Kinetic study of CO_2 reforming of propane over Ru/Al_2O_3

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The rate of reaction of propane over a Ru/Al_2O_3 catalyst was determined as a function of the partial pressures of the reactants, C_3H_8 and CO_2 at 600 and 650 °C. The order of the reaction was found to be fractional with respect to carbon dioxide, indicating its involvement in the rate-determining step of the reaction. The order of the reaction was zero in propane indicating the fast reaction of propane over the catalyst. The apparent activation energies for propane and the formation of hydrogen and carbon monoxide were investigated. Values for the formation of hydrogen and carbon monoxide indicated a decrease in the $CO:H_2$ ratio with an increase in temperature. Modelling of the kinetic data was inconclusive in the selection of a possible mechanism as good fits were observed for a Langmuir–Hinshelwood and a Mars–van Krevelen mechanism.

KEY WORDS: carbon dioxide; propane; reforming; ruthenium catalyst

1. Introduction

The most economical product of biomass gasification is the production of a clean synthesis gas stream for an integrated combined cycle [1]. The advances currently being made in gasification technology/design have led to the complete elimination of tarry hydrocarbons under certain conditions and with the use of guard beds such as dolomite [2]. However, the contamination of the gas stream by smaller hydrocarbons such as methane and propane, even at low concentrations can cause serious problems in the end use of the gas stream. Short chain hydrocarbons such as propane are often a constituent of the product gas from biomass gasification and are also present (in small quantities) in natural gas. This paper presents a kinetic study for the reaction of carbon dioxide with propane (equation (1)) over the catalyst, 1 wt% ruthenium on alumina,

$$3CO_2 + C_3H_8 \rightleftharpoons 6CO + 4H_2 \tag{1}$$

This catalyst was selected as it has been shown to have a longer life and better selectivity than other catalysts tested for the CO_2 reforming of hydrocarbons in a model gas stream (42 mol% H_2, 15.5 mol% CO, 5.1 mol% CH_4, 19.0 mol% CO_2 and 18.3 mol% C_3H_8) [3].

2. Experimental

The catalyst selected for the investigation was 1 wt% ruthenium on alumina catalyst (20 mg for each experiment) and was prepared by wet impregnation [3]. Before each experiment the catalyst was reduced *in situ* in a flow of 20% H_2/N_2 at 400 °C for 1 h. A stabilised, active catalyst was employed for each experiment. The reactant partial pressure was varied, keeping the total flow rate constant at 60 $ml\,min^{-1}$ by adding argon ballast to the system. The propane conversion was below 10% for all temperatures investigated and preliminary experiments showed the system to be in the kinetic regime with particle sizes smaller than 600 μm. The temperatures at which the experiments were carried out were 600 and 650 °C. Preliminary experiments with the Ru/Al_2O_3 catalyst were performed and the catalyst showed a good stability at 650 °C over a period of 30 h with no evidence of carbon formation. Mass balances for C, H and O were maintained for each experiment within ±5%.

Kinetic orders for the reaction with respect to C_3H_8 and CO_2 were determined by following the rate of C_3H_8 consumption. For these measurements the partial pressure of one of the reactants was held constant while the other was varied. For the determination of orders with respect to C_3H_8, the partial pressure of CO_2 was held constant at 50.65 kPa while that of C_3H_8 was varied between 6.75 and 23.64 kPa. For the determination of orders with respect to CO_2, the partial pressure of C_3H_8 was held constant at 23.64 kPa while that of CO_2 was varied between 16.88 and 50.65 kPa. Activation energy was investigated experimentally by maintaining a constant reactant flow rate and catalyst volume and varying the temperature from 500 to 700 °C in 50 °C steps.

