Asian Journal of Chemistry Vol. 15, No. 1 (2003), 95–104

Hydrogenolysis of Propane over Sol-Gel Pt-Rh/SiO_2: Activity, Selectivity and Kinetics

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The catalytic properties of Pt_xRh_{1-x} (x = 0, 0.2, 0.4, 0.5, 0.6, 0.8, 1.0) bimetallic catalysts supported on SiO_2 and prepared by the sol-gel method have been investigated in the hydrogenolysis of propane in the temperature range of 150–550°C. The measured BET surface area of these catalysts is relatively high (*ca.* 580 m^2/g). Their temperature of 100% conversion of propane to ethane and methane at $H_2/C_3H_8 = 3$ and space velocity of 12,000 h^{-1} is relatively low (200–270°C). All Pt-Rh/SiO_2 catalysts are very active in this respect, whereas Pt/SiO_2 is relatively inactive. Their selectivity towards the production of ethane is *ca.* 50%. The kinetic parameters for this reaction over $Pt_{50}Rh_{50}/SiO_2$ are also reported, where increasing the hydrogen pressure has an adverse effect on the rate of this conversion. The reaction order with respect to hydrogen pressure is strongly negative (–2). Propane pressure has a slight effect on the rate of conversion, and is with an observed reaction order of +0.55. The apparent activation energy was determined and found to be 123 ± 7 kJ/mol.

Key Words: Hydrogenolysis, Propane, Pt-Rh/SiO_2, Selectivity, Kinetics.

INTRODUCTION

In the last decade, supported metallic catalysts prepared by sol-gel method gained high scientific and industrial interests. These catalysts are highly dispersed and have large BET surface area, as well as strong metal-support interaction[1–5]. Sol-gel catalysts proved to have good stability and catalytic properties in many reactions[1, 4–8]. For example, Lopez *et al.*[1] reported the unusual catalytic and structural effects of sol-gel Pd/SiO_2 in the hydrogenation of 1-hexene and of phenylacetylene. The hydrogenation of benzene and the hydrogenolysis of *n*-pentane by sol-gel Ru/SiO_2 have also been reported[6].

Recently, hydrogenolysis of propane and/or other alkanes over many supported metal catalysts has been the subject of many studies because of its scientific and/or industrial importance[9–33]. The kinetic parameters, such as the reaction order and the activation energy of this reaction over many supported metals have also been investigated[9–21]. SiO_2 has proved to be a good support and superior to many supports in this respect[19–25]. Although platinum metal is a good catalyst for many reactions, has been reported to have low activity in this reaction[20, 23, 26]. Rhodium metal, as reported by many researchers, has an excellent activity in the hydrogenolysis of alkanes in general and of propane in particular[19–21, 26, 27].

In spite of its high hydrogenolysis activity, rhodium has poor stability and ethane selectivity at high temperatures[19, 21]. For instance, at temperatures above *ca.* 280°C Rh/SiO_2 was found to be selective towards methane in the hydrogenolysis of lower members of alkane family[19], and was also found to deactivate fast in the hydrogenolysis of propane[21].

In this work, we report the catalytic properties of sol-gel Pt_x-Rh_{1-x}/SiO_2 [x = 0, 0.2, 0.4, 0.5, 0.6, 0.8, 1.0] in the hydrogenolysis of propane, and in the temperature range of 150–550°C. We also report the effect of changing hydrogen and/or propane pressure on the conversion of propane. The kinetic parameters of this reaction, such as the activation energy and reaction order are also reported.

Because of its known high catalytic activity in the hydrogenolysis of alkanes, rhodium metal was chosen as a major constituent of the bimetallic catalysts used in this investigation[24]. Also, the choice of platinum metal as another constituent emerged from its well-known good catalytic properties, thermal stability and deactivation resistance. Sol-gel SiO_2 support was chosen because of its relatively high BET surface area, strong metal-support interaction, and the good catalytic properties of SiO_2 itself in this particular reaction[34]. Therefore, by preparing Pt-Rh/SiO_2 catalysts *via* the sol-gel method, we aimed at making catalysts that possess the good catalytic properties of rhodium and of SiO_2, the high BET surface area produced from the sol-gel technique, and the improvement inflicted from the incorporation of platinum on these catalysts. Moreover, supported Pt-Rh bimetallic catalysts have good catalytic properties and stability in many reactions, such as the hydrogenolysis of alkanes[19], the hydrogenation of toluene[28], dehydrogenation and hydrogenolysis of cyclohexane[24], and in propane oxidation and steam reforming[25].

