CHAPTER IV
RESULTS AND DISCUSSION

4.1 Catalyst Characterization

BET surface area, total pore volume and average pore diameter results of prepared catalysts are given in Table 4.1. As shown in Table 4.1, it was found that BET surface areas of the prepared Al_2O_3 and Ba/Al_2O_3 supports by sol-gel technique were close to one another and higher than that of commercial alumina. The surface area, total pore volume and average pore diameter of these catalysts were independent of amount and sequence of metal loading.

The percentage of gold loading of prepared catalysts from Atomic Adsorption Spectroscopy analysis are shown in Table 4.2.

Table 4.1 BET Surface Area Results

Catalyst	Surface area [a] (m^2/g)	Pore volume [b] (cc/g)	Pore diameter [c] (^0A)
0.7%Au / Al_2O_3 (SSG)	389.6	0.7125	90.04
0.7%Au (imp) on commercial Al_2O_3	179.1	0.2820	63.01
0.7%Au (imp) on Al_2O_3 (SG)	461.7	1.0210	100.92
Al_2O_3 (SG)	463.3	1.0160	100.35
0.5%Au (imp) on Al_2O_3 (SG)	464.3	1.2950	111.60
1.0%Au (imp) on Al_2O_3 (SG)	466.1	1.2510	107.35
0.7%Au (imp) on 5%Ba/Al_2O_3 (SG)	422.9	1.1420	87.35
0.7%Au (imp) on 10%Ba/Al_2O_3 (SG)	404.6	0.8846	87.44
0.7%Au (imp) on 15%Ba/Al_2O_3 (SG)	419.4	0.9064	86.44
10%Ba/Al_2O_3 (SG)	468.7	1.0230	91.26
0.5%Au (imp) on 10%Ba/Al_2O_3 (SG)	476.3	1.0200	85.66
1.0%Au (imp) on 10%Ba/Al_2O_3 (SG)	437.2	0.9415	86.13
10%Ba (imp) on 0.7%Au/Al_2O_3 (SG)	317.2	0.7367	92.90

a: From 5 points BET

b:Total pore volume for pore with diameter less than 31853 ^0A at P/P_0= 0.9999

c: Average pore diameter

SSG: Single step sol-gel method

SG: Sol-gel method

Imp: Impregnation method

Table 4.2 % Gold Loading from AAS

Catalyst	% Gold loading
0.7%Au / Al_2O_3 (SSG)	0.58
0.7%Au (imp) on commercial Al_2O_3	0.54
0.7%Au (imp) on Al_2O_3 (SG)	0.73
0.5%Au (imp) on Al_2O_3 (SG)	0.46
1.0%Au (imp) on Al_2O_3 (SG)	0.98
0.7%Au (imp) on 5%Ba/Al_2O_3 (SG)	0.66
0.7%Au (imp) on 10%Ba/Al_2O_3 (SG)	0.68
0.7%Au (imp) on 15%Ba/Al_2O_3 (SG)	0.69
0.5%Au (imp) on 10%Ba/Al_2O_3 (SG)	0.49
1.0%Au (imp) on 10%Ba/Al_2O_3 (SG)	1.02
10%Ba (imp) on 0.7%Au/Al_2O_3 (SG)	0.60

XRD patterns identified the kinds of support structures and metal loading on the supports. Figure 4.1 shows the XRD patterns of 0.7%Au/Al_2O_3 catalysts for different preparation methods, and no difference was observed. Figure 4.2 illustrates the XRD pattern of Al_2O_3 (sol-gel) catalyst and Au impregnated on Al_2O_3 (sol-gel) catalysts with different percentage of gold loadings. It was found that intensity of gold peaks increased with increasing percentage of gold loading. In the same trend as for barium loading of Au impregnated on Ba/Al_2O_3 (sol-gel) catalysts shown in Figure 4.3, barium peaks intensity increased with increasing percentage of barium loadings. The XRD patterns of Au/Ba/Al_2O_3 catalysts with different percentage of gold loadings were shown in Figures 4.4. The intensity of gold peaks increased with increasing percentage of gold loadings. The relative intensity of barium peaks decreased with increase the percentage of gold loadings since ratio of barium:gold loadings decreased. The XRD patterns of Au/Ba/Al_2O_3 catalysts with different impregnation sequences were shown in Figure 4.5.