3. Results

3.1. The effect of varying temperature and C_3H_8 partial pressure on the rate of reaction

Figure 1 shows the order of the reaction with respect to $P_{C_3H_8}$, determined from a plot of the natural log of the rate C_3H_8 consumption *versus* the natural log plot of $P_{C_3H_8}$. The partial order is close to zero in C_3H_8. The rate of reaction of the C_3H_8 consumed is almost constant as the partial pressure of C_3H_8 is increased. The change in temperature shows that

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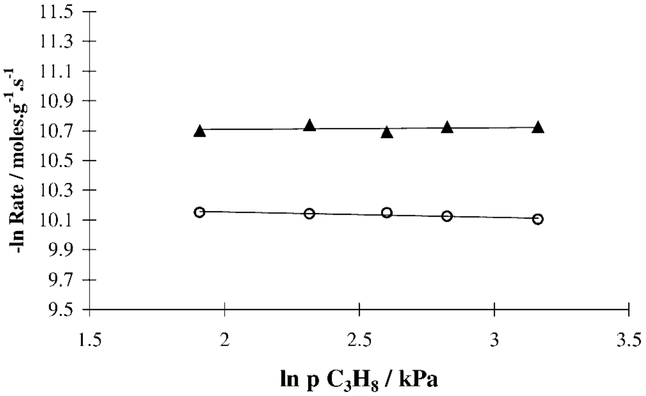


Figure 1. Order with respect to C_3H_8 based on C_3H_8 consumption, the partial pressure of CO_2 being kept constant at 50.65 kPa. (▲) 600 and (○) 650 °C.

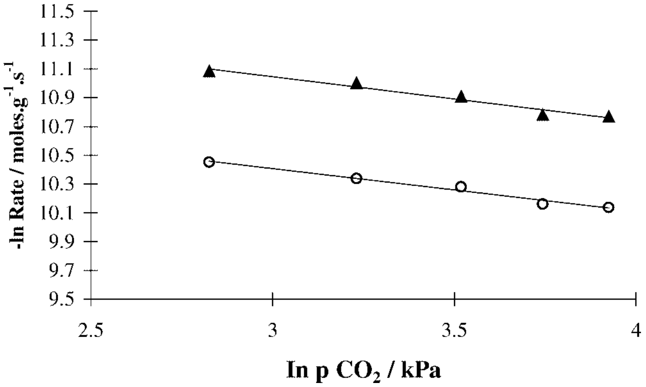


Figure 2. Partial order with respect to CO_2 for C_3H_8 consumption the partial pressure of C_3H_8 being kept constant at 23.64 kPa. (▲) 600 and (○) 650 °C.

the rate of C_3H_8 consumption increased as the temperature was increased from 600 to 650 °C.

3.2. The effect of varying temperature and CO_2 partial pressure on the rate of reaction

Figure 2 shows the order with respect to P_{CO_2}, determined from a plot of the natural log, of the rate consumption of C_3H_8 *versus* the natural log plot of P_{CO_2}. The rate of conversion of C_3H_8 increases as a function of the partial pressure of the CO_2 over the range investigated. The partial order for C_3H_8 consumption in CO_2 is 0.3.

Thus the reaction order with respect to C_3H_8 is zero order. While the order with respect to CO_2 is 0.3 (equation (2)). The change in temperature shows that the rate of propane consumption increased as temperature increased from 600 to 650 °C.

$$\nu = k\big[C_3H_8\big]^0\big[CO_2\big]^{0.3}. \tag{2}$$

3.3. Activation energies for CO_2 reforming of C_3H_8

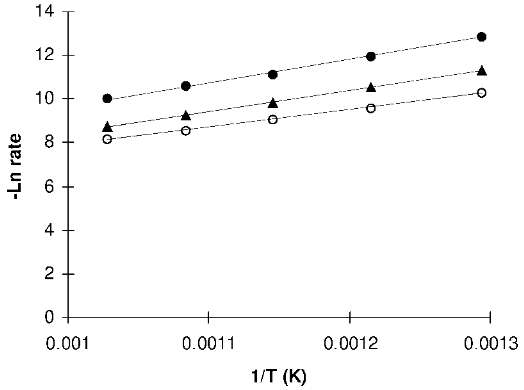


Figure 3. Arrhenius plot for temperature range 500–700 °C for the consumption of CO_2. (●) C_3H_8 conversion, (○) CO production and (▲) H_2 production.

Figure 3 shows the Arrhenius plot for the activation of C_3H_8 and the formation of H_2 and CO. The linear portion of an Arrhenius plot may be used to calculate the activation energy of a reaction. The activation energy of the C_3H_8 conversion was calculated as 86 kJ mol^{-1}. From the temperature dependence of the rates of H_2 and CO production the activation (figure 3) energies were calculated as 80 and 66 kJ mol^{-1}, respectively.

