CHAPTER V

RESULTS AND DISCUSSIONS

In this research, the selective hydrogenation of acetylene was carried out in a fixed bed reactor. An attempt has been made to improve the performance of palladium catalyst by alloying with silver serving as a promoter and adding nitrous oxide to the promoted catalyst. The results are catagorized into six parts as follows:

5.1 Selecting an optimum operating condition

The hydrogenation of acetylene in the presence of large excesses of ethylene was conducted at temperatures from 40 to 80 °C, gas hourly space velocities from 2000 to 7000 h^{-1} and atmospheric pressure. Of the metals which catalyse the hydrogenation of acetylene, Bond et al. [4] have shown that palladium has an outstanding ability to give a highly selective production of ethylene. Therefore, because of its superiority, the alumina-support palladium catalyst was used to determine the optimum operating condition. The reaction conditions as mentioned above were carried out after 48 hours on stream to establish the suitable condition. Temperature dependence of acetylene conversions at various space velocities is shown in Figure 5.1. As seen from the graph, acetylene conversion increases directly with temperature, i.e., temperature has a direct relationship with the kinetics of the system. This implies that increasing the temperature causes an increase in reaction rate because the kinetic energy of the system increases.

Figure 5.2 shows the selectivity to ethylene versus space velocity at various temperatures. The result indicates that the selectivity gradually increases as space velocity increases. Since the reactor volume is fixed, an increase in flow rate increases the space velocity. This means that a given volume of reactants travels through the reactor in a shoter time. This reduction in contact time or residence time effectively enhances the selectivity to ethylene. On the contrary, an increase in ethylene loss may occur at lower space velocity due to a longer period of contact

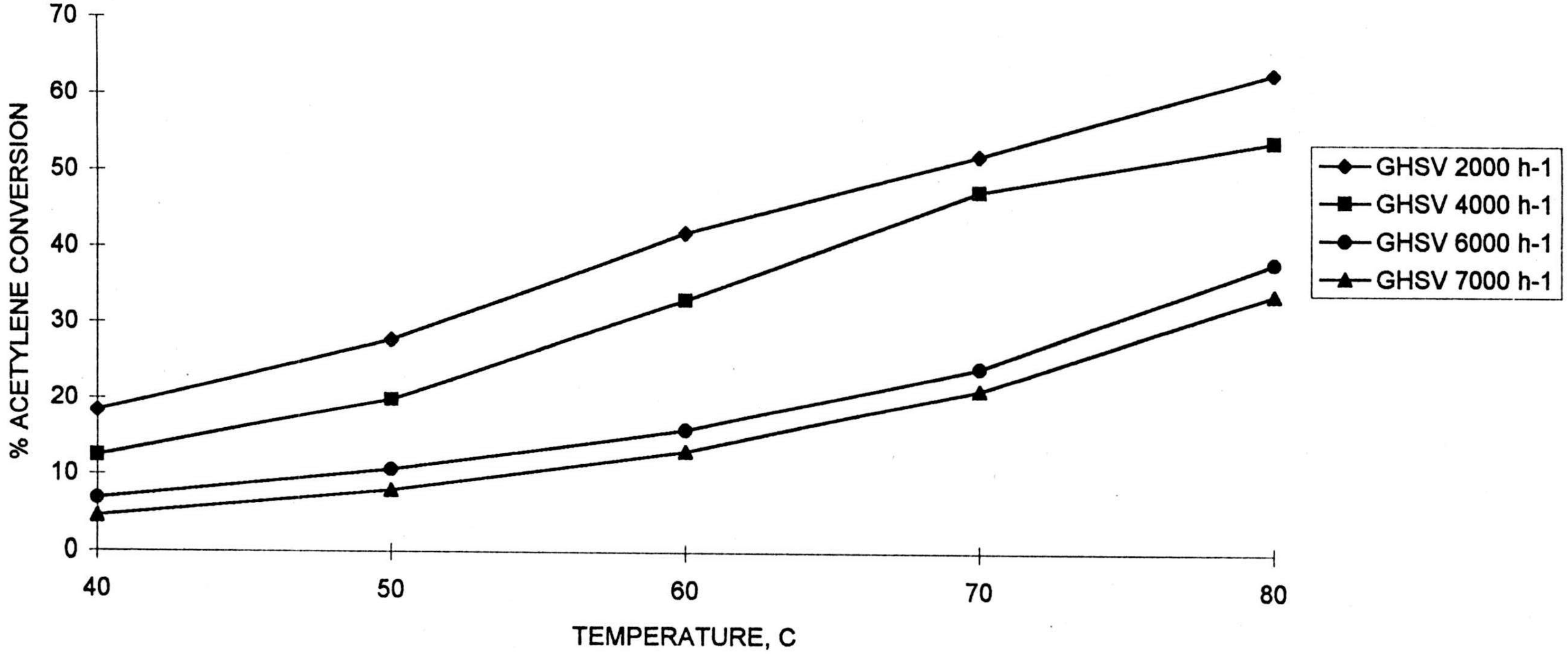


Figure 5.1 Temperature dependence of acetylene converrsions at various space velocities

