Methanol–steam reforming on Cu/ZnO/Al₂O₃ catalysts. Part 2. A comprehensive kinetic model

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Abstract

Surface mechanisms for methanol–steam reforming on Cu/ZnO/Al₂O₃ catalysts are developed which account for all three of the possible overall reactions: methanol and steam reacting directly to form H₂ and CO₂, methanol decomposition to H₂ and CO and the water-gas shift reaction. The elementary surface reactions used in developing the mechanisms were chosen based on a review of the extensive literature concerning methanol synthesis on Cu/ZnO/Al₂O₃ catalysts and the more limited literature specifically dealing with methanol–steam reforming. The key features of the mechanism are: (i) that hydrogen adsorption does not compete for the active sites which the oxygen-containing species adsorb on, (ii) there are separate active sites for the decomposition reaction distinct from the active sites for the methanol–steam reaction and the water-gas shift reaction, (iii) the rate-determining step (RDS) for both the methanol–steam reaction and the methanol decomposition reaction is the dehydrogenation of adsorbed methoxy groups and (iv) the RDS for the water-gas shift reaction is the formation of an intermediate formate species. A kinetic model was developed based on an analysis of the surface mechanism. Rate data were collected for a large range of conditions using a fixed-bed differential reactor. Parameter estimates for the kinetic model were obtained using multi-response least squares non-linear regression. The resultant model was able to accurately predict both the rates of production of hydrogen, carbon dioxide and of carbon monoxide for a wide range of operating conditions including pressures as high as 33 bar. © 1999 Elsevier Science B.V. All rights reserved.

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1. Introduction

Recently, the possibility of using an on-board methanol–steam reformer to generate hydrogen for a fuel cell engine in various transportation applications has resulted in an increased interest in the study of the methanol–steam reforming process. The most promising type of fuel cell for this application is the low temperature proton exchange membrane (PEM) fuel cell. However, at the operating temperature of PEM fuel cells, the electrocatalyst at the anode is extremely sensitive to CO poisoning. For this reason it is highly desirable to have a kinetic model of methanol–steam reforming which is able to not only predict the rate of production of hydrogen but also the rate of production of undesirable by-product CO.

An enormous amount of research has been published on the surface processes which occur on Cu/ZnO/Al₂O₃ catalysts during methanol synthesis. Various reviews and extensive kinetic studies have been...
published in the last decade [1–4]. The continuation of various debates concerning the reaction mechanism for over three decades is an indication of the complexity of the process. Less has been published concerning the water-gas shift reaction on Cu/ZnO/Al₂O₃ but the debate over whether the mechanism is associative via an intermediate formate or regenerative via a redox reaction involving a special form of copper has continued for a similar period of time [4–7]. By contrast, the literature to date on methanol–steam reforming is relatively limited and only a few studies have attempted to develop kinetic models based on surface reaction mechanisms [8–13].

This paper presents the development of a comprehensive model for the kinetics of methanol–steam reforming on Cu/ZnO/Al₂O₃ catalysts. Surface mechanisms for the main reactions were developed using information from the literature. Progressive improvements were made to the mechanisms based on observations from an extensive experimental program. A set of Langmuir–Hinshelwood rate expressions were then derived based on a steady-state analysis of the final surface mechanisms. The kinetic and thermodynamic parameters for these rate expressions were then obtained by non-linear least squares regression. The model is referred to as comprehensive because it accounts for both the rates of production of hydrogen and of the by-product carbon monoxide.

2. Previous studies of surface mechanisms on Cu/ZnO/Al₂O₃ catalyst

2.1. Methanol synthesis

Based on extensive temperature-programmed reaction and desorption studies, as well as in situ FTIR surface studies, Waugh with various co-workers developed a surface mechanism which proposes that the active site for the predominant reaction in methanol formation from synthesis gas is solely metallic copper [1]. According to Waugh, the other components of the catalyst do not play an active role in the reaction mechanism but are crucial to maintaining a crystal form which provides a large stable surface area with small copper crystallites.