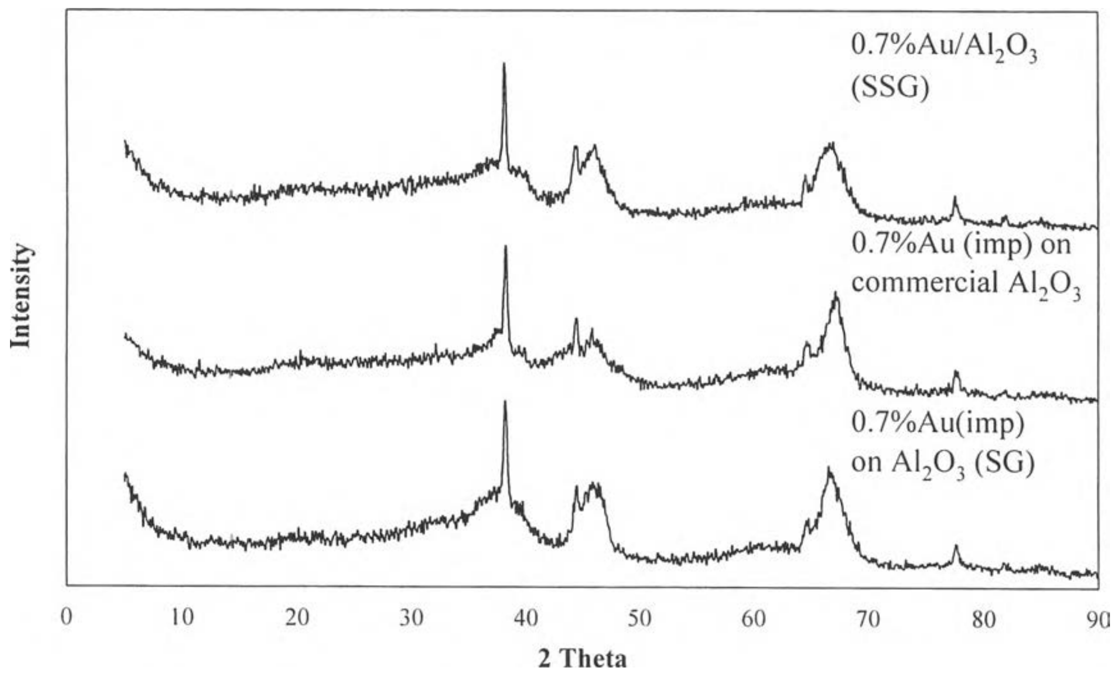

Figure 4.1 XRD patterns for 0.7%Au/Al_2O_3 catalysts with different preparation methods

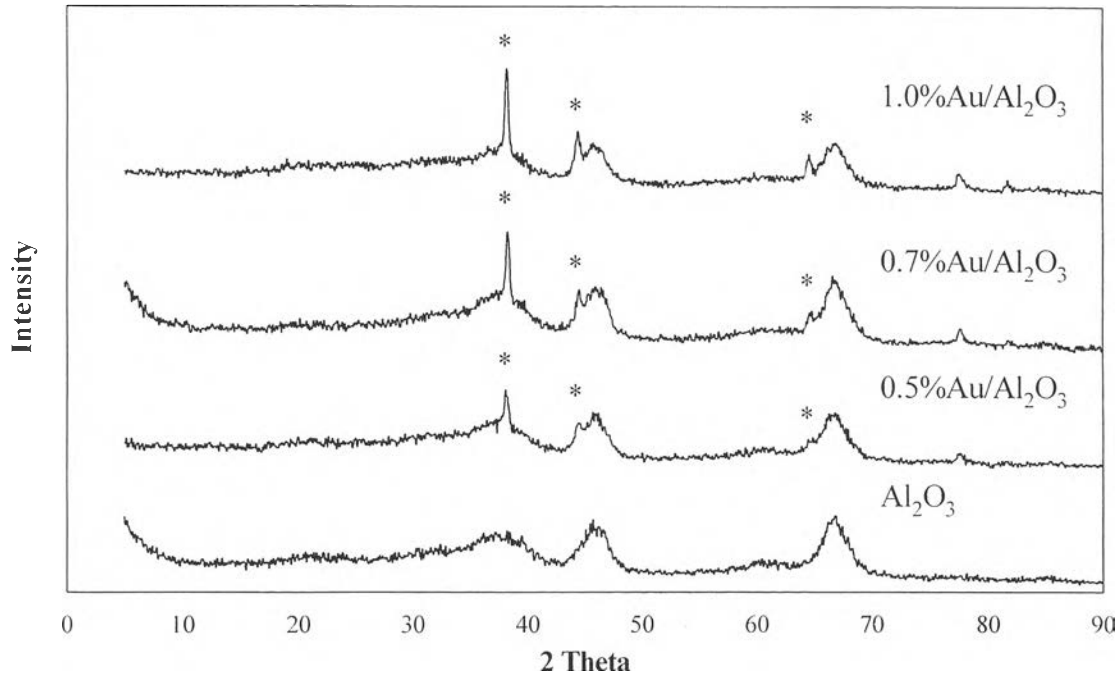

Figure 4.2 XRD patterns for Al_2O_3 (sol-gel) catalyst and 0.5-1.0%Au (imp) on Al_2O_3 (sol-gel) catalysts, [* : gold]