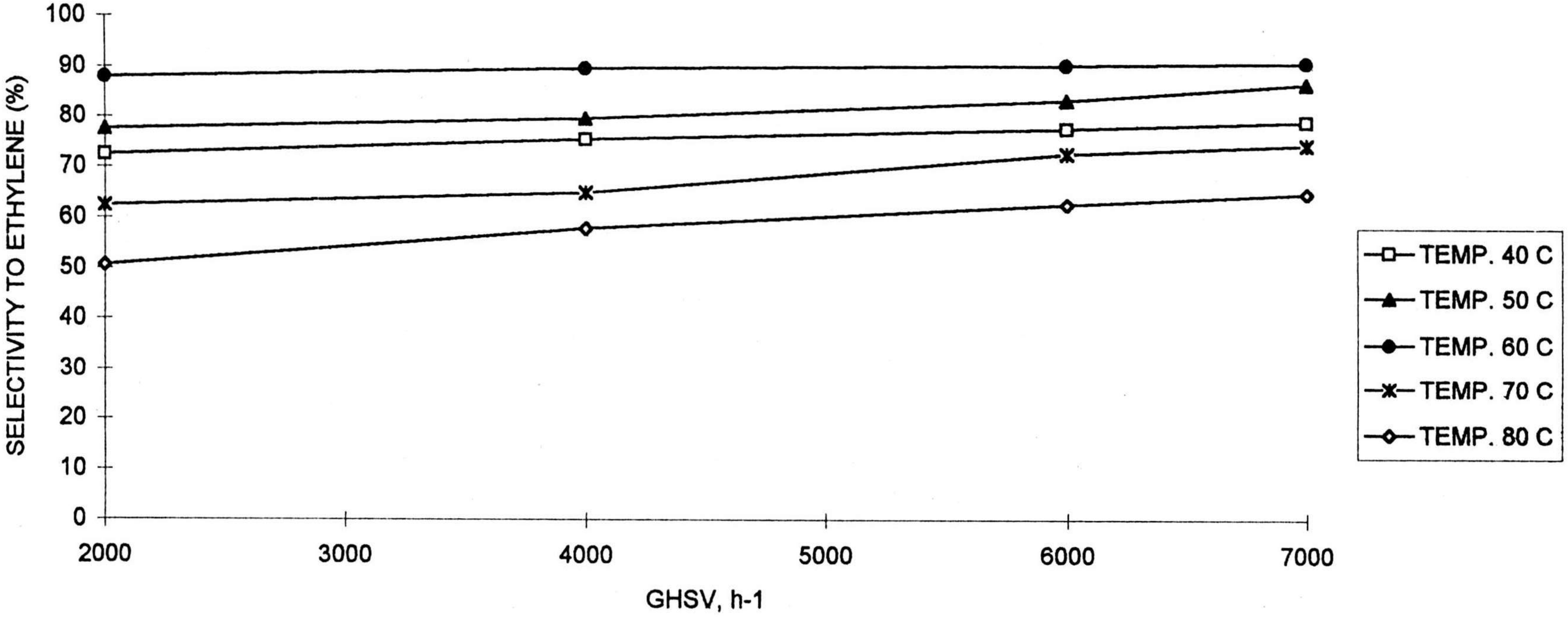


Figure 5.2 Selectivity to ethylene versus space velocity at various temperatures

time. Several aspects of the effect of temperature may be noted from the Figures. First, increasing temperature promotes the reaction rate resulting in high conversions of acetylene. A temperature of 60 °C promotes higher ethylene selectivities. Further increasing temperature (higher than 60 °C), however, decreases ethylene selectivity. This effect may be related to high kinetic energy. Even though increasing the temperature causes an increase in reaction rate of the system, the rate of undesired reaction also increases leading to lower selectivity. In this case, the latter seems to be dominant. Therefore, increasing the temperature exceeding 60 °C is probably beyond the optimal temperature.

As can be concluded from the above results, at 2000 h^{-1} and 60 °C the catalyst exhibits a better performance than any other condition considered. Therefore, the most suitable operating conditions (temperature and space velocity) should be 60 °C and 2000 h^{-1}.

The catalysts prepared hereinafter in this research were tested at 60 °C, 2000 h^{-1}, atmospheric pressure and time on stream 2 hours.

5.2 Effect of palladium loading

The performance of catalyst versus the amount of palladium loading ranging from 0.01 to 0.09 wt% is given in Figure 5.3. Increasing small amount of Pd loading on the catalyst increases the yield per pass (YPP). However, above 0.04 wt% Pd loading, a decrease in YPP takes place. The possible reason for this happening could be the closer distance between the active palladium sites. This increases the chance of the β-phase Pd-hydride formation [15] which has been found to be both more active and less selective than the more common α-phase, thus resulting in a decrease in the catalyst performance. The blank test using pure support instead of support with metal loading was also carried out. The result shows that support without metal loading causes no changes in acetylene hydrogenation.