EXPERIMETAL

Pt_xRh_{1-x}/SiO_2 (x = 0, 0.2, 0.4, 0.5, 0.60, 0.80, 1.0) catalysts were prepared of 5% metal loading on SiO_2 by the sol-gel method. Platinum and rhodium were obtained as $PtCl_4$ and $RhCl_3\cdot 3H_2O$, respectively (Jansen Chimica). The SiO_2 sol-gel support was prepared from tetraethoxysilane of 98% purity (Fluka). Propane gas used in this reaction was of > 99.5% purity (Matheson). Helium and hydrogen gases (Arab Gas Co.) were purified from water vapour and oxygen by using proper traps.

Catalyst Preparation

Samples of the sol-gel catalysts (*ca.* 5 g each) were prepared by mixing aqueous solutions (*ca.* 50 mL) of proper concentrations of $PtCl_4$ and $RhCl_3\cdot 3H_2O$ with 18 mL absolute ethanol in a 250 mL round bottom flask. The pH of the solution was adjusted to <1 by adding drops of concentrated HCl (aq). This solution was heated to 60°C and then, 18 mL of tetraethoxysilane were added dropwise while stirring. The mixture was then refluxed until gelation took place.

The formed gel was left overnight in air, so that moisture was absorbed and hydrolysis was completed. The gel was dried in an electric oven at 110°C under air for 24 h. The resulting solid mass was crushed, powdered, and calcined in a quartz fixed-bed flow reactor in flowing air (100 mL/min), at 350°C for 1 h. After that, helium gas was passed through it for 5 min, and then hydrogen gas was introduced at a flow rate of 60 mL/min at 450°C for 4 h. At the end of this oxidation/reduction process, the catalyst was cooled slowly to room temperature under helium atmosphere. This process produces sol-gel catalysts with high surface area (Table-1). The BET surface area of the obtained sol-gel catalysts was measured using a specially built, modified and calibrated N_2 adsorption single-point apparatus[35].

Reactions

A 0.50 g sample of each catalyst was placed on the catalyst bed of a vertical 30 cm long × 1.5 cm I.D. quartz reactor. The catalyst bed is a quartz fitted-disc located at 10 cm above the bottom of the reactor. An electric tubular quartz oven with a temperature controller (Digi-sense) was used for heating the reactor. Prior to any experiment, hydrogen gas was passed through the catalyst sample at 450°C for 30 min, for catalyst activation. Helium, hydrogen and propane gases were introduced to the reactor after mixing, *via* a four-channel electronic mass flow controller (Matheson, model 8274). Their flow rates were 80 mL/min, 15 mL/min and 5 mL/min, respectively. The temperature was gradually increased from 100 to 550°C and the produced gaseous mixture was analyzed by gas chromatography. The % conversion of propane at all reaction temperatures was calculated, and the temperature of 100% conversion was determined for each catalyst (Table-1).

TABLE-1
BET SURFACE AREA, CATALYTIC SELECTIVITY, AND TEMPERATURES OF 100% CONVERSION OF ALL SOL-GEL CATALYSTS

Catalyst[a]	BET surface area (m^2/g)	Ethane selectivity[b] (%)	Temperature of 100% conversion (°C)
Rh	554	< 50	215
$Pt_{20}Rh_{80}$	562	< 50	220
$Pt_{40}Rh_{60}$	570	50	210
$Pt_{50}Rh_{50}$	578	50	200
$Pt_{60}Rh_{40}$	576	50	230
$Pt_{80}Rh_{20}$	597	50	268
Pt	595	50	550

[a] All metal catalysts are supported on SiO_2 and prepared by sol-gel method.

[b] Ethane selectivity = (% ethane/% conversion) × 100%, at % conversions < 100%.

To determine the effect of hydrogen pressure on this reaction, another set of experiments was performed on a 0.50 g sample of $Pt_{50}Rh_{50}/SiO_2$ catalyst. Hydrogen gas was passed over the catalyst sample 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 180, 190 and 200°C. A third set of experiments was carried out to determine the effect of propane pressure. Propane gas was passed over 0.50 g of $Pt_{50}Rh_{50}/SiO_2$ at 200°C with flow rates of 2.5 to 25 mL/min, hydrogen gas flow rates of 7.5 to 75 mL/min ($H_2/C_3H_8 = 3$) and helium gas was passed to complete the total flow rate to 100 mL/min. Also, 2.5 to 30 mL/min propane gas, 7.5

mL/min hydrogen gas and helium gas which completes the total flow rate to 100 mL/min were passed over a 0.50 g sample of $Pt_{50}Rh_{50}$ at 200°C.

