 shows the dependence of the catalyst activity on the platinum loading at various reaction temperatures. It shows that the 1.5% Pt/Al_2O_3 catalyst gives the highest NO conversion among other platinum loading catalysts and a maximum NO conversion of 32% occurs at 300°C.

4.2.1.3 Silver Supported on Titania (Ag/TiO_2)

The silver loading was varied in the range of 0.5, 1.0, 2.0 and 3.0 wt%. Figure 4.7 shows the dependence of the catalyst activity on the silver loading at various reaction temperatures. It shows that the 2% Ag/TiO_2 catalyst gives the highest NO_x conversion among other silver loading catalysts and a maximum NO_x conversion of 42 % occurs at 400°C.

4.2.1.4 Platinum Supported on Titania (Pt/TiO_2)

The platinum loading was varied in the range of 0.5, 1.0, and 1.5 wt%. Figure 4.8 shows the dependence of the catalyst activity on the platinum loading at various reaction temperatures. It shows that the 1.5% Pt/TiO_2 catalyst gives the highest NO_x conversion among other platinum loading catalysts and a maximum NO_x conversion of 61% occurs at 250°C.

From figures, the NO_x conversion results show the negative value because NO_x was adsorbed on the catalyst surface at low temperature range. After increasing the reaction temperature NO_x was desorbed from the catalyst

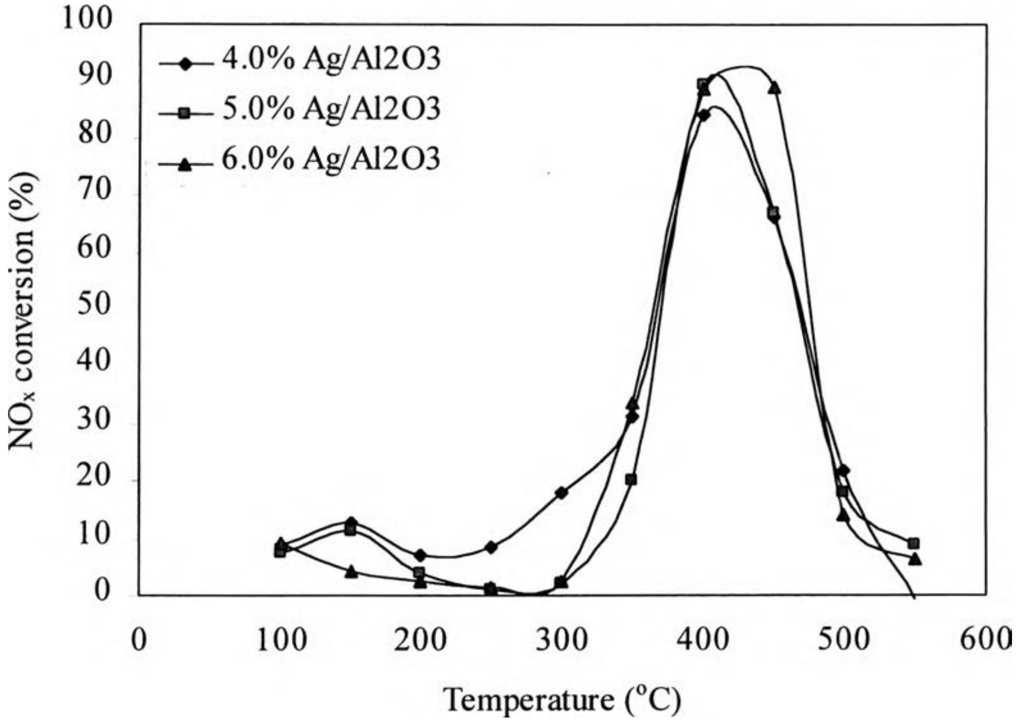

Figure 4.5 NO_x conversion at various reaction temperatures over Ag/Al_2O_3 catalysts with different silver loadings.

