CHAPTER IV

RESULTS AND DISCUSSION

The results presented here were obtained at the condition of 0.2 grams catalyst, and the feed amount of NO and NH_3 at 0.115 volume% each. The factors which affected the conversion of NO in the present studies are reaction temperature, space velocity, the presence of O_2 (3.45 volume%) in the feed, and the composition of catalysts.

4.1 Effect of reaction temperature

The temperature effect on the conversion of NO is shown in Figure 4.1-4.6. The result indicates that the conversion of NO will increase when the temperature rises from 100 °C to 300 °C. This result conforms to the basic thermodynamics principle which indicates that the reaction tends to favourably occur when the temperature rises (the negative values of $(\Delta G_R^{\circ})_T$ of the first and the second reaction in Table 2.1 increase as the rising of temperature). Conversely, as temperature reaches 400 °C the conversion of NO decreases which does not follow the basic thermodynamics principle mentioned above. It may result from the combustion of NH₃ which the $(\Delta G_R^{\circ})_T$ of NH₃ combustion (in Table 2.1) indicates that it is favourable. The NH₃ combustion will produce NO or N₂ and a little

amount of N₂O. Odenbran et al. (1985) reported that NO readily occurred from the combustion of NH₃. Besides, Cavani et al.(1980) found N₂ and N₂O occurred from the same reaction. The combustion of NH₃ with O₂ is expressed as the ninth, the tenth, and the eleventh reaction in Table 2.1. In the absence of O₂, N₂O may occur from the side reaction of NO-NH₃ expressed as the twelfth reaction in Table 2.1. However, the amount of N₂O may be too low to be detected by gas chromatography. Niiyama et al.(1980) and many researchers have found the similar temperature effect to this work even with different kinds of catalysts.

4.2 Effect of space velocity

The effect of space velocity are shown in Figure 4.7-4.12. The result indicates that the NO conversion will reduce when the space velocity increases from 18820-75280 hr^{-1} for all catalysts with and without O₂ in the reaction. This can be explained by the reason that the increasing of space velocity reduces the contact time at the active sites and leads to the incompleteness of NO reduction.

4.3 Effect of addition O2 into NO-NH3 reaction system

This effect is shown in Figure 4.1-4.6. The result points out that, in the presence of O_2 , more percentage of NO conversion was obtained than that in the absence of O_2 for all catalysts. Addition of

28

3.45 volume% O_2 increases approximately one fold the NO conversion, these results are similar to the work of Inomata et al.(1980). In the presence of O_2 , Table C7-C12 show that the mole ratio of NO:NH₃ is approximately 1:1. This reveals that the reaction between NO and NH₃ may occur as the following reaction

$$4NO + 4NH_3 + O_2 \longrightarrow 4N_2 + 6H_2O$$
 (4.1)

However, the measuring N_2 amount is slightly higher than 100% in comparison with N_2 calculated from the actual conversion of NO of reaction (4.1). This may be due to the oxidation of NH_3 to N_2 and N_2O as explained in section 4.1.

In absence of O_2 , Table C1 - C6 show that the mole ratio of NO:NH₃ is about 1:0.892 which is not likely the stoichiometry of NO:NH₃ of 1:0.667 in reaction (4.2).

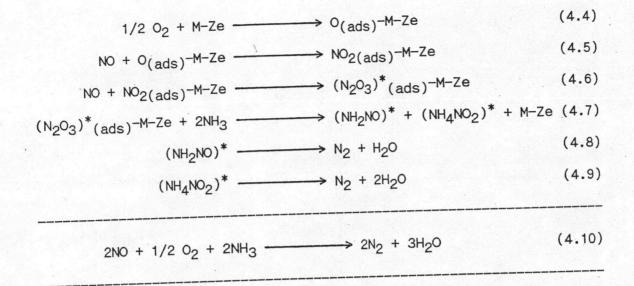
$$6NO + 4NH_3 \longrightarrow 5N_2 + 6H_2O \qquad (4.2)$$

And the percentage of measuring N_2 is approximately 87 % in comparison with N_2 calculated from the actual conversion of NO of reaction (4.2). The disappearance of 13% N_2 and mismatch of NO:NH₃ mole ratio may be the result from the side reactions such as reaction (4.3).

 $8NO + 2NH_3 \longrightarrow 5N_2O + 3H_2O$ (4.3)

This reaction is favourable confirmed by the value of $(\Delta G_R^{O})_T$ of the twelfth reaction in Table 2.1. However, very small minute amount of N₂O may be produced from the NO-NH₃ reaction either in the presence or absence of O₂.

From the experimental results, the participation of O_2 in the reaction of NO-NH3 has two different pathways which depend on each type of used catalysts in this work. In case of cationexchanged zeolite, O_2 has a role in the step of NO oxidation. Firstly, O2 adsorbs on surface of zeolite at cation sites called oxygen surface. Subsequently, NO2 species are produced by the reaction between NO (from the feed) and oxygen surface. Considering the characteristic of electron transfer in the reaction of NO-NH3-O2 system which is expressed in reaction 2.12-2.14, these sets of reactions indicate that electron receivers are NO and O_2 , by the fact that the electron affinity of NO_2 is much higher than that of O_2 (see Table 4.1). This means that it can attract electron from $\rm NH_{3}$ easier than O_2 . Therefore, the oxidation of NO by O_2 is the important step although the values of $(\Delta G_R^O)_T$ of NO oxidation, the third reaction in Table 2.1, indicates that this reaction is unfavourable. This reaction is promoted by cation exchanged zeolite that has high electron field and transition metal cations have the ability to change valence state easily, and can therefore function as an intermediate storage for electrons that are needed in the reaction. So, these are sufficiently reasonable to propose a general mechanism for the reduction of NO by NH3 as expressed in the following set of reactions;



where M-Ze stands for a cation exchanged zeolite, M is cation such as Cu^{2+} and Pt^{2+} , (ads) denotes an adsorbed species and ()* is a reaction intermediate.

Table 4.1 Ionization potential energy and Electron affinity for one electron transfer

species	IP (EV)	EA (EV)
NO	9.25	
NO2	9.75	3.91
0 ₂	12.06	0.45
		1

From : Brandin et al." Catalyst reduction of nitrogen oxide on mordenite some aspect on the mechanism" Journal of Catalysis Today, Volume 4,(1989); PP 197.

