Propane Hydrogenolysis over Alumina-Supported Pt-Rh Catalyst

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Bimetallic catalysts of various Pt/Rh ratios supported on Al_2O_3 have been prepared and used in propane hydrogenolysis reaction. The reaction order with respect to hydrogen was determined and found to equal -2 indicating inhibiting action of hydrogen. The activation energy of propane hydrogenolysis was calculated for Rh, Pt_{30}-Rh_{70} and Pt_{50}-Rh_{50} and found to have the following values: 201, 221 and 201 kJ/mol, respectively. The effect of %Rh mass content on the reaction rate was also studied.

INTRODUCTION

Hydrogenolysis of alkanes over supported transition metals has gained much interest and has been the subject of many scientific studies[1-12]. This is due to scientific and industrial importance of such reactions. In addition, kinetic studies of these reactions, particularly reaction order and activation energy determination have been investigated[13-15]. We are concerned here in the hydrogenolysis of propane over Al_2O_3-supported Pt-Rh bimetallic catalysts.

Al_2O_3 support provides acidic sites as well as stability and large catalyst surface area. Al_2O_3 is expected to furnish a BET surface area of *ca.* 100 m^2/g for the prepared bimetallic catalysts. Moreover, this kind of support possesses sintering resistance and thermal stability for reaction temperatures up to 500°C.

Pt and Rh metals are the sources of the metal sites on the surface of these Pt-Rh/Al_2O_3 catalysts. Pt metal has good catalytic effects in many reactions, but it shows low activity in the hydrogenolysis of propane[16]. Whereas, Rh metal has shown very high catalytic activity in the hydrogenolysis of alkanes[16-18]. However, it has moderate stability and selectivity[17]. Consequently, the high stability and selectivity of Pt are combined with

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the high catalytic activity of Rh to obtain bimetallic sites with enhanced catalytic properties. This bimetallic catalyst is supported on Al_2O_3 in order to have maximum thermal stability and optimum selectivity, as well as high activity. In this paper, a kinetic study of the hydrogenolysis of propane using Al_2O_3 supported Pt/Rh bimetallic catalyst is reported.

EXPERIMENTAL

α-Al_2O_3 was purchased from Merck and used as catalyst support. $PtCl_4\cdot xH_2O$ and $RhCl_3\cdot3H_2O$ salts (Jansen Chimica) were used as metals sources. Propane gas > 99.5 % purity was purchased from Matheson. Helium and hydrogen gases (Arab Gas Co.) were purified from water vapour and oxygen by using proper traps.

Catalyst preparation: The bimetallic catalysts were prepared by the co-impregnation technique. After impregnation, the formed paste was dried overnight in an electric oven at 110 °C, then crushed and powdered. The obtained fine powder was calcined in flowing air at 250 °C for 2 h to produce Al_2O_3-supported metal oxides. These oxides were reduced in flowing hydrogen gas at 400 °C for 4 h to produce Pt-Rh bimetallic catalysts supported on Al_2O_3 (Table-1). Calcination and reduction processes were carried out in a tubular quartz reactor (30 cm long × 2 cm ID) inserted in an electric oven. Heating was performed by an electronic temperature controller (Digi-sense).

Hydrogenolysis reactions: Pure propane, hydrogen and helium gases were used in these reactions. An electronic mass flow controller was used to measure and control the flow rates of these gases. An electronic programmable temperature controller (Digi-sense) was used to control the reaction temperature. Kinetic parameters were determined by measuring conversion percentages of propane at different temperatures.

A 0.50 g sample of each catalyst was placed on the catalyst bed of a vertical 30 cm long × 2.0 cm ID quartz reactor. The catalyst bed is a quartz fritted-disc located at 10 cm above the bottom of the reactor. An electric tubular quartz oven with a temperature controller was used for heating the reactor. Prior to any experiment, hydrogen gas was passed through the catalyst sample at 450 °C for 0.5 h, for catalyst activation. Helium, hydrogen and propane gases were introduced into the reactor after mixing, *via* a four-channel electronic mass flow controller (Matheson, model 8274). Their flow rates were 80, 15 and 5 mL/min, respectively. The temperature was gradually increased from 170 to 350 °C and the produced gaseous mixture was analyzed by gas chromatography. This was done to determine optimum reaction temperatures for each catalyst. The conversion percentages of propane at all reaction temperatures and gases partial pressures were calculated for each catalyst.

A second set of experiments was performed on a 0.50 g sample of each catalyst to determine the effect of hydrogen pressure on this reaction. Hydrogen gas was passed over the catalysts at different flow rates (0-80 mL/min) along with 7.5 mL/min propane gas and 92.5-12.5 mL/min helium gas at the determined optimum reaction temperatures (Table-2).

Due to the high catalyst surface coverage and thus saturation, with propane as also found previously[15], varying propane pressure showed no noticeable effect on the kinetics of this reaction and therefore it was not included in this study.