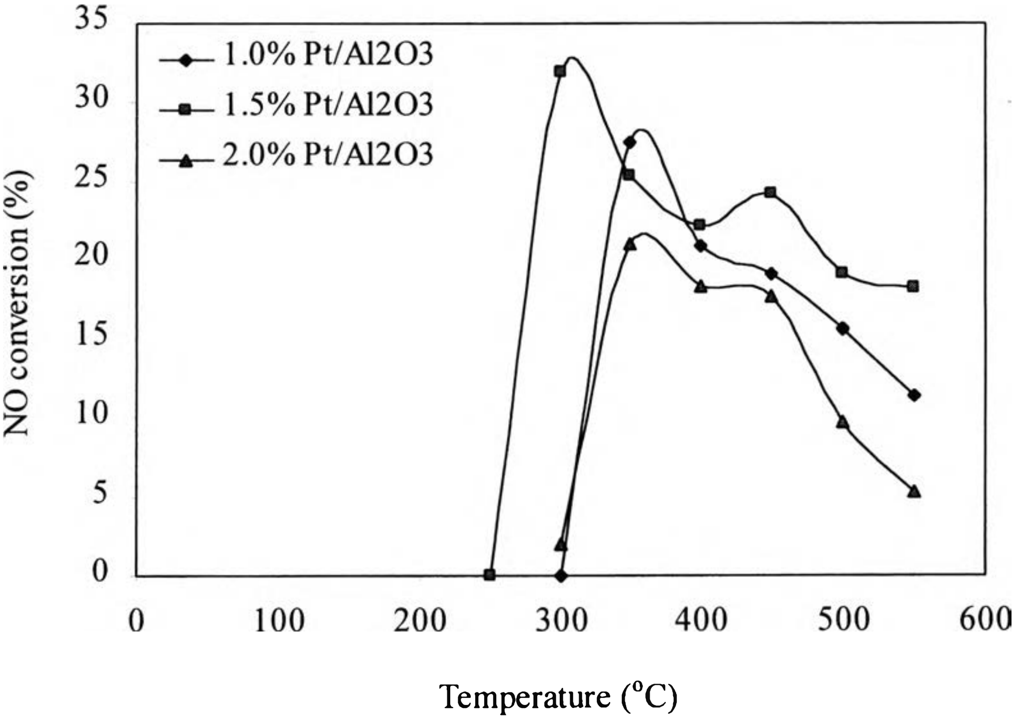

Figure 4.6 NO conversion at various reaction temperatures over Pt/Al_2O_3 catalysts with different platinum loadings.

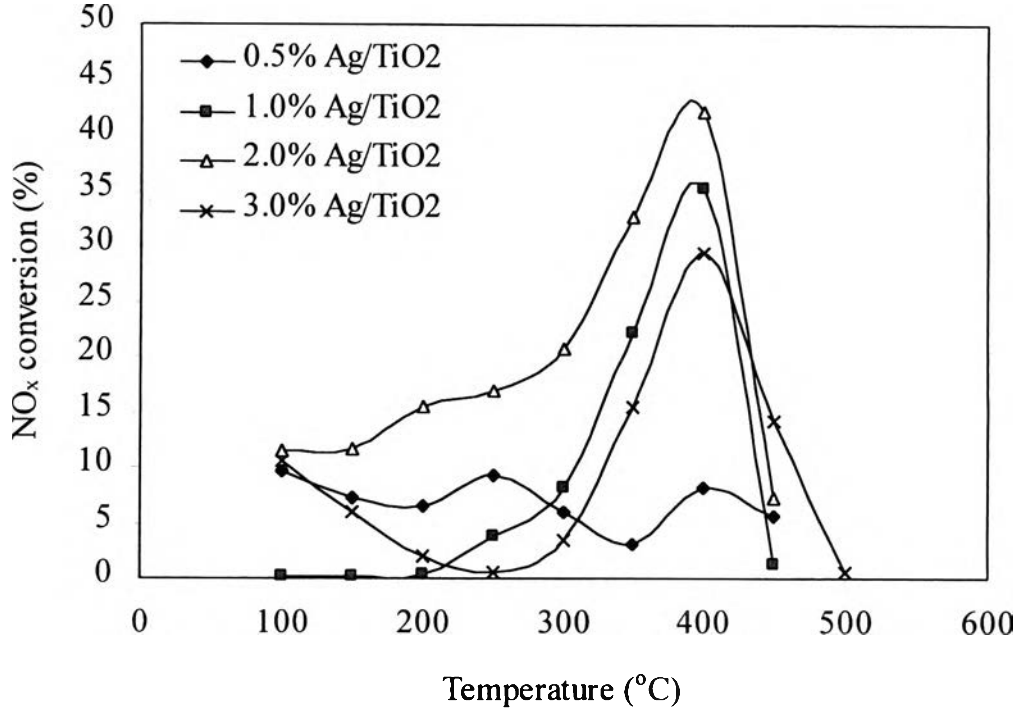

Figure 4.7 NO_x conversion at various reaction temperatures over Ag/TiO_2 catalysts with different silver loadings.