31

The formation of a N_2O_3 -like intermediate could be a fast step, since it is known that in the gas phase the equilibrium of NO-NH₃ with N_2O_3 is established within microseconds. It seems reasonable to assume that step (4.7)-(4.9) are fairly fast step too. Intermediate N_2O_3 reacts on the catalyst surface either with gas phase ammonia or with ammonia bound to Lewis and Bronsted acid centers. Farber and Harris confirmed NH₂NO intermediate formation, by mass spectrometry, with a lifetime of about 100 microseconds. The work of Farber and Harris is refered by Luck and Roiron (1989). Lastly, lifetime of intermediate NH_4NO_2 is extremely short, at current temperature involved in NO reduction. In the absence O_2 in feed gaseous reactant, the formation of NO_2 is established by disproportionation of NO as described by the reaction below

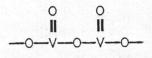
$$3NO \longrightarrow N_2O + NO_2$$
 (4.11)

However, the amount of established NO₂ from reaction (4.11) may be less than in the presence of O₂ by the reason that the capability to draw electron of three molecules of NO is equal. Therefore, the NO conversion in the presence of O₂ is higher than in the absence of O₂. Further details of this mechanism, however, should be clarified by IR or other methods.

In case of vanadium oxide catalyst, the participation of O_2 in the reaction of NO-NH₃ is directly supplied from the lattice oxygen of the catalyst. It seems reasonable to explain that the quantity of lattice oxygen of vanadium oxide catalyst is much more than that of

32

adsorbed oxygen and the lattice oxygen of catalyst can diffuse easily from bulk to surface. This explanation is confirmed by the work of Inomata et al.(1980). Consider the molecular structure of vanadium oxide as V_2O_5 below,



the structure indicates that the arrangement of oxygen atoms are set as the balanced state which conforms to octave rule. So, O_2 from gaseous reactants hardly attracts on surface of V_2O_5 by the method of adsorption at V⁵⁺=O species. For the reaction of NO-NH₃ to take place, NH₃ is the first species which adsorbs at V⁵⁺=O species by hydrogen bonding. The adsorption of NH₃ is easier than the adsorption between V⁵⁺=O and O₂ because V⁵⁺=O can polarize oxygen atom as the negative polar and NH₃ can polarize hydrogen atom as the positive polar whereas gaseous O₂ can not self-polarize. The opposite polarity of the two species can result in weak bonding. Thus, it seems reasonable to suggest that the active site of V₂O₅ as catalyst for NO-NH₃ reaction is V⁵⁺=O species. Subsequently, adsorption of NO on the adsorbed NH₃ occurs through the hydrogen bonding between oxygen atom of NO and two hydrogen atoms of adsorbed NH₃. The participation of O₂ in the reaction can be expressed by the set of reactions below.

$$V^{5+=0} \longrightarrow N_2 + H_2 0 + V$$
 (4.12)

From reaction (4.13), gaseous O_2 from the feed is used to convert the reduction site to an oxidation site. In the presence of O_2 , the V⁵⁺=O species on the surface is reproduced by reaction (4.13) with the expense of bulk V⁵⁺=O species, followed by the formation of V⁴⁺ ion in bulk. As a consequence, the quantity of V⁵⁺=O should decrease completely after the long duration of NO-NH₃ reaction in the absence of gaseous O_2 and the conversion of NO is lower than in the presence of gaseous O_2 . This mechanism has been proposed by Miyamoto et al.(1982) and the scheme is shown in Figure 2.2. In the present study, TiO₂ is used as the supporting material. TiO₂ is useful for V₂O₅ catalyst as the storage of lattice oxygens which are used in NO-NH₃ reaction. So, V₂O₅-TiO₂ should be better than pure V₂O₅.

4.4 Influence of catalyst compositions

In the present study, catalysts can be classified to two main types. The first type of catalyst is cation-exchanged zeolite which is composed of Pt-HY and Cu-Pt-HY. The other is vanadium pentoxide with and without TiO₂ as the supporting material. In case of cation-exchanged zeolite, Figure 4.13-4.20 show that Cu-Pt-HY gave higher activity than Pt-HY for all conditions. The enhanced activity on the conversion of NO can be explained by the fact that Cu was able to adsorb O₂ especially in a very dilute concentration since O₂ is necessary to oxidize NO to NO₂ species. This reason is confirmed by the suggestion of Niiyama et al.(1980) which stated that catalyst of low O₂-adsorptive properties have no ability to adsorb NO as NO₂ species. Therefore, loading of Cu into Pt-HY increases an active site for O₂ adsorption.

34

Moreover, at high temperature and in the presence of O_2 , Pt^{2+} is more likely to reduce itself to pure metal than Cu^{2+} . This behaviour is confirmed by the standard redox potential energy of the metal as shown in Table 4.2. So, the activity of Pt-HY catalyst is maintained by Cu.

couple	E/V
$Cu^{2+} + e^{-} \longrightarrow Cu^{+}$	0.16
$Cu^{2+} + 2e^{-} \longrightarrow Cu$	0.34
$Cu^+ + e^- \longrightarrow Cu$	0.52
$Pt^{2+} + 2e^{-} \longrightarrow Pt$	1.20

Table 4.2 The standard redox potential energy of Cu and Pt at 25 °C

From: M.S. Antelman. "The Encyclopedia of Chemical Electrode Potentials", Plenum, New York, 1982.

In case of V_2O_5 -TiO₂, Figure 4.13-4.20 indicate that NO conversion increases with higher content of V_2O_5 on TiO₂ for all conditions. This result can be explained by the fact that the active site ($V^{5+}=0$ species) increases with increasing of V_2O_5 content. However, pure V_2O_5 gives the lowest NO conversion in comparison with the other V_2O_5 -Ti₂O₂ catalysts in the absence of O₂. This may be due from the impregnation of V_2O_5 on TiO₂ causing the structure to be defective and this will result in the easy transfers of electron at the catalyst surface. This effect enhances NO conversion to occur

higher than that in case of pure crystalline V₂O₅. In the presence of O₂, pure V₂O₅ gives the higher NO conversion than V₂O₅-TiO₂ as 8.54 wt% of V₂O₅. This result may be due from the amount of active sites (V⁵⁺=O species) of pure V₂O₅ having more than V₂O₅-TiO₂ as 8.54 wt% content of V₂O₅. Comparatively, the order of NO conversion affected by various catalysts can be arranged like this 25.61 wt% V₂O₅ > 15.0 wt% V₂O₅ ≥ Cu-Pt-HY > 8.54 wt% V₂O₅ ≥ pure V₂O₅ > Pt-HY. Table 4.3 Percentage of apparent N₂ in comparison with theory; Condition A : NO(0.119%)-NH₃(0.119%)-O₂(free) Condition B : NO(0.115%)-NH₃(0.115%)-O₂(3.45%) Catalyst : Pt-HY (Pt = 5.0 wt%)

reaction	space	percentage of N ₂	
temperature, ^o C	velocity,hr ⁻¹	condition A	condition B
100	18820	83.20	104.94
	37640	82.23	106.70
	56460	81.22	103.27
	75280	78.76	102.16
200	18820	86.48	106.71
	37640	85.98	105.69
	56460	85.41	105.02
	75280	84.04	95.97
300	18820	87.33	107.24
	37640	87.05	106.36
	56460	86.48	106.05
	75280	85.66	103.38
400	18820	87.10	107.10
	37640	86.67	106.33
	56460	86.05	105.89
	75280	84.37	103.14

