CHAPTER V

RESULTS AND DISCUSSIONS

In this research, it was purposed to increase activity of nickel catalyst by adding platinum. Small amount of platinum was used to promote nickel catalyst. Steps of study are devided in two 5 parts as follows.

A. To study the conditions for reducing catalyst : The reducing condition of nickel catalyst were studied. The suitable condition was those resulting in the highest activity or highest conversion of nickel catalyst

B. To study the sequence of metal loading influence on the activity of catalyst: Three preparation methods were studied: Impregnated platinum prior to nickel; co-impregnation of platinum and nickel; and impregnated nickel prior to platinum. These catalysts were tested to find out which preparation method would bring result in the highest activity.

C. To study the effect of platinum on the activity of nickel catalyst: Percentage of platinum loading were varied in the range of 0.5-2.0% Pt/Ni (metal/metal). The relation ship between benzene conversion (benzne hydrogenation) and platinum loading and synergistic effect on this platinum-nickel catalyst.

D. Characterization of catalyst :   It is better to

characterize the sites on surface of catalyst in order to explain how increasing of activity. Function of platinum on this catalyst was discussed in this section.

E. Surface area and metal loading measurment: This section was used to confirm that there are nickel and platinum on the catalyst and content of these metals in close to the calculated design value or not? what are the difference in the surface area of the individual catalysts?

5.1 Effect of Reduction Time

In this research the calcination temperature was fixed at 300 °C for 60 minutes, using a heating rate of 10 °C/minute. The reduction temperature was used at 400 °C. These conditions were those used in the work of Suphot [52] and the effect of reduction period on supported nickel catalyst was studied in micro-fixed bed reactor by benzene hydrogenation (see section 4.3.2). The reduction period was varied from 45 -120 min. The result are shown in Figure 5.1. At the shorter period of reduction (45-90 minutes), the activity, defined as conversion per gram of catalyst increased with time. On the other hand, the activity decreased with time when the reduction period was longer than 90 minites. From this result, it indicated that the maxinum activity would be obtained when the reduction time was 90 minutes at 400 °C. With the above-mentioned conditions, the maximum activity might have occured due to 8%Ni/Al₂O₃ undergoing the maximum reduction. When the reduction period was longer than 90 minutes, It might bring about sintering of nickel metal on support, finally resulting in losing activity
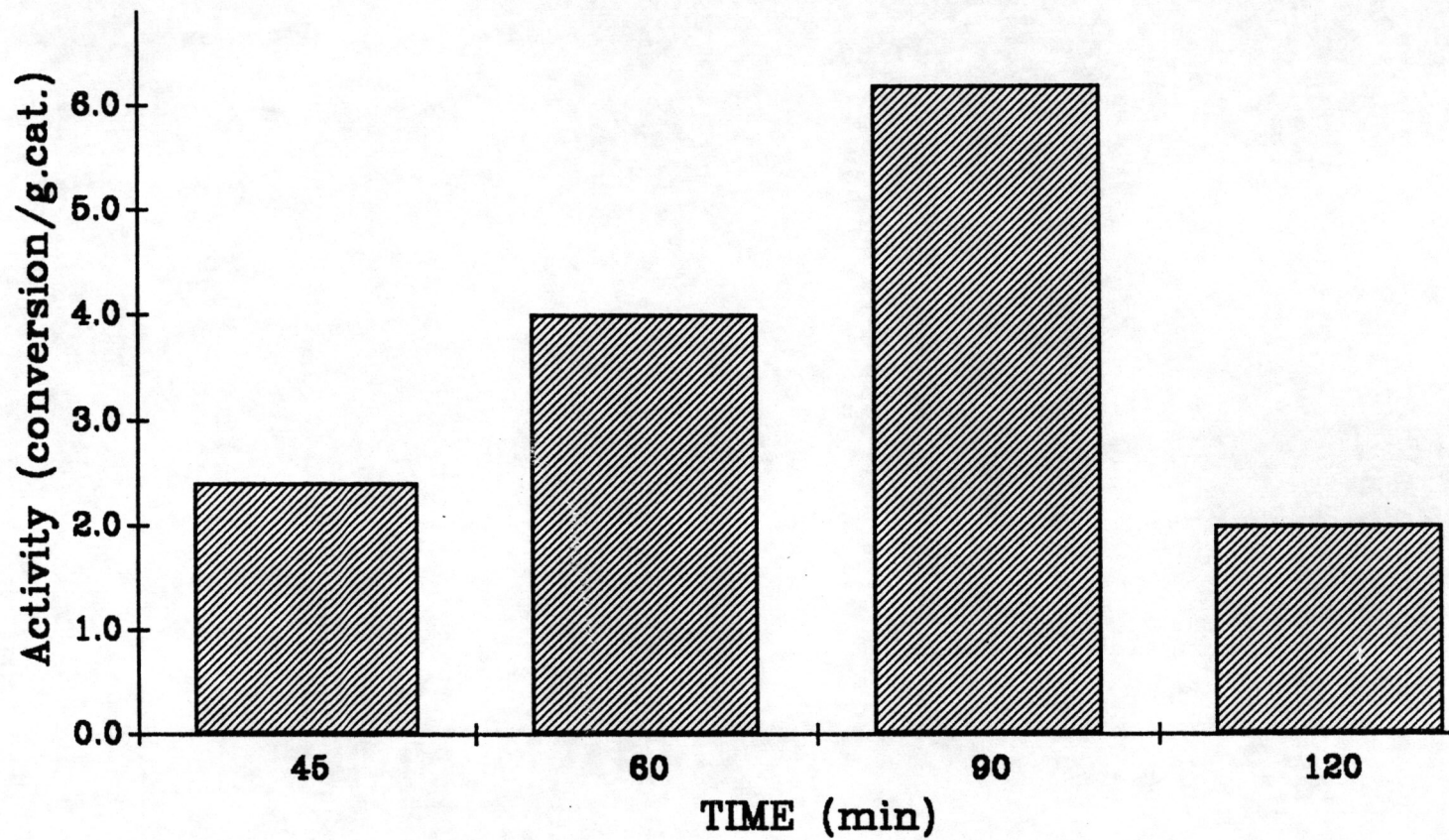
Fig. 5.1 Effect of reduction time, for 8%NI/Al₂O₃ catalyst, reduction
temperature = 400 ℃, calcined temperature = 300 ℃, heating rate 10 ℃/min.

5.2 Effect of Preparation Method

From this study, the order of the impregnation of platinum and nickel in catalyst preparation step is vary important and has influence on the activity of catalyst. Three catalysts, all of which were 0.5%Pt on 8%Ni/Al$_2$O$_3$, were prepared by different methods as shown in Table 5.1. The activity of the catalysts were tested by the same condition in section 5.1 with reduction time was 90 minutes. The results are shown in Figure 5.2. The catalyst of highest activity was CAT.C which was prepared by impregnating platinum prior to nickel.

Table 5.1 Catalysts and its preparation.

