CHAPTER IV
RESULTS AND DISCUSSION

4.1 Catalyst Characterization

All of the catalysts from coprecipitation and sol-gel methods were prepared at 5% total metal loading. Catalysts containing 5%Ag, 2.5%Ag / 2.5%Au, and 5%Au supported on Al_2O_3 were prepared to study the effect of Ag and Au loading. To study the calcination temperature effect, the sol-gel catalysts of 5%Ag and 2%Ag were prepared and calcined at 300, 400, 500, 600, and 700°C.

The effect of Ag and Au loading and calcination temperature on surface area, pore volume, and pore radius of catalysts were shown in Table 4.1. For both methods of catalyst preparation, the surface area increased in proportion to the increasing of percent silver on the catalyst. Sol-gel catalysts gave very high surface area when compared to coprecipitation catalysts, espectially 5%Ag from sol-gel method gave about 4 times of total surface area comparing to coprecipitation method. For the effect of calcination temperature, the total surface area decreased with increasing calcination temperature due to the sintering of Al_2O_3 support. All catalysts had a very small pore size between 6.8 to 7.5 °A.

XRD patterns, shown in Figures 4.1-4.3, taken from all of the catalysts showed the internal structure of the catalysts. For 5%Au and 2.5%Ag / 2.5%Au sol-gel catalysts which were shown in Figure 4.1, gold tended to agglomerate to form larger crystals. These large crystals had the activity less

Table 4.1 Catalyst Charaterization

Catalyst	Method	Calcination Temperature (°C)	Surface Area[a] (m^2/g)	Pore Volume[b] (cm^3/g)	Pore Radius[c] (°A)
5%Au	Coprecipitation	300	86.90	0.03159	7.271
2.5%Ag/2.5%Au	Coprecipitation	300	88.78	0.03221	7.257
5%Ag	Coprecipitation	300	127.8	0.04461	6.982
5%Au	Sol-gel	300	511.0	0.1773	6.938
2.5%Ag/2.5%Au	Sol-gel	300	520.6	0.1860	7.144
5%Ag	Sol-gel	300	534.5	0.1904	7.126
5%Ag	Sol-gel	400	449.2	0.1608	7.161
5%Ag	Sol-gel	500	391.3	0.1385	7.079
5%Ag	Sol-gel	600	356.4	0.1302	7.307
5%Ag	Sol-gel	700	299.6	0.1160	7.452
2%Ag	Sol-gel	300	540.4	0.1931	7.147
2%Ag	Sol-gel	400	529.4	0.1805	6.819
2%Ag	Sol-gel	500	430.9	0.1549	7.188
2%Ag	Sol-gel	600	358.3	0.1310	7.310
2%Ag	Sol-gel	700	299.9	0.1107	7.381

a : From 5 point BET

b : Total pore volume for pores with radius less than 8 °A at $P/P_0 = 0.10640$

c : Average pore radius

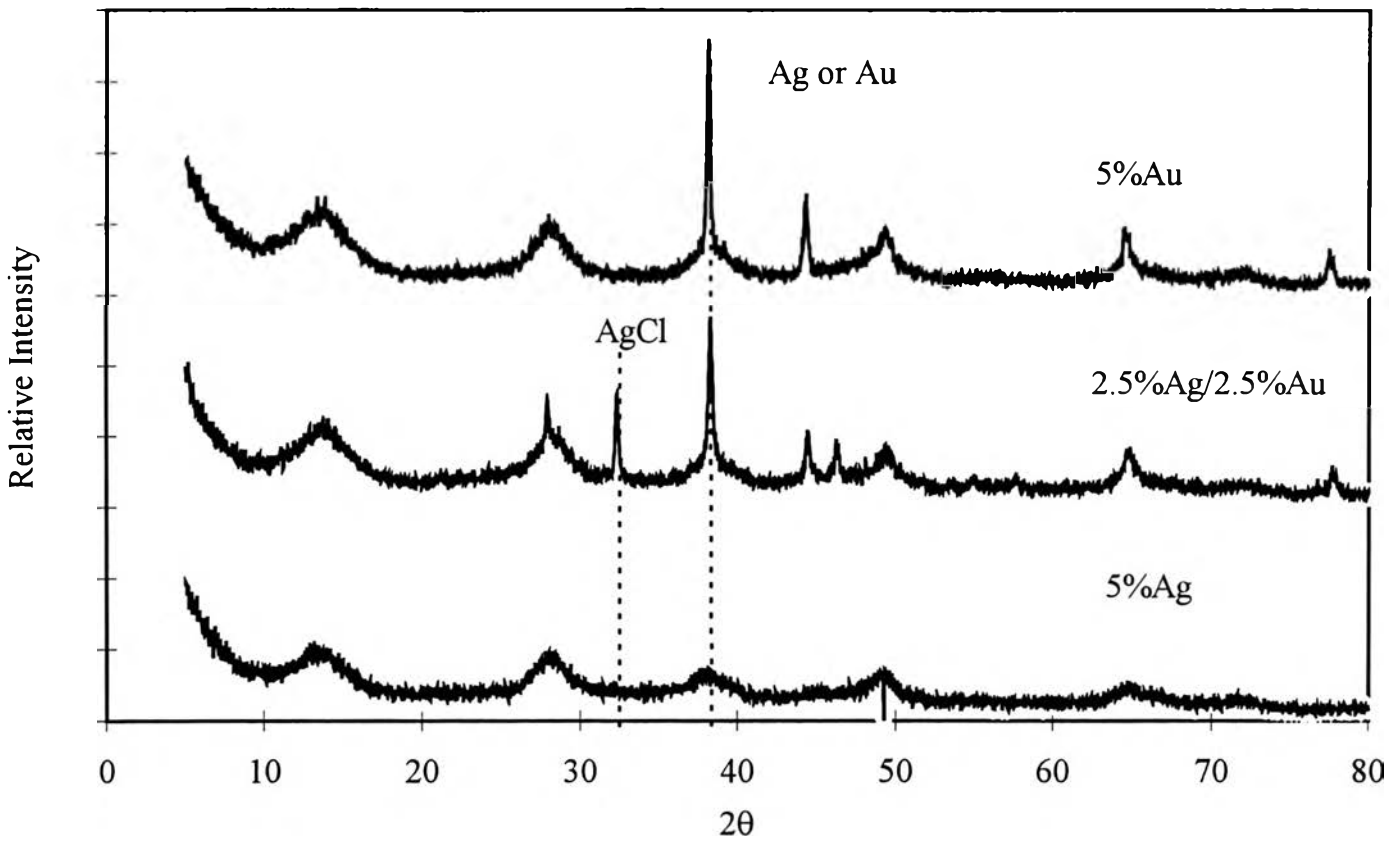


Figure 4.1 X-ray diffraction patterns for sol-gel catalysts calcined at 300°C.