3.4. Modelling of the kinetic data

From the apparent reaction orders presented, two kinetic models can be selected for consideration. The Eley–Rideal model is not a suitable model for the reaction since a first-order dependency for the component reacting from the gas phase is required. The adsorption of carbon dioxide can be associative or dissociative and may occur on the same or different sites than those for adsorption of propane. According to the Langmuir–Hinshelwood mechanism four equations can be derived which describe the dependence of the reaction rate on the partial pressure of propane and carbon dioxide.

Model LH1: adsorption on the same sites with associative adsorption of carbon dioxide

$$\nu_{LH1} = \frac{k b_{CO_2} p_{CO_2} b_{C_3H_8} p_{C_3H_8}}{\big(1 + b_{CO_2} p_{CO_2} + b_{C_3H_8} p_{C_3H_8}\big)^2}. \tag{3}$$

Model LH2: adsorption on the same site with dissociative adsorption of carbon dioxide

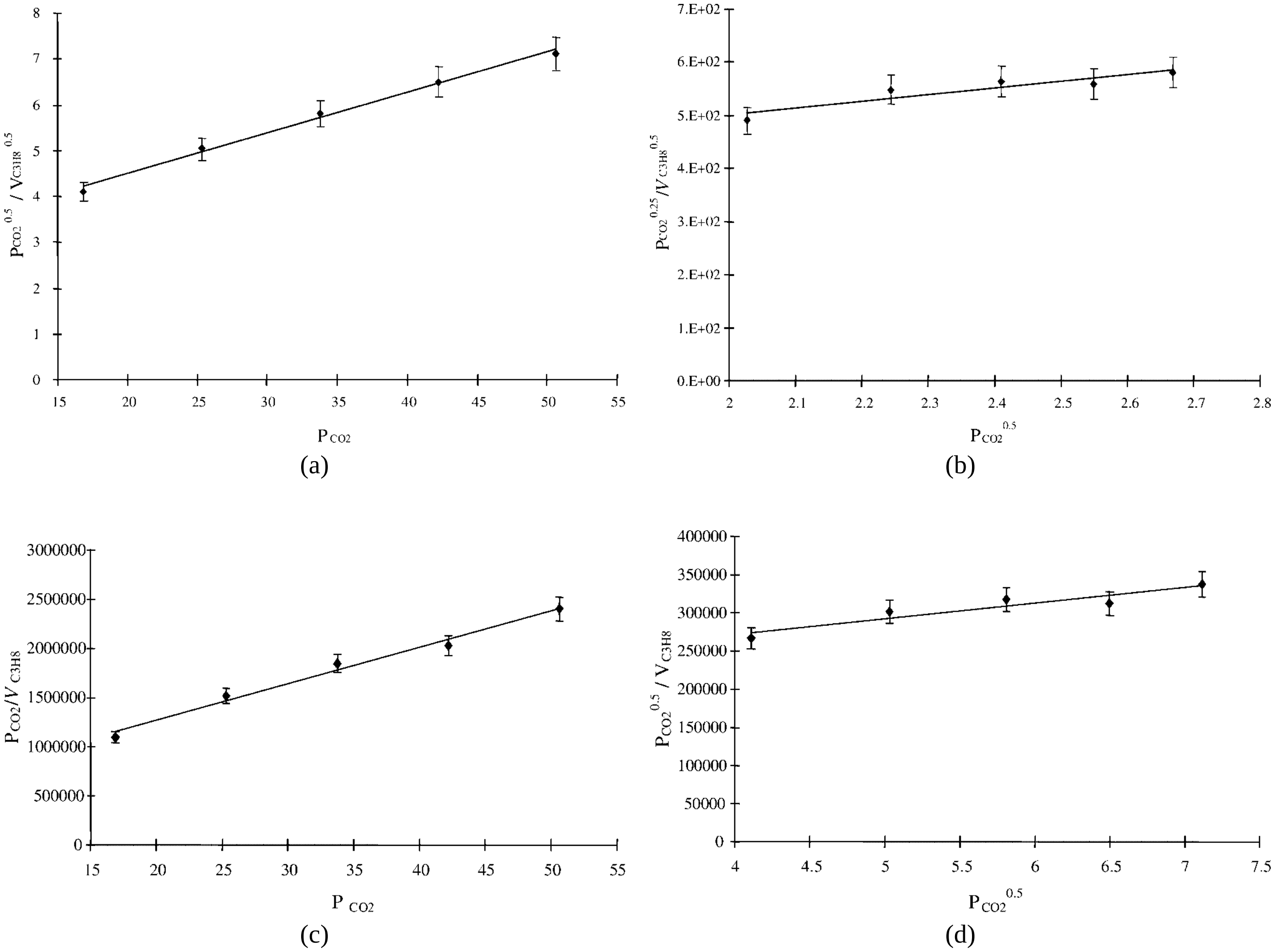
$$\nu_{LH2} = \frac{k\sqrt{b_{CO_2} p_{CO_2}}\, b_{C_3H_8} p_{C_3H_8}}{\big(1 + \sqrt{b_{CO_2} p_{CO_2}} + b_{C_3H_8} p_{C_3H_8}\big)^2}. \tag{4}$$