5.3 Effect of a second metal

General feature of acetylene hydrogenation on supported Pd in the presence of large amount of ethylene and in the absence of carbon monoxide, is

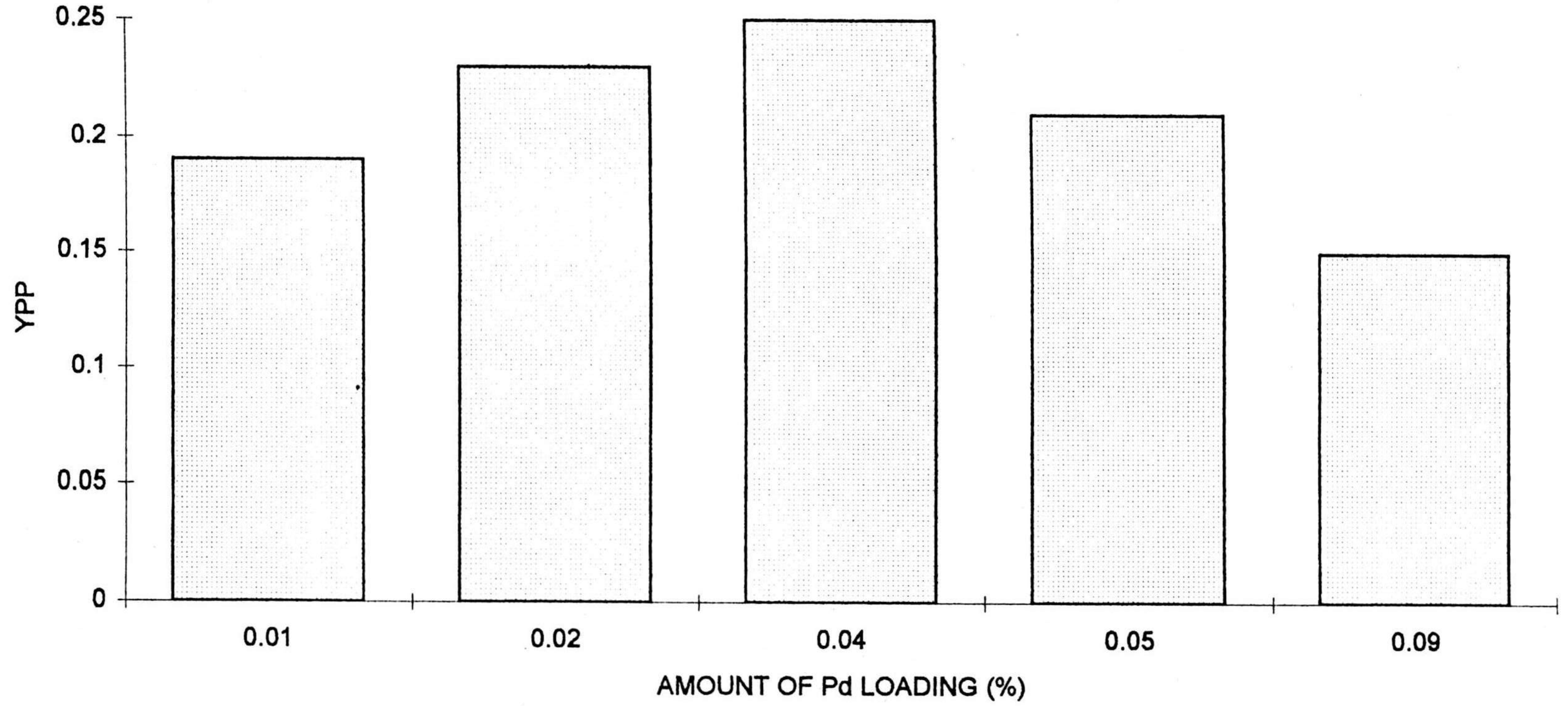


Figure 5.3 Performance of catalyst versus the amount of palladium loading in a range of 0.01 to 0.09 wt%