The effect of catalyst mass and the activation energy of this reaction were determined by passing a mixture of helium gas (80 mL/min), hydrogen gas (15 mL/min) and propane gas (5 mL/min) over four samples of different masses (0.10, 0.25, 0.50, 1.0 g) of $Pt_{50}Rh_{50}/SiO_2$, and in the temperature range of 150 to 300°C. For the purpose of investigating the stability of this catalyst with time on stream, the above experiments were also run continuously at 200°C for 24 h.

Analysis

A gas chromatograph (HP 5890) with TCD connected to an electronic integrator (Spectra-Physics) was used for analyzing samples of the gaseous mixtures. A six-port valve with a 50 μm sampling loop was used for sample injection. The separation of the mixture was performed on a 2.0 m long × 3.0 mm O.D. S.S. column packed with 10% squalene on 80–100 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 G.C./M.S. (VG Analytical Instruments, VG 7070 E) for structure confirmation.

RESULTS AND DISCUSSION

Generally, all catalysts have shown large and close BET surface areas *ca.* 580 m^2/g (Table-1). Rh/SiO_2 has a surface area of *ca.* 40 m^2/g lower than Pt/SiO_2. This difference in surface area is due to the higher rate of sintering of rhodium catalysts compared to platinum catalysts.

Activity and Selectivity

In the hydrogenolysis of propane, the temperature of 100% conversion was taken as a measure of catalytic activity, where lower temperatures indicate higher activity. Rh/SiO_2 and all other rhodium-containing catalysts have shown very high conversions at lower temperatures (Table-1). For instance, the temperature of 100% conversion for all catalysts, except Pt/SiO_2, was in the range of 200 to 268°C. $Pt_{50}Rh_{50}/SiO_2$ was superior to all other catalysts. Pt/SiO_2 is the least active; it needed a temperature of *ca.* 550°C to reach 100% conversion. This high activity of rhodium catalysts is inherent in rhodium itself, which is known to be very active in this respect, whereas platinum catalysts were reported to be of much lower activity[19, 22, 24]. Oliver *et al.*[19] have reported that Rh/SiO_2 catalyst prepared by conventional impregnation methods is *ca.* 1.7×10^3 times more active in the hydrogenolysis of propane than Pt/SiO_2. Here, it has been found that Pt/SiO_2 is relatively inactive when compared to the other catalysts. It did not show significant conversions at temperatures below 350°C, whereas Rh/SiO_2 reached 100% conversion at 215°C. Therefore, it is impossible to make an accurate comparison between these two catalysts in this respect. It is worth mentioning that Rh/SiO_2, contrary to the other catalysts, deactivates fast. This is in agreement with other reports[20].

The catalyst's selectivity is defined here as the (% ethane/% conversion) × 100%, at temperatures below the temperature of 100% conversion. All catalysts, except Rh/SiO_2 and $Rh_{80}Pt_{20}/SiO_2$, have a selectivity of 50% (Fig. 1), whereas Rh/SiO_2 and $Rh_{80}Pt_{20}/SiO_2$ have a selectivity slightly favouring the production of methane (Table-1). This may be due to the high rhodium activity, which has led to high successive demethylation of propane. At temperatures of 100% conversion, the methane selectivity of all catalysts was drastically shifted to 100% (Fig. 1). This observation, which is in agreement with results of similar studies[32], suggests that the conversion of propane over all used catalysts may follow the following two consecutive steps:

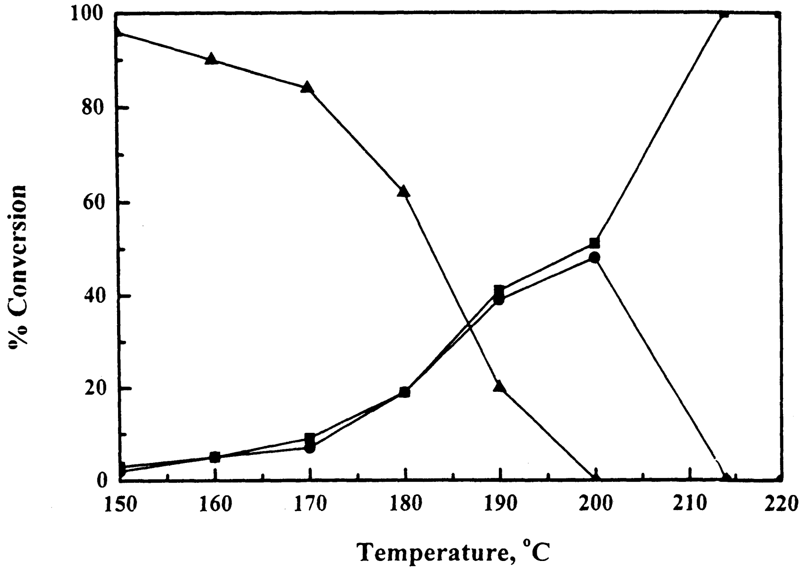

Fig. 1. Hydrogenolysis of propane over sol-gel $Pt_{50}Rh_{50}/SiO_2$ catalyst as a function of temperature: ▲, Propane; ●, ethane; ■, methane.

$$C_3H_8 \xrightarrow{H_2} C_2H_6 + CH_4 \tag{1}$$

$$C_2H_6 \xrightarrow{H_2} 2CH_4 \tag{2}$$

The step represented by equation (2) is observed only at % conversions of 100%, because at lower % conversions propane would be present, and its conversion is easier than that of ethane, whereas at a 100% conversion (zero propane), ethane is the only hydrocarbon present with C—C bond, and thus it is hydrogenolyzed. Another possibility is that a change in mechanism at high temperatures may have taken place, causing the reaction to select the path represented by equation (3). However, at lower temperatures, the route in equation (3) seems not to be present here, because CH_4/C_2H_6 ratio is constant and equals unity at all conversions of < 100%.

$$C_3H_8 \xrightarrow{2H_2} 3CH_4 \tag{3}$$

Kinetic Parameters for $Pt_{50}Rh_{50}/SiO_2$ Catalyst

The reaction rates were determined from equation (4), where

$$R = (F_{prop.} \cdot C)/M_{cat} \tag{4}$$

R = Rate of conversion of propane (mmol g^{-1} s^{-1}).

F_{prop} = Flow rate of propane gas at 1.0 atmosphere, 20°C and in mmol s^{-1}.

M_{cat} = Mass (g) of catalyst sample used in a particular experiment, and is equal to 0.50 g for all experiments, except those related to the variation in the catalyst mass.

C = Conversion of propane in a particular experiment, and it has values ranging from 0 to 1.

The rate of conversion of propane at 200, 190 and 180°C was strongly reduced when hydrogen pressure was increased from 0.10 to 0.70 atm (10–70 mL/min) (Fig. 2A). At all temperatures, as hydrogen pressure increases, the rate of conversion decreases until it reaches a minimum. For instance, at 200°C and $P_{H_2} = 0.225$ atm, the conversion increased to 100%, and then it starts to decline as P_{H_2} increases until it reached < 20% at $P_{H_2} = 0.70$ atm. This decrease in % conversion upon increasing P_{H_2} is due to high surface coverage with hydrogen. This is also emphasized at $P_{H_2} > 0.30$ atm, where % conversion becomes drastically reduced. While at $P_{H_2} = 0.225$ atm (H_2/C_3H_8 ratio = 3), a conversion of 100% was observed. Moreover, at $P_{H_2} < 0.225$ atm the % conversion was initially high, but it declined rapidly as P_{H_2} decreased (% conversion = 0 at $P_{H_2} < 0.05$ atm). This is due to the rapid deactivation of the catalyst caused by an extensive C—H bond cleavage, which is initiated by the low availability of hydrogen and thus coke formation on the catalyst surface.

Determination of the reaction order: The power rate law [equation (5)] was used to calculate the reaction orders, (n and m), with respect to propane and hydrogen partial pressures ($P_{C_3H_8}$ and P_{H_2}),