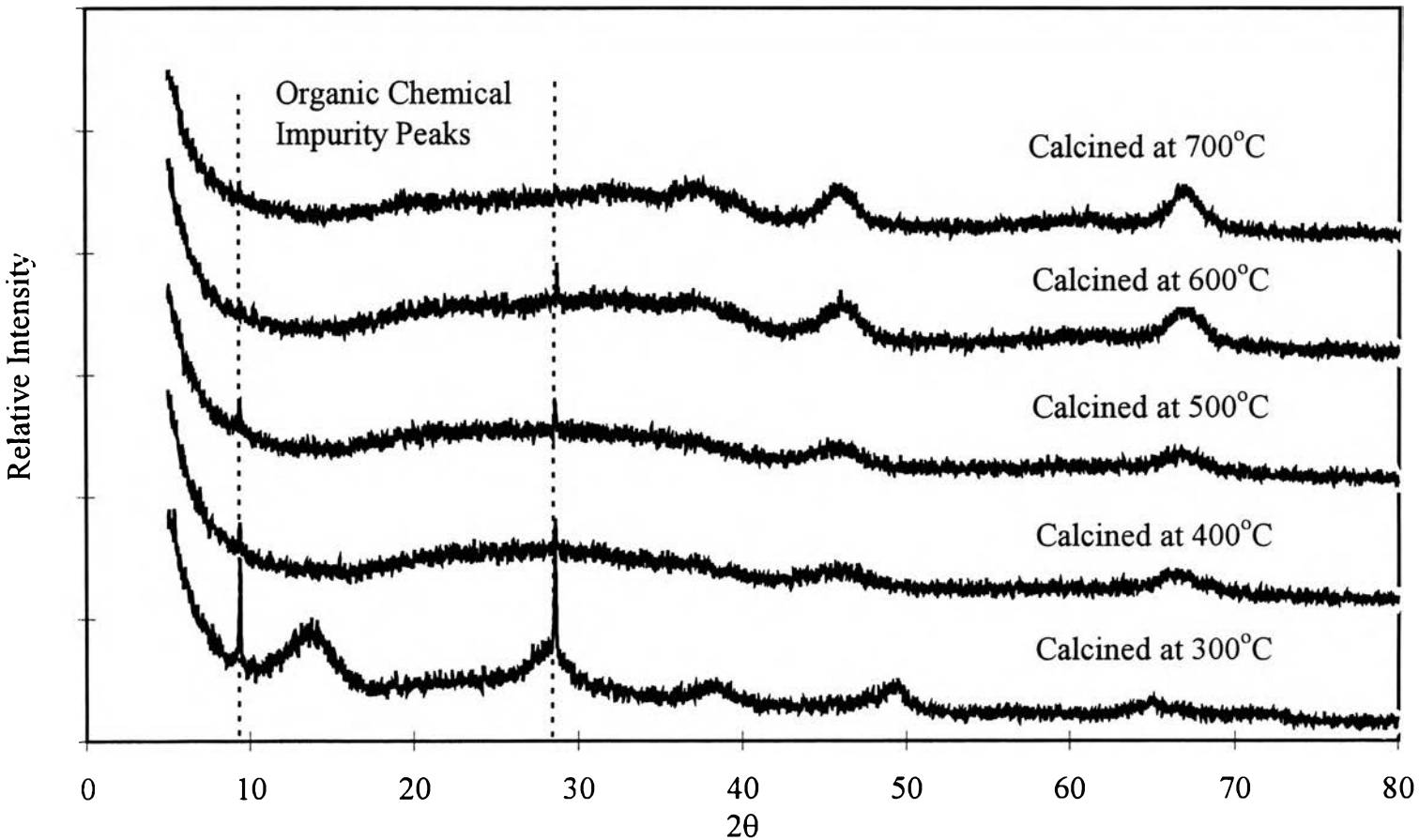


Figure 4.2 X-ray diffraction patterns for 2%Ag sol-gel catalysts.

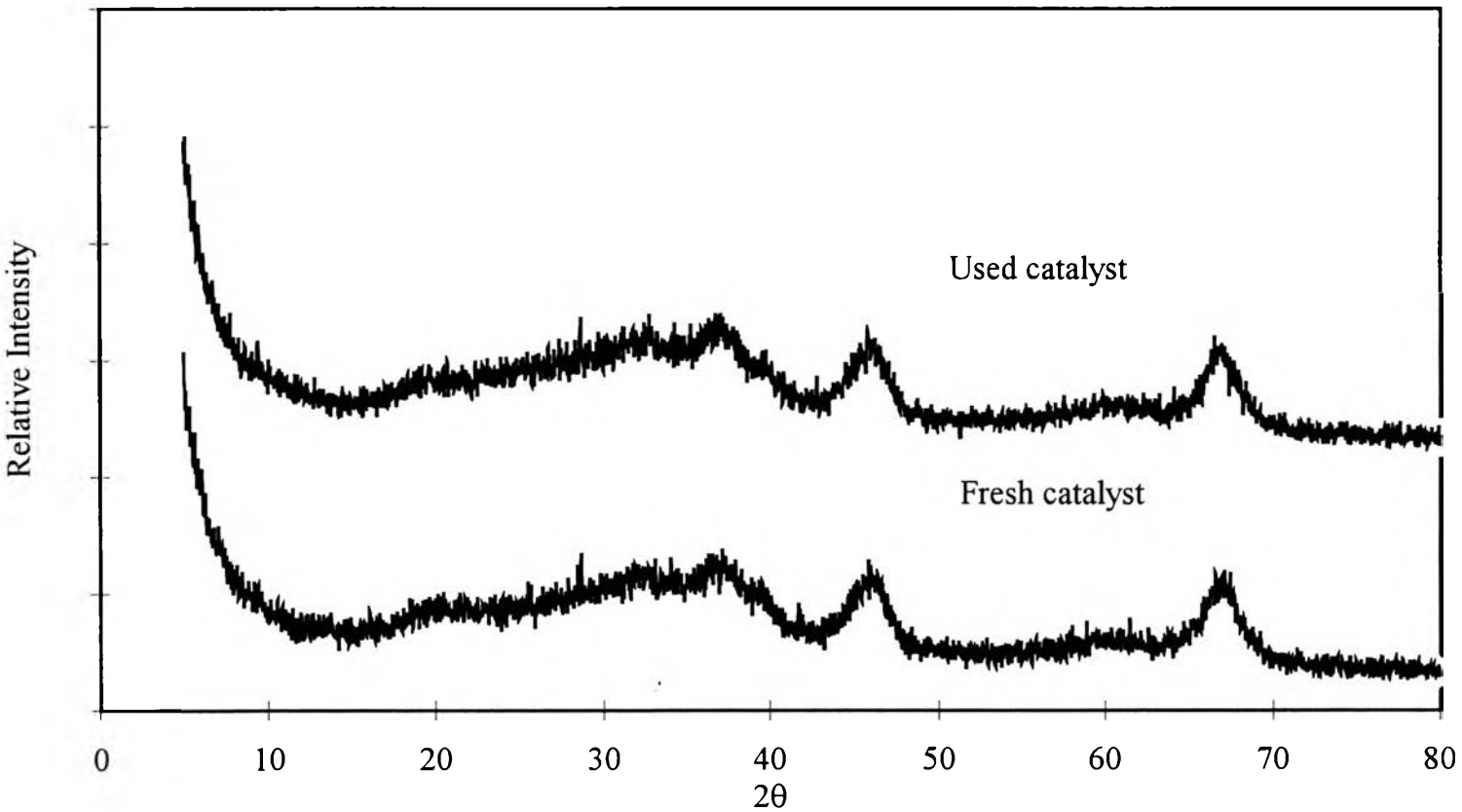


Figure 4.3 X-ray diffraction patterns for 5 % Ag sol-gel catalysts calcined at 600°C.

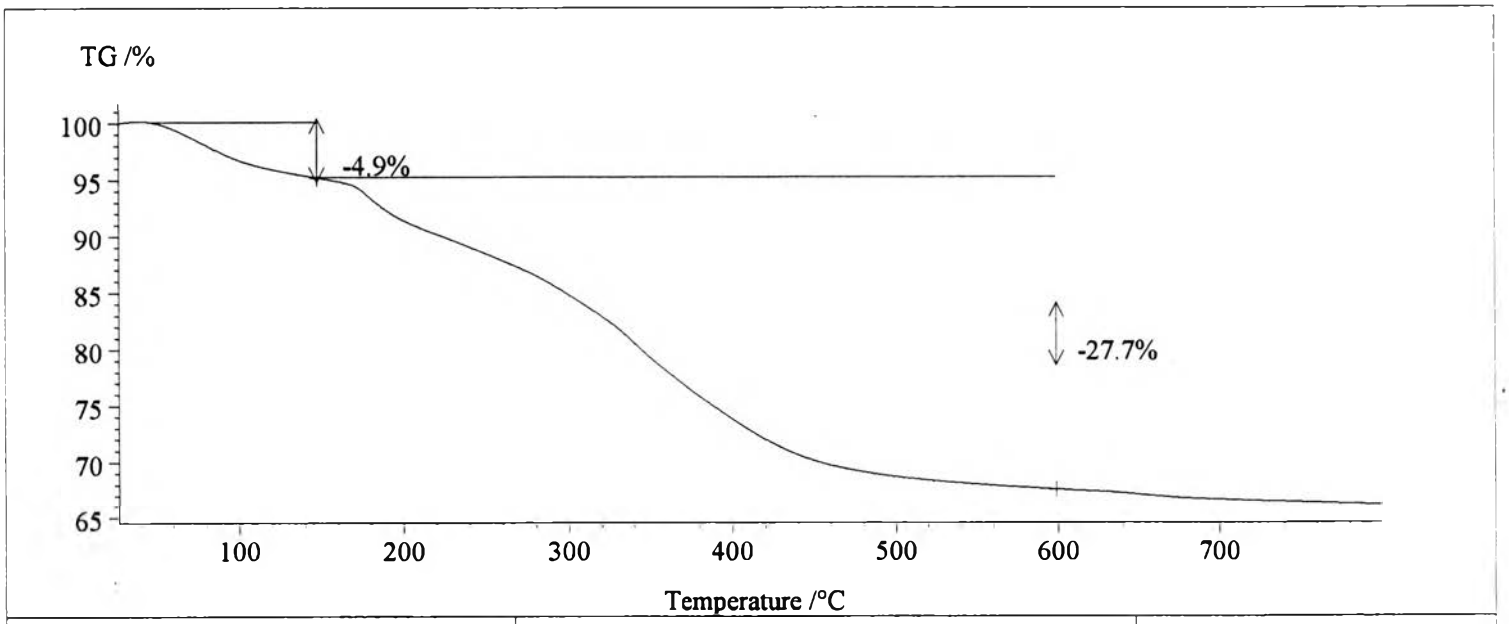
than fine dispersing crystals liked silver which dispersed over Al_2O_3 support. The effect of calcination temperature did not change the XRD pattern of Al_2O_3 support significantly. It reduced the BET surface area a lot. All catalysts calcined at various temperature as shown in Figure 4.2 were appeared to be amorphous in structures. This amorphous structure was very useful for the catalytic reaction. This was favorable for most of the reactions (Heck and Farrauto, 1995). Figure 4.3 shows that even though the used catalysts have the same catalyst structure based on the XRD pattern. Some organic chemical impurities shown in the XRD pattern in Figure 4.2 could be burnt off when the calcination temperature increased. This organic chemical removal could increase the activity of the reaction.