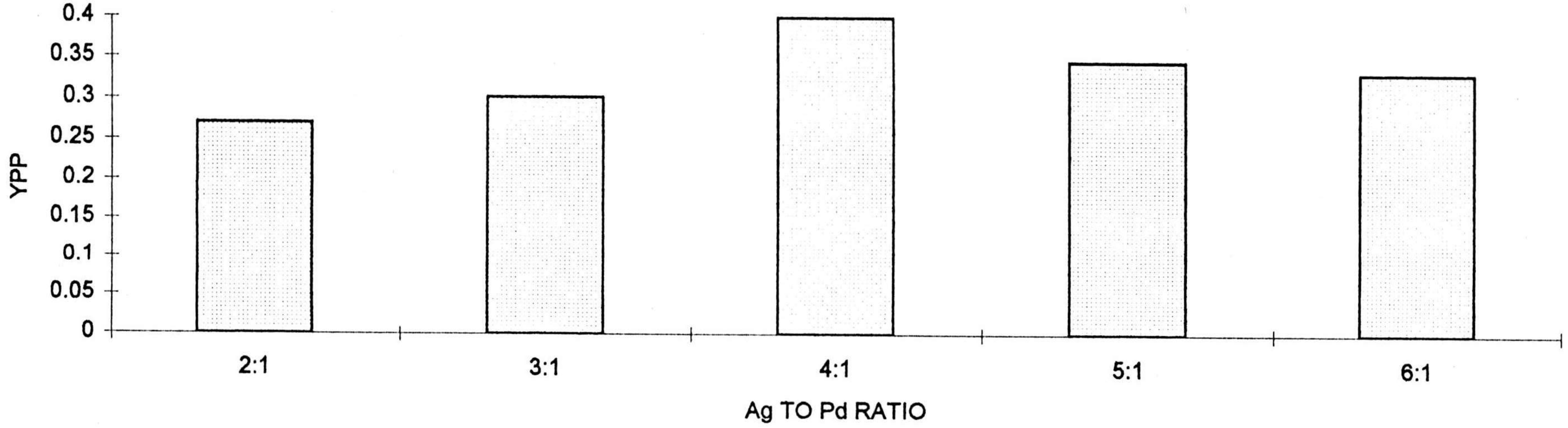


Figure 5.4 Effect of the addition of Ag with Ag to Pd ratio between 2:1 and 6:1 on the performance of catalyst

the formation of large amount of ethane. The non-selectivity can be slightly modified by the addition of a second metal (Ag) as shown in Figure 5.4. 0.04 wt% Pd/Al_2o_3 catalysts were impregnated with silver having Ag to Pd ratio ranging from 2:1 to 6:1. The YPP increases as the Ag to Pd ratio increases up to 4:1. A significant decrease in YPP is observed when Ag to Pd ratio is greater than 4:1. This might be because of a possible reason that exessive amount of silver could cause a depletion in the active palladium sites responsible for ethylene formation, hence, leading to a decrease in the perfomance of catalyst. Apparently, the performance of the silver-promoted 0.04 wt% Pd/Al_2O_3 catalyst is found to be higher than that of the unpromoted one. The two possible explanations for such phenomenon come from the following findings (Leveness et al., 1984):

1) Breakup of the Pd-H system which exists even on supported Pd. Borodzinski et al. [15] have shown that the β-phase Pd-hydride is both more active and less selective than the more common α-phase, which is more selective in acetylene hydrogenation. It has also been found that a palladium catalyst with a high degree dispersion was unable to form the β-phase and exhibited a high selectivity. For these reasons, If the β-phase exists at all on Ag-free catalysts, which seems unlikely due to the very low metal loading, it certainly does not exist on the Ag-containing catalysts.

2) Insertion of Ag into Pd matrix. This co-metal acts like an atomic spacer to increase the distance between the active palladium sites causing the number of multiple sites responsible for dissociative adsorption decreases. As a result, the amount of polymer and the amount of ethane formed directly from acetylene decrease. The former leads to a decrease in ethylene hydrogenation. This is because Ag insertion may provide desorption sites for spillover hydrogen; these sites would otherwise be active for ethylene hydrogenation.

5.4 Effect of nitrous oxide addition

In this part, attention was paid to investigate the influence of nitrous oxide on the nature of silver-promoted palladium catalyst. In other word, to find out whether it can improve the performance of catalyst. Figure 5.5 illustrates the