The model of Waugh also proposed that methanol is synthesised almost entirely by the hydrogenation of CO₂ via a bidentate surface formate. The rate-determining step (RDS) in Waugh’s model is the hydrogenation of this surface formate species to formaldehyde or the adsorbed species, hydroxycarbene ion. Millar et al. [14] used infrared spectroscopy to prove the existence of the intermediates involved in Waugh’s mechanism. Fig. 1 is a schematic drawing of the RDS for the mechanism of methanol synthesis from CO₂ proposed by Waugh [1]. The formation of methanol from CO and H₂, which historically was considered to be the reaction path for methanol synthesis, was reported to be 100 times slower than methanol synthesis from CO₂ and H₂.

According to the concept of micro-reversibility [15] it should, theoretically, be possible to use the reverse of the methanol-synthesis mechanism for the methanol–steam reforming process. Attempts to do this, however, were unsuccessful, probably due to the large differences between the operating conditions of the two processes. For example, in methanol–steam reforming the average partial pressure of methanol is much greater and the partial pressure of CO is much less than during methanol synthesis; hence, it would be expected that competitive adsorption of methanol with CO and CO₂ would have a less significant effect on the kinetics of methanol synthesis than on the kinetics of methanol–steam reforming. Indeed, in the review by Skrzypek et al. [2] of the various kinetic models which have been proposed for methanol synthesis, only three of the 15 models included terms for the adsorption of methanol.

Reversible methanol-synthesis mechanisms could be applied to methanol–steam reforming by simply adding terms for the adsorption of other intermediates if the difference in adsorption effects was the only issue. However, recent works by Kalchev et al. [5] and Clausen et al. [16] have shown that the chemical state of Cu/ZnO/Al₂O₃ catalysts is strongly affected by the
reducing potential of the reactant mixture. The much higher partial pressure of CO and the lower partial pressure of steam during methanol synthesis would result likely in the catalyst surface being in a different chemical state than during methanol–steam reforming. Considering these factors, it is unlikely that the reverse of methanol-synthesis rate expressions would be able to explain the kinetics of methanol–steam reforming.

2.1.1. Adsorption of reactants and products in methanol synthesis

Despite the fact that reversible rate expressions for methanol synthesis failed to provide an adequate model of the kinetics of methanol–steam reforming, the literature on the surface processes which occur during methanol synthesis provided a significant amount of information for developing surface mechanisms for the methanol–steam reforming process. Skrzypek et al. [2] have reviewed a large number of publications concerning the adsorption of various reactants, products and possible intermediates in methanol synthesis on Cu/ZnO/Al₂O₃ catalysts. Table 1 provides a brief summary of their review. A great deal of information about the surface processes occurring on Cu/ZnO/Al₂O₃ catalysts is contained in this table. Two key pieces of information which will be used in developing the mechanism for methanol–steam reforming on Cu/ZnO/Al₂O₃ catalysts are:

1. CH₃OH, H₂O, CO₂ and CO all competitively adsorb. This indicates that there is at least one type of active site common to the adsorption of all these species.
2. Hydrogen does not adsorb competitively with the other products and reactants but appears to have a unique mode of adsorption.

2.2. Water-gas shift reaction on Cu/ZnO/Al₂O₃

The exact nature of the surface mechanism for the water-gas shift reaction on Cu/ZnO/Al₂O₃ catalysts has been a matter of debate for many decades. The central issue is whether the reaction proceeds via an associative mechanism or a regenerative mechanism. In the associative mechanism, H₂O and CO react to form an adsorbed intermediate surface formate which then decomposes to form H₂ and CO₂. In the regenerative mechanism, also known as the redox mechanism, copper oxide reacts with CO to form CO₂ and copper metal. Water then dissociates to produce H₂ and a surface oxygen which re-oxidises the copper.