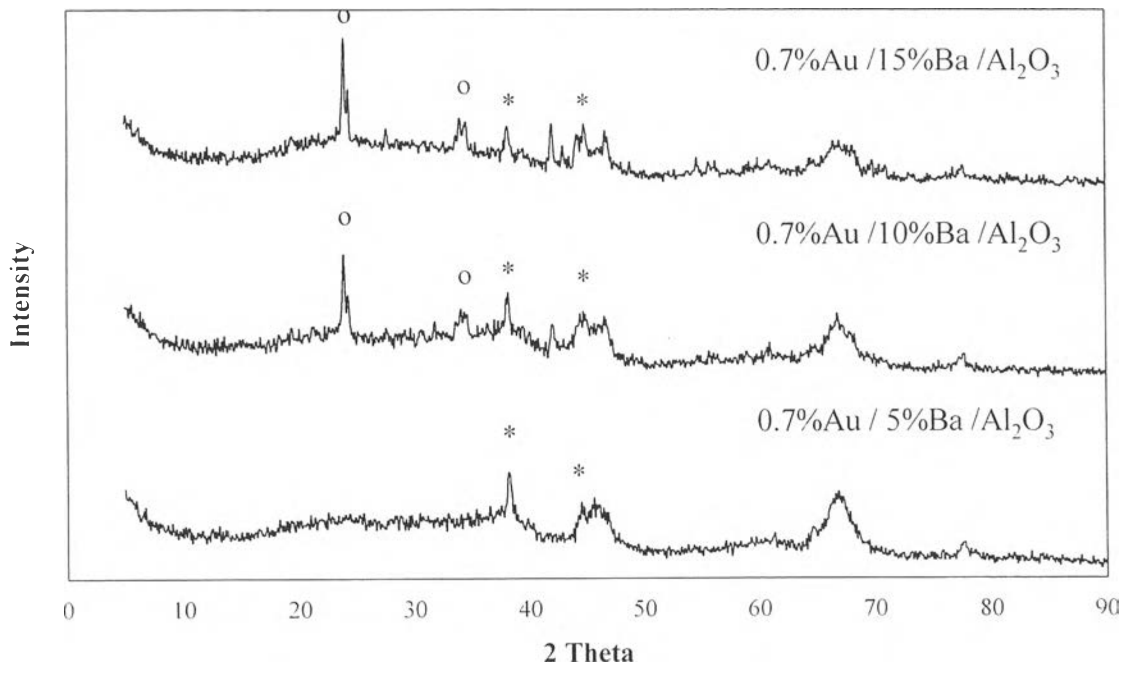

Figure 4.3 XRD patterns for 0.7%Au (imp) on 5-15%Ba/Al_2O_3 (sol-gel) catalysts. [* : gold, o : barium]

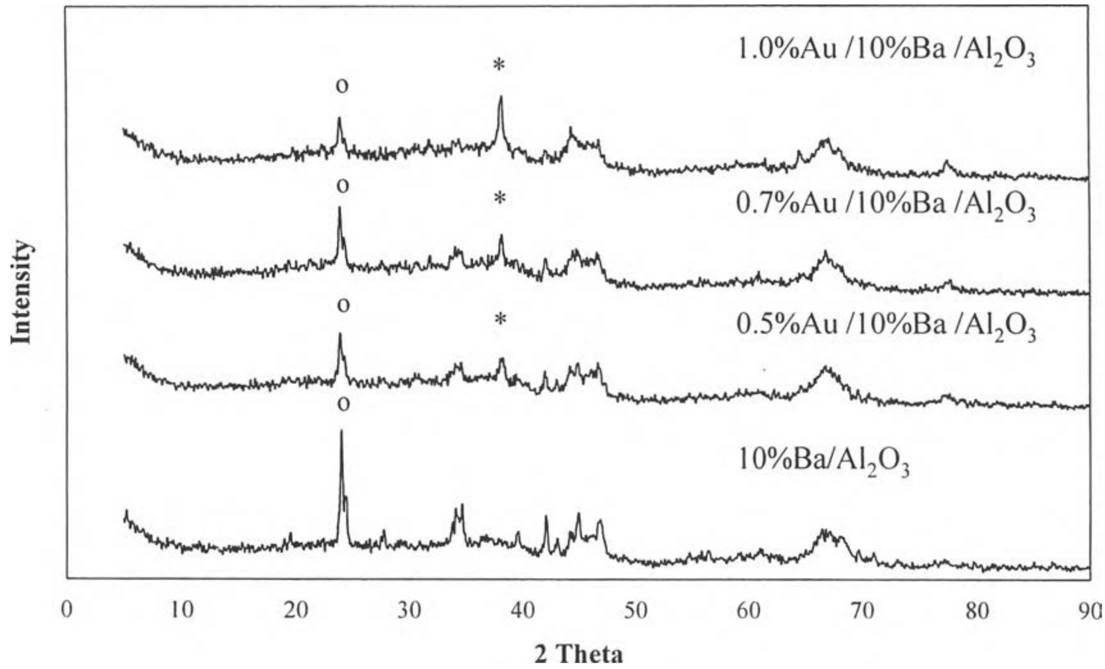

Figure 4.4 XRD patterns for 10%Ba/Al_2O_3 (sol-gel) and 0.5-1.0%Au (imp) on 10%Ba/Al_2O_3 (sol-gel) catalysts, [* : gold, o : barium]

