Hydrogenation of Benzene over Rhodium-Copper Alloy Crystallites Supported on Alumina

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ABSTRACT

Supported bimetallic Rh–Cu/Al$_2$O$_3$ catalysts of different copper fractions ($X_{Cu} = N_{Cu}/(N_{Cu} + N_{Rh})$ atomic ratios) were prepared by impregnating a monometallic 3.8 wt.%Rh/Al$_2$O$_3$ catalyst with copper. Benzene hydrogenation over the prepared catalysts was studied with a fixed bed reactor using a 1×10^5 Pa gaseous stream of 10% benzene in hydrogen. In a reaction-temperature range between 373 and 423 K, the observed reaction order varied significantly with their alloy phase on the surface of dispersed metallic crystallites. A rhodium-rich phase dominated the surface of bimetallic catalysts at low X_{Cu} (< 0.3) and exhibited a higher activity than the mono-metallic rhodium. On increasing the copper fraction of bimetallic catalysts to $X_{Cu} > 0.5$, the activity decreased dramatically because the surface of dispersed bimetallic crystallites was covered by a copper-rich phase.

Key words: Rhodium; Copper; Bimetallic catalysts; Hydrogenation.

INTRODUCTION

Bimetallic catalysts have been used in many practical applications (1), i.e., the naphtha reforming, the ammonia oxidation and abatements of vehicle emissions. Theoretically, an alloying of active monometallic catalyst with inert metals may cause two kinds of modification to catalytic activity, the ensemble (geometric) effect and the ligand (electronic) effect. (2)

In a classical study, Sinfelt studied the catalytic effect of adding inert copper to nickel catalysts. (3) The alloying greatly reduced their catalytic activity towards ethane hydrogenolysis (a demanding reaction) but affected negligibly the catalytic activity of nickel towards the cyclohexane dehydrogenation (a facile reaction). Although copper and nickel are miscible, the surface of their alloy-granules is significantly enriched with copper due to its relatively lower surface energy. As a consequence, nickel granules lost 70% of their capability towards hydrogen uptake upon alloying with 10% copper. (4,5)

Based on results of a combined NMR-H$_2$ chemisorption study, we presented the effect of alloying a 3.8 wt. % Rh/Al$_2$O$_3$ sample with different fractions of copper [$X_{Cu} = N_{Cu}/(N_{Cu} + N_{Rh})$] on the surface

structure of dispersed bimetallic crystallites. (6) Copper has a lower surface energy ($\gamma = 1.35$ J m^{-2}) than rhodium ($\gamma = 2.00$ J m^{-2}) and, therefore, segregated also to the surface of bimetallic crystallites. A formation of two kinds of alloy phases, i.e., a rhodium-rich phase [designated as (Rh), with $X_{Cu} = 0.05$] and a copper-rich phase [(Cu), with $X_{Cu} = 0.8$], on the surface of resulted bimetallic crystallites was confirmed. The average size of rhodium crystallites in the starting Rh/Al$_2$O$_3$ was around 2 nm (with a dispersion of 0.46 according to oxygen chemisorption on assuming a stoichiometry of $N_O/N_{Rh} = 1$). A complete coverage of the bimetallic crystallites with the (Rh) phase was reached at a copper fraction of $X_{Cu} = 0.02$. Patches of (Cu) phase (with $X_{Cu} = 0.8$) gradually substituted the (Rh) phase on the metallic surface on increasing X_{Cu} of bimetallic catalysts. Dispersed bimetallic crystallites were covered completely with a layer of (Cu) phase when the fraction of copper on was raised to $X_{Cu} \sim 0.4$. Copper atoms further added on $X_{Cu} > 0.4$ tended to dilute the (Cu) phase with pure copper.

It became a pertinent project in our laboratory to pursue "Effects of the characterized compositions on surface of the Rh-Cu/Al$_2$O$_3$ bimetallic catalysts on their catalytic properties". Four samples with different surface compositions, i.e., pure (Rh), mixture of (Rh) and (Cu), pure (Cu) and copper diluted (Cu), were selected for the study. Following benzene hydrogenation was tested as the model reaction:

$$C_6H_6 + 3H_2 \rightarrow C_6H_{12} \qquad -\Delta H = 206 \text{ kJ mol}^{-1} \qquad (1)$$

This exothermic reaction is used in chemical industry to manufacture cyclohexane, an important intermediate in nylon syntheses. This reaction has been suggested to proceed through the Langmuir-Hinselwood mechanism over supported precious metals of Pt (7,8), Pd (9) and Rh (10-12). Hydrogen was unambiguously chemisorbed on metallic surface in the reaction mechanism. Reacted benzene may be adsorbed either on the support of catalysts or on the surface of dispersed crystallites.

Experimental

Detailed procedure of catalyst preparation has been described in the previous paper (6). In short, a series of Cu-Rh/Al$_2$O$_3$ bimetallic catalysts of different copper composition were prepared by impregnating a 3.8 wt. % Rh/Al$_2$O$_3$ sample ($D_{Rh} = 46\%$) with different amounts of CuNO$_3$. Table 1 summarizes the nomenclature and the physical properties of catalysts used in this study. Isotherms of hydrogen chemisorption over prepared samples were pursued at 300 K in a volumetric apparatus of a glass vacuum system that may be evacuated to 1×10^{-2} Pa.