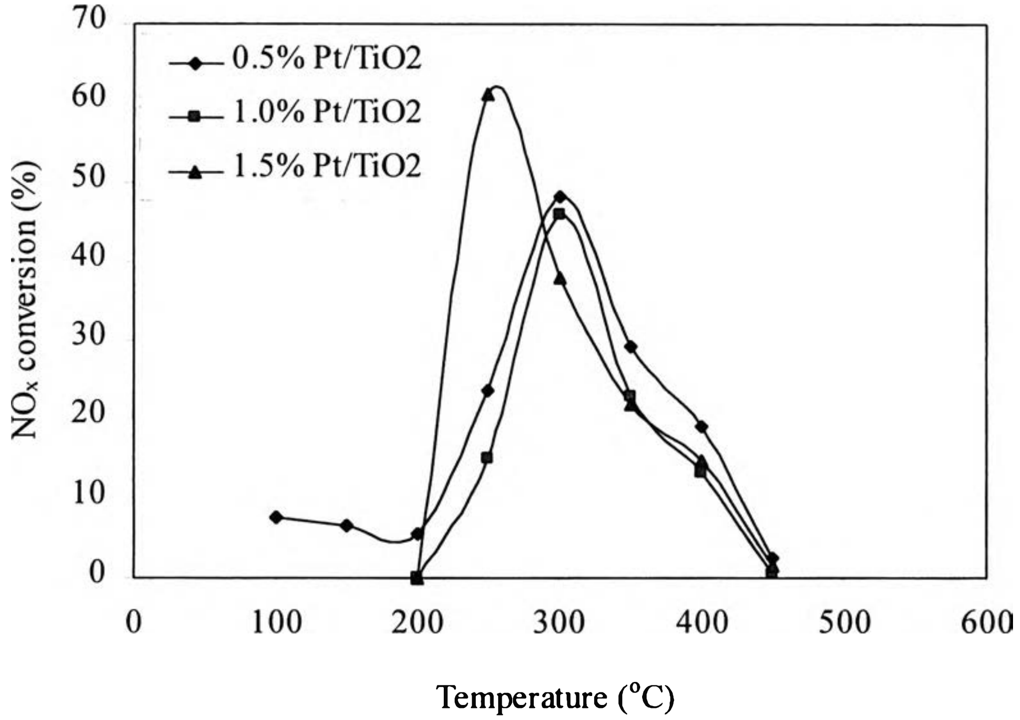

Figure 4.8 NO_x conversion at various reaction temperatures over Pt/TiO_2 catalysts with different silver loadings.

surface then it was mixed together with the unreacted gas. Therefore the concentration of NO_x in the product gas was higher than the reactant gas.

4.2.2 Effect of Water Vapor

Experimental results are presented in Figures 4.9-4.12. Feed gas stream contains 0% water for dry reaction and 3% water for wet reaction. The Ag/Al_2O_3 and Pt/TiO_2 catalysts had higher activity for the selective catalytic reduction of nitric oxide in the presence of water, while the activity of the Pt/Al_2O_3 and Ag/TiO_2 catalysts decreased significantly in the presence of water vapor.

The effect of water on the Ag/Al_2O_3 catalyst was small. The silver on the Ag/Al_2O_3 catalyst is supposed to be in the metal state under the reaction conditions, since silver oxide decomposed to metallic silver and oxygen at temperatures above 300°C. Pt/Al_2O_3 catalyst consists of metal oxides and are subject to interference of water vapor because water adsorbs strongly on those oxides.

For titania catalysts, water and NO competed for the active sites and allowed for the possibility of a dissociative adsorption of water as H^+ and OH^-. The proton would get associated with the coordinatively unsaturated (cus) O^{2-} site and the hydroxyl with the (cus) cation site. The initial activity could be restored only after regeneration at high temperatures. Dispersion of the active species as well as the nature of the support play an important role in increasing the stability of catalysts.

For Pt/Al_2O_3 and Ag/TiO_2 catalysts, the conversion curves for NO_x were shifted to higher temperature range. Water vapor is always present in automobile exhaust. Therefore the catalysts will always be exposed to water vapor in the exhaust. The effect of this inhibitor may be compensated by improving the overall activity of catalysts and enhancement in activity resulting from modifications to the alumina or titania supports.

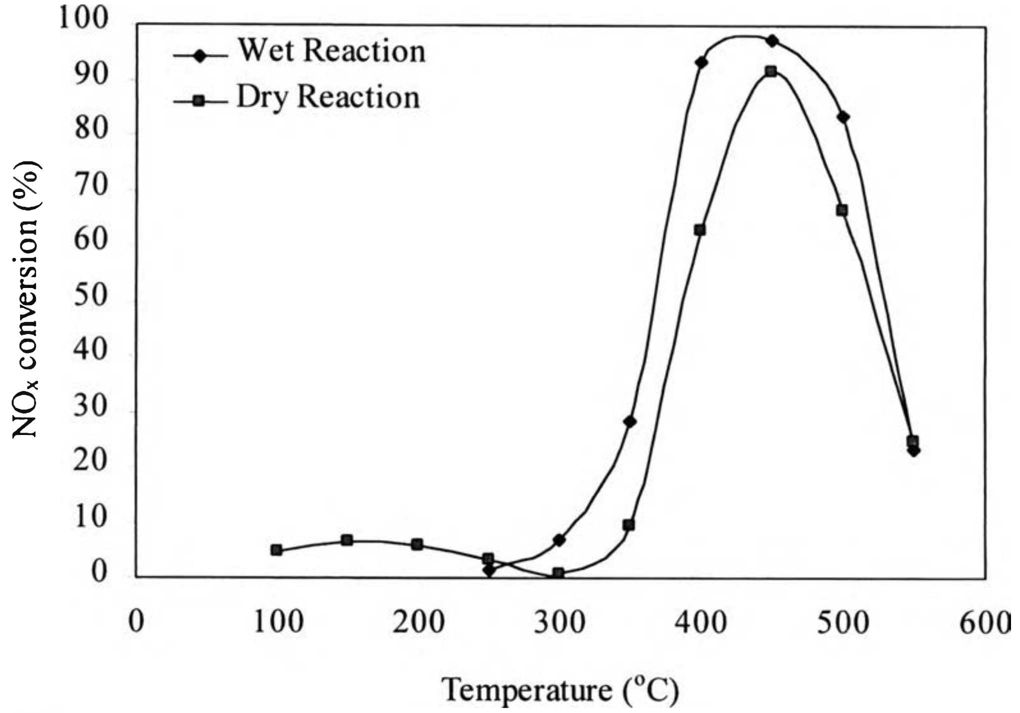

Figure 4.9 Effect of water vapor on the activity of 6.0% Ag/Al_2O_3 catalyst.