Model LH3: adsorption on different sites with associative adsorption of carbon dioxide

$$\nu_{LH3} = \frac{k b_{CO_2} p_{CO_2} b_{C_3H_8} p_{C_3H_8}}{\big(1 + b_{CO_2} p_{CO_2}\big)\big(1 + b_{C_3H_8} p_{C_3H_8}\big)}. \tag{5}$$

Model LH4: adsorption on different sites with dissociative adsorption of carbon dioxide

$$\nu_{LH4} = \frac{k\sqrt{b_{CO_2} p_{CO_2}}\, b_{C_3H_8} p_{C_3H_8}}{\big(1 + \sqrt{b_{CO_2} p_{CO_2}}\big)\big(1 + b_{C_3H_8} p_{C_3H_8}\big)}. \tag{6}$$



(a) (b)

(c) (d)

Figure 4. Linearisation of the P_{CO_2} dependence according to models LH1 (a), LH2 (b), LH3 (c) and LH4 (d) at 600 °C.

For the above equations p_{CO_2} and $p_{C_3H_8}$ are the partial pressures of carbon dioxide and propane, respectively. b_{CO_2} and $b_{C_3H_8}$ are adsorption coefficients for carbon dioxide and propane, respectively, and k is the reaction rate constant. The linearised versions of the above four models can be seen in figure 4 (a)–(d). The correlation coefficients for straight line fits to the various mechanistic models were calculated. These coefficients indicate the suitability of each model to the experimental data obtained.

The correlation coefficient for the Langmuir–Hinshelwood models at 600 and 650 °C are given in table 1.

Figure 4(a) shows a plot of $(P_{CO_2}/r)^{0.5}$ as a function of P_{CO_2} which has a good correlation coefficient (0.994 at 600 °C and 0.989 at 650 °C) for the LH1 model. This model assumes adsorption on the same site for propane and carbon dioxide with associative adsorption of carbon dioxide. The figure 4(b) shows a plot of $P_{CO_2}^{0.5}$ as a function of $P_{CO_2}^{0.25}/r^{0.5}$. The LH2 model which assumes dissociative adsorption of carbon dioxide on the same site of propane has a correlation coefficient which, compared with LH1, is not good evidence of this model (0.896 at 600 °C and 0.878 at 650 °C).

Table 1
Correlation coefficient for linearised Langmuir–Hinshelwood expressions.

Model	T 600 °C	T 650 °C
LH1	0.994	0.989
LH2	0.896	0.887
LH3	0.986	0.993
LH4	0.825	0.894

The plots for linearisation of the models LH3 and LH4 in which it is assumed that propane and carbon dioxide adsorb on different sites are represented in figure 4 (c) and (d). Figure 4(c) shows a plot of $P_{CO_2}/V_{C_3H_8}$ as a function of P_{CO_2} which has a correlation coefficient of 0.986 at 600 °C and 0.993 at 650 °C, which assumes associative adsorption of carbon dioxide on different sites. The plot of $P_{CO_2}^{0.5}/V_{C_3H_8}$ a function of $P_{CO_2}^{0.5}$ has a correlation coefficient of 0.825 at 600 °C and 0.846 at 650 °C. These values are a poor fit for the model, where the carbon dioxide is dissociatively adsorbed on a different site to the propane.