One gram of a sieved (20-30 mesh) catalyst was packed between two layers of quartz sands in an integral fixed-bed reactor for hydrogenation tests. Changing the loading of packed catalyst in the reaction has eliminated the probability of diffusion control in the catalytic system. After a pretreatment of a 2 h purge with nitrogen and a 2 h reduction with hydrogen at 473 K, a gas stream of 13% of benzene in hydrogen was passed through the catalyst for activity measurements. The pressure of reaction system was maintained at one bar (1×10^5 Pa) and the reaction temperature was varied between 373 and 423 K. Cyclohexane was found to be the sole product of the hydrogenation according to gas-chromatographic analyses using a Carbowax column and a flame-ionization detector. The contact time of reactants, expressed in $(GHSV)^{-1}$, was controlled by the flow-rate of the reaction gas. Fresh

catalysts showed an activity drop at beginning of the hydrogenation reaction. An elapse-time of ten minutes was therefore waited before each benzene-conversion measurement. Since then, rate of benzene conversion generally good ($\pm 3\%$ in conversion) in a period of 8 h.

RESULTS and DISCUSSION

Chemisorption Studies

Figure 1 displays isotherms of total (including reversible and irreversible) hydrogen uptake (N_H^t) measured at 300 K for all of the selected catalysts. Calculated uptakes always increased with the over pressure of hydrogen (P_H). Observed slope was steep at initial but decreased and approached a limiting slope on increasing P_H. The hydrogen-uptake ability (N_H^t) for each catalyst was estimated from its corresponding isotherm by extrapolating uptakes in the limiting slope region to $P_H = 0$ (6).

The fifth column of Table 1 lists N_H^t uptakes determined for all of the catalysts studied. Evidently, an alloying of copper to the 3.8 wt. % Rh/Al_2O_3 catalyst has a profound effect on N_H^t. A higher N_H^t uptake was found for 2Cu-Rh than the monometallic Rh/Al_2O_3. This uptake increase has not been found from alloying nickel with copper. Nickel granules lost 70% of their hydrogen-uptake ability upon alloying with 10% copper. (4,5) The difference may be caused by miscibility of bimetallic samples. Nickel mixed well with copper to form homogeneous solid solutions at all compositions. However, rhodium and copper are only partially miscible to each other and tended to form two alloy phases: a rhodium rich phase (designated as (Rh) with a $X_{Cu} = 0.05$) and a copper-rich phase (designated as (Cu) with a $X_{Cu} = 0.8$). Evidently from Fig. 1, (Rh) phase has a higher ability of hydrogen-uptake than the monometallic rhodium. (6) Probably, copper atoms in the surface (Rh) phase can also chemisorb hydrogen.

Figure 2 presents the effect of temperature on the hydrogen uptake isotherms from 2Cu-Rh sample. The uptake generally decreased on increasing the adsorption temperature. An isostere heat of adsorption with E_{ad} around 55 kJ (mol H_2)$^{-1}$ was estimated from these isotherms in a hydrogen uptake (N_H/N_{Rh}) range between 0.3 to 0.4. The temperatures also affect the uptake isotherm of hydrogen on Rh/Al_2O_3. (Fig. 3) A similar E_{ad} has also been evaluated for a dissociative adsorption of hydrogen on the monometallic Rh/Al_2O_3 catalyst. (12) Accordingly, the strength of hydrogen adsorption on (Rh) phase is similar to that on the monometallic rhodium.

A mild N_H^t decrease was found in Table 1 on increasing the X_{Cu} of bimetallic samples from 0.02 and 0.40. The decrease in N_H^t was resulted by a partial substitution of (Rh) phase on crystallites' surface by (Cu) patches. The substitution increased with X_{Cu} and reached a completion on increasing the copper composition of the bimetallic catalysts to $X_{Cu} = 0.4$. Accordingly, 41Cu-Rh sample should

be covered by a layer of (Cu) phase. Conceivably, (Cu) phase has a slightly less ability towards the hydrogen chemisorption than (Rh) phase.

As the copper composition was raised to $X_{Cu} > 0.4$, part of lately added copper dissolved into the (Cu) phase on the surface of crystallites to form a copper-diluted (Cu) phase. Evidently from Table 1, this phase does not chemisorb hydrogen appreciably and N_H^t of 83Cu-Rh was very small. The fourth column of Table 1 summarizes alloy phases proposed for the surface of metallic crystallites dispersed on bimetallic catalysts. On comparing to the determined N_H^t, these phases displayed the following sequence of hydrogen-chemisorption ability:

$$(Rh) > Rh > (Cu) >> \text{copper-diluted (Cu)} \qquad (I)$$

Kinetic order studies

The kinetics of benzene hydrogenation may be expressed with an empirical equation of:
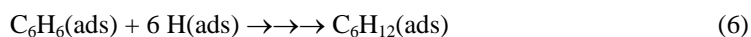
$$Rate = k\theta_B^b \theta_H^h \qquad (II)$$

Where θ_B and θ_H denote the coverage of benzene and hydrogen on active sites of catalysts, and superscripts b and h denote the kinetic order of benzene and hydrogen, respectively. System temperatures significantly affected the kinetic order of reaction 1. (7) According to a recent TPD study, benzene molecules adsorbed on clean rhodium surfaces at low temperatures tended to decompose into adsorbed hydrogen and carbonaceous deposit, i.e.,

$$C_6H_6 + * \rightarrow C_6H_6(ads) \qquad (2)$$
$$C_6H_6(ads) \rightarrow \text{carbonaceous deposit} + m\, H(ads) \qquad (3)$$