Catalyst		Preparation mothod
Cat.A	0.5%Pt-8%Ni/Al$_2$O$_3$	Impregnated Ni prior to Pt
Cat.B	0.5%Pt-8%Ni/Al$_2$O$_3$	Co-impregnated of Pt & Ni
Cat.C	0.5%Pt-8%Ni/Al$_2$O$_3$	Impregnated Pt prior to Ni

The differences in activity of three catalysts might have resulted from metal poisoning due to formation of surface metal chloride, or it enhance sintering via the formation of volatile metal chlorides [53]. In the perparation of CAT.C, chlorie was removed from the catalyst before impregnated with nickel. Therfore, CAT.A was largely affected by chlorides and lower on CAT.B, whereas effect of chloride was vary low on CAT.C.
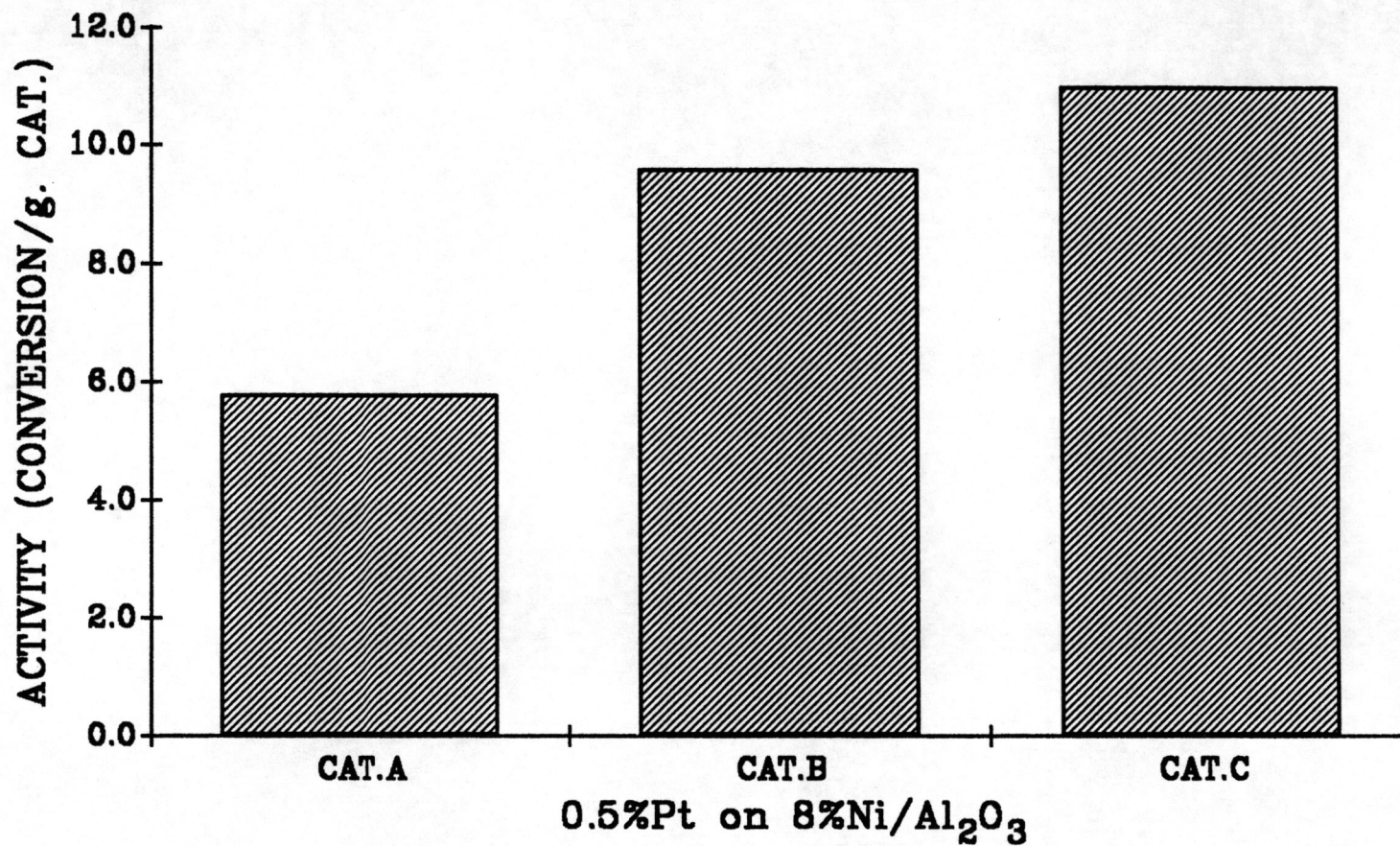
Fig. 5.2 Effect of preparation method, CAT.A = impregnated Ni prior to Pt,

CAT.B = co-impregnated of Pt & Ni, CAT.C = impregnated Pt prior to Ni.

5.3 Effect of Platinum on Nickel Catalyst

The impregnation of platinum incorporated with the nickel catalysts was consequently carried out. By varing the percentage of platinum loading (g.Pt/g.Ni), the effect of platinum presence and of platinum loading on the activity of nickel catalyst was studied in this section

The catalysts were prepared by the procedure as in section 4.3.3.2 using the best conditions from section 5.1, 5.2. The catalysts were impregnated with platinum in range of 0.5%-2.0% Pt/Ni and the detail is shown in Table 5.2

Table 5.2 The detail of the series of catalysts was used in this experiment

Name	Catalyst
P00	8%Ni/Al$_2$O$_3$
P05	0.5%Pt on 8%Ni/Al$_2$O$_3$
P05N	0.5%Pt/Al$_2$O$_3$ (amount of Pt is the same as P05)
P10	1.0%Pt on 8%Ni/Al$_2$O$_3$
P15	1.5%Pt on 8%Ni/Al$_2$O$_3$
P20	2.0%Pt on 8%Ni/Al$_2$O$_3$

All catalysts were tested by benzene hydrogenation reaction to study the effects on the activity of nickel catalyst which incorporated by small amounts of platinum.

The effect of platinum on the activity of nickel catalyst are shown in Figure 5.3. The activity of catalyst P05, P10, P15, and P20 were plotted in comparison with that of nickel catalyst (P00). In this section, the activity of the catalysts was presented by benzene conversion per gram of catalyst.

5.3.1 Effect of platinum on activity of nickel catalyst

It was apparent that the activity of nickel catalyst incorporated with platinum was higher than that of pure nickel catalyst. This was concluded due to the following results:

1) The activity of benzene hydrogenation of catalyst P05, P15 and P20 are higher than catalyst P00. This result is similar to the previous work of Nawak and Koros [19], who found that the hydrogenolysis of n-heptane was enhanced by platinum, incorporated in alumina supported nickel catalyst.