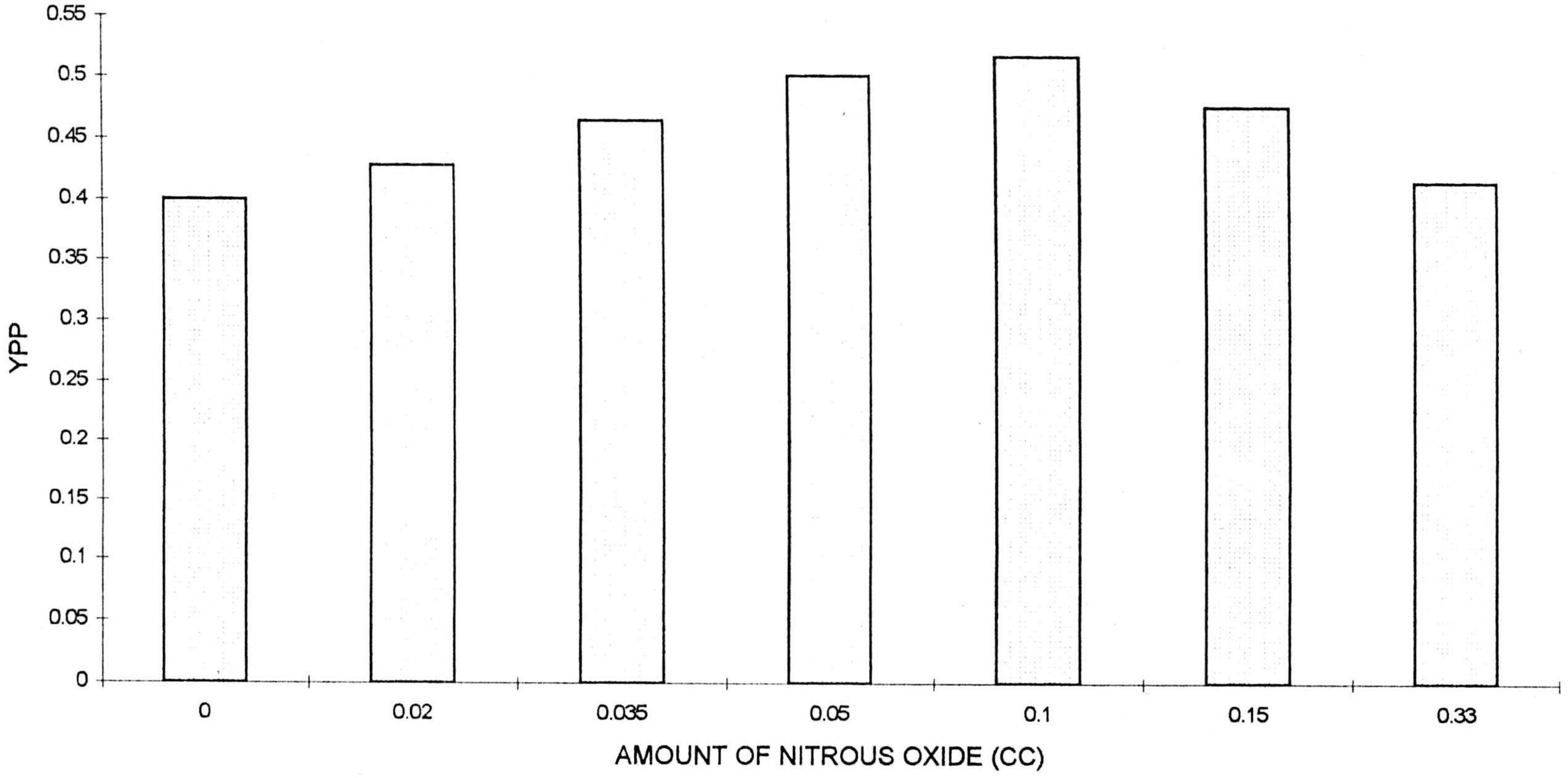


Figure 5.5 Performance of 0.04 wt% Pd-Ag/Al_2O_3 (Ag:Pd = 4:1) versus the amount of nitrous oxide ranging from 0.02 to 0.33 cc

performance of 0.04 wt% Pd-Ag/Al_2O_3 (Ag:Pd = 4:1) versus the amount of nitrous oxide addition ranging from 0.02 to 0.33 cc. Here, it is obvious that a small amount of added nitrous oxide (0.02 cc) has a positive effect on the catalyst performance. Increasing amount of nitrous oxide further increases YPP. During this nitrous oxide addition, YPP appears to go through a maximum value (0.1 cc) and a marginal decrease is observed above this value. This could probably be attributed to simultaneous Pd active sites opening and destroying, especially the sites responsible for ethylene production from acetylene.

5.5 Effect of catalyst aging

Figures 5.6 and 5.7 shows the effect of catalyst aging on acetylene conversion and on ethylene selectivity over both untreated and N_2O-treated 0.04 wt% Pd-Ag/Al_2O_3, respectively. As can be seen from the graph, both catalysts show similar results on aging; decreasing ethylene selectivity, while acetylene conversion does not change greatly during the course of time. After 60-100 hours of operation, both catalysts show an apparent steady state selectivity. It is obvious that when compared between untreated and treated catalysts the former exibits both lower activity and selectivity than those of the latter under the reaction conditions. The possible explanations to this result are given below.

It may be summarized from several previous investigations (Al-Ammar et al [6,7,8], Bernt et al. [9], Margitfalvi et al. [13,14], Moses et al. [16] and Weiss et al. [21]) that four main types of surface site are involved in the hydrogenation of acetylene and ethylene. Three types which are responsible for conversion of acetylene to ethylene, ethane production from acetylene and oligomer formation from acetylene are on the metal surface whereas the other which accounts for the hydrogenation of ethylene to ethane is on the support. A decrease in ethylene selectivity (increase in ethylene hydrogenation) during aging has been related to the amount of carbonaceous deposits on the catalyst surface [12,20] which apparently act as bridges promoting hydrogen spillover from Pd to the support. Acetylene hydrogenation and oligomerization, which occur on Pd sites, remain unaffected during this support activation. A decrease in ethylene hydrogenation on the support