Both the associatively adsorbed benzene and the dissociatively adsorbed hydrogen started to desorb from the metal surface on raising the TPD temperature over 423 K. (10) At low temperatures (around 373 K), kinetic orders of the hydrogenation were found to be zero and 0.5 for benzene and hydrogen, respectively. The zero order of benzene indicates saturation coverage of benzene on the surface. The experimental orders usually increased on raising the reaction temperature over 423 K, probably due to a substantial decrease in the coverage of reactants. In this study, we confined our reaction condition to T < 423 K with a hope to minimize the reactant desorption.

Figure 4 presents experimental results from the hydrogenation over the monometallic Rh/Al_2O_3 catalyst. The partial pressure of benzene in the product stream decreased linearly with the contact time for all reaction temperatures. Obviously, the rate of benzene conversion was independent to the benzene concentration in the temperature range used. The reaction order of benzene, in the hydrogenation, was therefore regarded as b = 0 over the monometallic rhodium catalyst.

Although the detailed kinetics of benzene hydrogenation over supported metallic catalysts is not yet well elucidated, (8) the reaction is generally regarded to proceed through a Langmuir-Hinshelwood mechanism of following steps:

$$C_6H_6 \Leftrightarrow C_6H_6(ads) \qquad\qquad (4)$$

$$H_2 \Leftrightarrow 2H(ads) \qquad\qquad (5)$$

$$C_6H_6(ads) + 6\,H(ads) \rightarrow\rightarrow\rightarrow C_6H_{12}(ads) \qquad\qquad (6)$$

$$C_6H_{12}(ads) \rightarrow C_6H_{12} \qquad\qquad (7)$$

In this mechanism, step 6 involves many consecutive mini-steps. Hydrogen and benzene were pre-adsorbed on active sites as precursors for step 6.

A zero order kinetics for benzene has been found in many studies (7-10) on its hydrogenation over monometallic noble metal catalysts at T < 427 K. A saturated coverage of benzene during the hydrogenation was generally suggested. Thermodynamically, benzene molecules are adsorbed stronger (E_{ad} = 100 kJ mol^{-1} (11)) than hydrogen ($E_{ad} \sim$ 55 and 21 kJ (mol H_2)$^{-1}$ for a dissociative and a molecule adsorption, respectively (13)) on the surface of dispersed rhodium crystallites.

Fig. 5 presents experimental results on hydrogenation over 2CuRh bimetallic catalysts. Time profiles of benzene pressure in the same temperature region deviated surprisingly from straight lines expected for b = 0. The kinetic order of benzene for the hydrogenation must have changed by alloying the rhodium crystallites of the Rh/Al$_2$O$_3$ catalyst with a small fraction of Cu (X_{Cu} = 0.02). Semi-log plots of Figure 6 suggested that the kinetic order for benzene was increased to b = 1 over the 2CuRh catalyst. Obviously, the coverage of benzene on the metallic surface was far from saturation.

Observed change in kinetic order by alloying the dispersed rhodium with 2% of copper is interesting. According to previous characterizations (6), supported bimetallic crystallites on this catalyst were dominantly covered with a layer of (Rh) phase. The adsorption strength of hydrogen on this phase has been found in Fig. 2 to remain the same as that on monometallic rhodium. Evidently, the adsorption of benzene molecules (step 2) is seriously hindered by the alloying rhodium with copper. Since the fraction of copper of the (Rh) phase is only X_{Cu} = 5%, it is hard to attribute the abrupt change in benzene coverage to a simple ensemble effect. Electronic effect must have played an important role. The expected electronic effect may be confirmed from a future study on XANES and heat of benzene adsorption.

A kinetic order for benzene of b = 1 was also found from Fig. 7 for hydrogenation over other bimetallic catalysts studied, i.e., 21Cu-Rh, 41Cu-Rh and 83Cu-Rh. The benzene coverage during their hydrogenation should also be far from a saturation ($\theta_b \ll 1$) and increase with the pressure of benzene. Obviously, benzene molecules were adsorbed only weakly on all of the bimetallic catalysts used in this study. Since alumina support has a decent affinity towards benzene molecules (with a q_{ad} = 40 kJ mol^{-1} (11)), they may be pre-adsorbed (step 4), besides on the metallic surface, also at the metal-support interface of bimetallic catalysts. The contribution of these two kinds of site to the hydrogenation probably varied with X_{Cu} composition of our catalysts.

Benzene conversions

Column six of Table 1 compares benzene conversions over different catalysts at a temperature of 373 K. The conversion of benzene on Cu-Rh bimetallic catalysts in the reaction 1 was similar as long as $X_{Cu} < 0.4$. Measured TOF was around 2 s^{-1} at a reaction temperature of 373 K. This TOF frequency is in the same order that reported for Pt/Al$_2$O$_3$ (7) and Pd/Al$_2$O$_3$ (9).