2) The activity of Pt-Ni catalyst in benzene hydrogenation reaction was increasing gradually with increasing of percentage platinum loading (see Fig. 5.3) from 0.5 - 2.0 %Pt/Ni. the effect of platinum on increasing conversion is shown in Figure 5.4, which indicated that higher percentages of platinum loading was not yield the effectiveness in line with lower percentage of platinum loading. The increasing in activity on higher platinum loading from 1.5-2.0% Pt may have been caused by platinum directly.
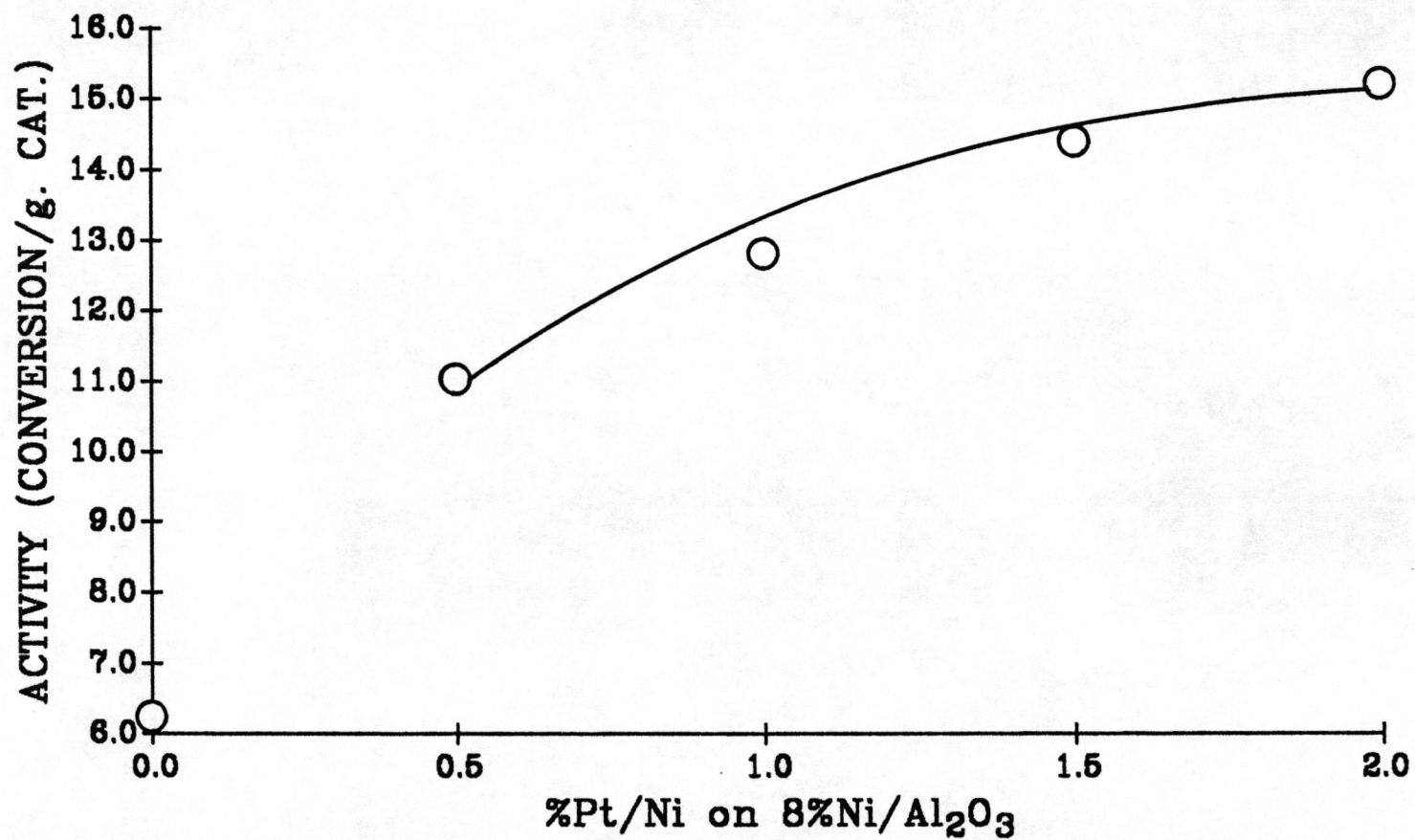
Fig. 5.3 Effect of platinum loading on the activity of 8%Ni/Al₂O₃, reaction
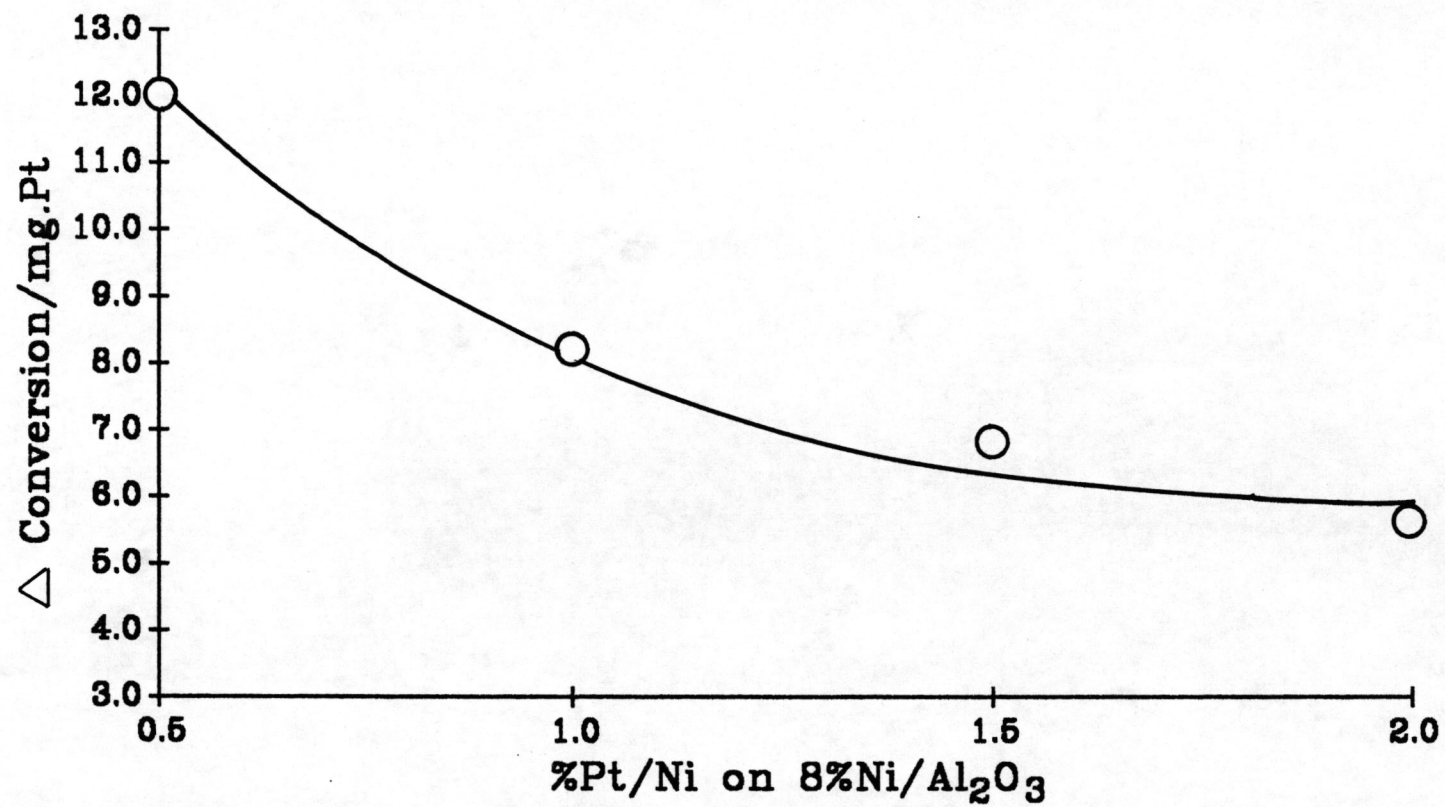temperature = 100 °C, hydrogen = 60 cm³/min, hydrogen:benzne = 89:2.

Fig. 5.4 Effeciency of loaded platinum on 8%Ni/Al$_2$O$_3$, reaction temperature = 100 °C,
hydrogen = 60 cm^3/min, hydrogen:benzne = 89:2.

5.3.2 Synergistic Effect

Synergistic effect was considered from the comparison between summation of activity of pure nickel catalyst and pure platinum catalyst and activity of platinum-nickel catalyst (amount of platinum and nickel was the same as pure nickel, platinum catalysts). If there is the synergistic effect occur in the catalyst preparation, the activity of platinum-nickel catalyst must be superior than that of the summation of activity of the pure nickel, platinum catalysts. To prove that there is synergistic effect, the catalysts P00, P05, P05N were used and the result as shown in Figure 5.5.

From figure 5.5, the highest activity was catalyst P05 when comparing with summation of catalyst P00+P05N. This must be the activity of synergistic effect from the preparation by impregnating platinum from the preparation by impregnating platinum prior to nickel on the same support. The synergistic effect of this system can be seen from the amount of difference between peak P05 and peak P00+P05N. Thus synergistic effect occured only when the nickel catalyst was incorporation with a small amount of platinum on alumina support.

With the above results it has been assumed of three possible causes which induce to the increaseing of activity of the catalysts when incorporated with platinum, as follows:

1) A lot of metal sites in the catalyst were increased by platinum.