$$R = k \cdot P_{C_3H_8}^{n} \cdot P_{H_2}^{m} \tag{5}$$

respectively. The reaction orders of the reactants were calculated from the data obtained from several experiments, in which the partial pressure of one gas was varied and the partial pressure of the other gas was kept constant. The total pressure was maintained constant at 1.0 atmosphere (atm) by varying the partial pressure of the inert gas, helium, in an open system. So ln R was plotted against ln P_{H_2} ($P_{H_2} = 0.025$ to 0.70 atm) at three different temperatures (180, 190 and 200°C), over $Pt_{50}Rh_{50}/SiO_2$ catalyst,and at constant propane partial pressure (0.075 atm). The reaction order with respect to hydrogen gas was then calculated from the slopes of the obtained straight lines in Figure 2B, and found to be –2. Figure 2B shows that at P_{H_2} lower than 0.10 atmosphere ($H_2/C_3H_8 = 1.33$), a deviation from linearity is observed at 180 and 190°C. Also, a similar behaviour was observed at 200°C, but at $P_{H_2} \leq 0.275$ atm. These deviations occur at high % conversions (> 80%) and at catalyst deactivation ($P_{H_2} \leq 0.10$) (Fig. 2). Fig. 2B shows a linear relationship between ln R and ln P_{H_2} at the three reaction temperatures and in the P_{H_2} range of 0.225–0.700 (22.5–70 mL/min), with a deviation from linearity in the 200°C case due to the higher rate of conversion at this temperature. At $P_{H_2} < 0.225$ atm, the catalyst suffers rapid deactivation. From the negative slopes of these plots, an order of –2 with respect to hydrogen was calculated. This negative value indicates that hydrogen pressure has a negative effect on the rate of conversion, and thus suggests the possibility of high hydrogen coverage on the metal surface at high P_{H_2}, as well as, strong hydrogen/metal-surface bonds.

Similarly, the order with respect to propane was calculated for the same catalyst at 200°C, constant hydrogen pressure (0.15 atm) and various propane partial pressures (0.025 to 0.300 atm). ln R was plotted against ln $P_{C_3H_8}$, and the order was calculated from the slope of the obtained straight line and found to equal +0.55 (Fig. 3A). At $P_{C_3H_8} > 0.175$ atm, a deviation from linearity was observed (Fig. 3), which is due to high surface coverage with propane (the order was calculated from points obtained at $P_{C_3H_8} \leq 0.175$ atm). The value so obtained has no contradiction with the values obtained in similar studies, where first-order values were reported[14–17]. The small magnitude (+0.55) of this order may indicate that a surface saturation with propane had occurred.

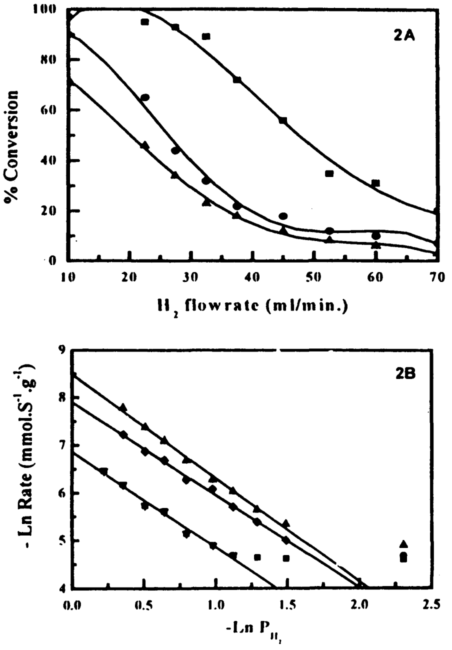

Fig. 2. The effect of changing hydrogen partial pressure on the rate of conversion of propane over $Pt_{50}Rh_{50}/SiO_2$ catalyst at different temperatures: ■, 200°C; ●, 190°C; ▲, 180°C. (A) The effect of hydrogen flow rate and temperature on the rate of conversion. (B) A plot of ln rate of conversion of propane *vs.* ln hydrogen pressure.

Increasing $P_{C_3H_8}$ from 0.025 to 0.30 atmosphere (2.5–30 mL/min) at a constant P_{H_2} (0.075 atm) and at 200°C had led to a strong decline in the % conversion of propane (Fig. 3B). It decreased from 100% at $P_{C_3H_8} = 0.025$, to 20% at $P_{C_3H_8} = 0.30$ atm. This decline in the % conversion is possibly due to two factors; firstly, at hydrogen/propane ratios less than three and at 200°C, an extensive C—H and C—C bonds cleavage occurred. This led to the formation of carbonaceous residues on the catalyst surface, and thus decreased the catalyst activity[27]. Secondly, the increase in propane pressure would certainly affect its rate of conversion in accordance with its reaction order. In Fig. 3B, two curves represent the effect of increasing $P_{C_3H_8}$; at $H_2/C_3H_8 = 3$; and at constant P_{H_2} (0.075 atm). In the first case, the decline in rate is minimal because of the fact that the formation of carbonaceous residues under these conditions is also minimal due the adequate availability of hydrogen. On the other hand, at $P_{H_2} = 0.075$ atm, the decline in rate is high because of the low availability of hydrogen and thus possible catalyst deactivation due to coke formation.