A gas chromatograph (HP 5890) with TCD detector connected to an electronic integrator (HP3950) was used for monitoring samples of the gaseous mixtures. A six-port valve with a 50 µL sampling loop was used for sample injection. The separation of the mixture was performed on a 2 m long × 3 mm OD SS column packed with 10 % squalene on 80-100 mesh chromosorb. Helium carrier gas was passed at a flow rate of 15 mL/min with the injector, detector and column temperatures of 150, 200 and 50 °C, respectively. Samples of the reaction mixture were also analyzed by GC/MS (VG Analytical Instruments, VG 7070 E) for structure confirmation.

Nitrogen adsorption and BET method were used to measure the surface area of the prepared catalysts and found to be *ca.* 105 m^2/g.

RESULTS AND DISCUSSION

Various alumina-supported catalysts with different Pt/Rh ratios (Table-1) had been prepared and investigated with respect to their catalytic behaviour in the hydrogenolysis of propane. Their catalytic activity was expressed by the initial reaction rate calculated according to eqn. 1

$$\text{Rate} = \frac{F_{HC}\, X}{\text{mass}_{cat}} \tag{1}$$

whereby, F_{HC} is propane flow rate, mass_{cat} is mass of catalyst sample and X is conversion of propane.

TABLE-1
MASS AND MOLE PERCENTAGES OF RHODIUM IN THE
PREPARED CATALYSTS

Catalyst*	Mass % Rh**	Mol % Rh**
Pt	0.0	0
$Pt_{50}Rh_{50}$	34.5	50
$Pt_{30}Rh_{70}$	55.2	70
Rh	100.0	100

*Total metal loading is 5 %. **Percentages of the metal loading.

The conversion percentages were kept below 15 % to ensure linearity between rate and conversion. For all these catalysts, the reaction order with respect to hydrogen as well as the activation energy were determined experimentally as follows:

Determination of the activation energy of propane hydrogenolysis

$$C_3H_8 + H_2 \longrightarrow C_2H_6 + CH_4$$
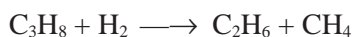
It is noteworthy that further cracking of C_2H_6 does not occur for conversions under 15 %. All results are therefore representative of the assumed reaction. The flow rates of propane, hydrogen and helium were adjusted and kept constant. The reaction mixture was allowed to pass over the catalyst, initially at low temperatures before being analyzed by gas chromatography. The temperature was then increased stepwise. The achieved conversions at the various temperatures were used to calculate the rate according to eqn. 1.

The activation energy was determined graphically by plotting ln rate or ln x, (It makes no difference since the rate is proportional to x) against 1/T. Fig. 1 shows this for the Rh, $Pt_{30}Rh_{70}$ and Pt_{50} Rh_{50} catalysts. The activation energy was accordingly estimated to be 201 and 221 and 201 kJ/mol, respectively.

Determination of the reaction order with respect to hydrogen

In general, $Rate = k \, P^n_{(propane)} \, P^m_{(H_2)}$, thus
$$ln \; rate = ln \; k + n \; ln \; P_{(propane)} + m \; ln \; P_{(H_2)} \qquad (2)$$

A series of experiments was done in which the partial pressure of propane was kept constant by keeping its flow rate constant, while that of hydrogen was varied systematically. The partial pressure of hydrogen was changed by changing its flow rate at the expense of helium flow rate. The total flow rate, F_{tot} which is the sum of the flow rates of all gases, was kept constant and equal to atmospheric pressure.

The partial pressure of hydrogen gas was calculated from the following relation:

$$P_{H_2} = \frac{F_{H_2}}{F_{propane} + F_{H_2} + F_{He}} \times P_{tot} \qquad (3)$$

Plotting ln rate against ln P_{H_2} yields a linear relationship according to eqn. 2 with m, the order with respect to hydrogen, as the slope. This is shown for the Rh, $Pt_{30}Rh_{70}$, $Pt_{50}Rh_{50}$ and Pt catalysts in Fig. 2. It is important to notice that these values were determined at different temperatures (Table-2). A negative order (*ca.* -2) means that hydrogen inhibits the hydrogenolysis process probably due to the competitive adsorption of propane on the active metal sites. As a result, the fraction of adsorbed propane will decrease leading to lower reaction rates.
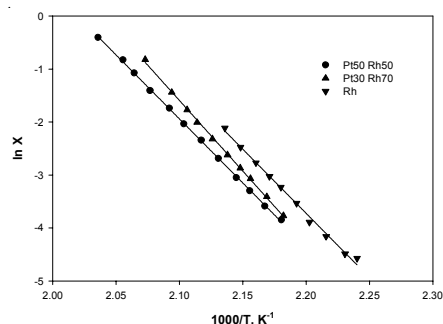
Fig. 1. Arrhenius plot for propane
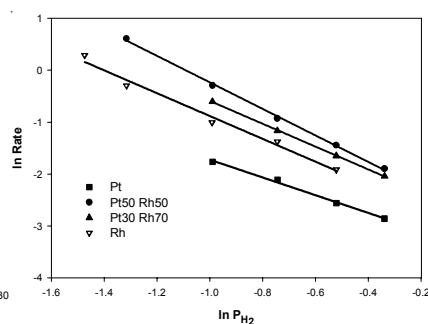hydrogenolysis over used
catalysts