Table 1
Summary of review by Skrzypek et al. [2] on adsorption of reactants during methanol synthesis on Cu/ZnO/Al₂O₃ catalysts

<table>
<thead>
<tr>
<th>Species</th>
<th>Type</th>
<th>ΔH (kJ mol⁻¹)</th>
<th>Competitive adsorbates</th>
<th>Remarks</th>
</tr>
</thead>
<tbody>
<tr>
<td>CO</td>
<td>Non-dissociative</td>
<td>50–70</td>
<td>All other species except H₂</td>
<td>Adsorbs perpendicular to surface with C towards surface</td>
</tr>
<tr>
<td>CO₂</td>
<td>Dissociative</td>
<td>80–128</td>
<td>All other species except H₂</td>
<td>Surface oxygen enhances adsorption by formation of carbonates</td>
</tr>
<tr>
<td>H₂</td>
<td>Dissociative</td>
<td>60 (as CO₂⁻)</td>
<td>–</td>
<td>Forms bonds directly with metal atoms</td>
</tr>
<tr>
<td>H₂O</td>
<td>Non-dissociative and dissociative</td>
<td>20 (θ=0.7)–67 (θ=0)</td>
<td>All other species except H₂</td>
<td>Heat of adsorption is a linear function of surface coverage, θ</td>
</tr>
<tr>
<td>CH₃OH</td>
<td>Dissociative</td>
<td>50–80</td>
<td>All other species except H₂</td>
<td>Hydrogen adsorption is stabilised by adsorption on ZnO to form OH(a)</td>
</tr>
<tr>
<td>HCOO⁻</td>
<td>–</td>
<td>–</td>
<td>All other species except H₂</td>
<td>Forms on all components of the catalyst either by the reaction of H₂ and CO₂ or by OH⁻ and CO</td>
</tr>
<tr>
<td>CH₃O⁻</td>
<td>–</td>
<td>–</td>
<td>All other species except H₂</td>
<td>Formed by dissociative adsorption of CH₃OH</td>
</tr>
<tr>
<td>HCO⁻</td>
<td>–</td>
<td>–</td>
<td>All other species except H₂</td>
<td>Formed by reaction of CO with the hydrided metal</td>
</tr>
</tbody>
</table>
A number of investigators, such as Dümpelmann [12], Waugh [1], and Vanden Bussche and Froment [4], claim that the matter has been settled. Rhodes et al. [6], however, in an extensive review of the literature, have shown that there are a number of issues which still have not been resolved. One of the most confounding factors is that the crystal structure of the catalyst varies for the range of experimental conditions which have been used for the kinetic studies reported in the literature. Rhodes et al. concluded that both regenerative and associative mechanisms may be occurring at comparable rates for some catalyst conditions, while certain catalyst-conditioning treatments may cause one or the other of the mechanisms to dominate.

Campbell and Ernst [7] studied the steady-state kinetics of the forward and reverse water-gas shift reactions on Cu(1 1 1) and the Cu(1 1 0) single-crystal surfaces at medium pressure (1–2000 Torr). They reported evidence of a hydrogen-induced surface reconstruction or phase transition which strongly affected the rate of reaction. Campbell and Ernst made the interesting suggestion that the mechanism may be regenerative but that there is a hydrogen-assisted mode of adsorption for CO2. Hence, CO2 adsorption may involve a H–CO2 bond that would be indistinguishable from the formate intermediate which is the basis of the associative mechanism.

The idea of a hydrogen-induced surface reconstruction of the surface assisting with the adsorption of CO2 introduces the question of the crystal structure of the catalyst and its importance to the mechanism of the water-gas shift reaction. Kalchev et al. [5] studied the relationship between the structure of Cu/ZnO/Al2O3 catalysts and their activity for the water-gas shift reaction. They used a wide array of physical characterisation methods to show that, for Raney copper catalysts, the activity of the catalyst for the water-gas shift reaction appears to depend on the formation of a hydroxy-carbonate structure on the copper crystal surface. This further reinforces the idea that the distinction between an associative versus a regenerative mechanism for the water-gas shift reaction may be an arbitrary choice depending on whether the hydroxy-carbonate crystal structure of the catalyst surface is considered as part of the mechanism.

Dümpelmann [12], in his investigation of methanol–steam reforming on a Cu/ZnO/Al2O3 catalyst, proposed an associative mechanism for the water-gas shift reaction which proceeds through an intermediate formate. Dümpelmann found that this mechanism agreed with his observations of the kinetics of the water-gas shift mechanism under typical operating conditions for methanol–steam reforming. Because of the issues concerning the structure of the catalyst under the operating conditions, discussed above, it was decided to use this mechanism as the basis for the mechanism of the water-gas shift reaction mechanism developed in this work with only minor variations which will be described below.