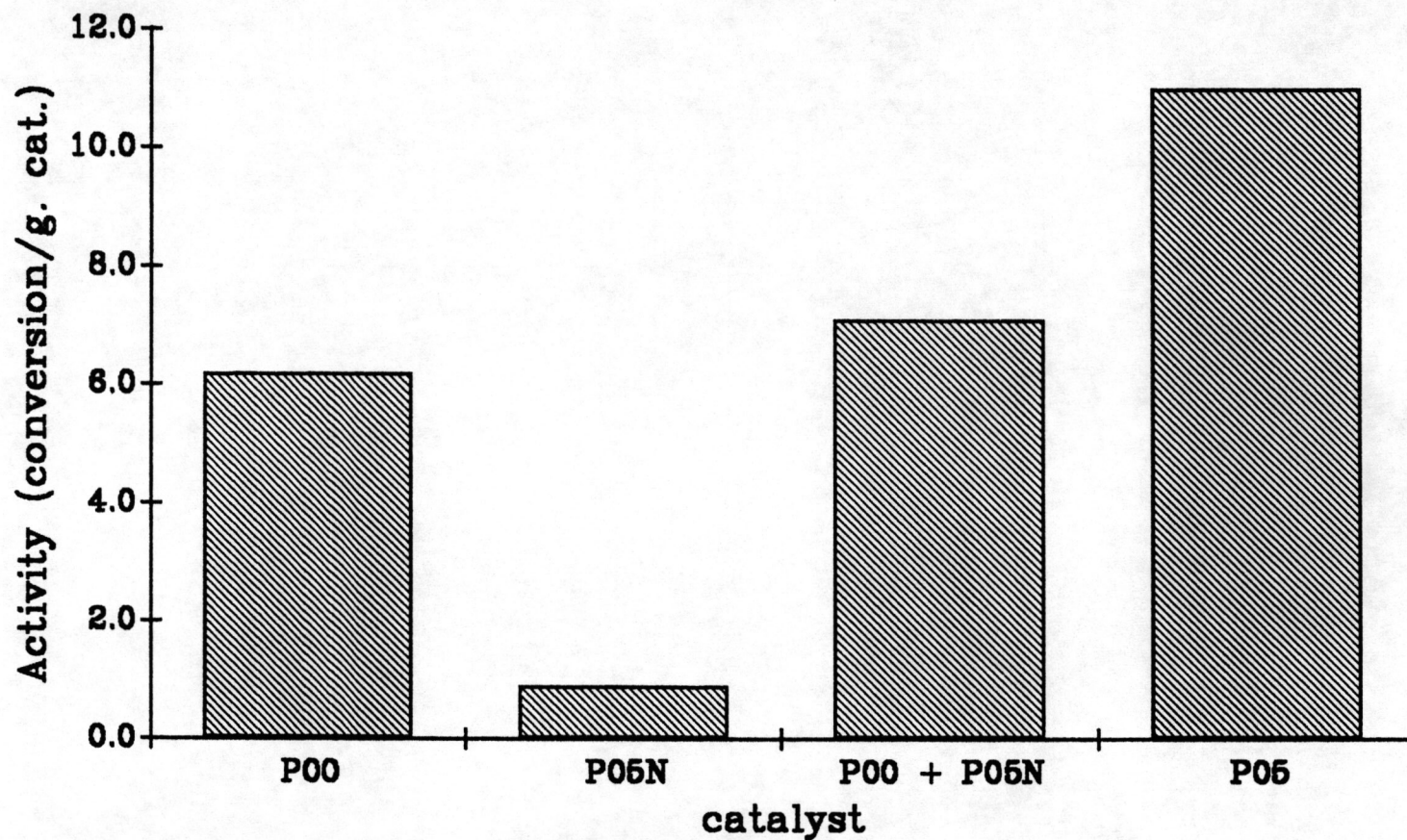2) The turnover number (TON) of catalyst was increased by platinum

Fig. 5.5 Synergistic effect by 0.5%Pt/Ni on 8%Ni/Al$_2$O$_3$, P00 = 8%Ni/Al$_2$O$_3$, P05N = 0.5%Pt on Al$_2$O$_3$, P00+P05N = summation of P00 and P05N, P05 = 0.5%Pt on 8%NiAl$_2$O$_3$.

3)   Both TON and metal sites were increased by platinum

The following exercise has been done to define the above possible causes.

5.4 Active Site Analysis

5.4.1 Metal Site

Generally, activity of catalyst is a function of metal site. Therefore, in order to find the cause of the increase in activity of nickel catalyst with incorporated platinum (Fig 5.3), metal site measurement was necessary to characterize these catalysts. CO-adsorption technique was used for the measurement. It was assumed that the ratio of adsorbed CO : Site was 1:1 and adsorption of CO was irreversible. The measurement procedure was explained in section 4.3.1. The result of metal site measurement was shown in Figure 5.6. A lot of sites were increased by platinum, $3.12*10^{19}$ site per gram of catalyst when 0.5% platinum incorporated with nickel catalyst. For 1.0-2.0% platinum loading, the sites were increased in straight line pattern (see Fig. 5.6). The cause of site increase were; (i) platinum sites which was incorporated in the nickel catalyst but very little ($>0.1810^{19}$ site/g cat/0.5%Pt), (ii) due to small amount of platinum catalysing hydrogen reduction of supported nickel oxide [19]. Therefore, increasing site on nickel metal by platinum could be concluded as a model which is shown in Figure 5.7. This model used the concept of spillover hydrogen of Hodnett [36] in section 3.4.
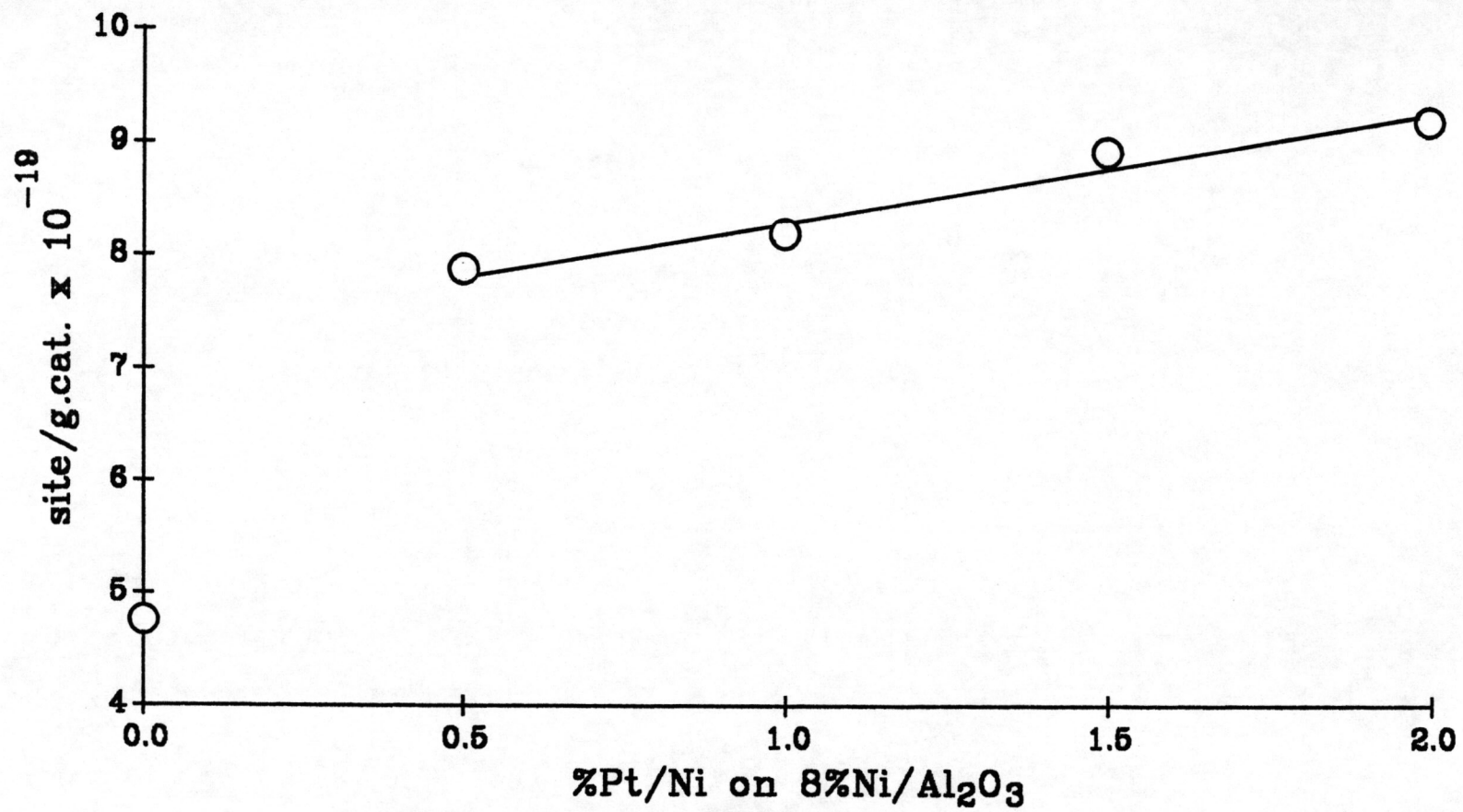
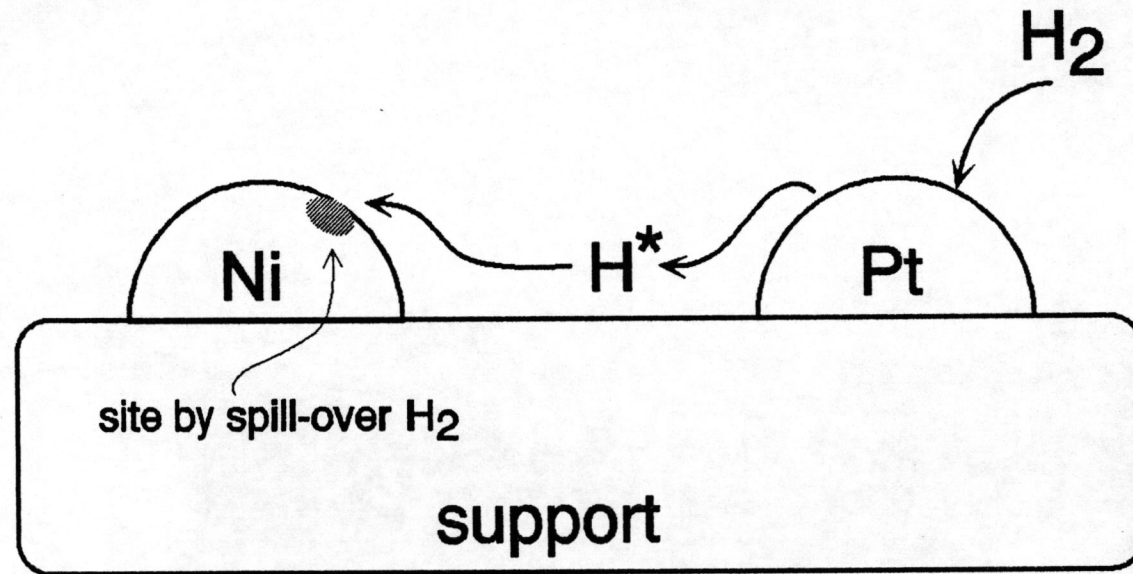Fig. 5.6 Effect of platinum on site of catalysts. He = 30 cm³/min, adsorbed temperature = 30 ℃.