Thermograms from thermogravimetric analysis (TGA) of 5%Ag and 2%Ag catalysts prepared by sol-gel method were shown in Figures 4.4-4.5. The weight of catalysts dramatically decreased from room temperature up to about 500°C. The thermogram results could support the XRD results that the increment of temperature could burn some organic chemicals off which made the deactivated active sites to be more active.

4.2 Catalyst Activities

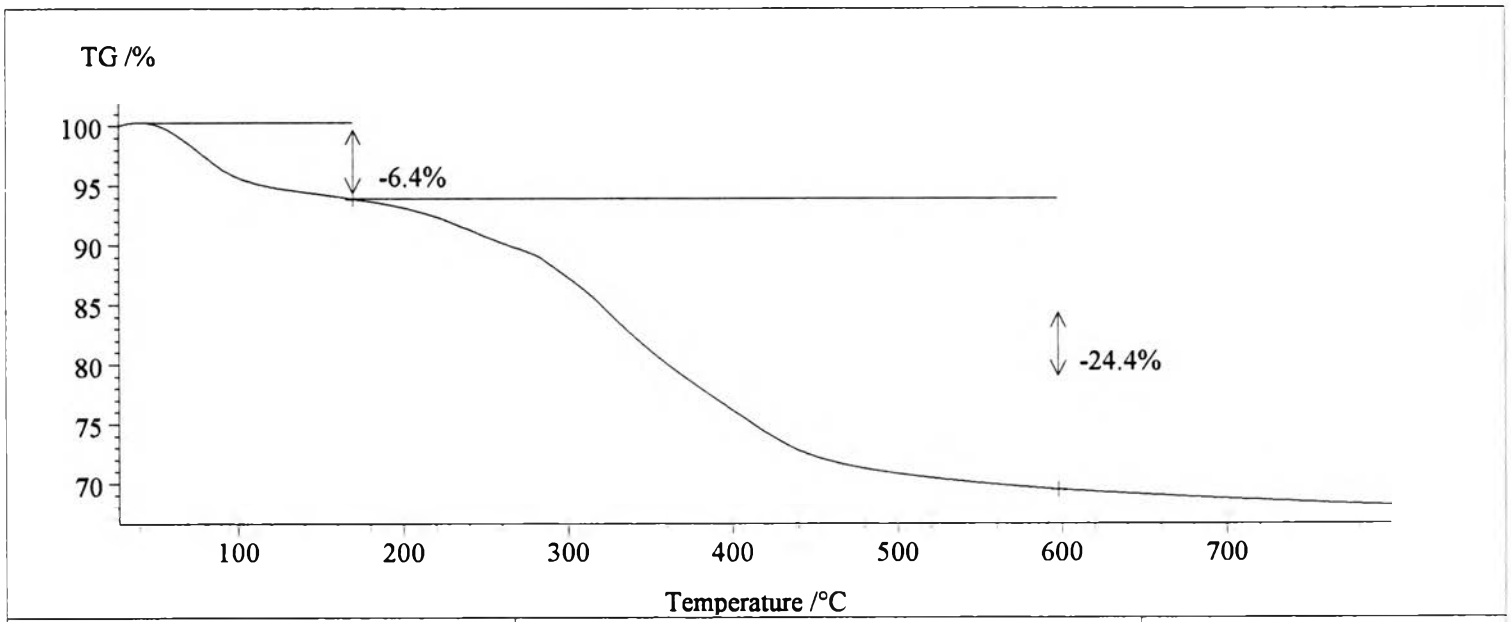
The catalysts prepared from coprecipitation method and sol-gel method were tested in the reaction of NO reduction with C_3H_6 in an oxidizing atmosphere.

The activity of catalyst was measured as a function of reaction temperature ranging from 100 to 550°C using simulated lean exhaust gas containing 1,000 ppm nitric oxide concentration, 0-2,000 ppm propylene



INSTRUMENT:	NETZSCH TG 209	SAMPLE:	5%Ag/Al2O3, sol-gel 12.054 mg	MODE:	Dynamic
FILE:	5AG_SOL2.DAT	REFERENCE:		RANGE:	26 °C/5.0/800 °C
IDENTITY:	5%Ag/Al2O3,Sol-gel,			SEGM:	1/ 1
DATE/TIME:	09.03.98 17:52	CORR-FILE:		CRUC:	Al2O3
LABORATORY:	Inclusion	REMARK:		ATMOS:	N2,20;
OPERATOR:	Paisan			CORR:	000

Figure 4.4 Thermogram of fresh 5%Ag sol-gel catalyst.



INSTRUMENT:	NETZSCH TG 209	SAMPLE:	2%Ag/Al2O3, sol-gel 10.900 mg	MODE:	Dynamic
FILE:	2AG_SOL.DAT	REFERENCE:		RANGE:	27 °C/5.0/800 °C
IDENTITY:	2%Ag/Al2O3, Sol-gel			SEGM:	1/ 1
DATE/TIME:	09.03.98 13:25	CORR-FILE:		CRUC:	Al2O3
LABORATORY:	Inclusion	REMARK:		ATMOS:	N2,20;
OPERATOR:	Paisan			CORR:	000

Figure 4.5 Thermogram of fresh 2%Ag sol-gel catalyst.

concentration, and 5% by mole of oxygen balanced with helium at total flow rate of 200 ml/min. The catalyst weight was varied from 0.05 to 0.2 g.

4.2.1 Effect of Ag and Au Loading

The effect of Ag and Au loading was studied with 0.2 g of catalyst prepared by coprecipitation and sol-gel method, and calcined at 300° C. The gaseous reactant fed at 200 ml/min containing approximately of 1,000 ppm of both NO and C_3H_6 and 5% O_2 balanced in helium. The experiments were conducted at various temperatures from 100°C to 550°C at atmospheric pressure.

Coprecipitation method

Figures 4.6-4.7 show the dependence of the catalyst activity on the silver and gold loading at various reaction temperatures. The 5%Au and 2.5%Ag / 2.5% Au catalysts showed no increase in the activity with reaction temperature. But for 5%Ag catalyst, the activity increased after 350°C and reached the maximum at about 500°C. After that the activity started to decrease.

Sol-gel method

The activities in terms of conversion of NO and NO conversion to N_2 were shown in Figures 4.8-4.9. All catalysts prepared by sol-gel method have the same level of activity up to 300°C. After 300°C, the activities of all catalysts started to increase. The 5%Ag catalyst showed a marked increase in activity. It resulted in temperature windows of highest activity (ca. 350-550° C). These temperature windows overlap very well with the temperature window expected for during actual operation on a lean-burn gasoline vehicle (Hoost et al., 1997).