2.3. Methanol–steam reforming

Until recently, the literature on the kinetics and mechanism of methanol–steam reforming on Cu/ZnO/Al2O3 catalysts was quite limited. Santacesaria and Carrà [8] published a paper which used an empirical approach to develop an expression for the rate of disappearance of methanol. Their rate expression was of the form of a Langmuir–Hinshelwood expression but it was not derived from an explicit mechanism. Amphlett et al. [9–11] reported studies of both the thermodynamics and the kinetics of methanol–steam reforming on Cu/ZnO/Al2O3 catalysts. Again, however, an explicit surface mechanism was not reported, although site blocking by CO adsorption was discussed.

Dümpelmann [12] developed a mechanism for methanol–steam reforming which included the direct formation of CO2 by the reaction of methanol and steam as well as the water-gas shift reaction. He assumed that the rate of the decomposition reaction was negligible. Using the method of analysis proposed by Boudart and Djéga-Mariadassou [17], Dümpelmann concluded that the RDS for methanol–steam reforming is the reaction of adsorbed formaldehyde via either of the following surface reactions:

\[
\text{CH}_2\text{O}^{(1)} + \text{O}^{(1)} \overset{k_{\text{HCOOH}}^{(1)}}{\rightleftharpoons} \text{HCOOH}^{(1)} + S_1 \quad (1)
\]

\[
\text{CH}_2\text{O}^{(1)} + S_1 \overset{k_{\text{CHO}}^{(1)}}{\rightleftharpoons} \text{CHO}^{(1)} + \text{H}^{(1)} \quad (2)
\]

For the WGS reaction the RDS was reported to be the surface reaction between adsorbed CO and surface hydroxyls to produce a formate species:
HO\(^{(1)}\) + CO\(^{(1)}\) $\xrightarrow{k_{\text{HCOO}^{(1)}}}$ HCOO\(^{(1)}\) + S\(_1\)  

Dümpelmann [12] derived a rate expression for methanol–steam reforming of the form

$$r_R = k_R \frac{K_{\text{CH}_3\text{OH}}}{K_{\text{H}_2}} \left( \frac{p_{\text{CH}_3\text{OH}}}{p_{\text{H}_2}} \right) \Theta^2,$$

where \(\Theta\) is the adsorption term, is the fraction of active sites available. The order of importance of adsorption, which presumably is associated with the degree of surface coverage during reaction, was reported as follows: CO\(_2>>\)H\(_2\)O>>CH\(_3\)OH≈CO>0.

Jiang et al. [13] explicitly defined a set of elementary surface reactions which could be analysed to obtain a true mechanistic Langmuir–Hinshelwood rate expression. Jiang et al. carried out a kinetic analysis of the reaction mechanism followed by a regression analysis of kinetic measurements of the rate of steam reforming on a Cu/ZnO/Al\(_2\)O\(_3\) methanol-synthesis catalyst. They obtained the following rate expression:

$$r_R = \frac{k_{\text{CH}_3\text{OH}} \left( K_{\text{CH}_3\text{OH}}/K_{\text{H}_2}^{1/2} \right) \left( p_{\text{CH}_3\text{OH}}/p_{\text{H}_2}^{1/2} \right)}{\left( 1 + \left( K_{\text{CH}_3\text{OH}}/K_{\text{H}_2}^{1/2} \right) \left( p_{\text{CH}_3\text{OH}}/p_{\text{H}_2}^{1/2} \right) + k_{\text{H}_2}^{1/2} p_{\text{H}_2}^{1/2} \right)^2} \left( C_{\text{S}}^T \right)^2,$$

where only the adsorption of methanol and the adsorption of hydrogen were found to have statistically significant effects on the rate of reaction. The kinetic expression developed by Jiang et al. [13] predicts the rate of disappearance of methanol and the rate of formation of CO\(_2\). They claim that the process is 100% selective for CO\(_2\) and that the rate of the WGS reaction is negligible. Although for industrial processes the rate of CO production could be considered negligible, for low temperature fuel-cell applications, where very low levels of CO contamination can severely poison the anode electrocatalyst, the decomposition reaction and the WGS reaction must be taken into account [18].