Fig. 5.7 Creation of an active site on nickel surface by
spill-over hydrogen from platinum.

5.4.2 Turnover Number (TON)

Amount of sites which was determined by CO-adsorption technique in section 5.4.1 and benzene conversion in section 5.3 were used to calculate turnover number (TON). The TON of various catalysts is shown in Figure 5.8. The increase of TON on nickel catlayst which was promoted by platinum can be devided into two intervals: First interval, TON increased rapidly by loading platinum on nickel catalyst in the range of 0.5-1.0% (Pt/Ni); and second interval, TON increased slightly and gradually with platinum loading in the range of 1.5-2.0% (Pt/Ni).

The result of TON increase in Fig 5.8 indicated that the increment in activity (in Fig. 5.2) was not only from the influence of increasing in site. If the activity was increased directly by the influence of the increasing of site, Then TON must be constant no matter what catalyst were used. Therefore, there must be some other effects from platinum on nickel catalyst.

As explained in section 5.4.1 and section 5.4.2, it can be seen that the site was increased by adding platinum into nickel catalyst and the site increase was not from the direct influence of the activity of catalyst alone. In order to find out the cause of TON increase therefore other parameter were also brought into consideration as well, i.e. adsorption of reactants of benzene hydrogenation reaction. In the next experiment all conditions were fixed to study the adsorption of the reactants, hydrogen and benzene, on surface of catalyst. these adsorbed species must be considered as the effecting parameter.
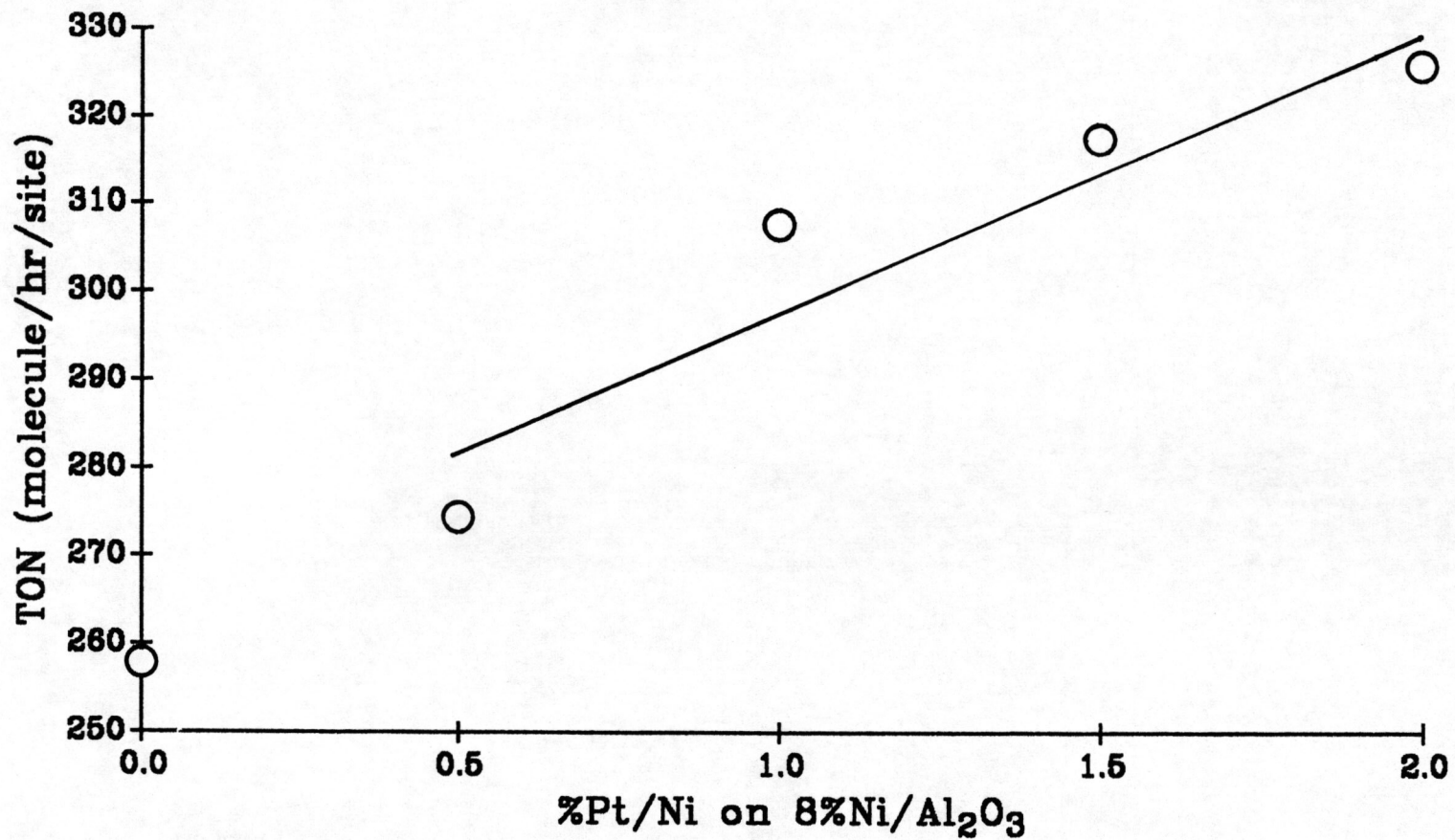
Fig. 5.8   Effect of loaded platinum on TON. Persentage of platinum loading
in range of 0-2.0% (Pt/Ni).