Interestingly, 2Cu-Rh and 21Cu-Rh exhibited a higher benzene conversion than the monometallic Rh/Al$_2$O$_3$. Since the surface of both bimetallic catalysts were covered mainly with (Rh) phase, we can conclude that this phase has a higher catalytic activity than the pure rhodium in reaction conditions performed in this study. This result is different to that reported for the same catalytic reaction over bimetallic catalysts of Cu-Pd/SiO$_2$ (15). An alloying of Pd/SiO$_2$ catalysts with Cu significantly reduced their catalytic activity (by a factor of ten or more) towards benzene hydrogenation. However, a promotion of catalytic activity on alloying metal catalyst with minor *B metal is not unique*. Sinfelt also reported a somewhat higher specific activity for cyclohexane dehydrogenation over Ni-Cu alloys after the addition of a small amount of Cu. (16)

Over the monometallic Rh/Al$_2$O$_3$ catalyst, metallic crystallites were covered with strongly adsorbed benzene. Under this situation, hydrogen was expelled from the surface by adsorbed benzene and θ_H is very small. The rate of hydrogenation reaction on this catalyst is thus limited by step 5, the pre-adsorption of hydrogen.

From the change in the reaction order of benzene, we have sensed that θ_b on the (Rh) deviated substantially from a saturation over all of bimetallic catalysts. Being a decent strong adsorbate (with an $E_{ad} \sim 55$ kJ mol^{-1}) on rhodium surface, hydrogen should have replaced benzene as the major adsorbate on the sites of (Rh) phase during hydrogenation. Accordingly, θ_H was high during hydrogenation over both catalysts of 2Cu-Rh and 21Cu-Rh when (Rh) phase represented the dominantly active sites. A good hydrogenation activity over (Rh) phase is therefore observed.

The benzene conversion in hydrogenation over 83-CuRh catalyst is shown in Table 1 to be very low (by a factor greater than 10 on comparing to other catalysts). According to the previous characterization, (6) the surface of metal crystallites on this bimetallic catalyst was dominated with a copper-diluted-(Cu) phase (with $X_{Cu} > 0.8$). Evidently, this phase is quite inactive towards the benzene hydrogenation.

Observed low hydrogenation activity of 83-CuRh may be resulted from its low ability towards hydrogen chemisorption. Figure 8 compares the total hydrogen uptake of bimetallic catalysts with their activity towards the benzene hydrogenation. The activity of the Cu-Rh bimetallic catalysts is proportional to their capability of hydrogen uptake when the (Rh) phase is the dominant active site (for

2Cu-Rh and 21Cu-Rh sample), but decreases dramatically when the surface of dispersed crystallites was replaced by the (Cu) or the copper diluted (Cu) phase.

Vannice et al reported apparent activation energies (E_a) determined for the catalytic hydrogenation over monometallic palladium and Cu-Pd alloys (14,15). At low temperatures (T < 425 K), a constant apparent activation energy of $E_a = 50$ kJ mol^{-1} was observed. Measured E_a, however, decreased on raising the reaction temperature over higher temperatures and became negative when T > 500 K. The decrease in E_a may be attributed, according to Eq. 2, to a decrease in θ_B and θ_H with the reaction temperature.

An $E_a < 50$ kJ mole^{-1} was found in the catalytic hydrogenation over Cu-Rh bi-metallic catalysts of the present study (last column of Table 1). Determined E_a generally decreased on increasing X_{Cu} of the catalyst in the reaction temperature of T < 425 K. Conceivably, θ_B and θ_H on these alloy catalysts should have decreased with an increasing in X_{Cu} at our reaction conditions.

CONCLUSIONS

An alloying the monometallic Rh/Al$_2$O$_3$ with partially miscible copper modified adsorption properties of dispersed metallic crystallites. Their affinity towards benzene was significantly decreased. Two alloy phases, (Rh) and (Cu), constitute the surface structure of dispersed alloyed crystallites. The (Rh) phase has a higher activity toward benzene hydrogenation than the monometallic rhodium because hydrogen replaced the benzene as the dominant adsorbate at the reaction conditions. The catalytic activity of the (Cu) phase is low because of low hydrogen and benzene coverage on this phase during reaction.

Acknowledgement

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Figure Captions

1. Effect of alloying copper to 3.8 wt.% Rh/Al_2O_3 on the total hydrogen uptake at 300 K.

2. Effect of temperature on the adsorption isotherms of hydrogen on 2Cu-Rh.

3. Effect of temperature on the adsorption isotherms of hydrogen on Rh/Al_2O_3
   (273 K,   296 K,   323 K,   348 K,   373 K,   398 K,   423 K,
       448 K,   475 K)

4. Time profiles for benzene remained in the product stream of benzene hydrogenation reactions performed over the monometallic rhodium catalyst.

5. Time profiles of benzene remained in the product stream of benzene hydrogenation reactions performed over 2CuRh bimetallic catalyst.

6. Pseudo-first-order plots of benzene remained in the product stream of benzene hydrogenation reactions performed over 2CuRh bimetallic catalyst.

7. Pseudo-first-order plots of benzene remained in the product stream of benzene hydrogenation performed at 373 K over different bimetallic catalysts.

8. Effect of total hydrogen uptake of the $Cu-Rh/Al_2O_3$ bimetallic catalysts on the conversion of benzene in benzene hydrogenation at 373 K and a contact time of 0.09 or 0.03 h.