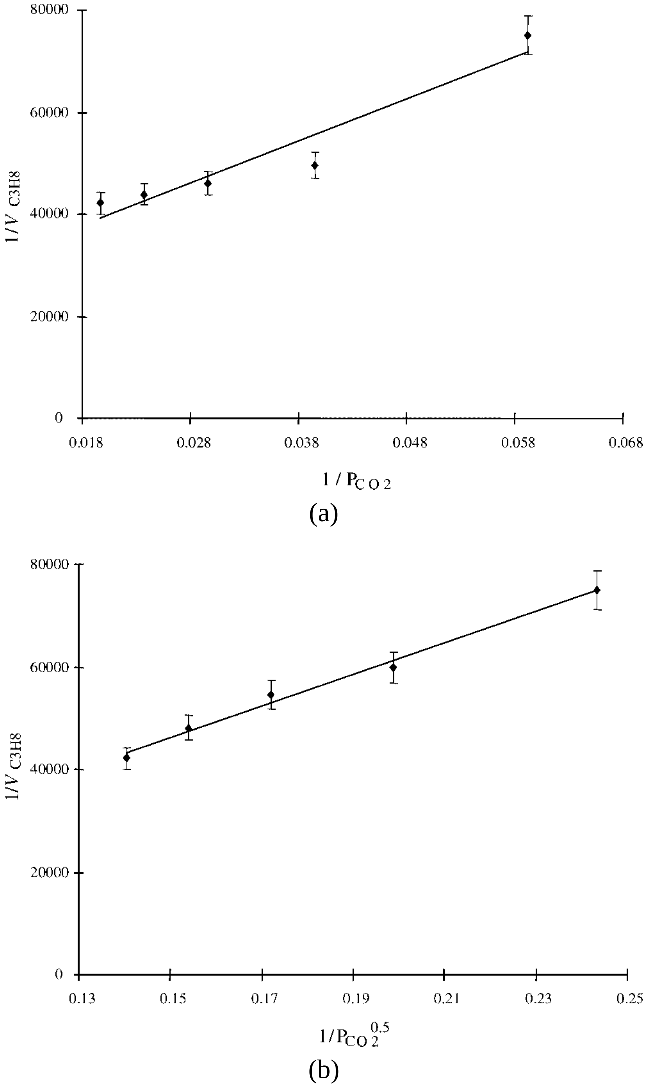


Figure 5. (a, b) Linearisation of the P_{CO_2} dependence according to the Mars–van Krevelen mechanism at 600 °C.

From the Langmuir–Hinshelwood model it is unclear which mechanism is taking place in the reaction. However, the resultant plots give some evidence to a non-dissociative adsorption of carbon dioxide based on the correlation data of the LH1 and LH3 models.

Investigation of the data for the Mars–van Krevelen model in figure 5 shows the plots for both cases of (a) associative adsorption of carbon dioxide and (b) dissociative adsorption of carbon dioxide.

The correlation coefficient for the Mars–van Krevelen models at 600 and 650 °C are given in table 2. The correlation coefficient for the case of associative adsorption of carbon dioxide at both temperatures is quite poor and is an unlikely mechanism for the reaction. The correlation coefficients for the case of dissociative adsorption of the carbon dioxide is consistent at 0.995 and 0.992 at both temperatures. This indicates the greater probability that the propane reacts with the lattice oxygen, while the carbon dioxide in the gas phase facilitates the re-oxidation of the lattice oxygen.

Table 2
Correlation coefficient for linearised Mars–van Krevelen expressions.

Model	T 600 °C	T 650 °C
MvK 1	0.876	0.789
MvK 2	0.992	0.995

4. Discussion

A literature search on the kinetics and mechanism for the carbon dioxide reforming of propane using appropriate data bases yielded no publications. However, there have been several studies on a similar reaction of carbon dioxide and methane, the kinetics and mechanism of which has been the subject of many publications. In the discussion of results reference will be made to available literature, on the reaction of carbon dioxide and methane over various catalysts. This approach may be supported by the fact, that both reactions are dry reforming reactions, and catalysed by Ru/Al_2O_3 catalysts. The similarities of the results and those published will be expanded upon and substantiated by literature and theory.