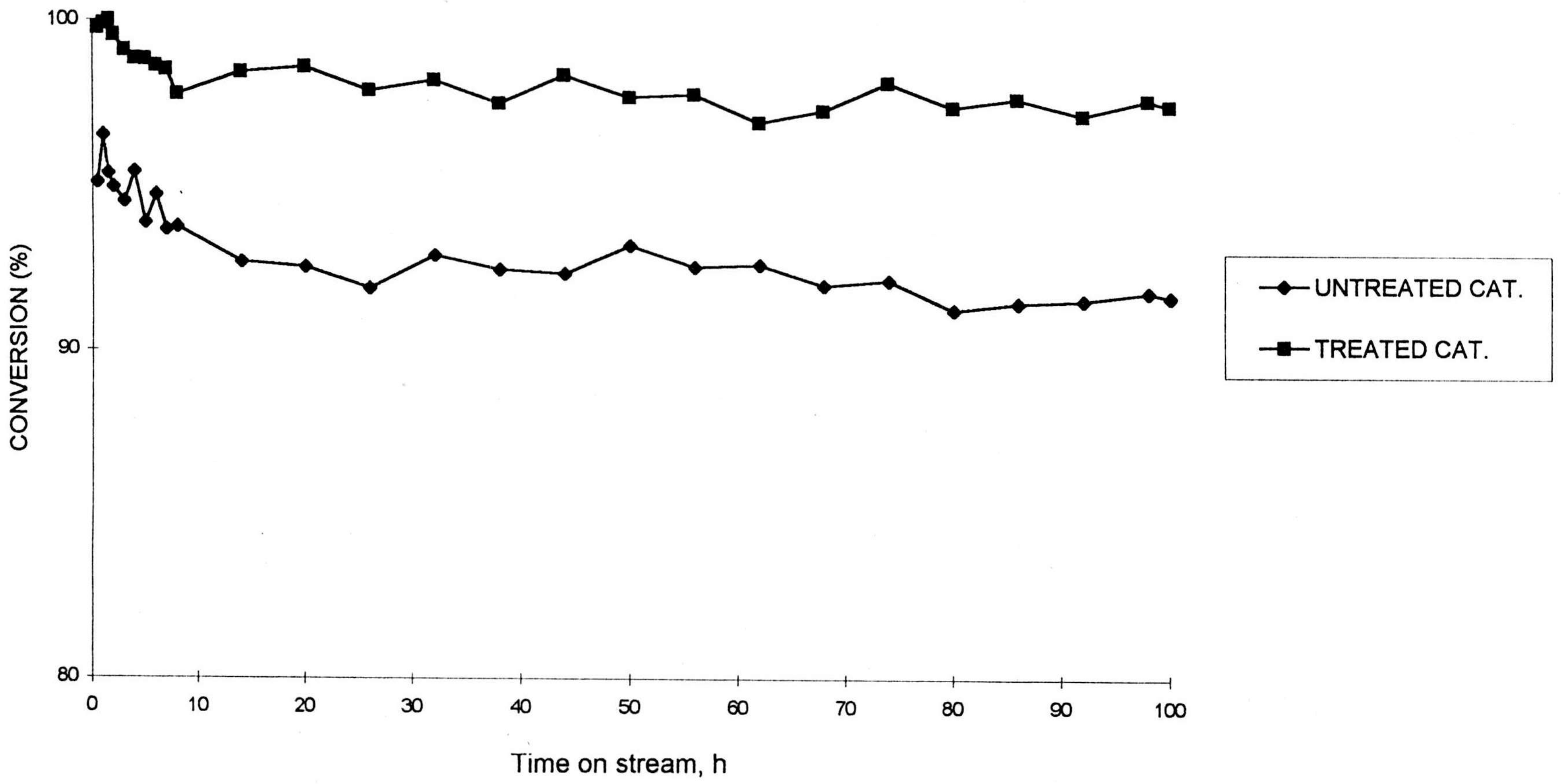


Figure 5.6 Effect of catalyst aging on acetyloene conversion over non-N_2O and N_2O Pd-Ag/Al_2O_3