Table 1 Physical characterizations of bimetallic $CuRh/Al_2O_3$ samples and their catalytic results on benzene hydrogenation.

Sample	Metal loading (wt%)		X_{Cu}*	Dominant phase on surface	N_H^t / (μmol g^{-1})	Benzene Conversion (%) at 373 K 1/GHSV=0.03 h	TOF (s^{-1})	b**	E_a (kJ/mol)
	Rh	Cu							
Rh	3.80		0.00	Rh	160.3	20.8	1.43	0	20.4
2Cu-Rh		0.05	0.02	(Rh)	173.1	37.1	2.36	1	33.7
21Cu-Rh		0.58	0.21	(Rh)+(Cu)	133.0	28.4	2.30	1	8.5
41Cu-Rh		1.34	0.41	(Cu)	109.3	10.4	1.05	1	-9.0
83Cu-Rh		9.75	0.83	diluted (Cu)	20.0	0.5	0.28	1	

* : Composition of copper in bimetallic crystallites.

** : Observed reaction order on benzene.
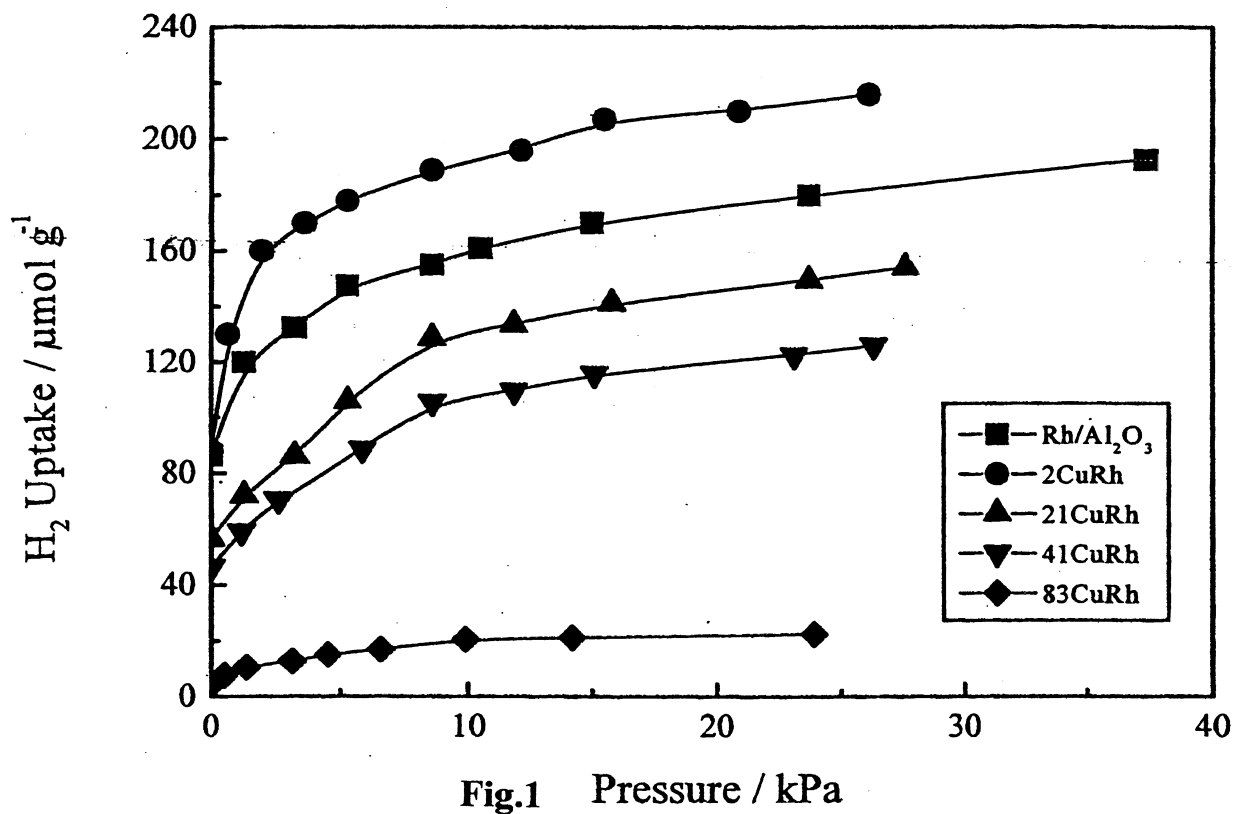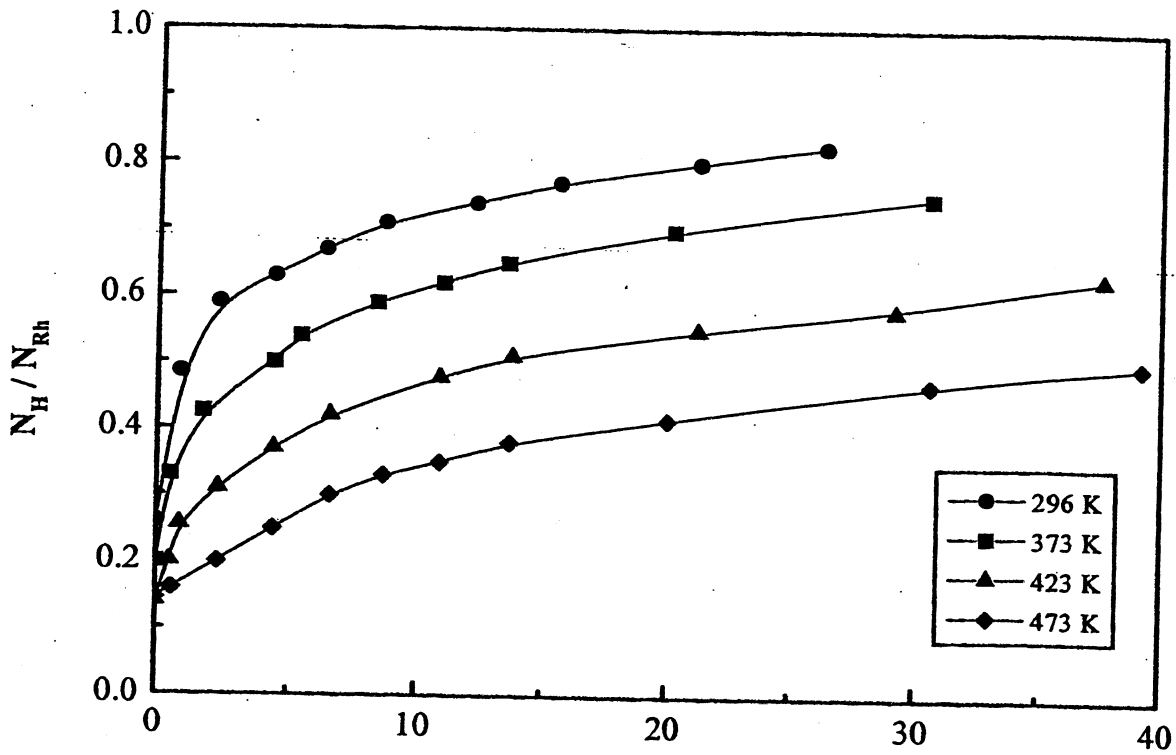
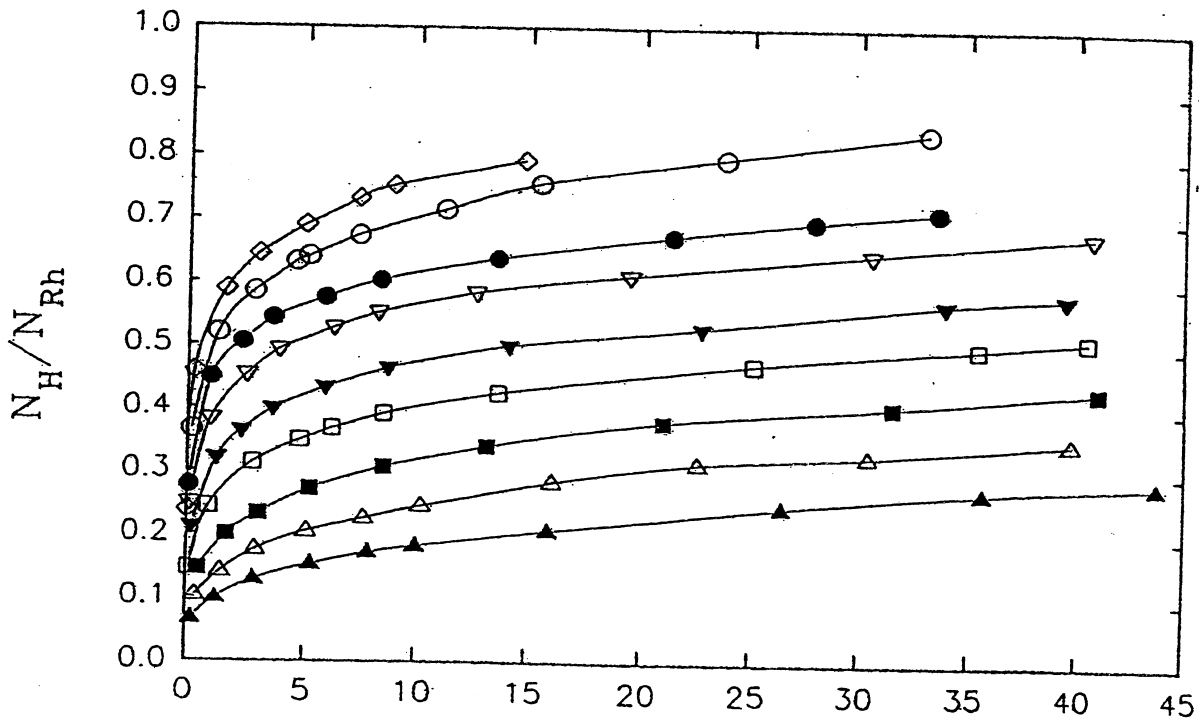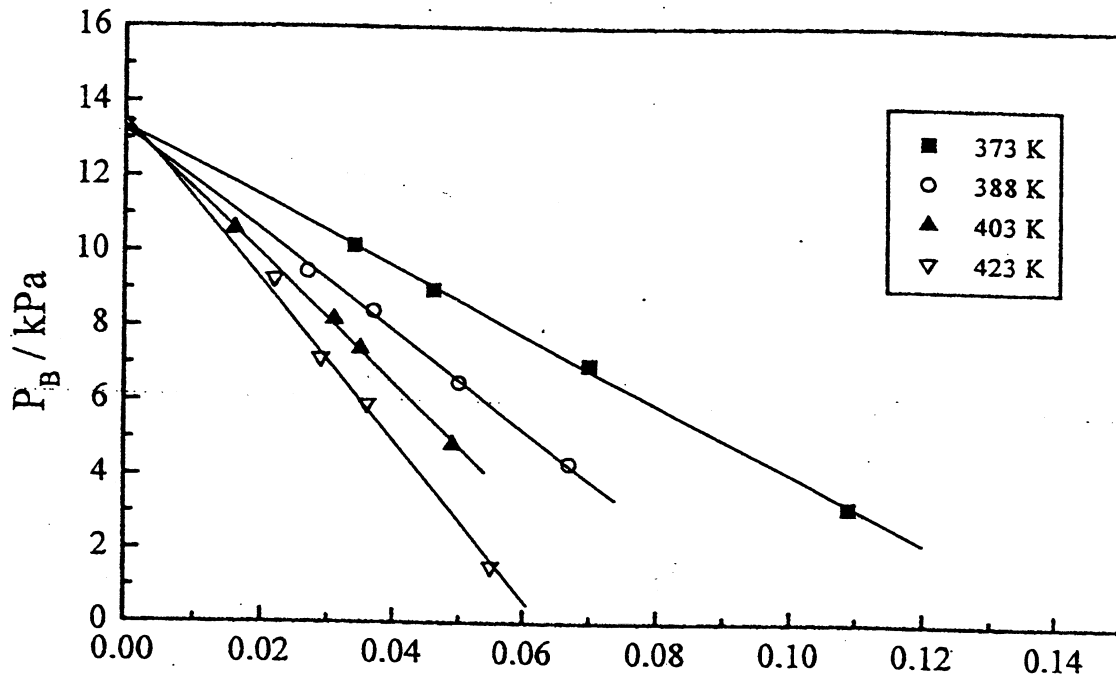Fig.1   Pressure / kPa