Fig. 2. Reaction order of propane
hydrogenolysis with respect
to hydrogen pressure

TABLE-2
REACTION ORDER WITH RESPECT TO HYDROGEN AT
REACTION TEMPERATURE

Catalyst	Order with respect to H_2	T (ºC)
Pt	-1.71	280
$Pt_{50}Rh_{50}$	-2.56	196
$Pt_{30}Rh_{70}$	-2.20	192
Rh	-2.20	185

To compare these catalysts with respect to their catalytic activity, values of their reaction rates at the same temperature should be available. Therefore, the experimentally determined activation energy can be used to calculate reaction rates at any temperature. Table-3 shows reaction rates for all catalysts calculated at same temperature (185 ºC).

TABLE-3
REACTION RATES PER MOLES OF Rh FOR DIFFERENT
CATALYSTS AT 185 ºC

Catalyst	Rate at 185 ºC*	Rate/n_{Rh}	Rate/rate (100 % Pt) × 10^{-3}
Pt	11.1×10^{-6}	–	1.0
$Pt_{50}Rh_{50}$	0.128	764	11.5
$Pt_{30}Rh_{70}$	0.138	516	12.4
Rh	0.218	448	19.6

*Rate is in mL propane/g $_{cat}$ min units.

Fig. 3 shows a plot of ln rate (any catalyst)/rate (100 % Pt) as a function of % Rh mass content in the metal phase in the supported catalyst (solid line). The dashed line represents calculated values for ln rate/rate

(Pt) obtained under the following assumptions: (i) The Pt atoms themselves were assumed to be inactive in the hydrogenolysis process. This assumption is justified by the fact that the catalytic activity of Rh is much higher than that of pure Pt (almost 20000 times higher). (ii) Alloying effects were neglected. (iii) The dispersion (particle size) is the same in all cases.

Accordingly, the rate of $Pt_{30}Rh_{70}$ catalyst (55.2 mass % Rh) is 55.2 % of that of the Rh catalyst and same is true for all catalysts.
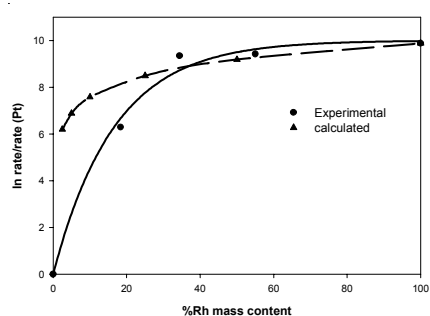

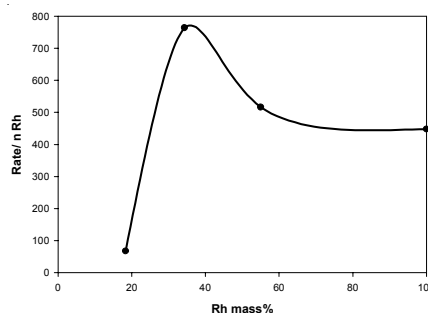Fig. 3. Plot of ln rate/rate of Pt *vs.* percentage of Rh mass content for used catalysts

Fig. 4. Catalyst activity as a function of rate per mole of rhodium *vs.* rhodium mass %

Two regions in Fig. 3 can be distinguished; one with Rh mass % < 26 % and one with Rh mass % > 26 % . In the first region, the calculated ln rate/rate Pt values are higher than the experimentally obtained ones. A possible reason for this behaviour is that under these conditions the catalyst surface is rich in Pt-atoms compared to Rh surface atoms. They act as a catalyst poison blocking thus the active Rh surface sites. On the other hand, in the second region there is no significant difference between the calculated and the experimentally obtained values of ln rate/rate Pt. This may be due to the fact that in this region the surface is richer in Rh-atoms, so that Pt-surface atoms may have a negligible deactivation effect. However, any enhancement on the rate of propane hydrogenolysis compared to the calculated (expected) values may be attributed to the alloying effects of Pt with Rh. However, it should be taken into account that the amount of the active component 'Rh' in the various catalysts is different. The catalytic activity per mole Rh can be determined for each catalyst (rate/n_{Rh}, Pt is inactive). It is a measure of the catalytic activity per Rh atom. It is obvious from Fig. 4 that Rh atoms possess different activities, depending on the Rh mass % of the catalyst. A maximum activity per mol Rh was obtained at Rh mass % of 34.5 %) ($Pt_{50}Rh_{50}$). This enhancement in catalytic activity of the bimetallic catalyst is probably due to alloying effect, as

well as, increase in dispersion. Finally, the reaction rate over Pt was found to be very low compared to that over Rh. Therefore much higher temperatures were needed in order to be able to measure observable conversions over Pt. In addition, deactivation of the Pt catalyst was found to take place rapidly. This may be due to the poisoning of the Pt active site by coke formation during reaction.

ACKNOWLEDGEMENT

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