Table 4.4 Percentage of apparent N₂ in comparison with theory; Condition A : NO(0.119%)-NH₃(0.119%)-O₂(free) Condition B : NO(0.115%)-NH₃(0.115%)-O₂(3.45%) Catalyst : Cu-Pt-HY (Cu = 4.9 wt%,Pt = 5.0 wt%)

reaction	space	percentage of N2	
temperature, ^O C	velocity,hr ⁻¹	condition A	condition B
100	18820	86.19	106.79
	37640	85.66	105.51
	56460	84.37	104.86
	75280	83.82	101.76
200	18820	88.38	115.23
	37640	88.04	107.30
	56460	87.09	104.45
	75280	86.81	104.43
300	18820	89.16	108.52
	37640	88.29	107.69
	56460	87.99	105.11
	75280	87.69	105.10
400	18820	88.80	108.30
	37640	87.89	107.53
	56460	87.69	104.86
	75280	87.29	104.80

Table 4.5 Percentage of apparent N₂ in comparison with theory; Condition A : NO(0.119%)-NH₃(0.119%)-O₂(free) Condition B : NO(0.115%)-NH₃(0.115%)-O₂(3.45%) Catalyst : V₂O₅-TiO₂ (V₂O₅ = 8.54 wt%)

reaction	space	percentage of N ₂	
temperature, ^o C	velocity,hr ⁻¹	condition A	condition B
100	18820	87.26	100.49
	37640	86.68	102.64
	56460	85.83	103.35
	75280	84.38	102.98
200	18820	88.56	102.20
	37640	88.11	104.04
	56460	88.06	104.73
	75280	87.16	104.75
300	18820	88.95	102.20
	37640	88.48	104.31
	56460	88.27	104.98
	75280	88.33	105.15
400	18820	88.76	101.80
	37640	88.29	103.75
	56460	88.09	104.59
	75280	87.65	104.80

Table 4.6 Percentage of apparent N₂ in comparison with theory; Condition A : NO(0.119%)-NH₃(0.119%)-O₂(free) Condition B : NO(0.115%)-NH₃(0.115%)-O₂(3.45%) Catalyst : V₂O₅-TiO₂ (V₂O₅ = 15.0 wt%)

reaction	space	percentage of N_2	
temperature, ^O C	velocity,hr ⁻¹	condition A	condition B
100	18820	87.05	101.02
	37640	86.67	103.16
	56460	86.19	103.59
	75280	79.61	103.37
200	18820	88.43	102.87
	37640	87.99	104.95
	56460	87.69	105.35
	75280	86.93	105.42
, 300	18820	89.09	103.35
	37640	88.35	105.33
	56460	88.21	105.74
	75280	87.79	105.58
400	18820	88.79	103.18
	37640	87.90	105.14
	56460	87.89	105.44
	75280	87.33	106.04

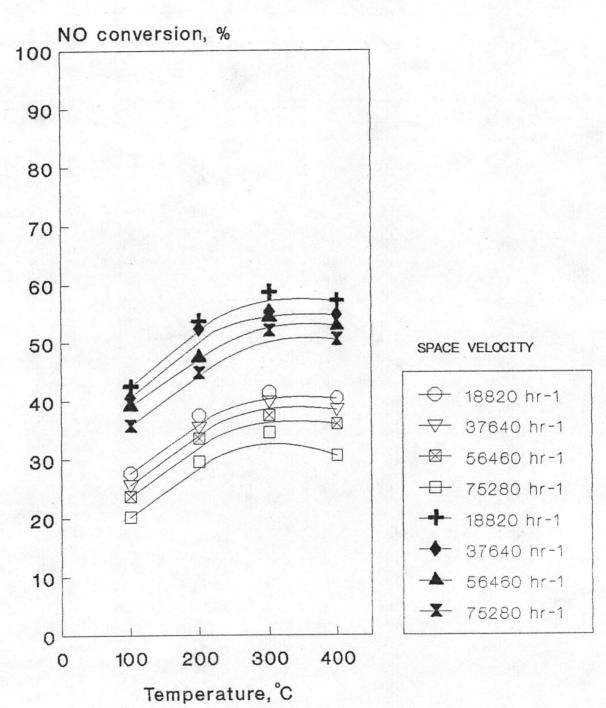
Table 4.7 Percentage of apparent N₂ in comparison with theory; Condition A : NO(0.119%)-NH₃(0.119%)-O₂(free) Condition B : NO(0.115%)-NH₃(0.115%)-O₂(3.45%) Catalyst : V₂O₅-TiO₂ (V₂O₅ = 25.61 wt%)

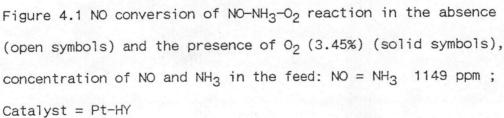
reaction	space	percentage of N ₂	
temperature, ^O C	velocity,hr ⁻¹	condition A	condition B
100	18820	86.86	101.15
	37640	86.51	103.50
	56460	86.33	104.15
	75280	84.96	103.94
200	18820	88.64	103.01
	37640	88.38	104.79
	56460	87.40	105.44
	75280	87.09	105.32
300	18820	89.30	103.60
	37640	88.80	105.33
	56460	88.10	105.90
	75280	87.33	105.88
400	18820	89.09	103.36
	37640	88.64	105.21
	56460	88.06	105.73
	75280	87.25	105.70

Table 4.8 Percentage of apparent N₂ in comparison with theory; Condition A : NO(0.119%)-NH₃(0.119%)-O₂(free) Condition B : NO(0.115%)-NH₃(0.115%)-O₂(3.45%)

reaction	space	percentage of N ₂	
temperature, ^o C	velocity,hr ⁻¹	condition A	condition B
100	18820	86.75	100.94
	37640	85.05	103.01
	56460	84.26	103.28
	75280	87.44	103.52
200	18820	87.21	102.91
1925	37640	86.02	100.56
	56460	85.61	95.32
	75280	91.19	104.71
300	18820	86.94	103.22
	37640	86.48	104.94
	56460	85.58	105.35
	75280	87.33	105.18
400	18820	87.66	102.87
	37640	85.66	104.85
	56460	84.26	104.85
	75280	83.51	105.85