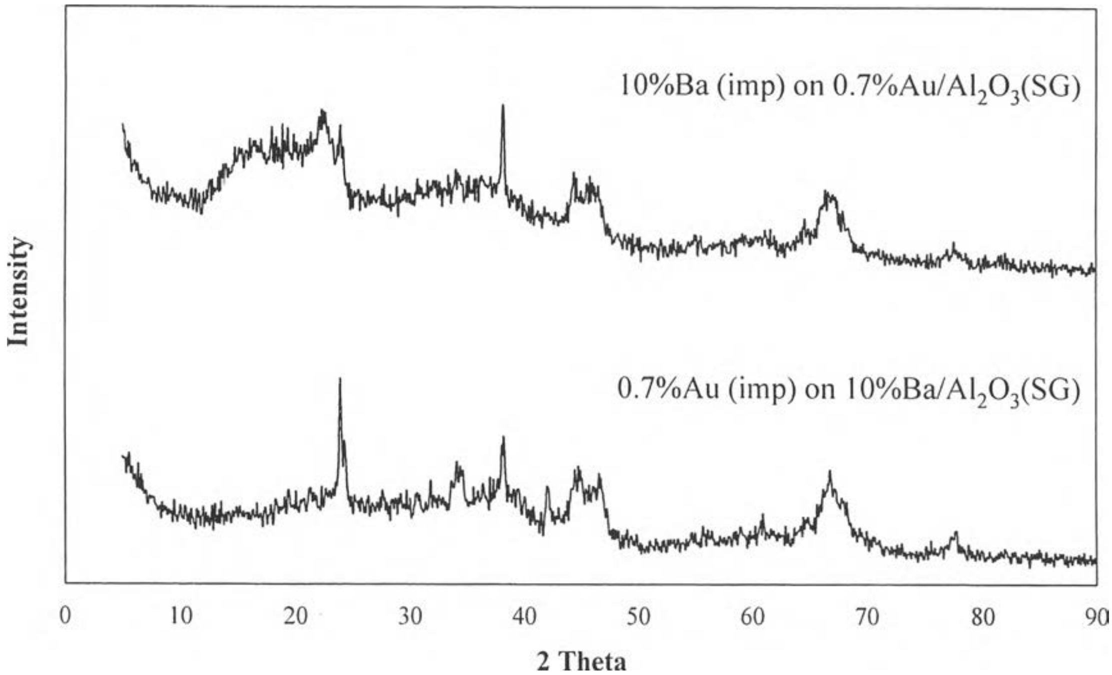

Figure 4.5 XRD patterns for 0.7%Au/10%Ba/Al_2O_3 catalysts with different impregnation sequences

4.2 Catalytic Activity Testing

4.2.1 NO_x Storage – Reduction

The results of this part could not be interpreted due to the equipments were not suitable for a pulse system. For example, a mass flow controller could not give the desired constant flow rate for a substantially short period and the NO_x analyzer had slightly long delay time. Furthermore, the outlet product especially N_2 gas was not detected in the correct time since the limitation of 6 ports valve GC. Thus, in case of the pulse system as cycle in NO_x storage-reduction system, GC-MS and FT-IR online should be set up.

4.2.2 Selective Catalytic Reduction

Since the simulated gases fed alternately under oxidizing and reducing conditions in NO_x storage-reduction were not suitable for our experimental setup, steady state system as selective catalytic reduction was performed. All of reactant gases were fed to the reactor containing catalyst, and the conversion was attained when gases concentrations were constant.

4.2.2.1 Effect of preparation method

The activity testing results for 0.7%Au/Al_2O_3 catalysts with different preparation methods were showed in Figure 4.6. It was found that 0.7%Au impregnated on sol-gel catalyst gave the highest activity at 475 ^{0}C. Furthermore, impregnation on sol-gel support catalyst gave higher activity than impregnation on commercial alumina one because sol-gel method can create higher surface area than commercial alumina does. The activity of gold impregnated on sol-gel catalyst was higher than single step sol-gel catalyst. It might be explained that gold on the support surface which created from impregnation on sol-gel support method is more active than gold in mixed oxide phase form which obtained from single step sol-gel method.