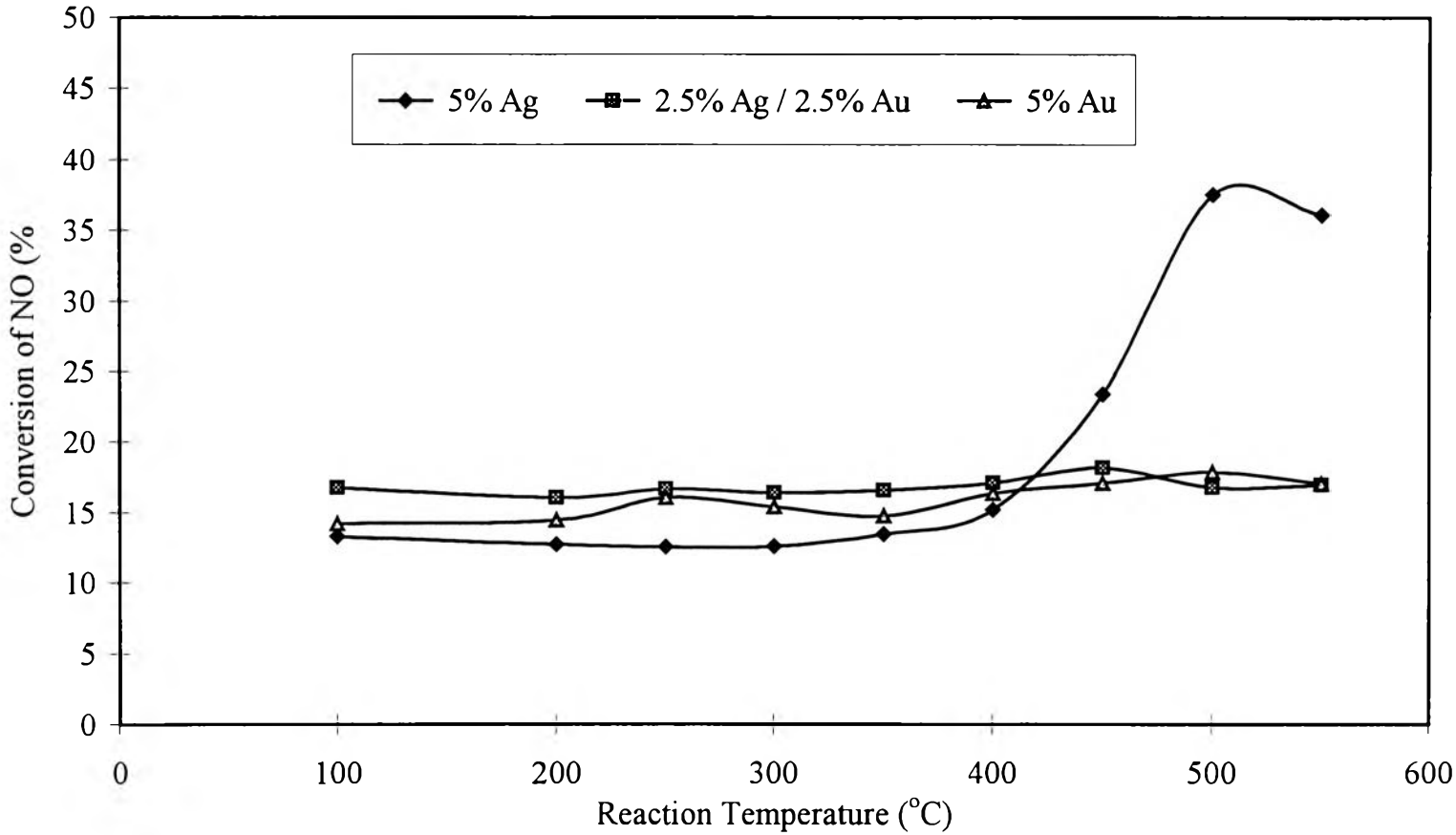


Figure 4.6 Conversion of NO at various reaction temperatures of coprecipitation catalysts.

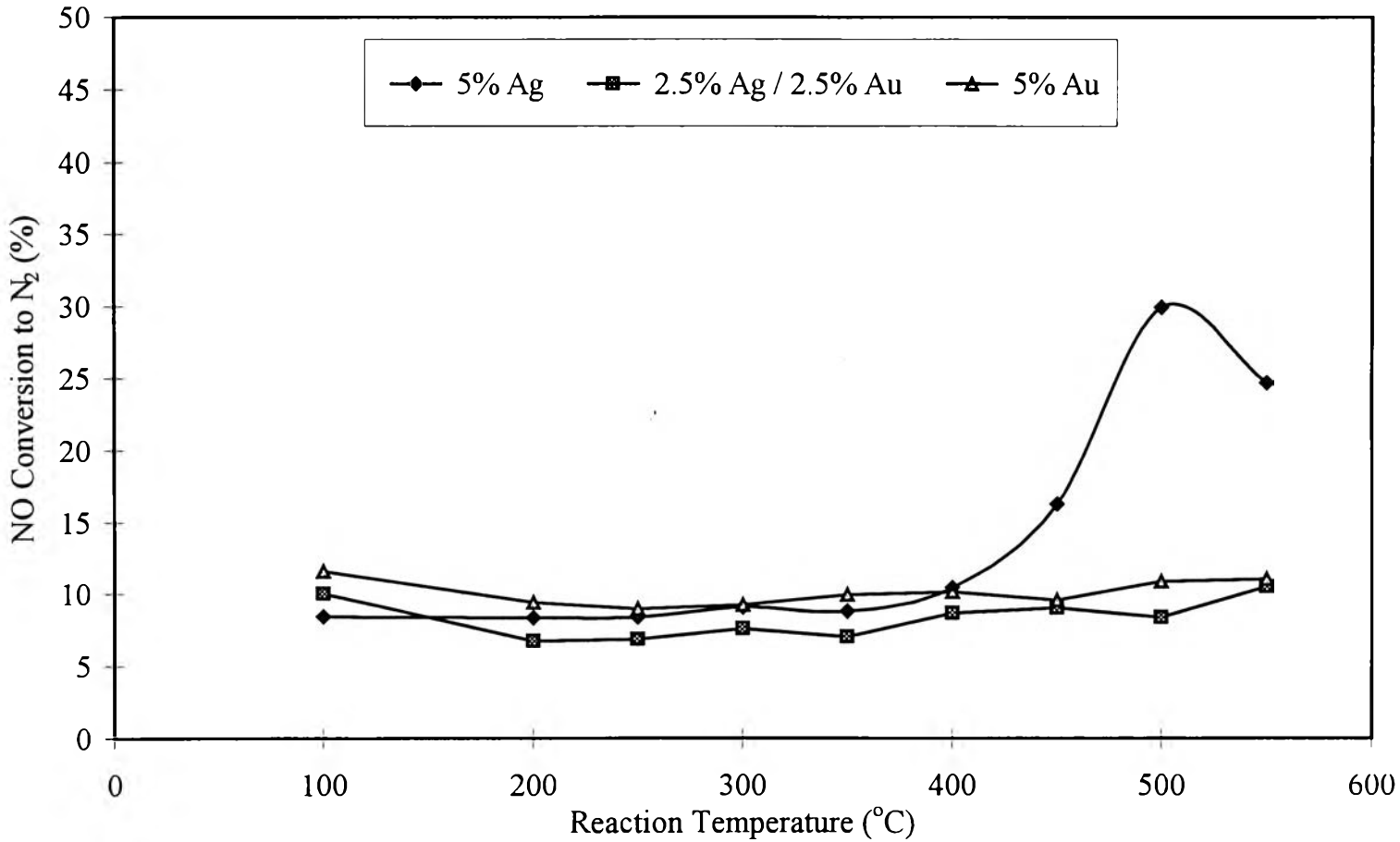


Figure 4.7 NO conversion to N_2 at various reaction temperatures of coprecipitation catalysts.

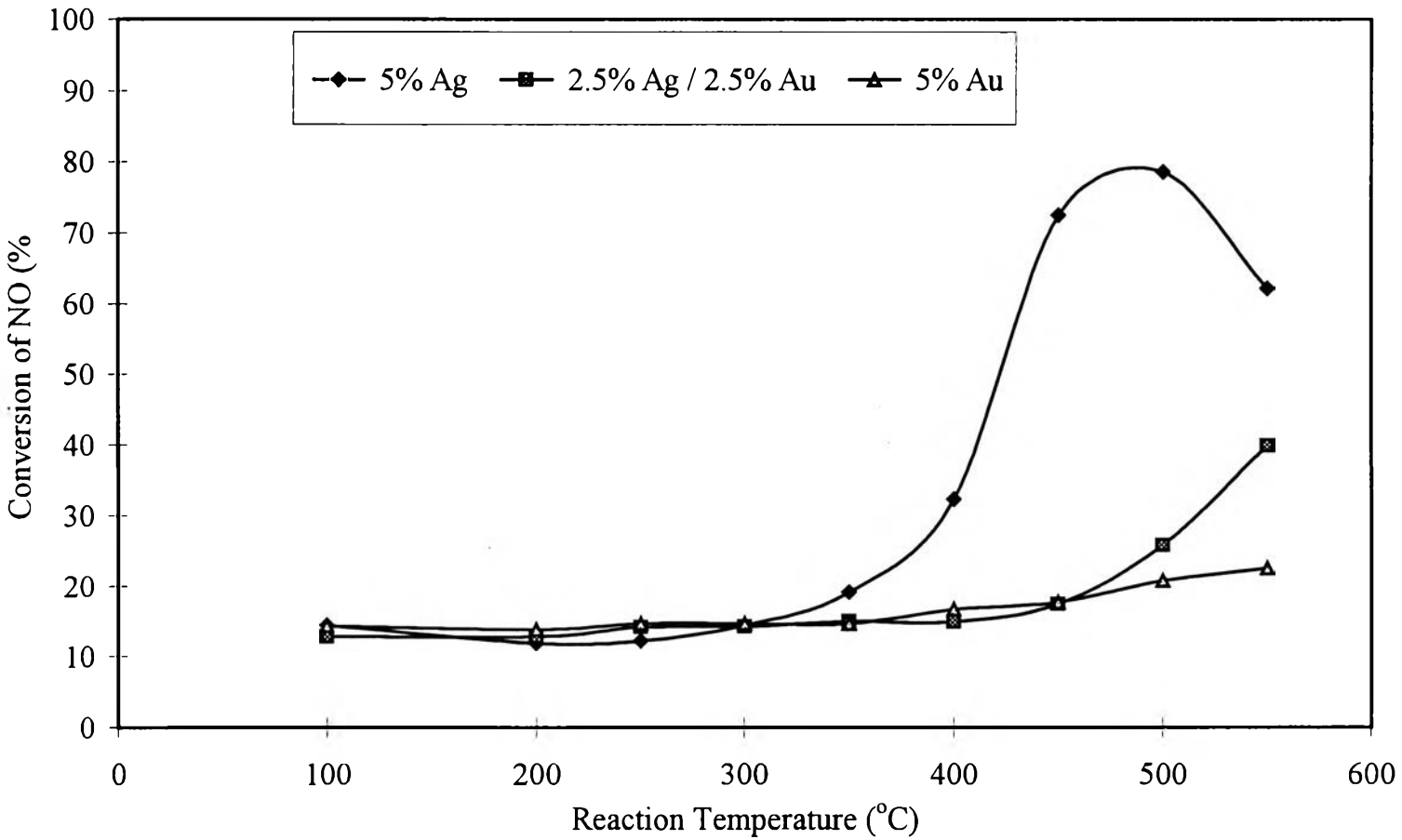


Figure 4.8 Conversion of NO at various temperatures of sol-gel catalysts.