Catalyst : pure V205





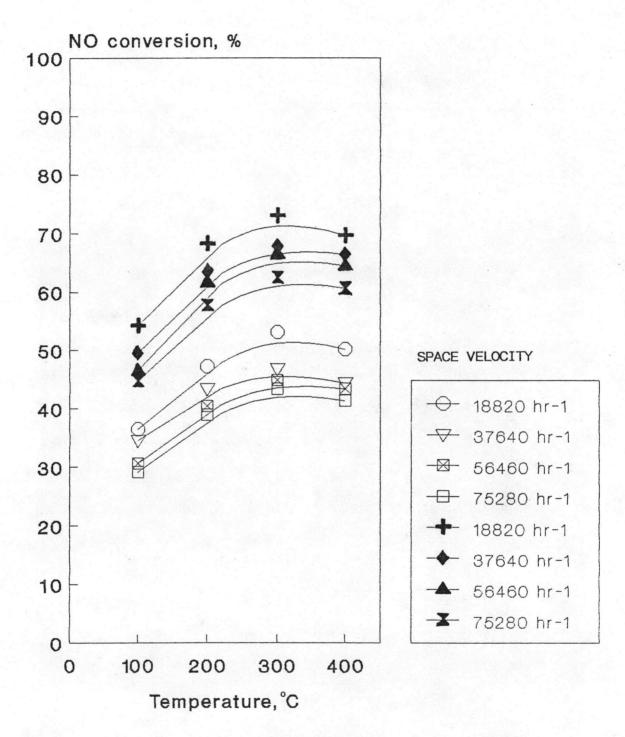
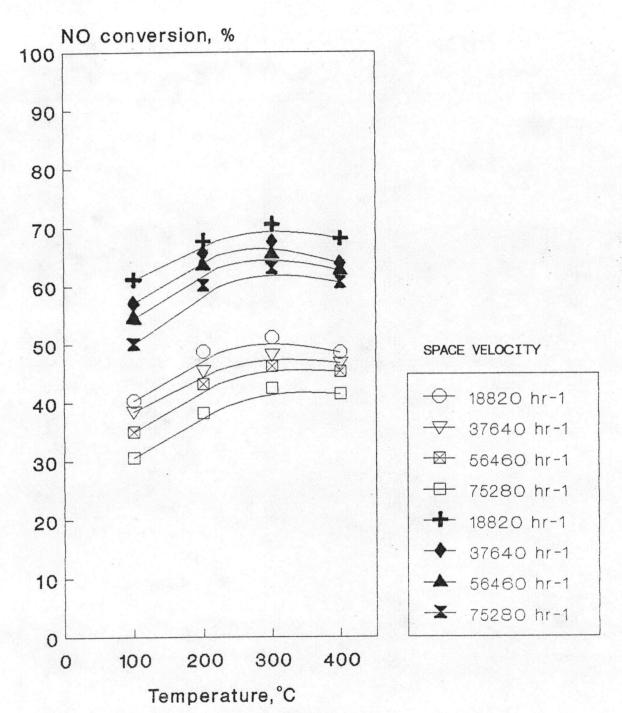
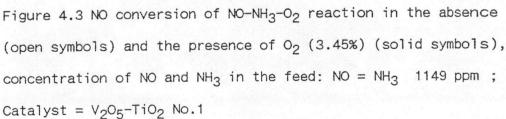


Figure 4.2 NO conversion of NO-NH₃-O₂ reaction in the absence (open symbols) and the presence of O₂ (3.45%) (solid symbols), concentration of NO and NH₃ in the feed: NO = NH₃ 1149 ppm ; Catalyst = Cu-Pt-HY





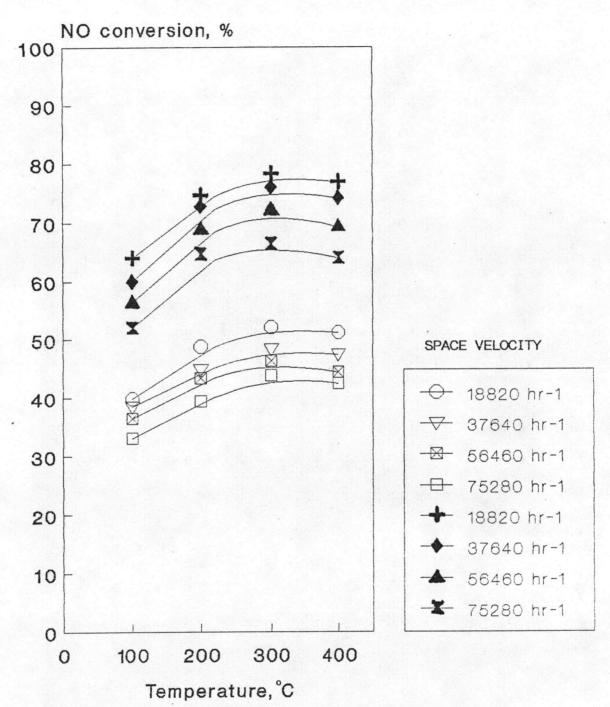


Figure 4.4 NO conversion of NO-NH₃-O₂ reaction in the absence (open symbols) and the presence of O₂ (3.45%) (solid symbols), concentration of NO and NH₃ in the feed: NO = NH₃ 1149 ppm ; Catalyst = V_2O_5 -TiO₂ No.2

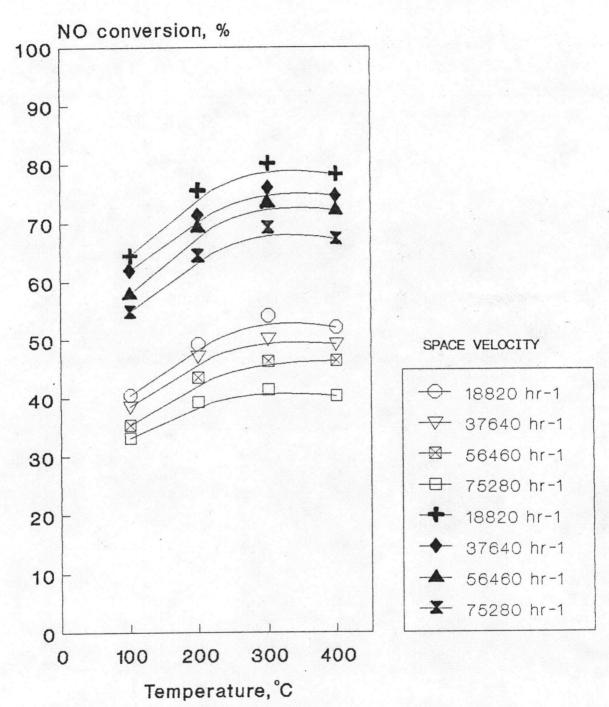
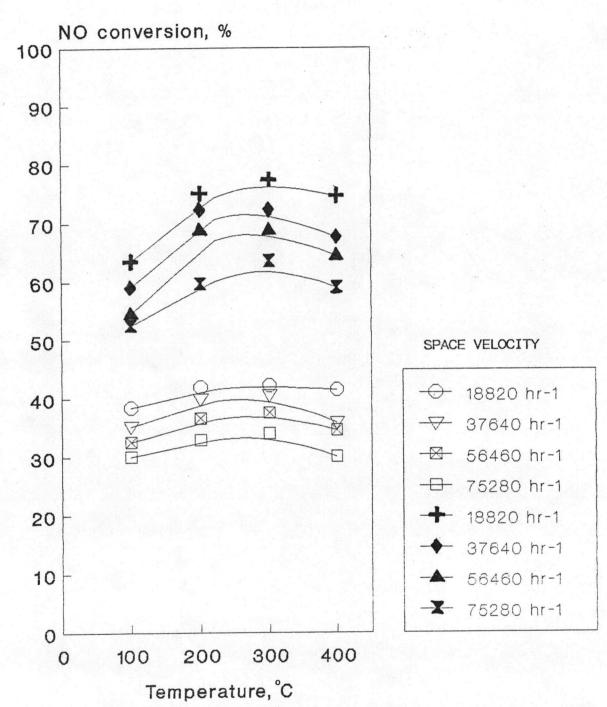
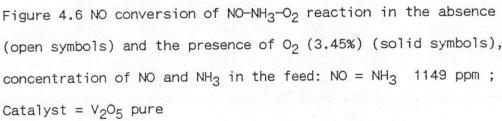