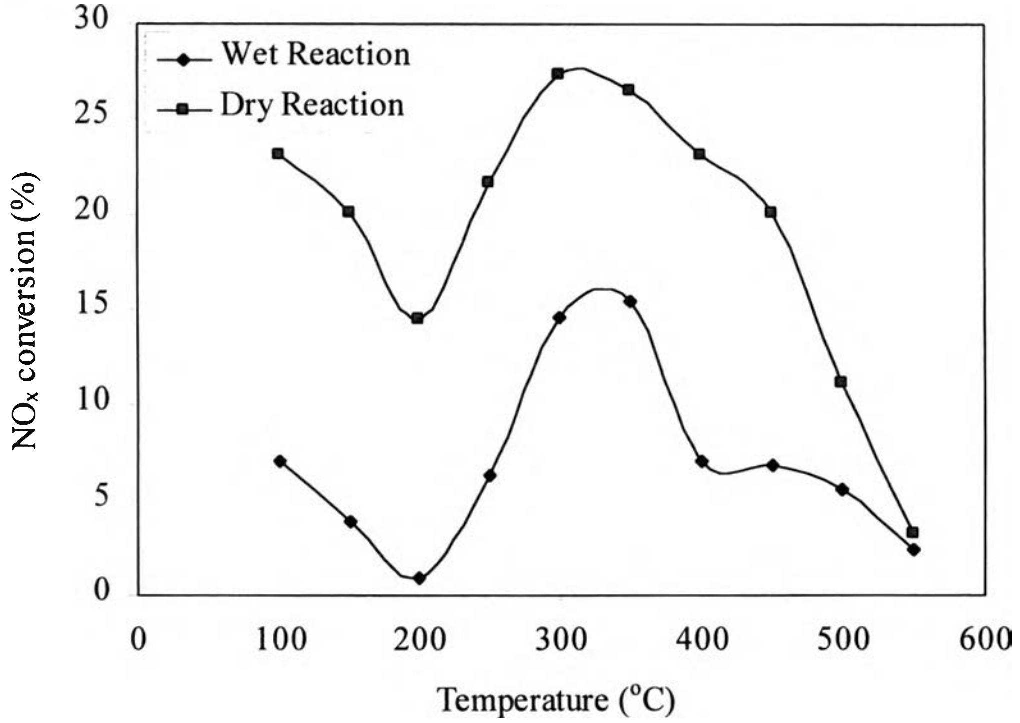

Figure 4.10 Effect of water vapor on the activity of 3.0% Pt/Al_2O_3 catalyst.

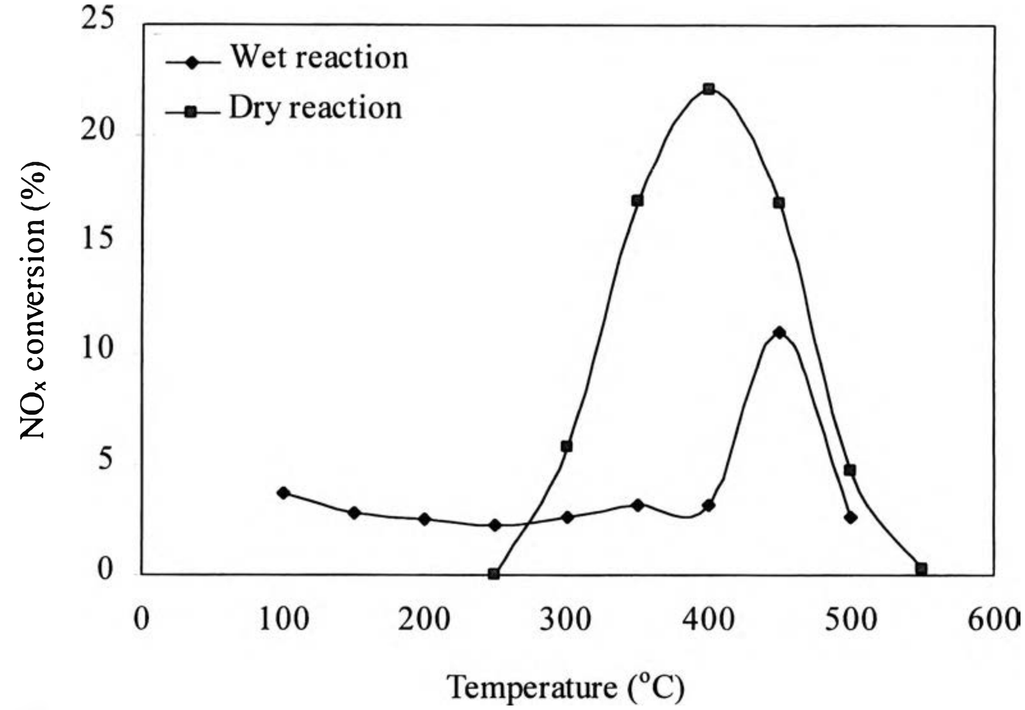

Figure 4.11 Effect of water vapor on the activity of 2.0% Ag/TiO_2 catalyst.