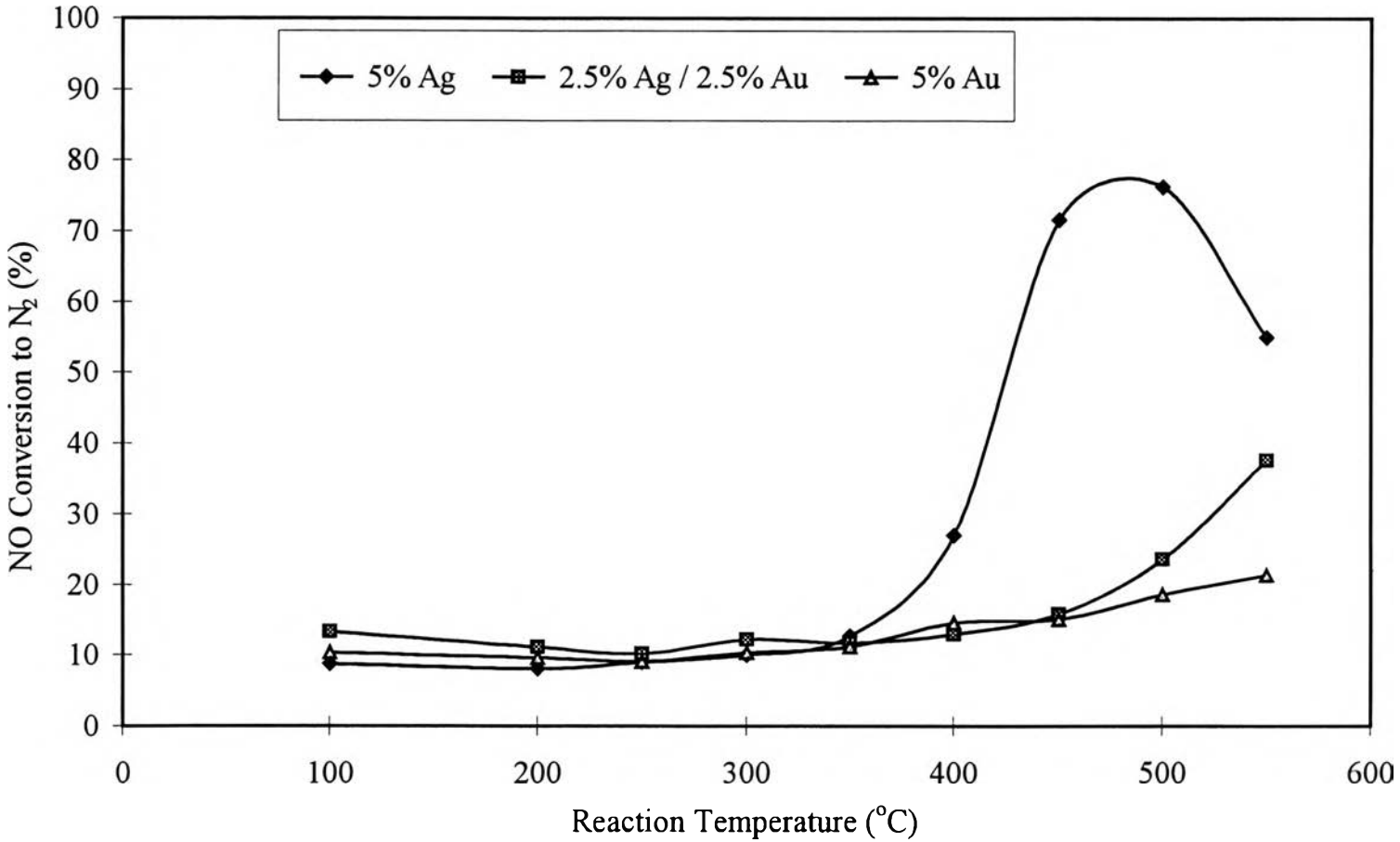


Figure 4.9 NO conversion to N_2 at various reaction temperatures of sol-gel catalysts.

4.2.2 Comparison of Coprecipitation and Sol-gel Methods

Figures 4.10-4.12 shows different activities between coprecipitation and sol-gel methods in terms of NO conversion to N_2. All catalysts prepared by sol-gel method had higher activity than coprecipitation method. It might be described that the coprecipitation catalysts did not have very well defined small crystallites. They had more impurities (Na^+ ion) which prevented them from being stable catalysts and also some of metals in coprecipitation catalysts were incoporated into alumina and were unavailable for reaction. Sol-gel catalysts showed rather unique catalytic properties and gave high porous structure (high surface area as shown in Table 4.1). The active sites which were well dispersed in the high porous structure resulted in high activity.

From both methods, 5%Ag catalyst had the highest activity which was later selected to be used for studying other effects.

4.2.3 Effect of Calcination Temperature

The effect of calcination temperature was studied with 0.2 g of 5% Ag sol-gel catalyst, which was calcined at 300, 400, 500, 600, and 700°C.

The results given in figures 4.13 shows that the activities of all catalysts which were calcined at various temperatures were constant up to about 300°C. They increased dramatically after 300°C and reached the maximum activity at about 450°C before decreasing at higher temperature. The activities increased with increasing in calcination temperature.

Figure 4.14 shows the activities of 2%Ag and 5%Ag sol-gel catalysts at various calcination temperatures which were studied with 0.1 g of catalyst at 450°C. At 5%Ag catalyst, the result was consistent with that shown in Figure 4.13. The activities markedly increased with increasing calcination temperature at the maximum activity temperature (450°C). Only slight

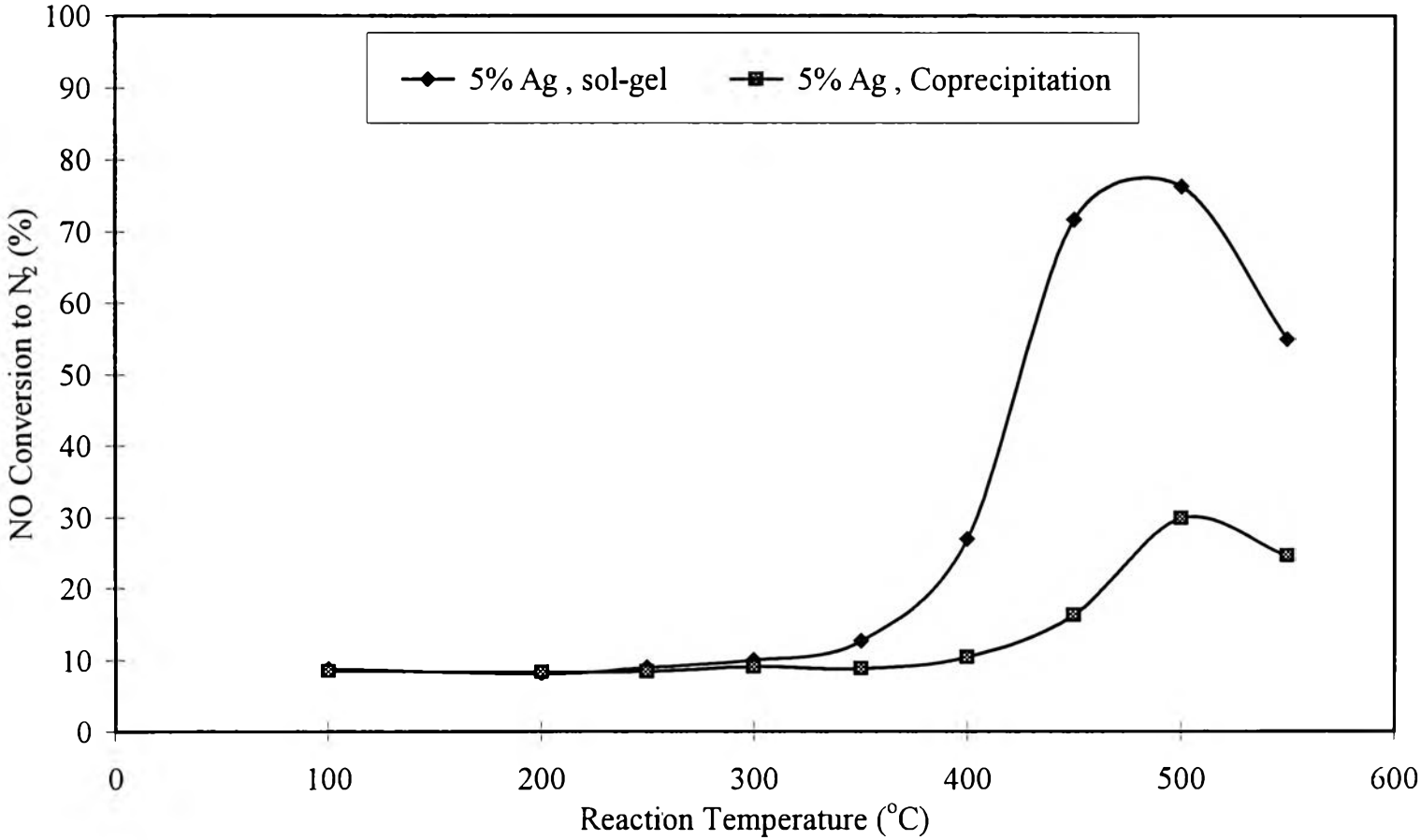


Figure 4.10 Comparison of coprecipitation and sol-gel methods over 5%Ag catalysts.