Figure 4.5 NO conversion of NO-NH₃-O₂ reaction in the absence (open symbols) and the presence of O₂ (3.45%) (solid symbols), concentration of NO and NH₃ in the feed: NO = NH₃ 1149 ppm ; Catalyst = V_2O_5 -TiO₂ No.3





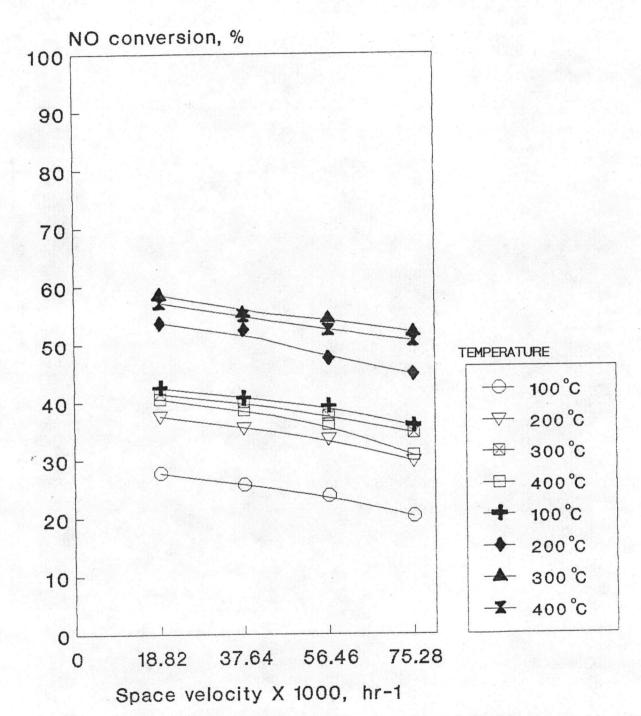


Figure 4.7 Effect of space velocity on NO conversion of NO-NH₃-O₂ reaction in the absence (open symbols) and the presence of O₂ (3.45%)(solid symbols) concentration of NO and NH₃ in the feed: NO = 1149 ppm, NH₃ 1149 ppm; Catalyst = Pt-HY

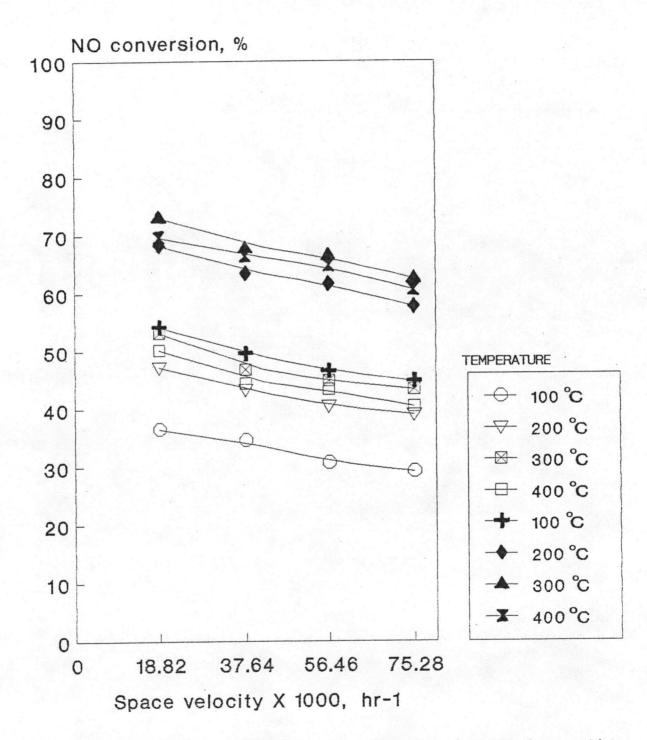


Figure 4.8 Effect of space velocity on NO conversion of NO-NH₃-O₂ reaction in the absence (open symbols) and the presence of O₂ (3.45%)(solid symbols) concentration of NO and NH₃ in the feed: NO = 1149 ppm, NH₃ 1149 ppm; Catalyst = Cu-Pt-HY

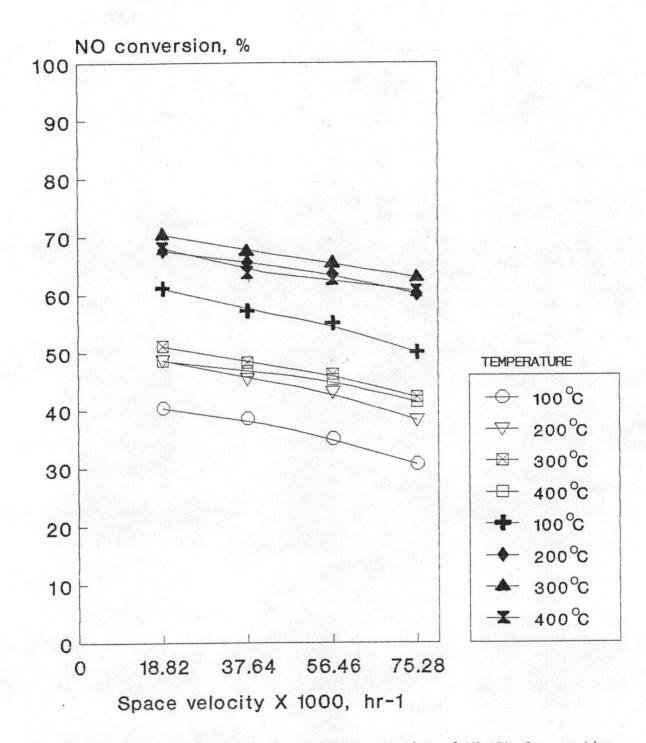


Figure 4.9 Effect of space velocity on NO conversion of NO-NH₃-O₂ reaction in the absence (open symbols) and the presence of O₂ (3.45%)(solid symbols) concentration of NO and NH₃ in the feed: NO = 1149 ppm, NH₃ 1149 ppm ; Catalyst = V₂O₅-TiO₂ No.1