4.1. Reaction orders for the CO_2 reforming of C_3H_8

The reaction orders with respect to carbon dioxide reforming of propane were determined and are shown in equation (2). The zero-order dependency in propane indicates that the reaction of propane is fast. This implies that the activation of propane and subsequent reaction occurs relatively rapidly over the Ru/Al_2O_3 catalyst. Zero-order dependency in methane for the carbon dioxide reforming of methane has been reported by several groups [4–7]. In 1984 Sakai *et al.* [4] reported kinetic results for carbon dioxide reforming of methane over a 10 wt% Ni/SiO_2 catalyst. The experimental data was collected between 550 and 700 °C under differential conditions. The order, with respect to carbon dioxide was reported as 0.5–0.6. While with respect to methane the order was 0.02–0.05. Erdöhelyi *et al.* [5,8] investigating the reaction over Rh on various supports, have reported a lower order dependency in methane indicating that the methane dissociation is rapid compared to that of carbon dioxide. Van Keulen [6], investigating the mechanism of the reforming of methane over a Pt/ZrO_2 catalyst, reported a zero-order dependency in methane and a positive order in carbon dioxide. This zero order implies that methane is not the rate-determining step as has been observed for the steam reforming of methane. O'Connor *et al.* [7] investigated the reaction over a Pt/ZrO_2 catalyst at 600, 650 and 700 °C. The reaction was found to be approximately first order, in carbon dioxide and zero order, in methane.

For the activation of hydrocarbons it is generally accepted that once the first C–H bond is broken the sequential reaction, to either intermediates or products occurs quite rapidly [9,10,15]. This appears to be the case for the carbon dioxide reforming of propane. It may also be proposed that since there was no evidence of other carbon-

Table 3
Bond strengths of methane and propane.

Bond	D^0_{298} (kcal mol^{-1})
CH_3–H	105
C_3H_7–H	95

containing products, the lifetime of any CH_x intermediates is very short, suggesting that the surface reaction rate of the CH_x species is greater than the formation and desorption of C_{2+} products. This may also be supported by the results of the carbon balance of each experiment which was 97–103% (average) also indicating the absence of hydrocarbon products.

The splitting of the propane molecule may occur on the Ru. This noble metal has been found to be quite active, for the dissociative adsorption of methane to CH_x species, followed by complete decomposition, resulting in adsorbed carbon and adsorbed hydrogen [8,11–13]. Ferreira-Aparicio *et al.* [17] reported the activation of methane to be irreversible over ruthenium on various supports. This was also demonstrated by van Keulen *et al.* [14] for platinum on zirconia catalyst. This irreversible cracking could be considered as a specific property of noble metals. On non-noble metals, like Ni, a large reversible activation was observed under the same conditions [15,16]. Several authors [8,9,15] have argued that the availability of adsorbed oxygen to react with adsorbed CH_x species enhances the activation of the C–H bond. It has also been shown by Ferreira-Aparicio *et al.* [17] that alumina-supported metals have a greater ability to dehydrogenate methane than other supports. It is possible that the same effect will be seen here because of the fast reaction of propane indicated by its zero-order activity. The adsorbed oxygen species will be from the dissociation of carbon dioxide as discussed later.

A propane molecule will be more easily activated than methane, since it is widely accepted that the activation of the first C–H bond is especially difficult for methane [9]. This is also reflected when one compares the bond strengths of propane and methane (table 3). The bond strength for the CH_3–H bond is reported as 105 kcal mol^{-1} while that of the C_3H_7–H bond is reported as 95 kcal mol^{-1} [18].

The reaction order for the reforming of propane was found to be approximately 0.3 in carbon dioxide (equation (2)). This suggests that the carbon dioxide is involved in the rate-determining step. Several authors [4–7,13,19] have reported that the carbon dioxide is involved in the rate-determining step for the reforming of methane. O'Connor *et al.* [7] reported that carbon dioxide was involved in the rate-determining step for the reforming of methane. It was suggested that this slow step may be the adsorption of carbon dioxide or the replenishment of the depleted lattice oxygen with an oxygen atom from the carbon dioxide. Van Keulen [6] showed that on switching from steam reforming to dry reforming of methane, that methane was not involved in the rate-determining step. He concluded that the dissociation of carbon dioxide was the rate-determining step for the reaction. Rostrup-Nielsen and Hansen [11] have also suggested that the rate-determining step may be the dissociation of carbon dioxide. Qin and Lapsezewicz [13], from TPR experiments on a Rh/MgO catalyst, suggested that the carbon dioxide reaction intermediate was an adsorbed oxygen and that the activation of the carbon dioxide may be the rate-determining step.