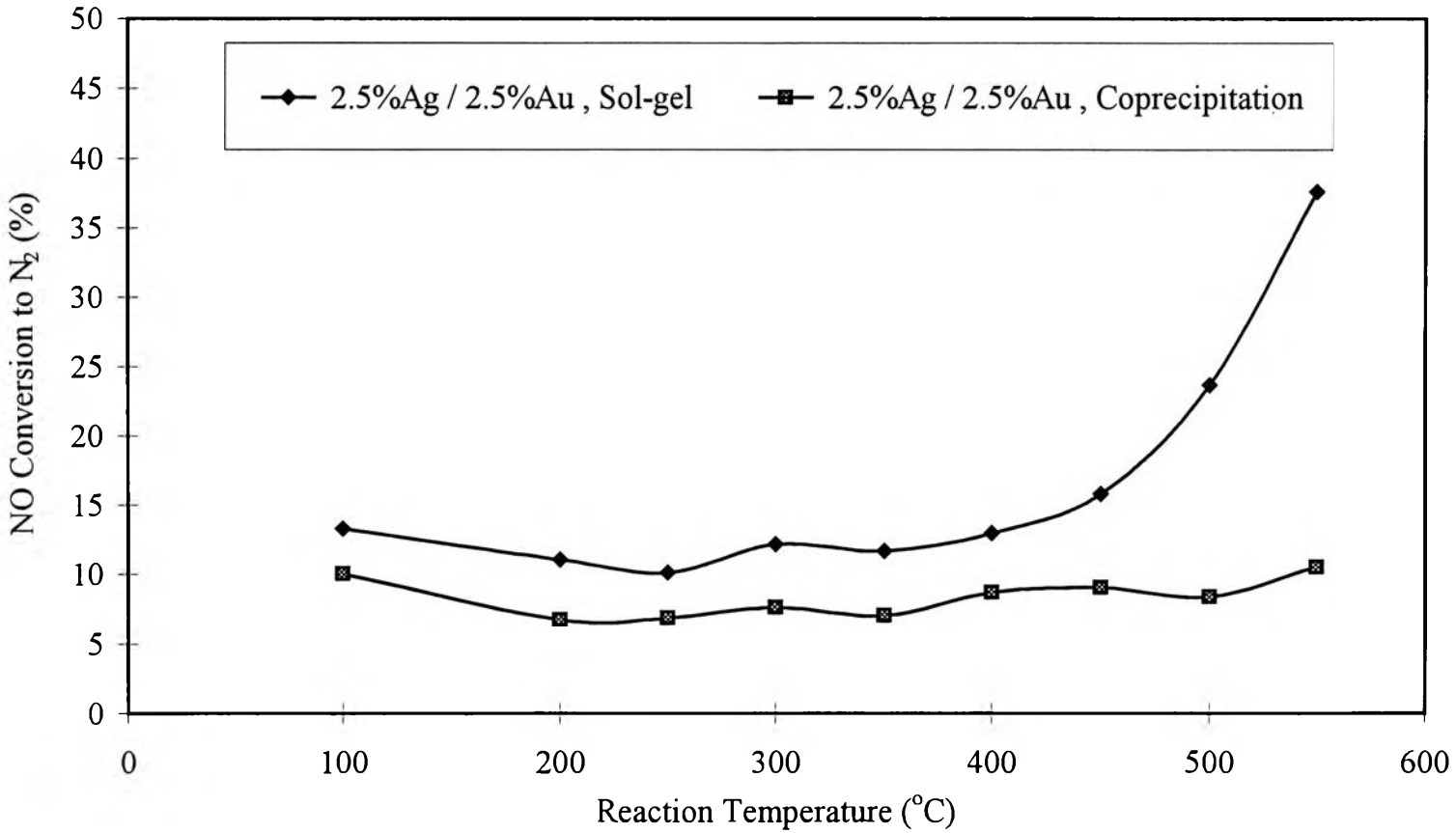


Figure 4.11 Comparison of coprecipitation and sol-gel methods over 2.5%Ag / 2.5%Au catalysts.

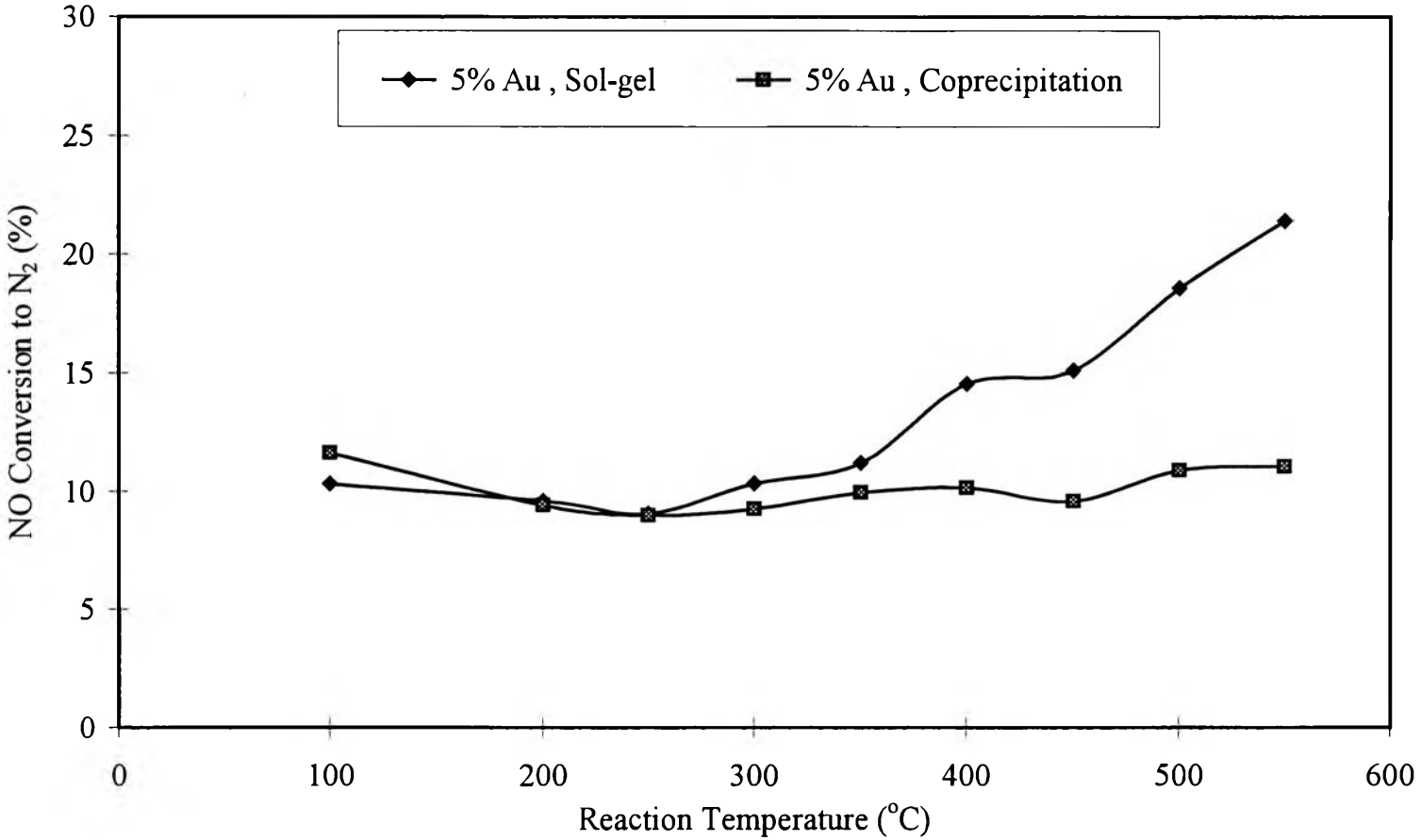


Figure 4.12 Comparison of coprecipitation and sol-gel methods over 5% Au catalysts.