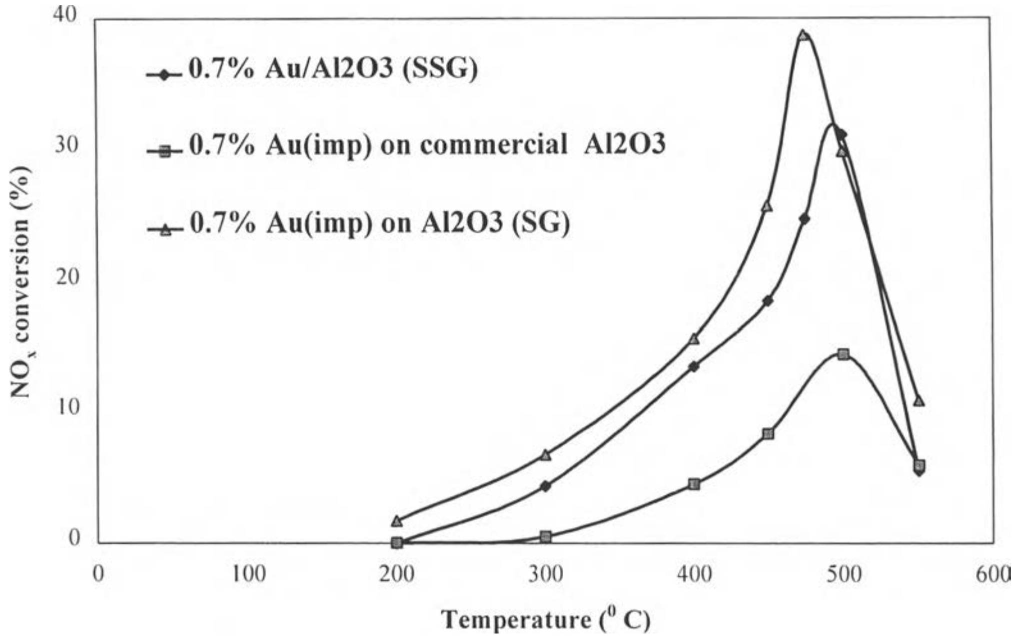

Figure 4.6 NO_x conversion over Au/Al_2O_3 catalysts with different preparation methods

4.2.2.2 Effect of % metal loading

Figure 4.7 shows NO_x conversion over Au/Al_2O_3 catalysts with different percentage of gold loadings in the range of 0.5-1.0%. It was observed that it had no significant difference on the catalytic activity. However 0.7%Au impregnated on Al_2O_3 sol-gel gave the highest conversion. This loading percentage is an optimum value for this study.

Figure 4.8 illustrates NO_x conversion over 0.7%Au impregnated on 5-15%Ba/Al_2O_3 (sol-gel) catalysts. The results show that the catalytic activity decrease with increasing the percentage of barium loadings. It might be described that a higher Ba content creates a higher $Ba(NO_3)_2$ formation. When $Ba(NO_3)_2$ is decomposed to NO_x as shown in the equation below at the outlet of the reactor, therefore, the outlet NO_x concentration is high. Then, the NO_x conversion decreases.

$$NO_x + O + BaO \longleftrightarrow Ba(NO_3)_2$$

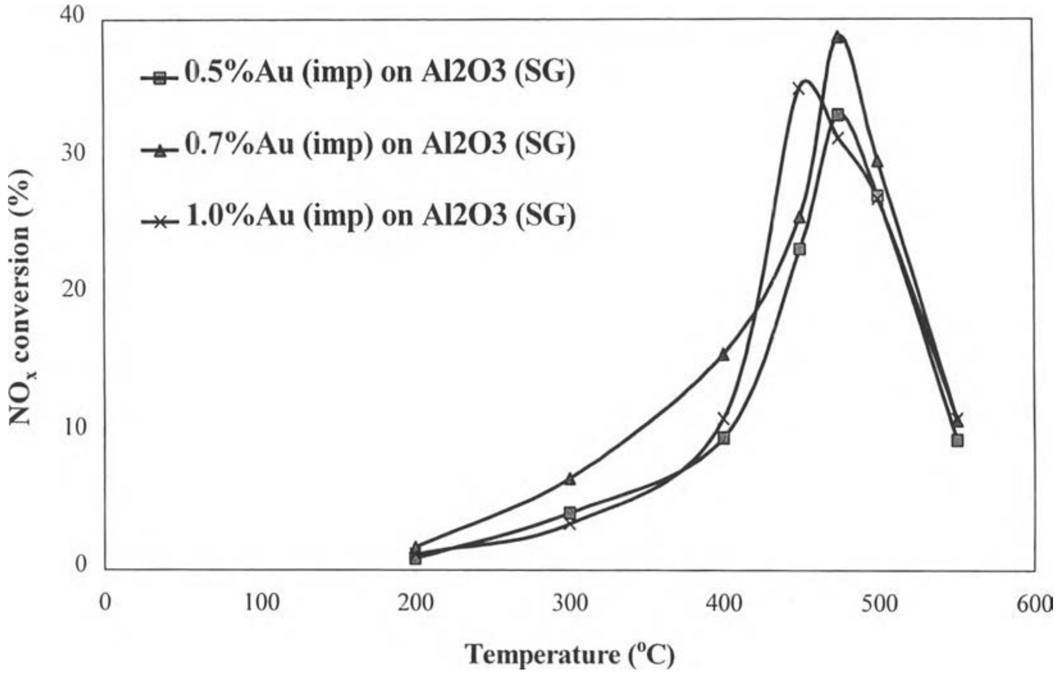

Figure 4.7 NO_x conversion over Au/Al_2O_3 catalysts with different percentage of gold loadings