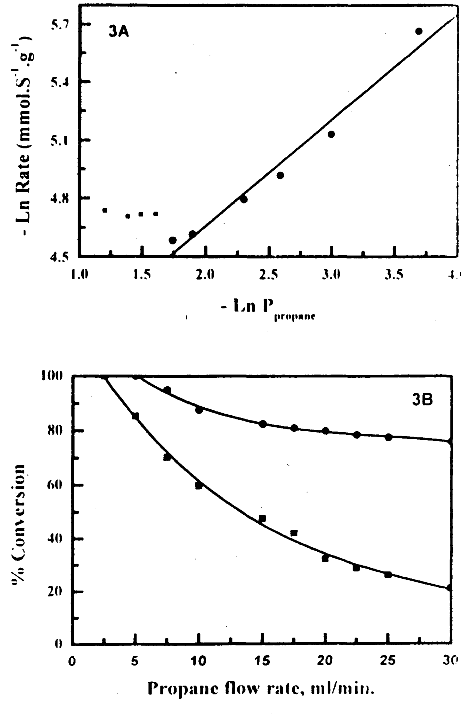

Fig. 3. The effect of changing propane partial pressure on the rate of conversion of propane over Pt$_{50}$Rh$_{50}$/SiO$_2$ catalyst at 200°C.A) A plot of Ln rate of conversion vs. Ln propane pressure, t 0.075 atm hydrogen pressure. B) The effect of propane flow rate on % conversion at different hydrogen flow rates: ■, hydrogen flow rate = 7.5 mL/min; ●, hydrogen/propne flow rates ratio = 3.

Determination of the activation energy: The conversion of propane to methane and ethane over the different catalyst masses was measured as a function of temperature (Fig. 4A). It is seen over all catalyst masses that % conversion increases rapidly with temperature. Also, at any temperature, as the catalyst mass increases the % conversion increases. To calculate the activation energy for this reaction over all the different masses of $Pt_{50}Rh_{50}/SiO_2$ catalyst, Ln R was plotted *vs.* 1/T (K) at constant P_{H_2} and $P_{C_3H_8}(H_2/C_3H_8 = 3)$, and in the temperature range of 150–250°C (Fig. 4B). A linear relationship was obtained for the four catalyst masses, with very similar slopes and very high correlation coefficients (> 0.99). The activation energy was then calculated from these slopes and found to equal 123 ± 7 kJ/mol. This value is better than other values reported for similar studies[13, 17, 19, 20]. For example, Oliver *et al.*[19] reported a value of 174 ± 10 kJ/mol for the hydrogenolysis of propane over Rh/SiO_2. Also, Bond *et al.*[20] reported activation energy values in the range of 202–242 kJ/mol.

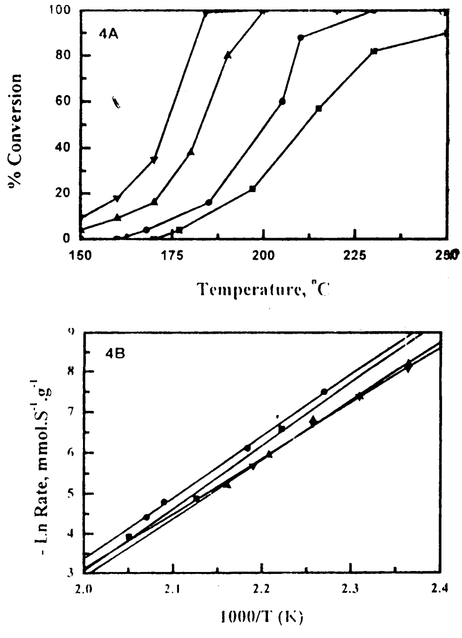

Fig. 4. The effect of changing catalyst mass on the conversion of propane over $Pt_{50}Rh_{50}/SiO_2$ catalyst: ■, 0.10 g; ●, 0.25 g; ▲, 0.50 g; ▼, 1.0g (.A) % conversion *vs.* temperature. (B) Arrhenius plots for the different $Pt_{50}Rh_{50}/SiO_2$ catalyst masses.

ACKNOWLEDGEMENTS

The author wishes to acknowledge financial support provided by the Deanship of Scientific Research and Graduate Studies at Yarmouk University.

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(*Received*: 13 May 2002; *Accepted*: 22 July 2002) AJC-2802