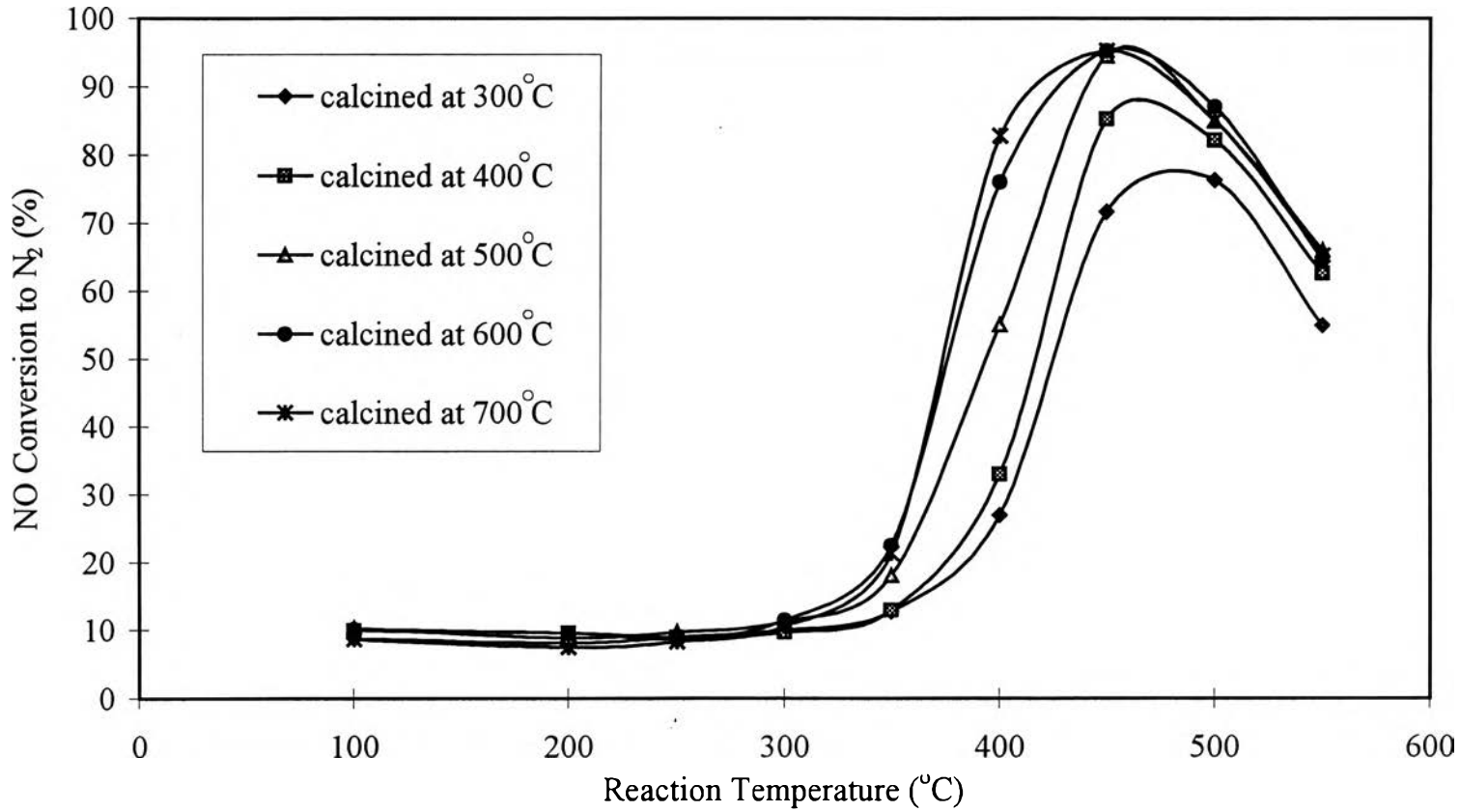


Figure 4.13 Effect of calcination temperature on the activity of 5%Ag sol-gel catalysts at various reaction temperatures.

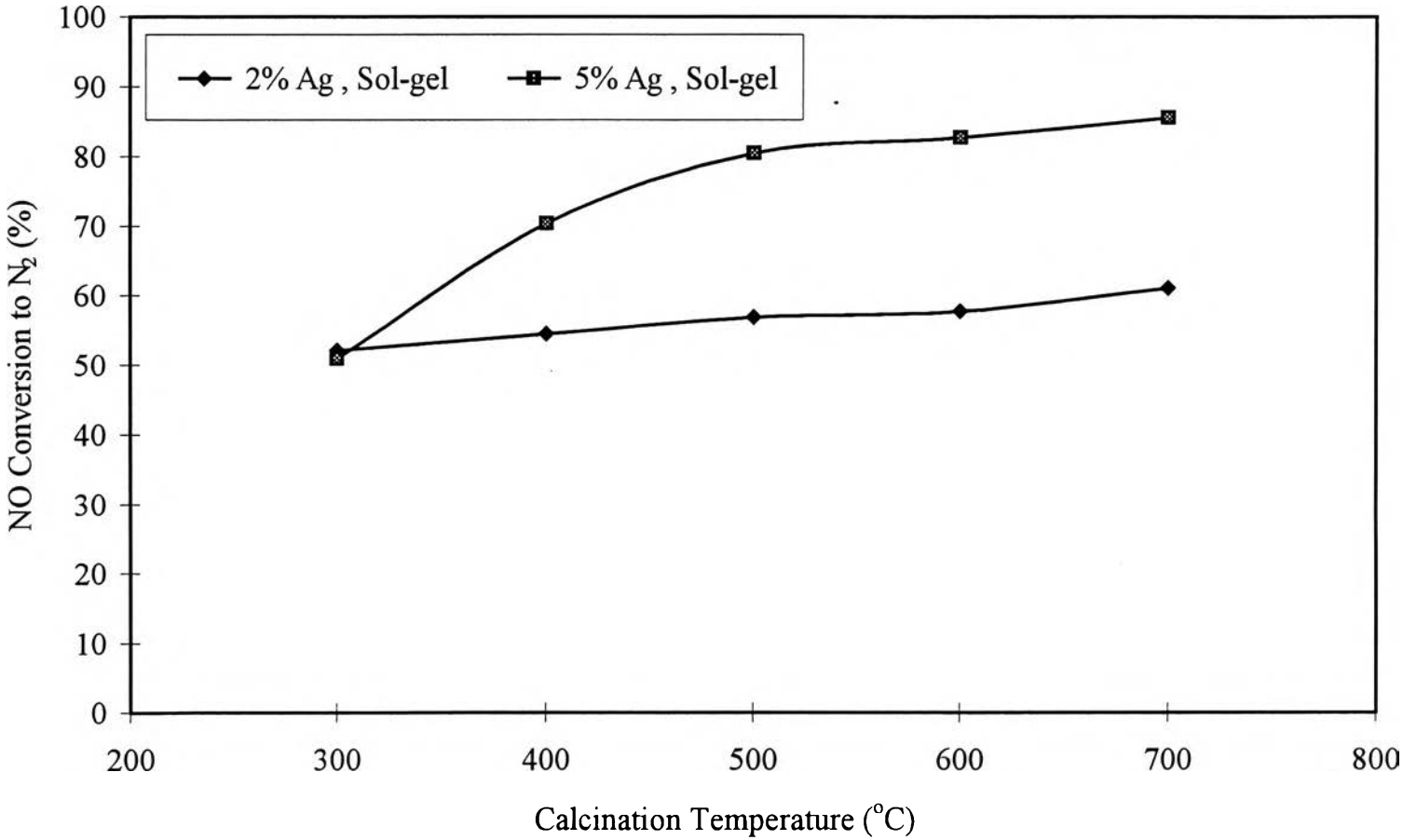


Figure 4.14 Effect of metal loading on the activity of sol-gel catalyst at various calcination temperatures.

increase in activity was found for 2%Ag catalyst. These behaviors might be described separately into two effects. First : the organic chemical imputiries (XRD patterns in Figure 4.2) traped inside the pores, might be burnt off when the calcination temperature was increased which caused the activity to be increased. Second : the subsidence of total surface area from increasing calcination temperature (Table 4.1) caused the activity to be subsided. Accordingly, for 5%Ag catalyst, the first effect was more influential than the second one. In contrast, these two effects had nearly the same influence for 2%Ag catalyst. Thus, in agreement with Maunula et al. (1998), the activity of alumina supported silver catalyst which was prepared by a sol-gel method was increased when calcined at 800°C instead of at 600 °C.

4.2.4 Effect of Metal Loading

From Figure 4.14, it shows that the activity is much higher over the higher loading sample. It appears that the sol-gel technique stabilizes the small crystallites of silver in the pores so that sintering is prevented even at the high temperatures. In this case, increasing the loading just increased the number of crystallites which gave rise to higher activity.