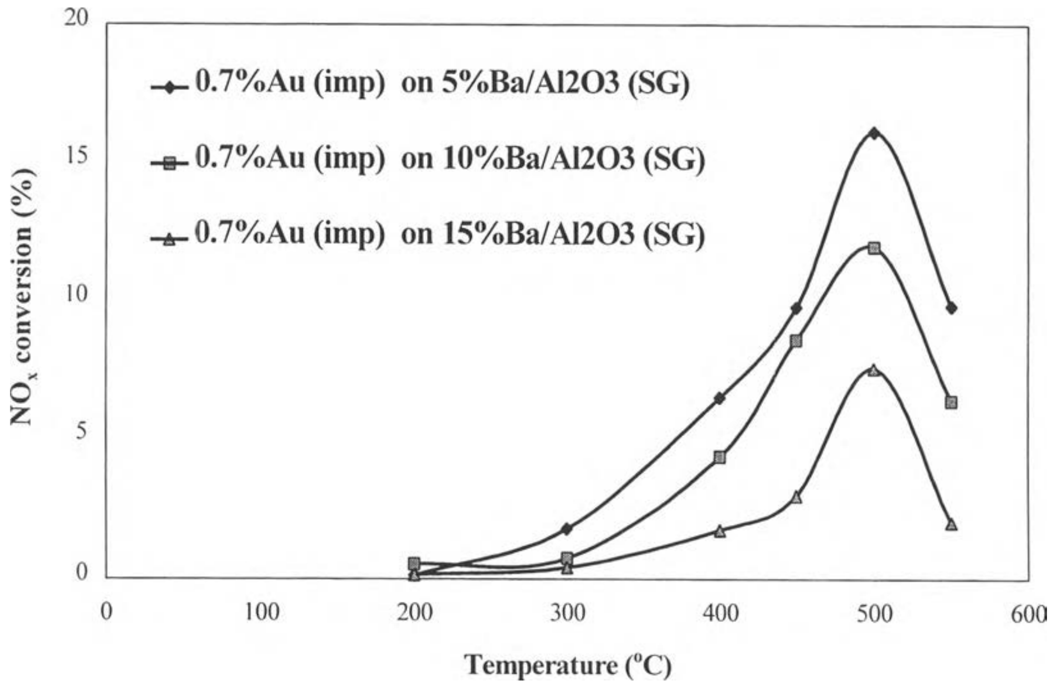

Figure 4.8 NO_x conversion over $Au/Ba/Al_2O_3$ catalysts with different percentage of barium loadings

When Figure 4.7 and 4.8 were compared, it was found that the activity of Au/Al_2O_3 catalysts decreased with adding barium content. It might be explained that the experiment was not performed in cycle as storage-reduction mode, but it was run in selective reduction mode

The results given in Figure 4.9 shows catalytic activity of Au impregnated on 10%Ba/Al_2O_3 (sol-gel) catalysts. For 0.5-1.0% Au impregnated on Ba/Al_2O_3 catalysts, no significant difference on activity was observed.

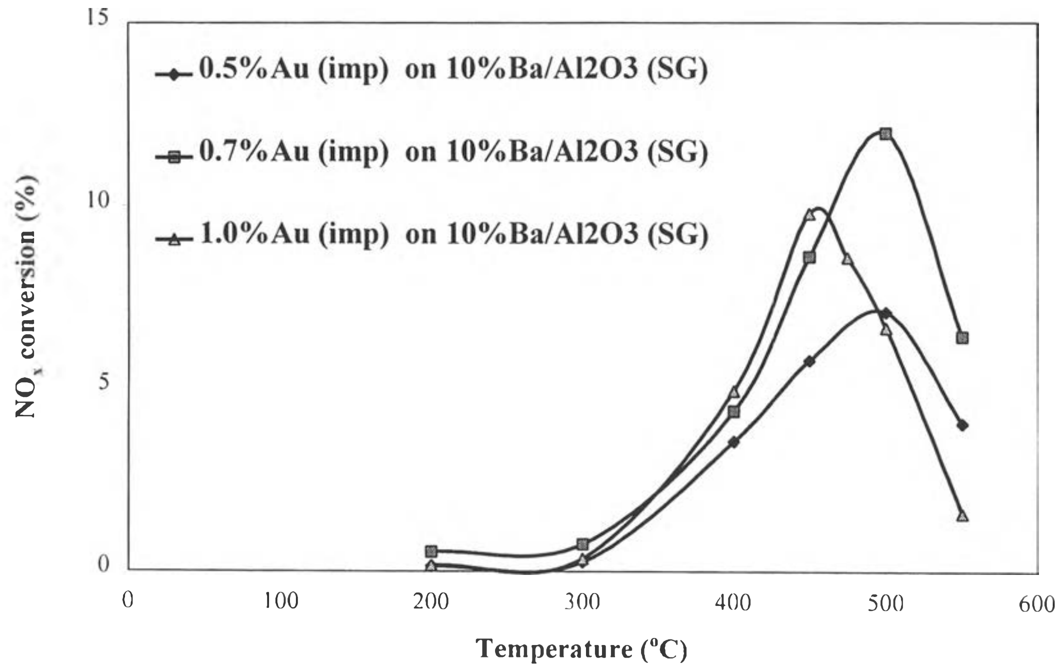

Figure 4.9 NO_x conversion over $Au/Ba/Al_2O_3$ catalysts with different percentage of gold loadings

4.2.2.3 Effect of impregnation sequence

Figure 4.10 exhibits NO_x conversion over $Au/Ba/Al_2O_3$ catalysts with different impregnation sequences. The results show that there is only slight difference on the activity.

4.2.2.4 Effect of water vapor

Effect of 3% water vapor content in feed stream was studied, and the results are shown in Figure 4.11- 4.12. It was found that water vapor have no effect over both 0.7%Au impregnated on Al_2O_3 (sol-gel) catalyst and 0.7%Au impregnated on 10%Ba/Al_2O_3 catalyst.