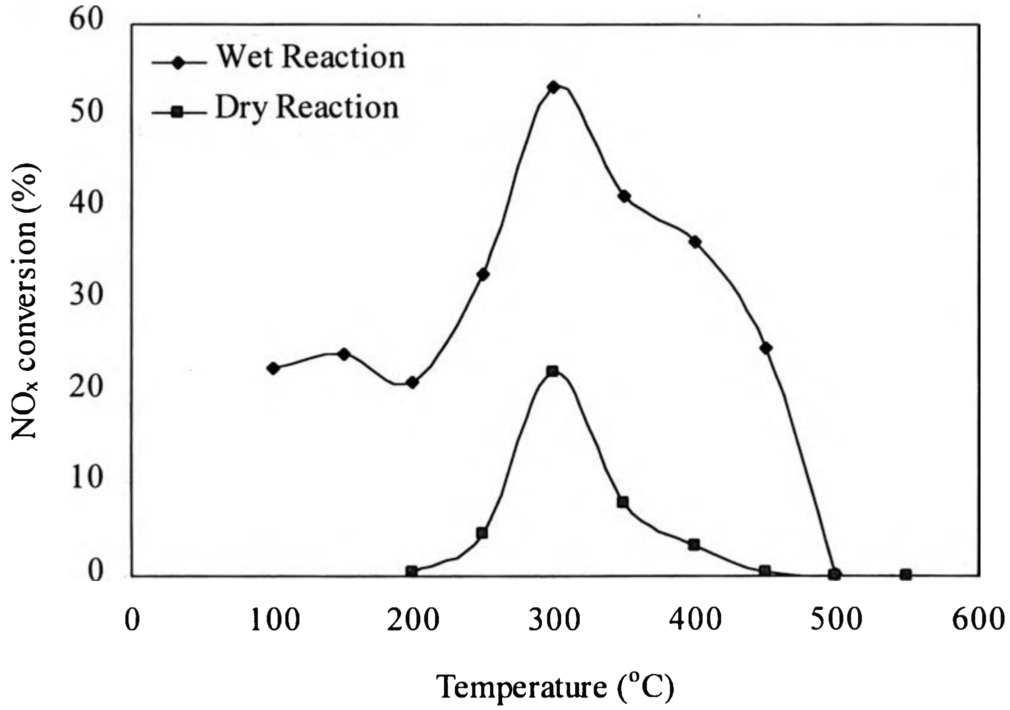

Figure 4.12 Effect of water vapor on the activity of 2.0% Pt/TiO_2 catalyst.

4.2.3 Study of Two Different Catalysts as a Double-bed

The study of double bed catalysts was performed by placing the two different catalysts together in series in the reactor. It is the sequential use of two NO reduction catalysts having different temperature windows, which have effective temperature range for NO reduction. It would broaden the temperature window for the NO reduction.

Let's take an example of catalyst A and catalyst B, the former having a higher effective temperature range for NO reduction than the latter. When catalyst A is placed before catalyst B with respect to the reactant gas flow, NO reduction is expected to take place over a wider temperature range, which is approximately the sum of the temperature windows of the two catalysts. When the two catalysts are placed reversibly, only the activity of catalyst B is anticipated because no more reductant remains at the inlet of catalyst A layer at the temperatures suitable for catalyst A.

The activities in terms of conversion of NO_x double bed catalysts were shown in Figures 4.13-4.16 respectively.

For Ag/Al_2O_3 and Pt/Al_2O_3 catalysts, it was found that Pt/Al_2O_3 showed good NO_x reduction activity at low temperature around 300°C and the maximum NO_x conversion is 28% where as Ag/Al_2O_3 catalyst was active at higher temperature of about 450°C and the maximum NO_x conversion is 89%. They were used as a double bed catalyst composed of Ag/Al_2O_3 layer followed by Pt/Al_2O_3 layer and found that it can broaden the effective temperature range which is shown in Figure 4.13. Then Ag/Al_2O_3 and Pt/Al_2O_3 were placed reversibly. The result shows much lower activity because only the activity of Pt/Al_2O_3 catalyst was effective as shown in Figure 4.14. The higher activity of platinum leads to hydrocarbon oxidation at low temperature. Thus, no hydrocarbon is available for silver-catalyzed NO_x reduction at higher temperature. On the other hand, hydrocarbons are available for silver-catalyzed NO_x reduction in a two-stage catalyst bed, because