Solymosi *et al.* [8] observed that the dissociation of carbon dioxide occurred only on reduced catalysts, which was carried out in the absence of adsorbed hydrogen. Adsorbed hydrogen has been shown to promote the dissociation of carbon dioxide [12,20]. It was proposed [8,13] that the activity sequence of the Pt group metals (Ru $>$ Pd $>$ Rh $>$ Pt $>$ Ir) in the dry reforming of methane reaction, reflects their ability to dissociate carbon dioxide and to produce adsorbed oxygen. The adsorbed oxygen scavenges the hydrogen of the CH_4 and hence promotes its dissociation. This is also a possibility for propane reforming.

4.2. Activation energies for the CO_2 reforming of C_3H_8

Kinetically controlled reactions have activation energies exceeding 25 kJ mol^{-1}, while those for diffusion controlled reactions rarely exceed 10–15 kJ mol^{-1}. The activation energy of propane was calculated over the Ru/Al_2O_3 catalyst as 86 kJ mol^{-1}, indicating that the process is not limited by diffusion at the temperatures investigated.

From the temperature dependence of the rate of hydrogen and carbon monoxide production, the apparent activation energies were determined. A higher value for the production of hydrogen (80 kJ mol^{-1}) than that of carbon monoxide (66 kJ mol^{-1}) was observed; as a result there was a decrease in the $CO:H_2$ ratio with an increase in temperature.

4.3. Reaction mechanism for the CO_2 reforming of C_3H_8

The results for the modelling of the kinetic data were not conclusive in the selection of a mechanism. There is a possibility that the reaction may proceed by a Langmuir–Hinshelwood mechanism or a Mars–van Krevelen mechanism. The two possibilities will be discussed.

The Langmuir–Hinshelwood plots (figure 4) give some evidence to a non-dissociative adsorption of carbon dioxide. This is based on the correlation data of the LH1 and LH3 models for the carbon dioxide reforming of propane. From these plots it seems probable that the reaction occurs, *via* non-dissociative adsorption of the carbon dioxide, either on a similar site as the adsorbed propane (figure 4(a)) or on a different site (figure 4(c)). Several authors [11,12,14,15,21,22] have reported that the over all reaction of carbon dioxide reforming of methane can be described by a Langmuir–Hinshelwood mechanism.

Based on the results, it may be tentatively proposed that the mechanism follows the generalised reaction sequence below:

$$C_3H_8 + \text{¤} \rightarrow C_3H_x\text{¤} + (8-x)H\text{¤} \qquad \text{(I)}$$

$$CO_2 + \text{¤} \rightleftharpoons CO_2\text{¤} \qquad \text{(II)}$$

$$C_3H_x\text{¤} \rightarrow C\text{¤} + xH\text{¤} \qquad \text{(III)}$$

$$CO_2\text{¤} + H\text{¤} \rightleftharpoons CO\text{¤} + OH\text{¤} \qquad \text{(IV)}$$

$$C\text{¤} + OH\text{¤} \rightarrow CO + H\text{¤} \qquad \text{(V)}$$

$$2H\text{¤} \rightleftharpoons H_2 + \text{¤} \qquad \text{(VI)}$$

$$OH\text{¤} + H\text{¤} \rightleftharpoons H_2O + 2\text{¤} \qquad \text{(VII)}$$

$$CH_x\text{¤} + OH\text{¤} \rightleftharpoons CH_xO\text{¤} + H\text{¤} \qquad \text{(VIII)}$$

$$CH_xO\text{¤} \rightarrow CO\text{¤} + \frac{x}{2}H_2 \qquad \text{(IX)}$$

$$CO\text{¤} \rightleftharpoons CO + \text{¤} \qquad \text{(X)}$$

However, support for such a reaction sequence could only be confirmed by experiments involving DRIFTS, TAPS or SSITK of the reaction.