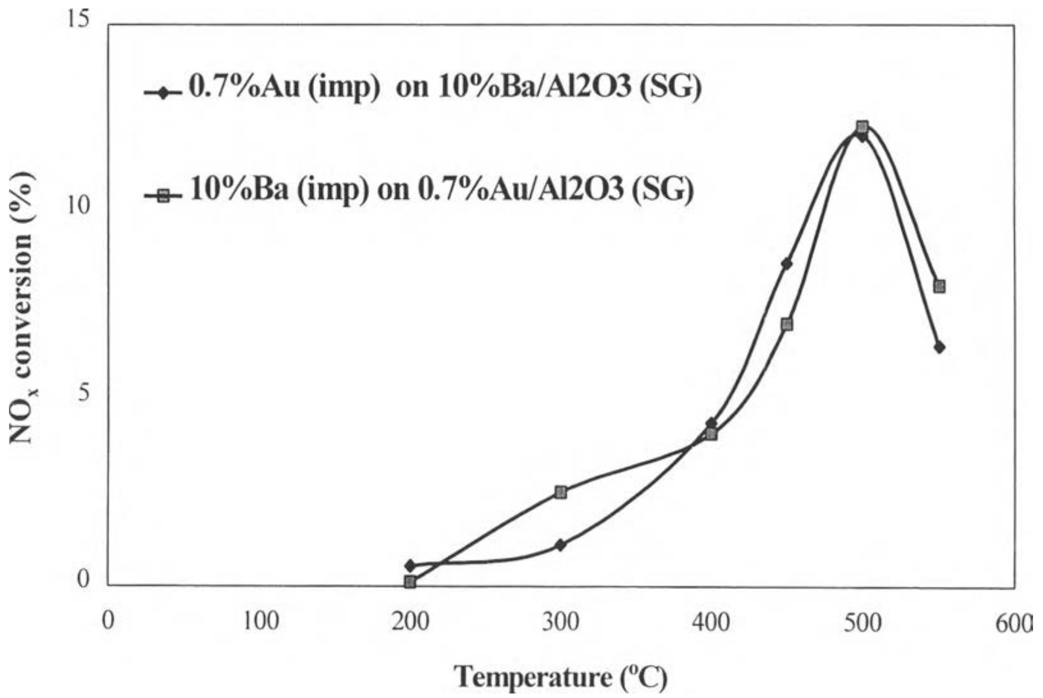

Figure 4.10 NO_x conversion over $Au/Ba/Al_2O_3$ catalysts with different impregnation sequences

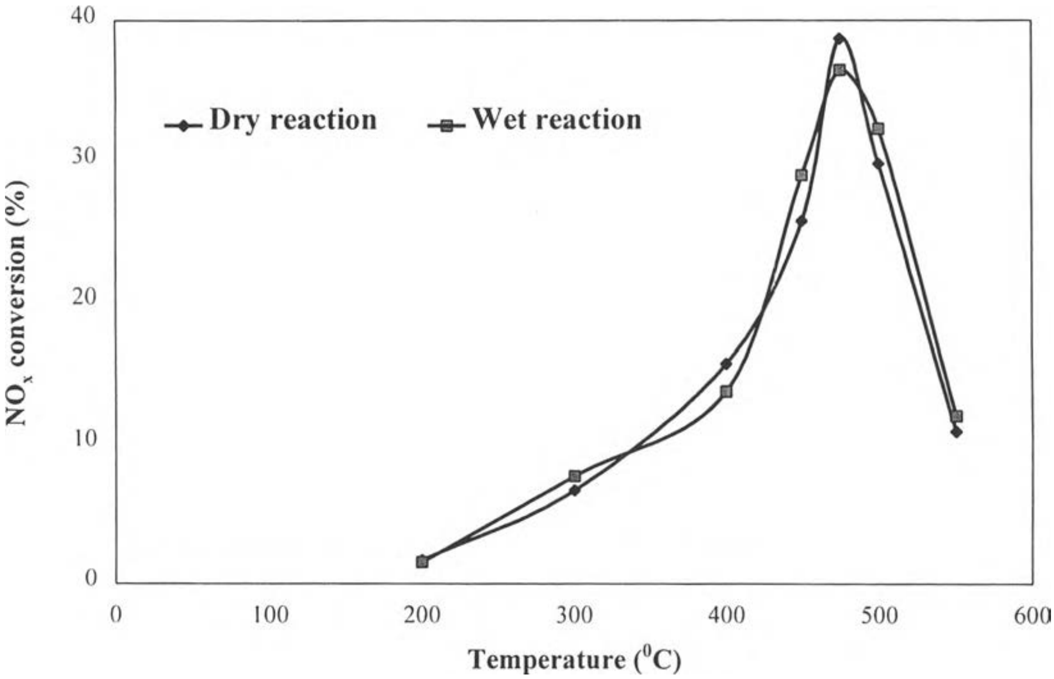

Figure 4.11 Effect of water vapor on the activity of 0.7% Au (imp) on Al_2O_3 (sol-gel) catalyst