5.4.3 Hydrogen adsorption

Hydrogen adsorption was measured by method which was discribed in section 4.3.2. adsorbed hydrogen by this method was irreversible adsorbed hydrogen. The result of adsorbed hydrogen is shown in Figure 5.9. The tendency of increasing was the same as that of the increasing site (Fig. 5.6). A lot of the adsorbed hydrogen was increased by incorporating 0.5% platinum into the nickel catalyst and then the adsorbed hydrogen increased slightly and gradually with platinum loading in the range of 1.0-2.0%. From this result,it could not be explained about the phenomena of an increasing TON which was discribed in section 5.3.2, so that adsorbed hydrogen per site was calculated as shown in Figure 5.10. The adsorbed hydrogen per site was rather constant for all catalysts. It indicated that adsorbed hydrogen was increasing directly with the site. Therefore, the TON increase in Figure 5.8 was not from the influence of the adsorbed hydrogen.

5.4.4 Adsorbed Benzene

Two types of benzene can be adsorbed on the surface of nickel catalyst, non-reactive adsorbed benzene and reactive adsorbed benzene [12]. Non-reactive adsorbed benzene can not react with hydrogen on the surface of catalyst so that this adsorbed form is not involve in the increase of TON. The reactive adsorbed benzene can react with hydrogen to form cyclohexane, Thus this adsorbed form may be involved in an increasing of TON. Measurement method of reactive adsorbed benzene was discribed in section 4.3.3. The result is shown in Figure 5.11. A lot of reactive adsorbed benzenes increased with 0.5% platinum loading and varied with % Platinum
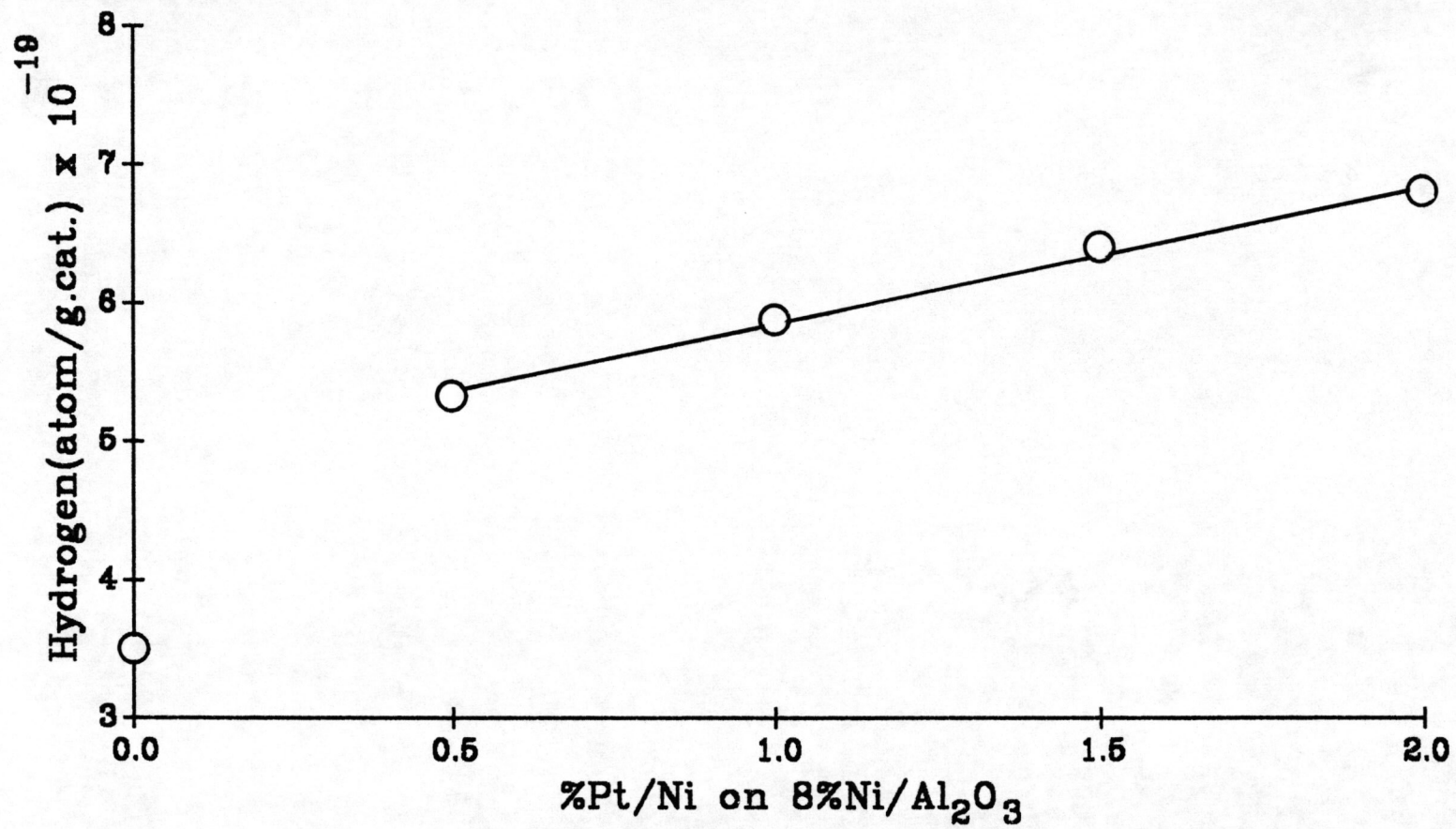
Fig. 5.9 Hydrogen adsorption on the catalysts. Ar = 30 cm³/min, adsorbed temperature = 30 °C.
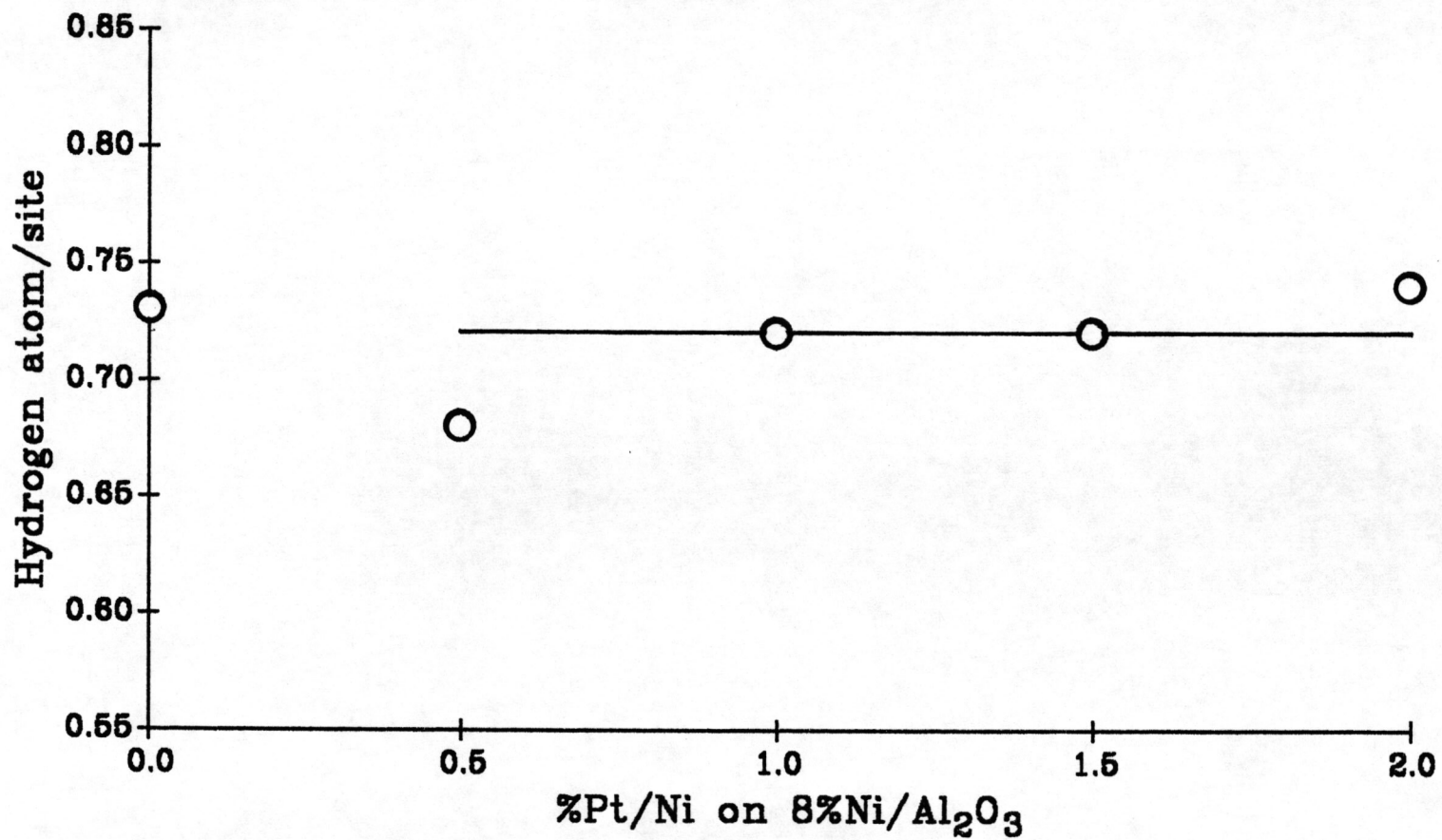
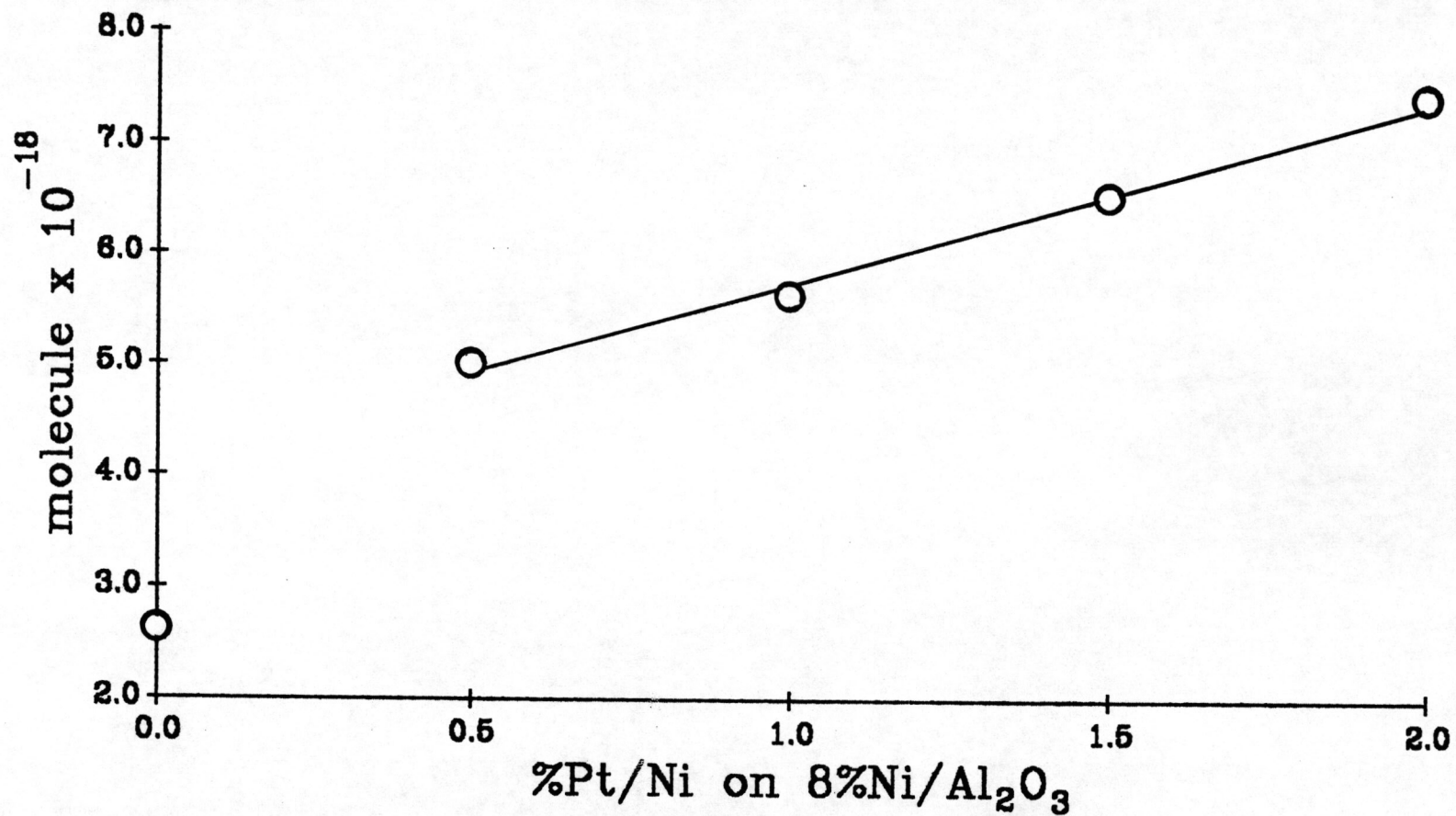Fig. 5.10 Ratio of adsorbed hydrogen per site of catalyst.