It is probable that the propane adsorbs and dissociates on the ruthenium to CH_x (C_{ads} and H_{ads}) (reactions (I) and (III)). Ferreira-Aparicio *et al.* [17], observed this for methane over the same catalyst and conditions during TAP experiments. This activation is reported to be irreversible for methane on noble metals [12,18] and is likely to be the case for propane. The H_{ads} mainly desorbs as hydrogen (reaction (VI)), however, one cannot rule out the possibility of the formation of H_2O (reaction (VII)). This may be a lesser reaction since no water was detected in the kinetic experiments carried out. The amount of water produced may be limited by the fast reaction of adsorbed carbide species (of which there will be significant quantities in the case of propane) with OH_{ads} species to form carbon monoxide and H_{ads} (reactions (V), (VIII) and (IX)). Alumina is well known to act as a reservoir of hydroxyl groups due to its large concentration of acid and basic sites. A similar explanation for the absences of water (for the carbon dioxide reforming of methane) was proposed by van Keulen *et al.* [14]. Consumed alumina hydroxyl groups may be regenerated by water formed during the process (reaction (VII)); this may also account for the absence of water as a major product [16].

Carbon monoxide can be formed by the reaction of adsorbed carbon dioxide with an adsorbed hydrogen atom (reaction (IV)). The fact that hydrogen can enhance the rate of dissociation of carbon dioxide and hence the formation of carbon monoxide has been reported by several authors [8,12,20]. It is also possible that CO will be formed by the reaction of carbon and a hydroxyl group (reaction (V)).

Although the kinetic data complies with a Langmuir–Hinshelwood mechanism, modelling of the data for Mars–van Krevelen also showed good correlation coefficients. This indicates the possibility for the propane reacting with the lattice oxygen, and the carbon dioxide in the gas phase facilitates the re-oxidation of the lattice. The possible reaction sequence is shown below:

$$C_3H_{8(g)} \rightarrow C_yH_{x(Ru^*)} \qquad \text{(XI)}$$

$$C_yH_x \rightarrow yC_{(Ru^*)} + xH_{(Ru^*)} \qquad \text{(XII)}$$

$$C_{(Ru^*)} + O_{(Al_2O_x^*)} \rightarrow CO_{(Al_2O_x^*)} \qquad \text{(XIII)}$$

$$CO_{2(g)} + \text{€}^{O-} \rightarrow CO_{(Al_2O_x^*)} + O_{(Al_2O_x^*)} \qquad \text{(XIV)}$$

$$2H_{(Ru^*)} \rightarrow H_{2(g)} \qquad \text{(XV)}$$

Propane first adsorbs on the ruthenium and then dissociates to give C_yH_x species, which then dissociate further to form atomic carbon and hydrogen. Reactions (XI) and (XII) appear to occur quite rapidly since the reaction is close to zero order in propane. Then, in accordance with a Mars–van Krevelen mechanism, the majority of surface carbon reacts with the lattice oxygen of the alumina, located close to the Ru–Al_2O_3 interface, to form adsorbed carbon dioxide (reaction (XIII)). The lattice oxygen is then replaced with oxygen from the carbon monoxide, in the gas phase to form carbon monoxide (reaction (XIV)). This is supported by evidence, that carbon dioxide is involved in the rate-determining step of the reaction. The H_{ads} mainly desorbs as hydrogen (reaction (XV)). Evidence for a Mars–van Krevelen mechanism has been demonstrated by O'Connor *et al.* [7], for the carbon dioxide reforming of methane over a platinum on zirconia catalyst. Mallens *et al.* [23] have also proposed such a mechanism for the partial oxidation of methane over a rhenium catalyst.

Based on the kinetic data alone it is not possible to identify the mechanism for the reaction. It may be possible that the two mechanisms play some part in the reaction.

5. Conclusions

The kinetics for the reforming reaction of propane over Ru/Al_2O_3 were found to be zero order in propane and 0.3 order in carbon dioxide. Carbon dioxide was identified as being involved in the rate-determining step of the reaction. The activation energy of propane was calculated as 86 $kJ\,mol^{-1}$, indicating that the process was not limited by diffusion at the temperature investigated. The activation energies for the formation of hydrogen and carbon monoxide were calculated as 80 and 66 $kJ\,mol^{-1}$, respectively. As a result there was a decrease in the $CO:H_2$ ratio with an increase in temperature. Analysis of the kinetic data indicated that the reaction may occur *via* a Langmuir–Hinshelwood mechanism, involving adsorption of carbon dioxide and propane on the same sites. However, a good fit of the data was also obtained for a Mars–van Krevelen mechanism. No clear distinction could be made between the two models. Further experiments are required to gain a clearer picture of the mechanism involved.

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