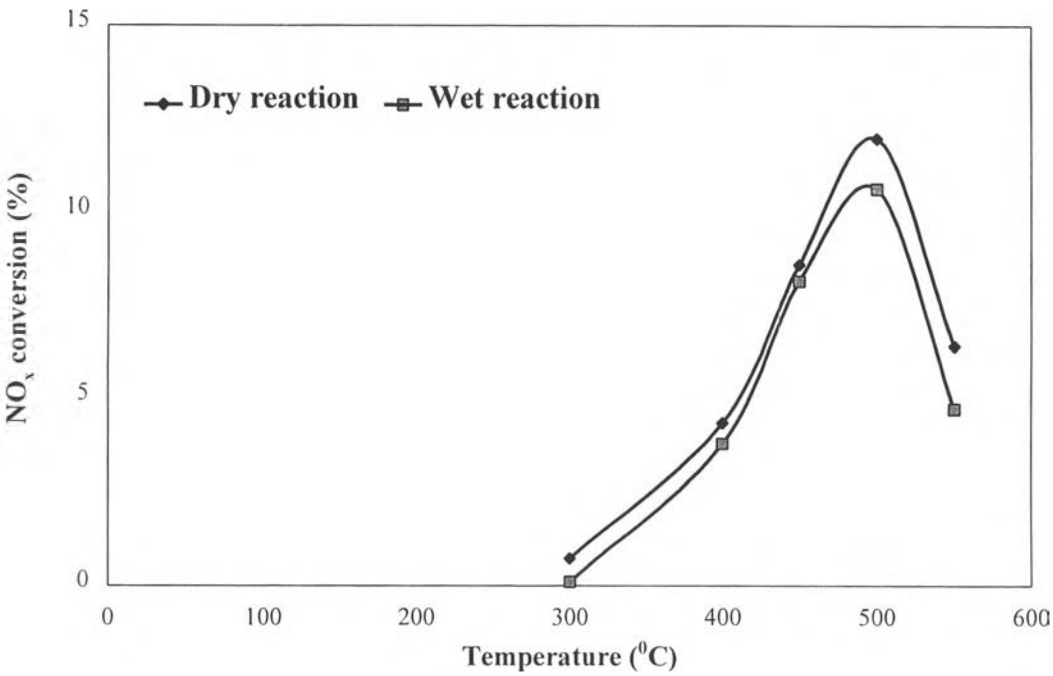

Figure 4.12 Effect of water vapor on the activity of 0.7% Au (imp) on 10%Ba/Al_2O_3 (sol-gel) catalyst

4.2.2.5 *Effect of pretreatment gas*

Effect of pretreatment gas was also investigated. Figure 4.13 shows NO_x conversion over 0.7%Au impregnated on Al_2O_3 (sol-gel) catalyst in the presence of water vapor content. The results indicated that there was slight difference on the activity. A gold activation using pretreatment gases has not well understood, further studies are required.

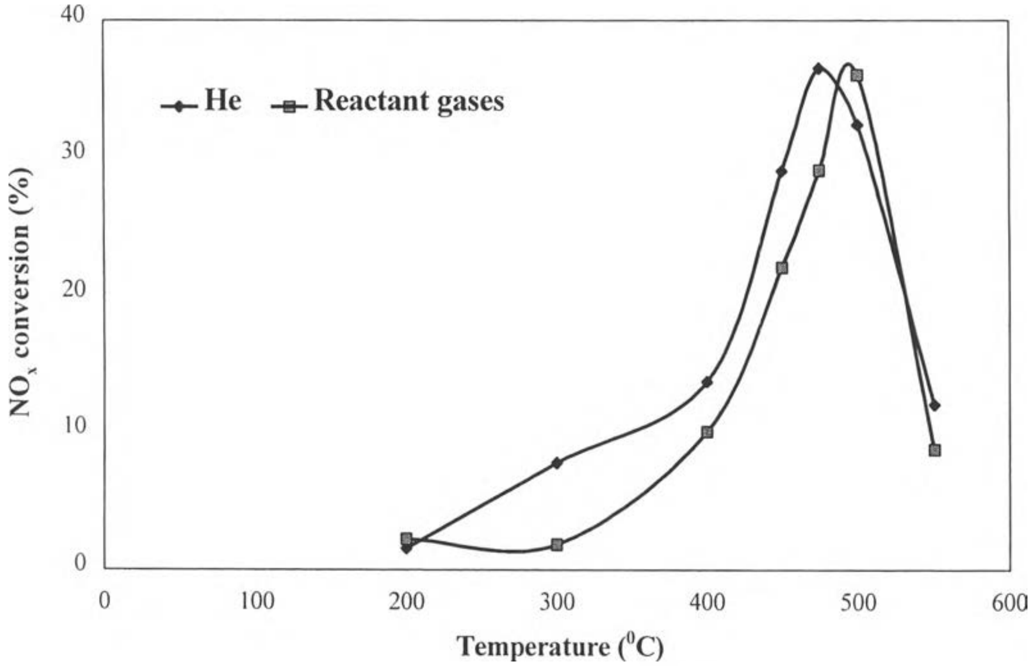

Figure 4.13 Effect of pretreatment gas on the activity of 0.7%Au (impregnation) on Al_2O_3 (sol-gel) catalyst in the presence of water vapor