Fig. 5.11 Effect of loaded platinum on reactive adsorbed benzene.

He = 50 cm^3/min. reaction temperature = 100 $^\circ$C.

loading. The increase of reactive adsorbed benzene was similar to the increasing site (Fig. 5.6). The ratio of reactive adsorbed benzene to site is shown in Figure 5.12. This indicates that reactive adsorbed benzene per site increased proportionally with percentage platinum loading. It could be conclude that the platinum could promote to increase the site of catalyst for the adsorption of reactive adsorbed benzene. To explain further about the increase of TON, the ratio of TON to the reactive adsorbed benzene pre site of the individual catalysts are calculated and shown in Figure 5.13. This ratio was quite the same for every catalysts. Therefore it could be concluded that the increase of the TON was definitely come from the reactive adsorbed benzene. The ratio of TON to reactive adsorbed benzene per site was nearly constant for all catalysts. So, it could be concluded that the increase of TON result from the increasing reactive adsorbed benzene caused by platinum.

The above-mentioned results, it shows that platinum promotes an adsorption of reactive adsorbed benzene which, in turn, caused of the increase of TON. The work of Mirodatos et al. [14] descirbed that an ensemble of about 4 nickel atoms occupied by a chemisorbed molecule of benzene (this benzene would be supplied by the loosely adsorbed resevoir that coats the whole surface of the catalyst, the chemisorption occuring as soon as suitable sites appear on the nickel surface) and then react with hydrogen to cyclohexane. This work match with the work of Marecot et al. [12] who had found that there were two types of adsorbed benzene, non-reactive adsorbed benzene and reactive adsorbed benzene. From those papers and this experiment, we were able to conclude that the platinum promotes an adsorption of reactive adsorbed benzene by increasing the suitable ensemble sites on the catalyst. This
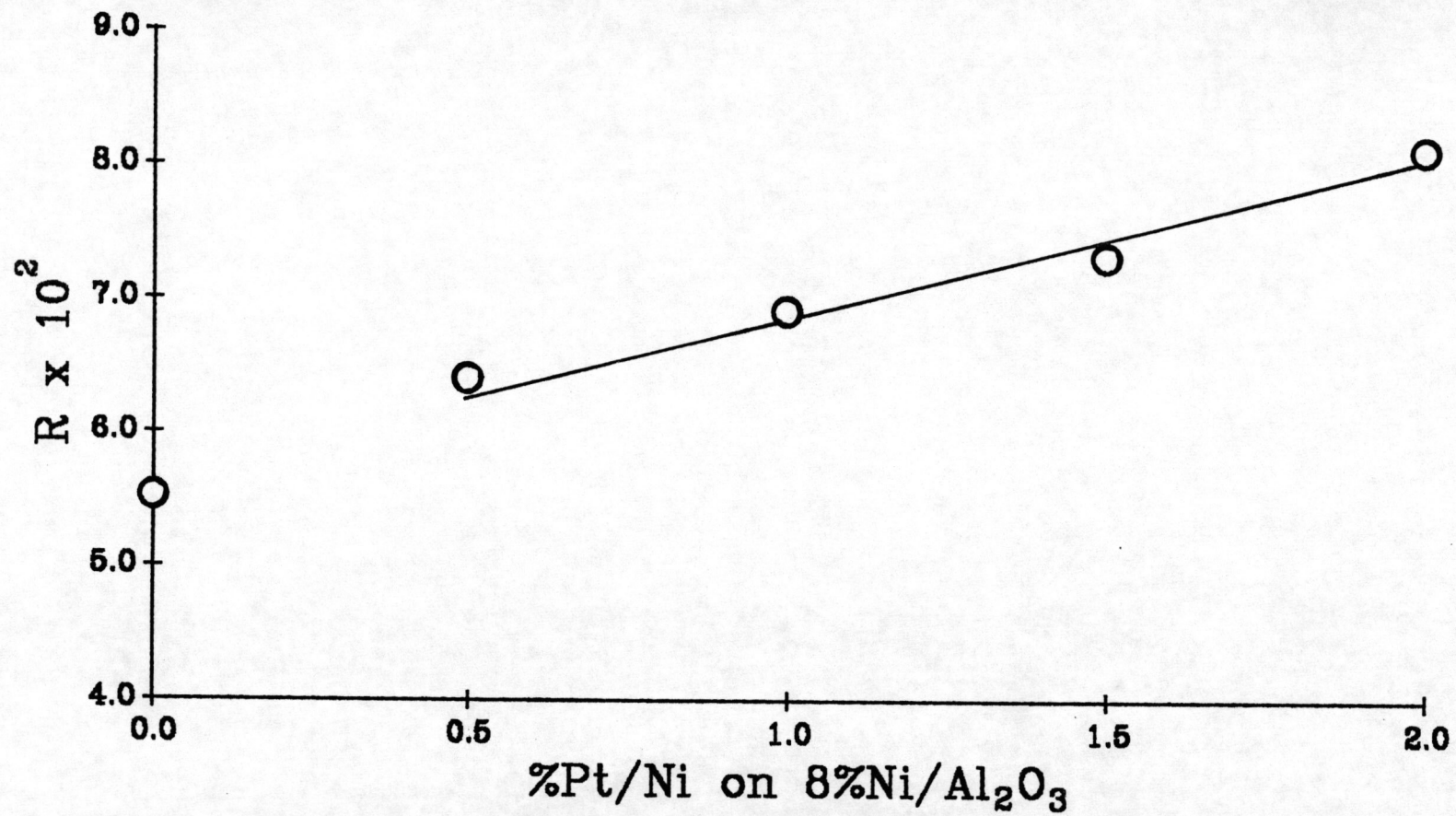
Fig. 5.12   Effect of loaded platinum to ratio of the reactive adsorbed benzene
to site, persentage of platinum loading in range of 0-2.0% (Pt/Ni).
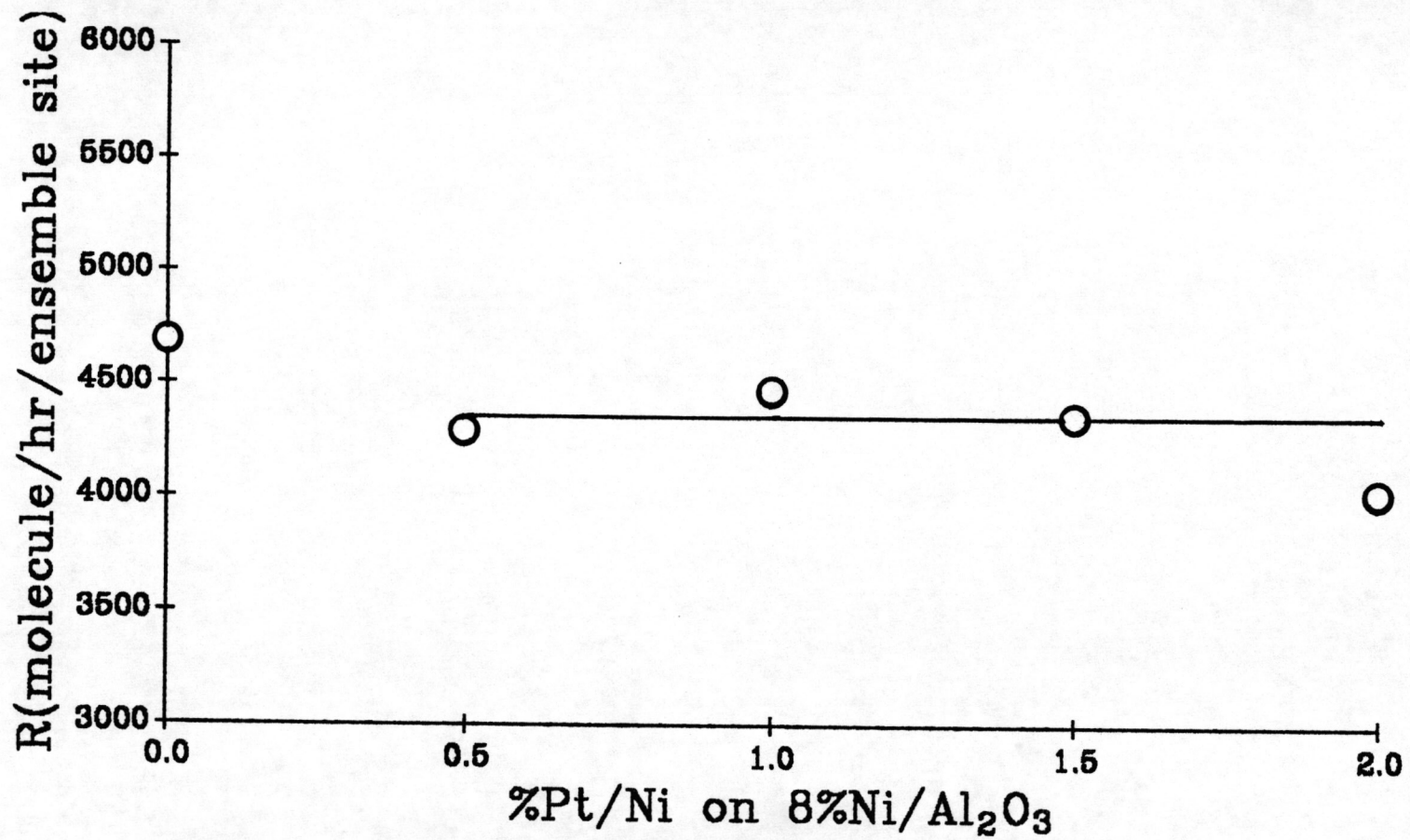R = Ratio of reactive adsorbed benzene : site.

Fig. 5.13 Ratio of TON to reactive adsorbed benzene per site.

conclusion follows assumption that the sites of benzene hydrogenation are the homogeneous sites.

5.5 Catalyst Analysis

The catalysts were analysed by BET for surface area and chemical analysis of catalyst was done by AA and ICPS for amount of nickel and platinum on catalysts respectively. The data of catalyst analysis are shown in Table 5.3.

Table 5.3 Catalyst analysis

catalyst	BET (m^2/g)	%Ni/catalyst	%Pt/Ni
8%Ni/Al$_2$O$_3$	284	8.10	–
0.5%Pt on 8%Ni/Al$_2$O$_3$	293	8.02	0.64
1.0%Pt on 8%Ni/Al$_2$O$_3$	299	8.30	0.98
1.5%Pt on 8%Ni/Al$_2$O$_3$	277	8.10	1.59
2.0%Pt on 8%Ni/Al$_2$O$_3$	270	8.10	2.07

The values of surface of area the catalysts from BET are rather constant. The result of the chemical analysis indicates that nickel and platinum are on the catalyst and every values are close to the design values.