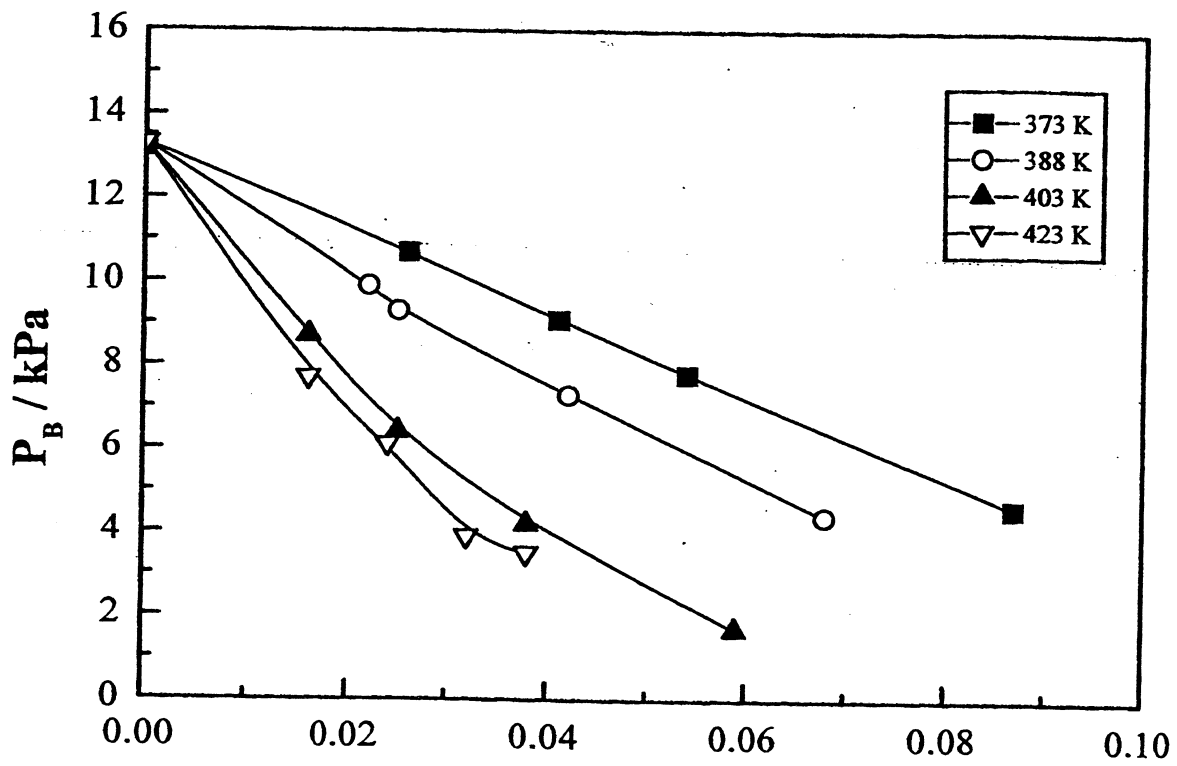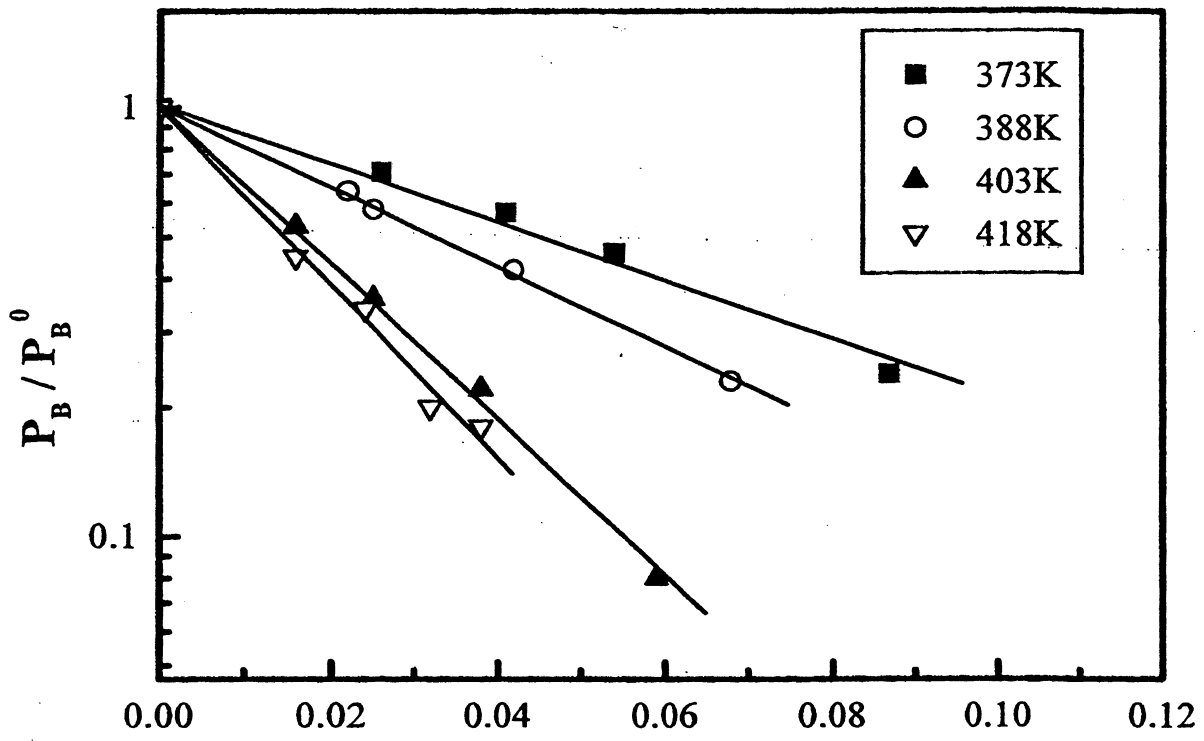Fig.2　Pressure /kPa