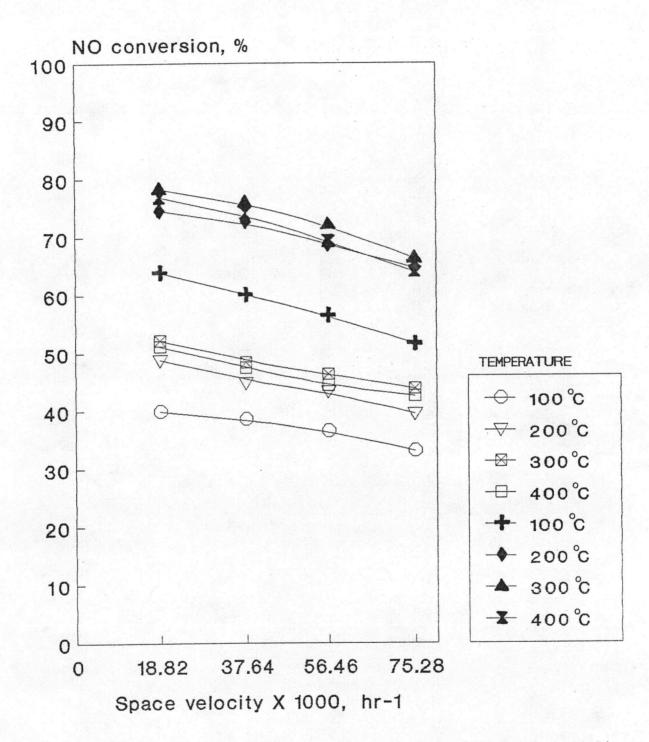


Figure 4.10 Effect of space velocity on NO conversion of NO-NH₃-O₂ reaction in the absence (open symbols) and the presence of O₂ (3.45%)(solid symbols) concentration of NO and NH₃ in the feed: NO = 1149 ppm, NH₃ 1149 ppm; Catalyst = V₂O₅-TiO₂ NO.2

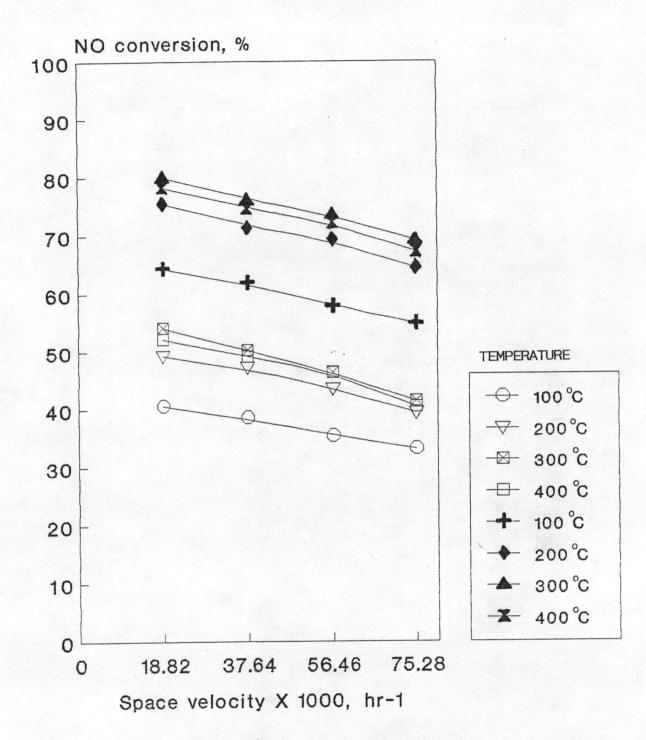


Figure 4.11 Effect of space velocity on NO conversion of NO-NH₃-O₂ reaction in the absence (open symbols) and the presence of O₂ (3.45%)(solid symbols) concentration of NO and NH₃ in the feed: NO = 1149 ppm, NH₃ 1149 ppm; Catalyst = V₂O₅-TiO₂ No.3

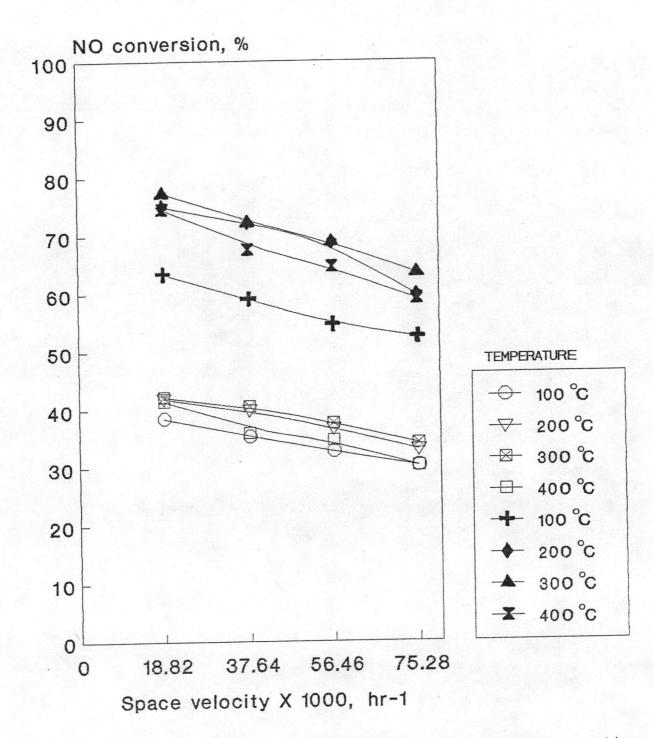


Figure 4.12 Effect of space velocity on NO conversion of NO-NH₃-O₂ reaction in the absence (open symbols) and the presence of O₂ (3.45%)(solid symbols) concentration of NO and NH₃ in the feed: NO = 1149 ppm, NH₃ 1149 ppm; Catalyst = V₂O₅ pure