4.2.5 Effect of Propylene Concentration

The effect of propylene concentration was studied with 0.2 g of 5%Ag sol-gel catalyst calcined at 600°C. The feed stream at total flow rate 200 ml/min was made up of 1,000 ppm of NO and 5%O_2 balanced with helium. The concentration of C_3H_6 was varied from zero to 2,000 ppm. The reaction temperature was fixed at 450°C at atmospheric pressure.

Figure 4.15 indicates that the activities increased as C_3H_6 increased from zero ppm up to 1,000 ppm and remained constant at nearly 100% conversion after 1,000 ppm. This catalyst also has some decomposition

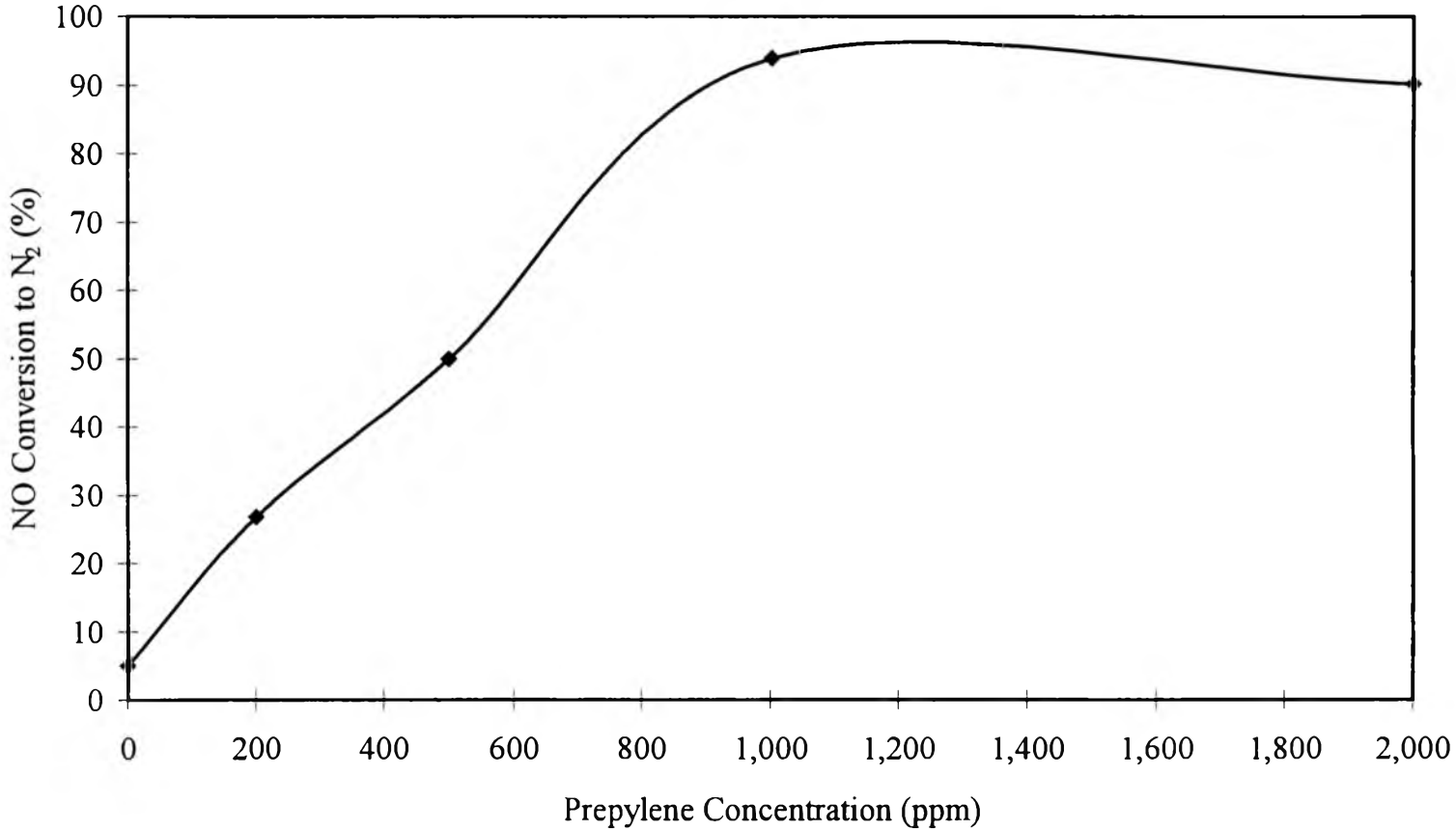


Figure 4.15 Effect of propylene concentration on the activity of 5%Ag sol-gel catalyst, calcined at 600°C.

activity (zero ppm of C_3H_6). The optimum condition between NO and C_3H_6 was found to be 1:1 as reported by Ueda et al. (1997).

4.2.6 Effect of Catalyst Amount

The effect of catalyst amount was studied with 0.05, 0.1, and 0.2 g of 5%Ag sol-gel catalyst and calcined at 600°C. The activity was measured under the same operating conditions as the previous part.

Figure 4.16 shows that in going from 0.05 g of catalysts to 0.1 g the activity almost double and after that the activity does not change much with going to 0.2 g.

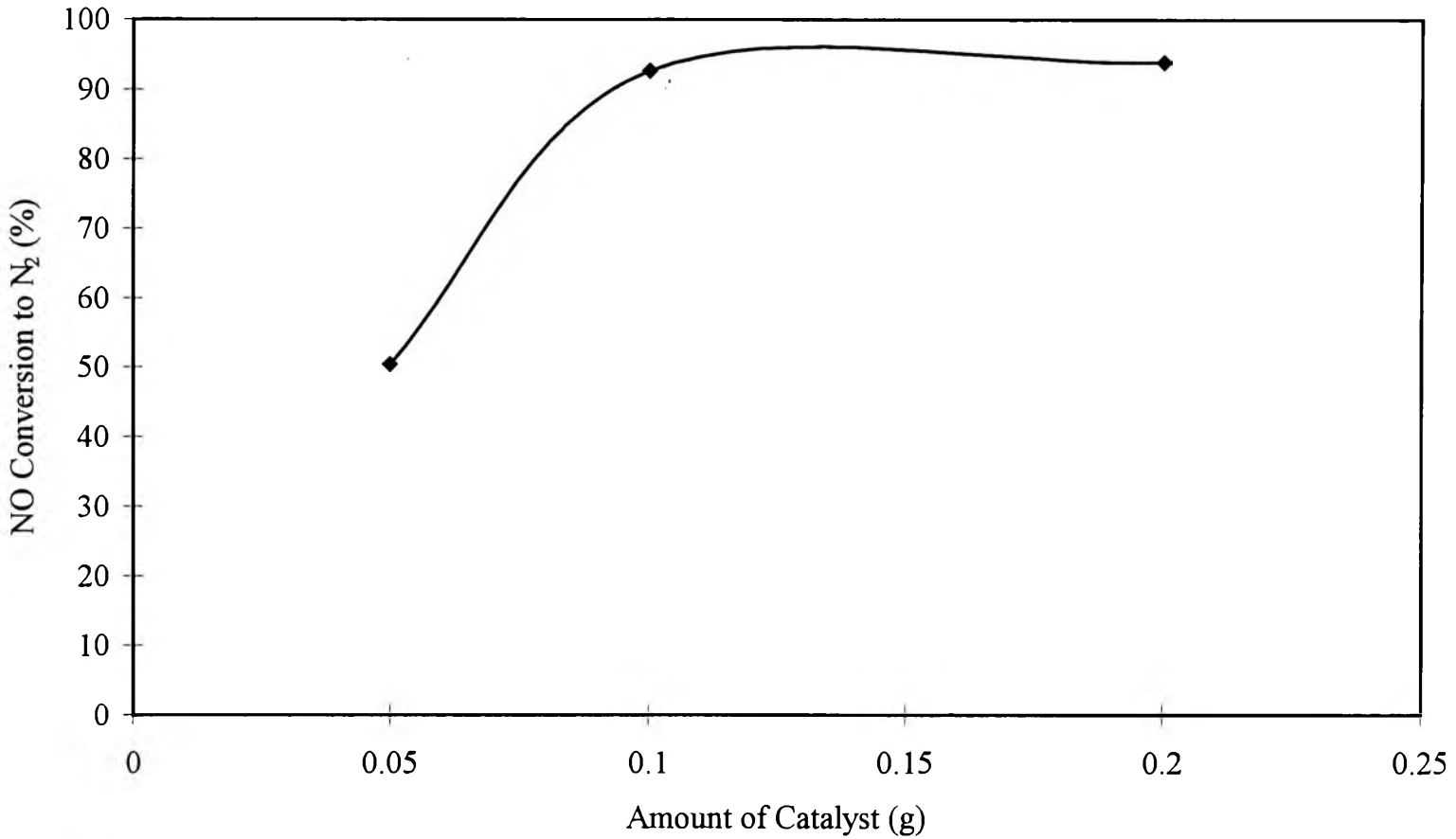


Figure 4.16 Effect of amount of catalyst on the activity of 5%Ag sol-gel catalysts, calcined at 600°C.