Fig.3　Pressure /kPa
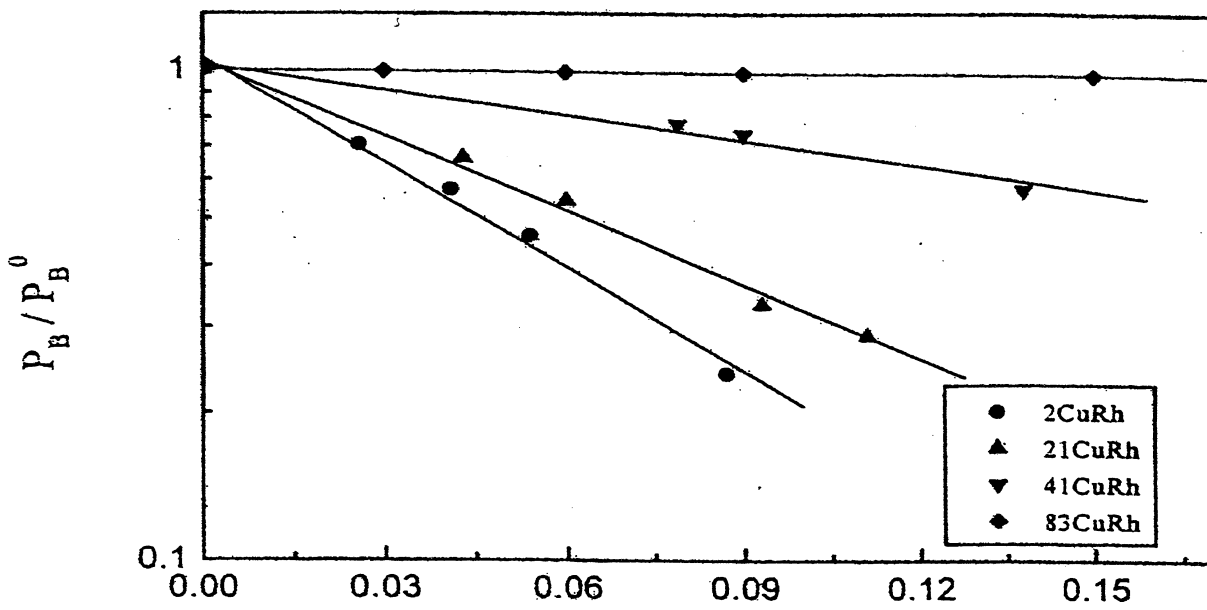
Fig.4   1 / GHSV , h

Fig.5   1/GHSV , h

Fig.6　1 / GHSV , h

Fig.7　1 / GHSV , h

Fig.8 N_H^t / umol g^{-1}