SPACE VELOCITY 18820 hr-1

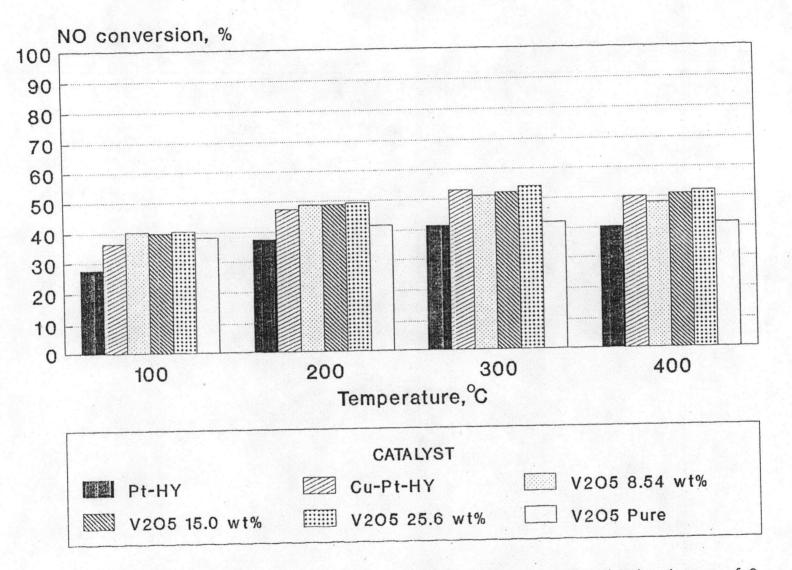


Figure 4.13 Catalytic activities of six catalysts on NO conversion in the absence of O_2 ; SV = 18820 hr⁻¹; concentration of NO and NH₃ in the feed : NO = 1149 ppm , NH₃ = 1149 ppm

SPACE VELOCITY 37640 hr-1

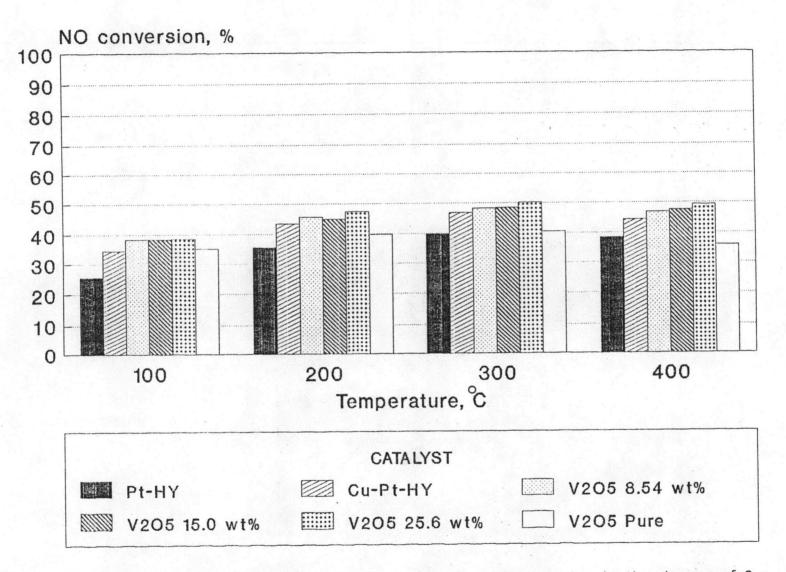


Figure 4.14 Catalytic activities of six catalysts on NO conversion in the absence of O_2 ; SV = 37640 hr⁻¹; concentration of NO and NH₃ in the feed : NO = 1149 ppm , NH₃ = 1149 ppm

SPACE VELOCITY 56460 hr-1

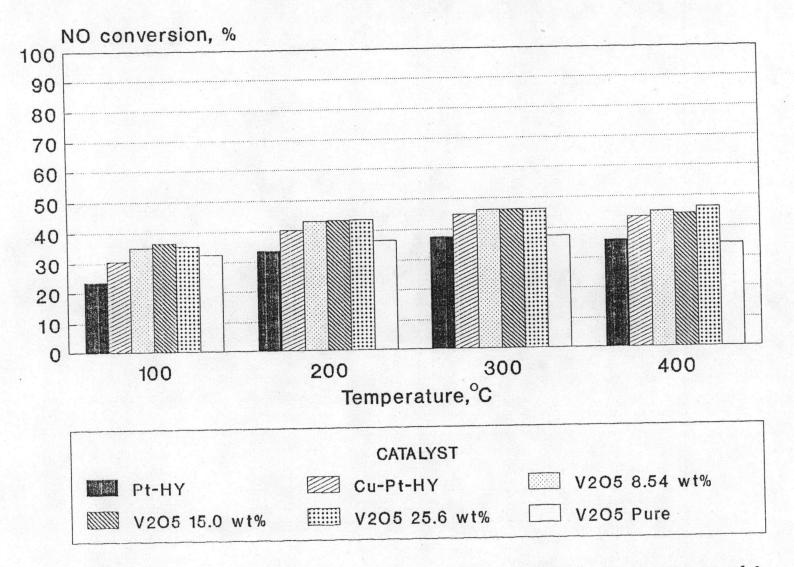


Figure 4.15 Catalytic activities of six catalysts on NO conversion in the absence of O_2 ; SV = 56460 hr⁻¹; concentration of NO and NH₃ in the feed : NO = 1149 ppm , NH₃ = 1149 ppm

SPACE VELOCITY 75280 hr-1

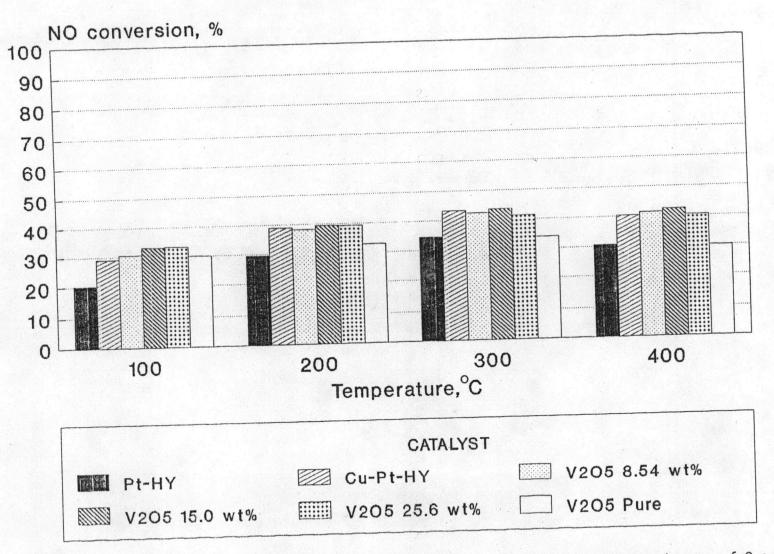


Figure 4.16 Catalytic activities of six catalysts on NO conversion in the absence of O_2 ; SV = 75280 hr⁻¹; concentration of NO and NH₃ in the feed : NO = 1149 ppm , NH₃ = 1149 ppm