Despite this simplification used by Jiang et al. [13], the surface mechanism which they propose provides the best explanation for the observed kinetic behaviour and also accounts for the high rate of methyl formate production which occurs when the S/M ratio is low. Their surface mechanism provided the starting point for the further development of the more comprehensive kinetic model presented in this work.

3. Development of a comprehensive mechanism for the reactions of methanol and steam on Cu/ZnO/Al\(_2\)O\(_3\) catalyst

The objective of developing a comprehensive surface mechanism for methanol–steam reforming is to be able to account for the variation in the CO content of the product gas as well as the rate of production of hydrogen. In a previous paper we have shown that it is necessary to include reaction paths which can account for the following three overall reactions [18]:

1. CH\(_3\)OH + H\(_2\)O $\xrightarrow{k_{R}}$ CO\(_2\) + 3H\(_2\)  
2. CO + H\(_2\)O $\xrightarrow{k_{W}}$ CO\(_2\) + H\(_2\)  
3. CH\(_3\)OH $\xrightarrow{k_{D}}$ CO + 2H\(_2\)

Only two of these reactions are linearly independent and any one of the reactions can be expressed as the sum or difference of the other two. Because of this it is not possible to measure the rate of each reaction separately, except in the special instance where one reaction is at equilibrium. The starting point for the mechanisms which were finally developed, therefore, relied heavily on fundamental information from surface studies and adsorption studies found in the literature. The reaction rate expressions derived from the surface mechanisms could only be evaluated against the experimental results as sums or differences of rates. Nevertheless, experimental data provided a number of significant insights into the form of the mechanism and the importance of specific surface processes. Details of the experimental data and the analysis have been presented in a previous publication [18].

3.1. Nature of the active sites

In developing surface mechanisms for Reactions (I)–(III), the basic assumption was made that there are two distinct types of active sites on the surface of the catalyst [18]. One type of site is assumed to be active for methanol–steam reforming and the water-gas shift reaction. It is believed that this type of site is created by the partial decomposition of a hydroxy-carbonate phase that supports the hydroxylation of the inter-
mediate surface formates. The second type of site (which may simply be the face-centred cubic form of elemental copper) was assumed to primarily support the decomposition reaction. Further work concerning the relationship between the crystal phase structure of the catalyst and its activity and selectivity is on-going.

Based on these assumptions concerning the active sites on the catalyst surface, a mechanism is proposed for methanol decomposition that is independent of the mechanism for the other two reactions. The elementary surface processes involved in the mechanisms for the methanol–steam reaction and the WGS reaction occur on Type 1 active sites while the decomposition reaction occurs on a separate and distinct Type 2 active site.

3.2. The RDS for methanol decomposition and methanol–steam reforming

The most frequently used method for determining the RDS for a given reaction mechanism is to test various derived kinetic expressions for goodness-of-fit against kinetic data based on a non-linear regression of a rate model. It has been shown, however, that there are numerous pitfalls and uncertainties associated with discriminating between kinetic models using rate data in this way [19]. On the other hand, information from adsorption studies and other methods of surface analysis can be used to develop a mechanism and postulate a most likely RDS directly. The substantial amount of information from methanol-synthesis research concerning surface processes occurring on supported copper catalysts provides an insight into the surface mechanism for methanol–steam reforming to an extent that is rare in studies of heterogeneous catalysis. In particular, a number of in situ FTIR studies of the surface of copper catalysts in the presence of various reactive atmospheres have shown which intermediates are most readily formed and which are the most stable [1,14].

The adsorption of methanol on oxidised and reduced copper on silica catalyst has been studied using in situ FTIR spectroscopy. Millar et al. [20] were able to show that methanol readily adsorbs dissociatively on copper to form adsorbed methoxy species at temperatures as low as 295 K. At higher temperatures the methoxy groups dehydrogenate to form formaldehyde, or its isomer oxymethylene, which subsequently is converted to a formate [20,21]. As shown in Fig. 2, we have confirmed these observations with diffuse reflectance in situ Fourier transform infrared spectroscopy (DRIFTS) which shows that methoxy and

![Fig. 2. FTIR spectra of surface of Cu/ZnO/Al₂O₃ catalyst after methanol–steam adsorption and heating from 120°C to 200°C, obtained using a Nicolet 510P with a Harrick environmental cell and a “praying mantis” diffuse reflectance attachment.](image-url)
formate groups dominate the surface of the catalyst when exposed to methanol and steam.