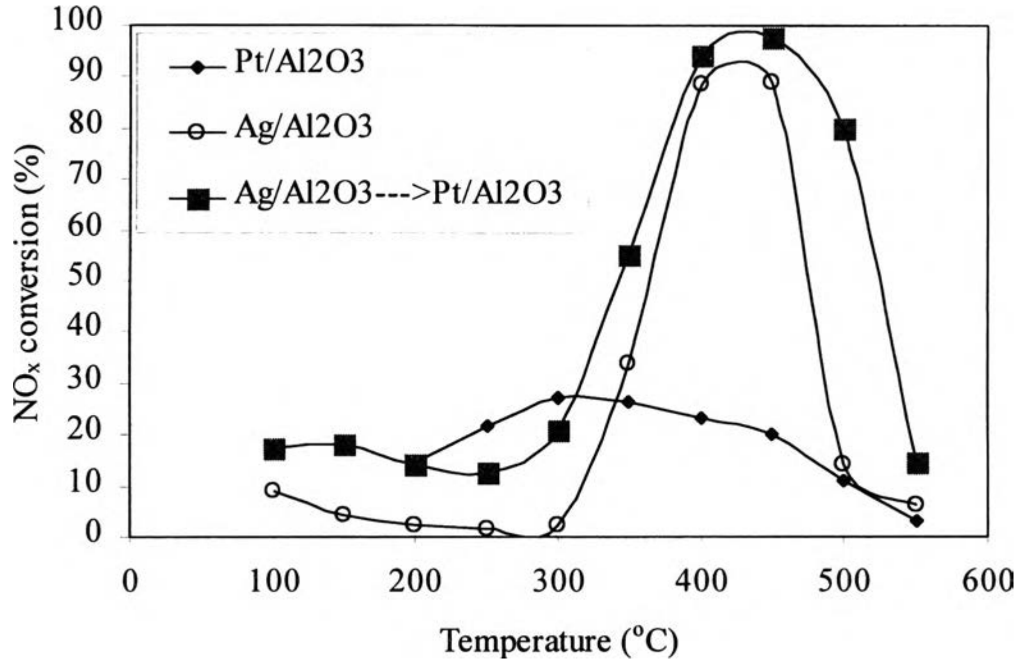

Figure 4.13 NO_x conversion at various reaction temperatures over a two-stage catalyst by placing Ag/Al_2O_3 catalyst followed by Pt/Al_2O_3 catalyst.

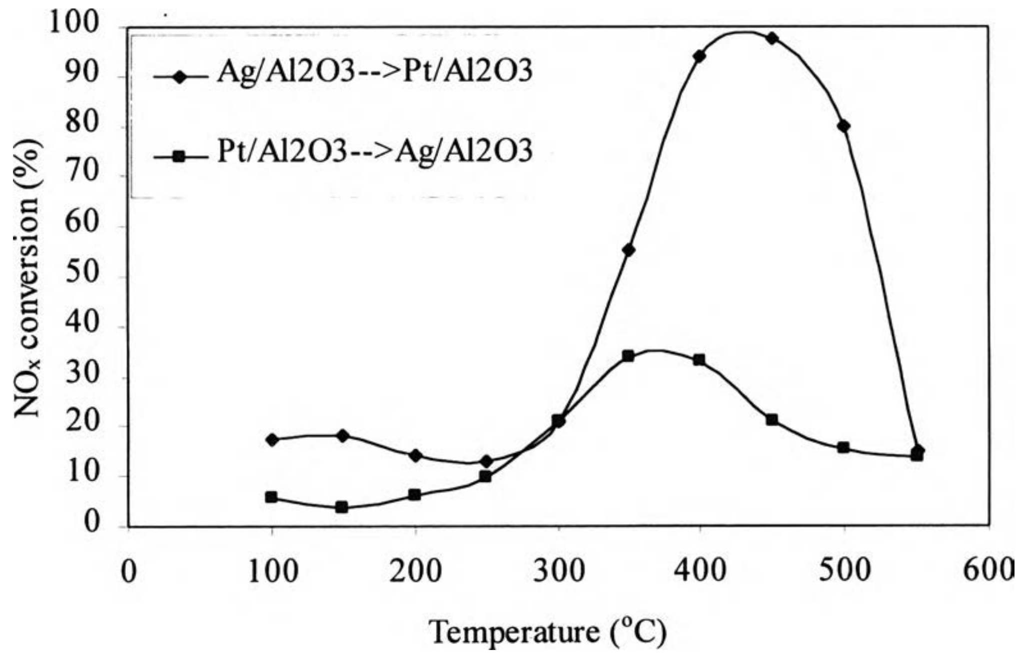

Figure 4.14 NO_x conversion at various reaction temperatures over a two-stage catalyst in a reactor composed of Ag/Al_2O_3 and Pt/Al_2O_3 catalysts.