SPACE VELOCITY 18820 hr-1

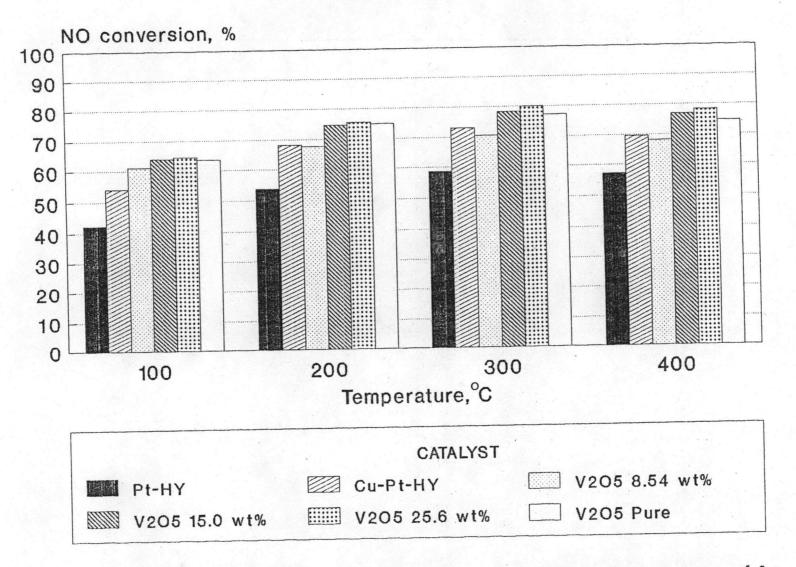


Figure 4.17 Catalytic activities of six catalysts on NO conversion in the presence of O_2 ; SV = 18820 hr⁻¹; concentration of NO and NH₃ in the feed : NO = 1149 ppm , NH₃ = 1149 ppm

SPACE VELOCITY 37640 hr-1

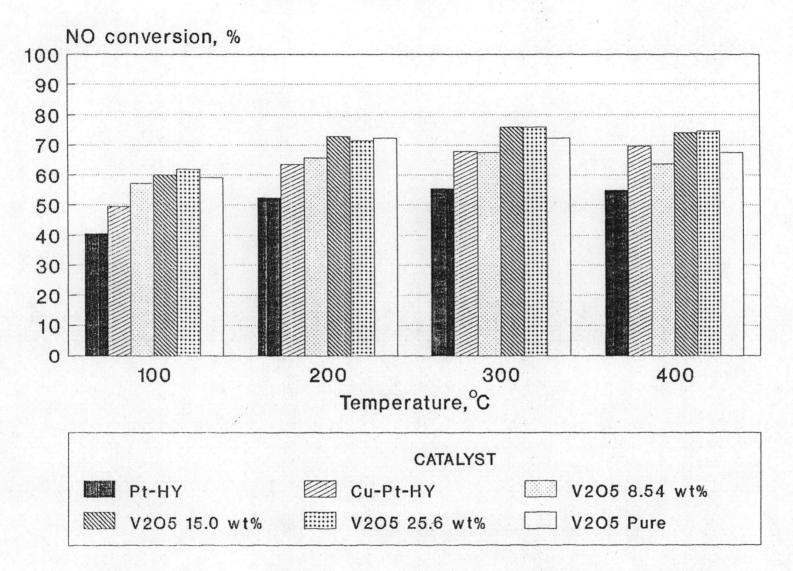


Figure 4.18 Catalytic activities of six catalysts on NO conversion in the presence of O_2 ; SV = 37640 hr⁻¹; concentration of NO and NH₃ in the feed : NO = 1149 ppm , NH₃ = 1149 ppm

SPACE VELOCITY 56460 hr-1

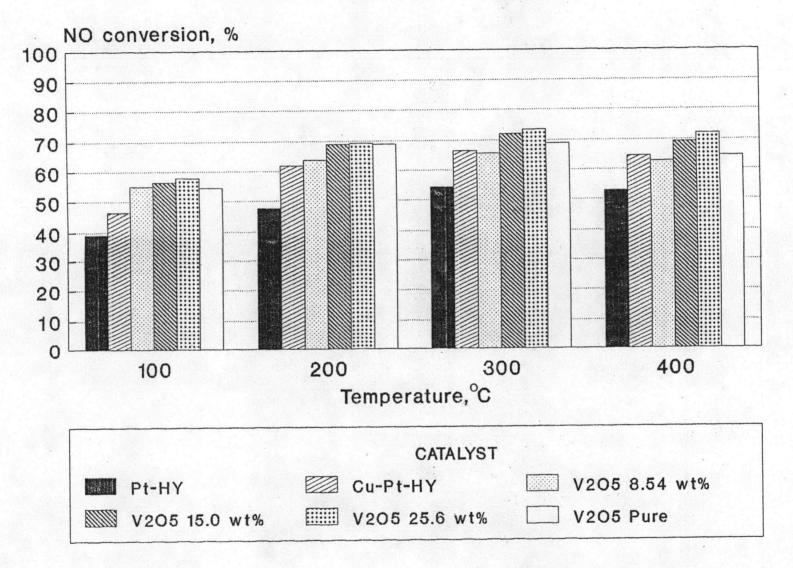


Figure 4.19 Catalytic activities of six catalysts on NO conversion in the presence of O_2 ; SV = 56460 hr⁻¹; concentration of NO and NH₃ in the feed : NO = 1149 ppm , NH₃ = 1149 ppm

SPACE VELOCITY 75280 hr-1

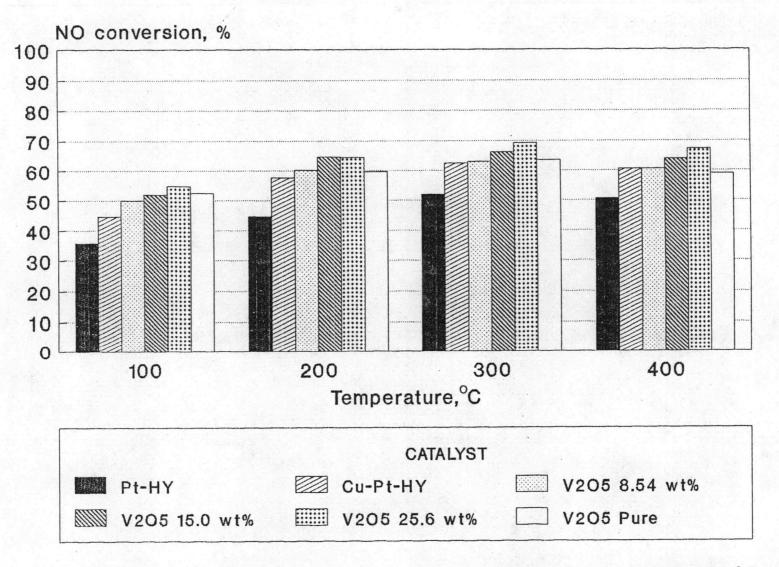


Figure 4.20 Catalytic activities of six catalysts on NO conversion in the presence of O_2 ; SV = 75280 hr⁻¹; concentration of NO and NH₃ in the feed : NO = 1149 ppm , NH₃ = 1149 ppm