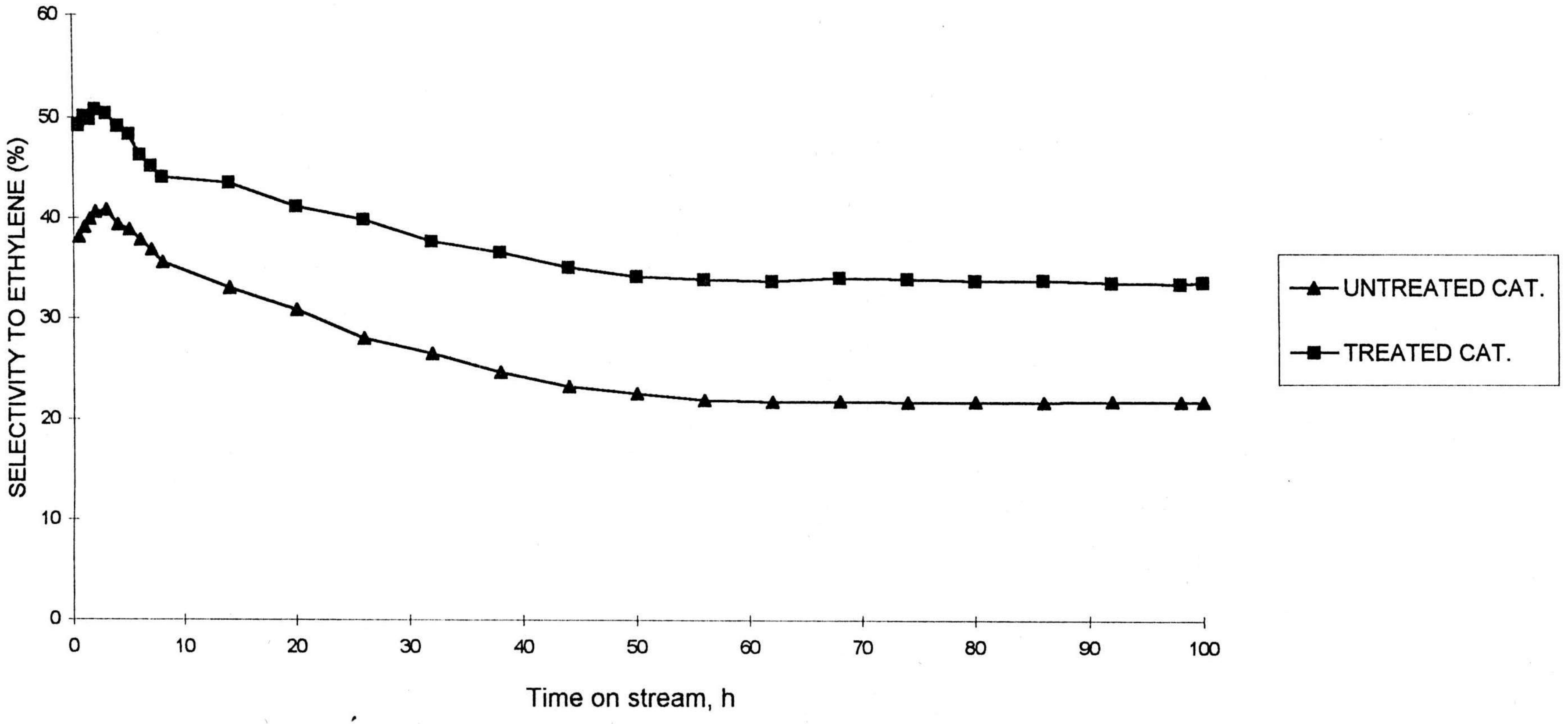
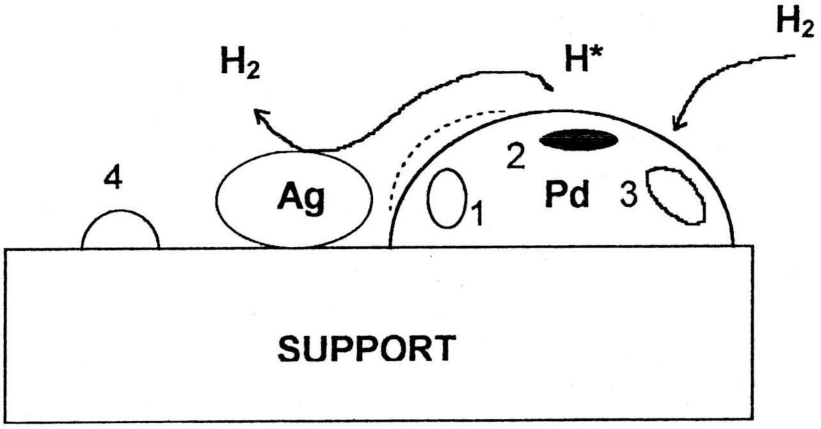


Figure 5.7 Effect of catalyst aging on ethylene selectivity over non-N_2O and N_2O Pd-Ag/Al_2O_3 catalyst



1 SITE FOR OLIGOMER FORMATION

2 SITE FOR DIRECT ETHANE FORMATION

3 SITE FOR ETHYLENE FORMATION

4 SITE FOR ETHANE PRODUCTION FROM ETHYLENE

.... CARBONACEOUS DEPOSIT BRIDGES

⬬ SITE COVERED BY Ag

Figure 5.8 Creation of a desorption site provided by Ag for spillover hydrogen migrating from metal to support by way of carbonaceous deposit bridges.

sites at steady state conditions upon the addition of Ag may be due to a reduction in the extent of hydrogen spillover for similar amounts of deposits, perhaps by providing desorption sites for spillover hydrogen which migrates from metal surface to support by means of carbonaceous deposit bridges illustrated as a model (Figure 5.8) postulated in section 3.9.