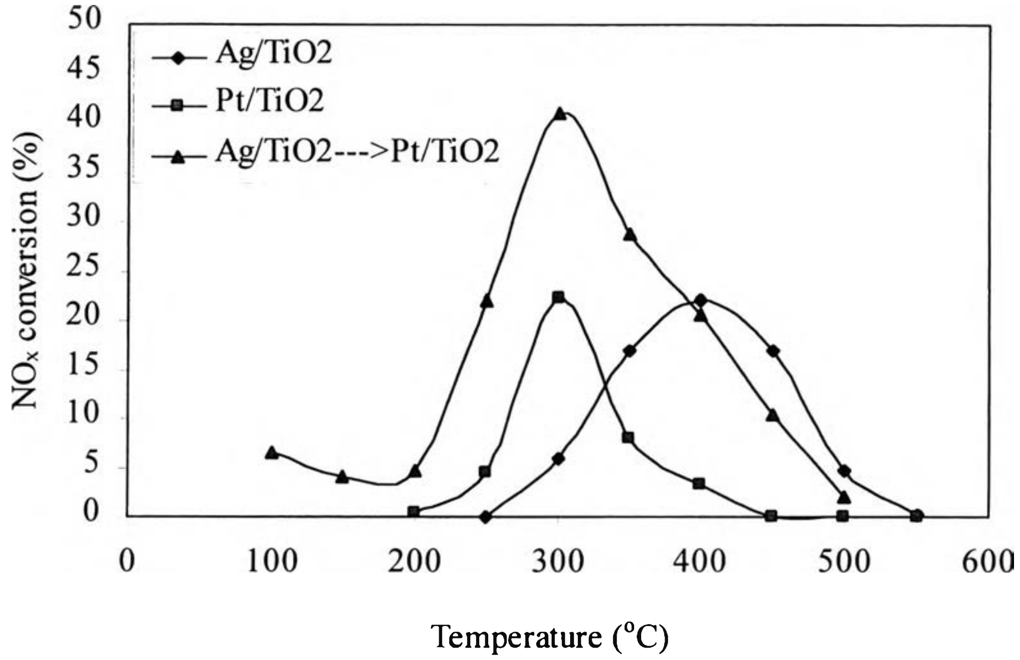

Figure 4.15 NO_x conversion at various reaction temperatures over a two-stage catalyst by placing Ag/TiO_2 catalyst followed Pt/TiO_2 catalyst.

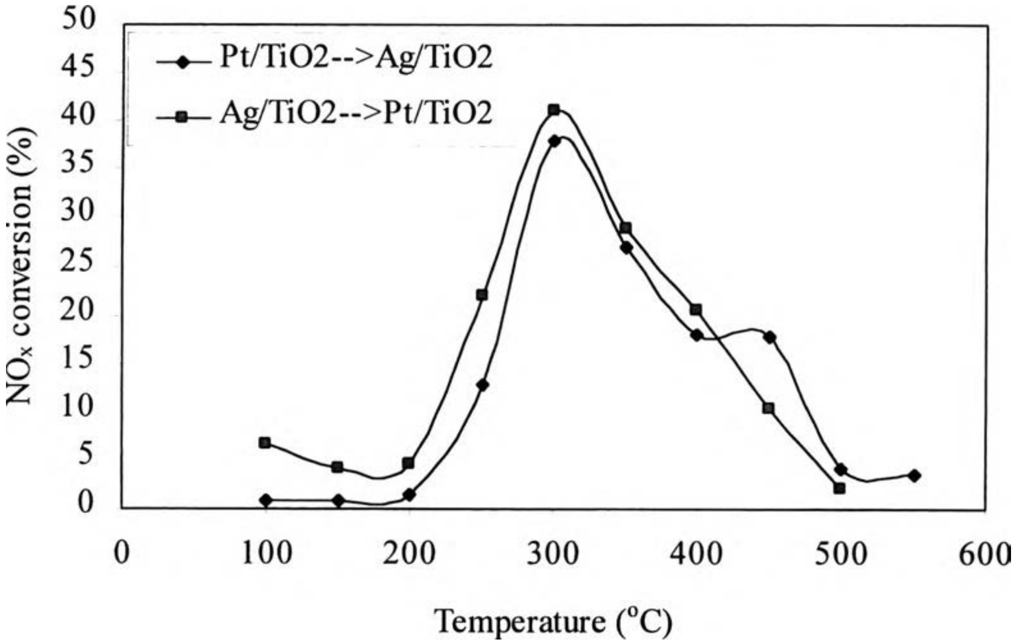

Figure 4.16 NO_x conversion at various reaction temperatures over a two-stage catalyst in a reactor composed of Ag/TiO_2 and Pt/TiO_2 catalysts.

platinum catalyst is downstream of silver catalyst. The phenomenon has been observed previously by Hamada (1997).

Pt/TiO_2 and Ag/TiO_2 catalysts showed a good NO_x reduction activity at 300°C and 400°C respectively. Therefore, they were used as a double bed catalyst in the reactor by placing Ag/TiO_2 catalyst followed by Pt/TiO_2 catalyst with respect to the reactant gas flow. Figure 4.15 shows that it can broaden the temperature window for the NO_x reduction. The maximum in NO_x conversion is 42%, occurred at 300°C. After reverse use of the two catalyst layers, the results show slightly lower activities as can be seen from Figure 4.16.

A wider NO_x conversion window is obtained if silver catalyst is placed upstream of platinum catalyst. In this configuration, the combined NO_x conversion efficiencies of both catalysts appear to be additive since they compare favorably with the algebraic sum of the individual catalysts conversion efficiencies.

A physical mixture of silver and platinum catalysts exhibits lower NO_x conversion than the two-stage catalyst as shown in Figures 4.17-4.18.