When untreated and treated catalysts are being compared, it is obvious that the catalyst with nitrous oxide addition exhibits both higher activity and selectivity than that without nitrous oxide throughout the course of reaction. It may be concluded from the evidence that the addition of nitrous oxide probably increases the sites responsible for ethylene production from acetylene and at the same time decreases the sites involving direct ethane formation from acetylene. In our case, the influence of the former prevails. Therefore, the untreated catalyst expresses high activity as well as does selectivity. Table 5.1 below shows comparison of various product compositions between 0.04 % Pd/Al_2O_3 and the above two mentioned catalysts at 5 minutes (initial stage) and at 44 hours on stream (long period of time). As can be seen from the 5-minute data, It can be interpreted with the assumption of no carbonaceous deposition on support that ethane shall be produced directly from acetylene rather than ethylene; i.e., only the sites on metal surface will be operative. When compared between base catalyst and promoted catalyst, the amount of ethane produced from acetylene in the former case is greater than that in the latter case. Also, the promoted catalyst exhibits acetylene conversion lower than that of the unpromoted one while the amount of ethylene is nearly the same. This implies that catalyst promoted by Ag improves selectivity probably by decreasing the site responsible for direct ethane formation from acetylene thus giving smaller amount of ethane. In case of N_2O catalyst, adding nitrous oxide to the promoted catalyst helps increase the amount of ethylene and at the same time decrease ethane formation while acetylene conversion is still higher. This implies that nitrous oxide addition augments the site responsible for ethylene formation and also reduces the site accounting for direct ethane formation. It should be noted that these explanations are in agreement with the above findings. At a longer period of time (44 hours on stream), however, the amount of ethane produced for the base catalyst is rather higher (increased by 5.67%) whereas the amount of ethylene and acetylene conversion show smaller values when compared to the promoted one. This may be due to carbonaceous deposit on catalyst surface of the base metal causing a decrease in acetylene conversion and at the same time ethylene itself can be further hydrogenated on the support to ethane leading to a decrease in selectivity. However, addition of a promoter (Ag) to catalyst will more or less enhance selectivity probably by providing desorption sites to spillover hydrogen. The amount of ethane formation is observed to increase by 0.85%. Again, we can obtain similar results for N_2O catalyst, i.e., a slight increase in the amount of ethane is found (0.71%) while the amount of ethyiene only slightly decreases.

Table 5.1 Raw chromatographic results; Conc% of hydrocarbon species

Feed			C_2H_2	C_2H_4	C_2H_6	CH_4
			0.2099	99.7708	0.0121	0.0072
Product	TOS	Catalyst	C_2H_2	C_2H_4	C_2H_6	CH_4
	5 min.	Base[A]	0.0037	99.8568	0.1321	0.0074
		Untreated[B]	0.0065	99.8566	0.1294	0.0074
		Treated[C]	0.0015	99.8784	0.1126	0.0073
	44 h	Base[A]	0.0192	99.8338	0.1396	0.0074
		Untreated[B]	0.0156	99.8465	0.1305	0.0073
		Treated[C]	0.0059	99.8731	0.1134	0.0075

[A] 0.04% Pd/Al_2O_3

[B] 0.04% $Pd\text{-}Ag/Al_2O_3$

[C] 0.04% $Pd\text{-}Ag/Al_2O_3$ treated with N_2O

5.6 Characterization of the catalyst

In this part, the catalysts were analysed by BET for surface area and CO - adsorption for metal site measurement. The results were as follows:

5.6.1 BET surface area

The data of BET surface area measurement is tabulated below.

Table 5.2 BET surface area measurement

Catalyst	BET (m^2/g)
0.04% Pd/Al_2O_3	4.74
0.04% Pd-Ag/Al_2O_3	4.11
0.04% Pd-Ag/Al_2O_3 (Aged, untreated)	4.36
0.04% Pd-Ag/Al_2O_3 (Aged, treated)	4.98

Table 5.2 shows the results of BET surface area. As can be obviously seen from the above tabulated results, the values of surface area of are rather constant among the test catalysts.

5.6.2 Metal active site measurement

The metal active site of catalyst was measured by CO adsorption technique and the results are shown in Table 5.3. As observed from the active site measurement results, it is apparent that silver-promoted Pd catalyst exhibits lower amount of active site than that of Pd catalyst. This may be due to alloy formation between both metals. It is also found that the addition of nitrous oxide to silver-promoted catalyst can enhance the amount of active site possibly by creating additional active sites on the metal thus resulting in higher conversion. Of all N_2O catalysts, promoted catalysts with 0.10 cc of N_2O gives the highest amount of active site (4.04×10^{17} site / gram of catalyst).

Table 5.3 The metal active site of catalyst measured by CO adsorption

Catalyst	Metal active site (site / gram of catalyst)
0.04 % Pd/Al_2O_3	3.30×10^{17}
0.04 % $Pd\text{-}Ag/Al_2O_3$	2.52×10^{17}
0.04 % $Pd\text{-}Ag/Al_2O_3$ (0.02 cc of N_2O)	3.14×10^{17}
0.04 % $Pd\text{-}Ag/Al_2O_3$ (0.035 cc of N_2O)	3.22×10^{17}
0.04 % $Pd\text{-}Ag/Al_2O_3$ (0.05 cc of N_2O)	3.70×10^{17}
0.04 % $Pd\text{-}Ag/Al_2O_3$ (0.10 cc of N_2O)	4.04×10^{17}
0.04 % $Pd\text{-}Ag/Al_2O_3$ (0.15 cc of N_2O)	3.37×10^{17}
0.04 % $Pd\text{-}Ag/Al_2O_3$ (0.33 cc of N_2O)	3.18×10^{17}