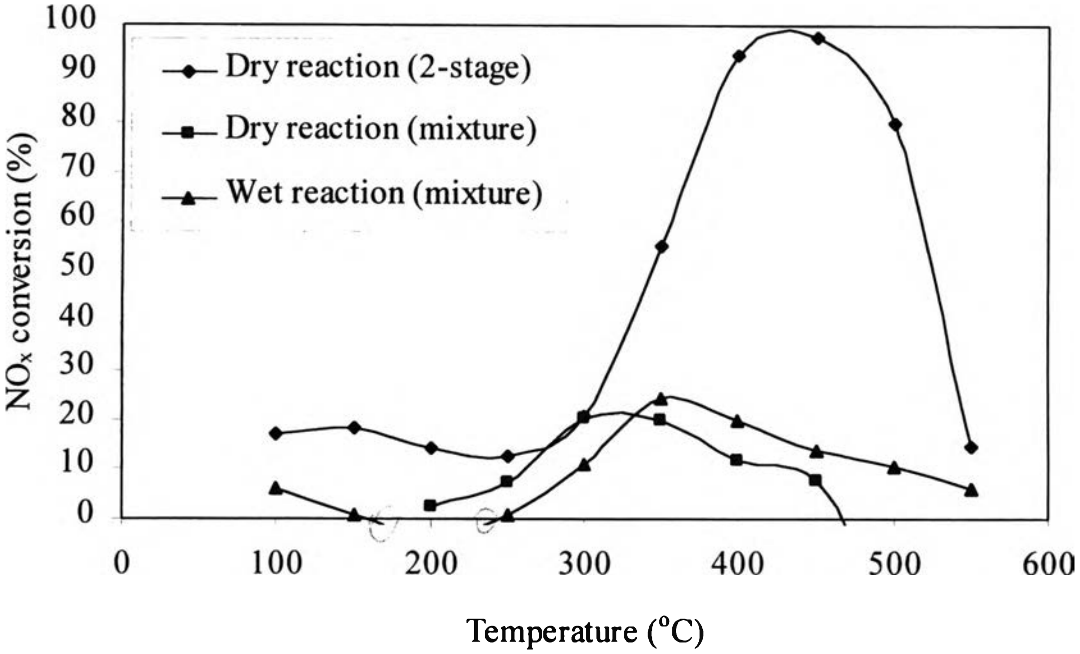

Figure 4.17 NO_x conversion at various reaction temperatures over Ag/Al_2O_3 and Pt/Al_2O_3 catalysts by comparing with mixture of Ag/Al_2O_3 and Pt/Al_2O_3 catalyst.

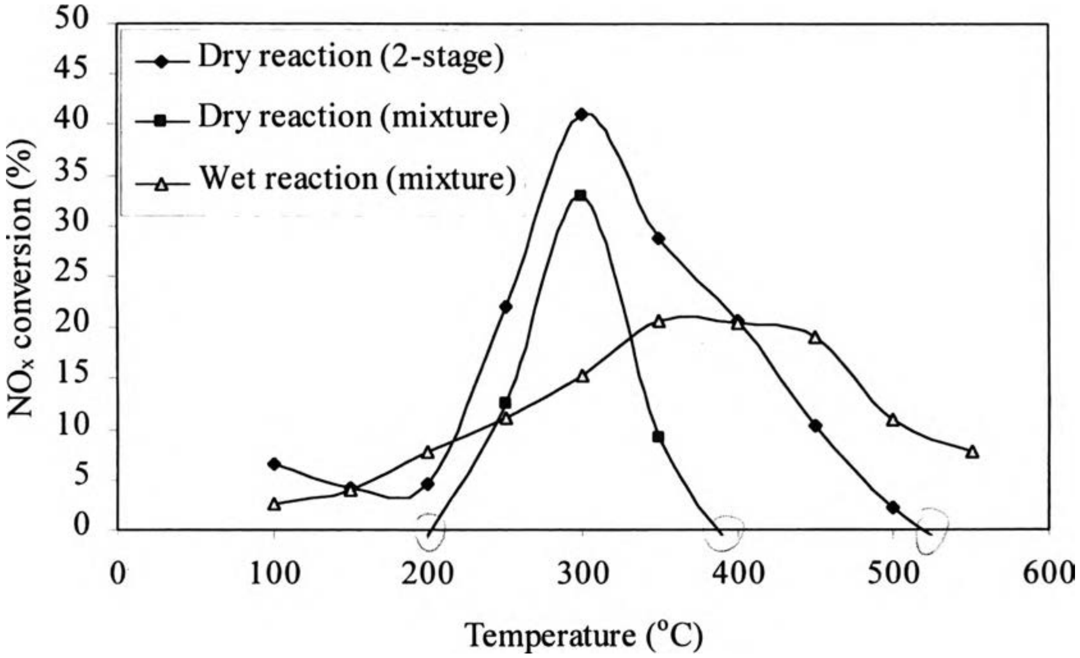

Figure 4.18 NO_x conversion at various reaction temperatures over Ag/TiO_2 and Pt/TiO_2 catalysts by comparing with mixture of Ag/TiO_2 and Pt/TiO_2 catalyst.