Millar et al. [14] proposed a surface mechanism for the formation of methyl formate from methoxy which involves the dehydrogenation of the methoxy to the adsorbed oxymethylene, which in turn rapidly reacts with a methoxy to yield methyl formate. They further showed that, in the absence of water on pure copper, this intermediate methyl formate decomposes to yield CO. Earlier work by Minachev et al. [22] showed that adsorbed formate decomposes to yield only CO₂ and H₂.

Jiang et al. [13], as part of the development of their dehydrogenation–hydrolysis mechanism for methanol–steam reforming, showed that the initial rate of formation of methyl formate from methanol had an activation energy equal to that observed for methanol–steam reforming. This observation indicates that either the adsorption of methanol or the dehydrogenation of the methoxy group is the RDS in methanol–steam reforming. Combining the observations of Jiang et al. [13] and Millar et al. [14] leads to the conclusion that methoxy dehydrogenation is the RDS in methanol–steam reforming. In situ FTIR spectroscopy studies of methanol adsorption on oxide-supported copper also support the hypothesis that methoxy dehydrogenation is the RDS in methanol decomposition [14].

3.3. Unique mode of adsorption of hydrogen

As pointed out in Table 1, adsorption studies have shown that hydrogen does not compete for the same sites that adsorb the oxygen or carbon-containing species. It is likely that the hydrogen adsorption sites are interstitial and may also involve spillover onto a ZnO/Al₂O₃ phase [23]. In a review paper, Burch et al. [24] report that the concept of H₂ spillover in Cu/ZnO/Al₂O₃ catalysts during methanol synthesis has been proposed by various investigators. This observation is also consistent with the concept of surface restructuring suggested by Campbell and Ernst [7] during the water-gas shift reaction on Cu/ZnO/Al₂O₃ catalyst. Active sites exclusively for hydrogen adsorption were therefore incorporated into the mechanism to account for these observations. The H₂ adsorbing site associated with the active phase for the methanol–steam reaction and the WGS reaction is designated as a Type 1a site and the H₂ adsorbing site for the second active phase is designated as a Type 2a site.

3.4. Elementary reactions occurring on Type 1 and Type 1a sites

The following surface mechanism for the methanol–steam reaction and the water-gas shift reaction during the methanol–steam reforming process is proposed. The majority of the elementary reactions are the same as those proposed by Jiang et al. [13]. The main differences involve the assumptions concerning the nature of the active sites and the incorporation of the water-gas shift reaction

\[
S_1 + S_{1a} + \text{CH}_3\text{OH}(g) \xrightleftharpoons{\text{h}_\text{CH}_3\text{OH}} k_{\text{CH}_3\text{OH}} \text{CH}_3\text{O}^{(1)} + \text{H}^{(1a)} \tag{6}
\]

\[
S_1 + S_{1a} + \text{H}_2\text{O}(g) \xrightarrow{\text{k}_{\text{H}_2\text{O}}} \text{OH}^{(1)} + \text{H}^{(1a)} \tag{7}
\]

\[
S_1 + \text{CO}_2(g) \xrightarrow{\text{k}_{\text{CO}_2}} \text{CO}_2 \tag{8}
\]

\[
S_1 + \text{CO}(g) \xrightarrow{\text{k}_{\text{CO}}} \text{CO}^{(1)} \tag{9}
\]

\[
2S_{1a} + \text{H}_2(g) \xrightarrow{\text{k}_{\text{H}_2}} 2\text{H}^{(1a)} \tag{10}
\]

\[
\text{CH}_3\text{O}^{(1)} + S_{1a} \xrightleftharpoons{\text{k}_{\text{CH}_3\text{O}}} \text{CH}_2\text{O}^{(1)} + \text{H}^{(1a)} \text{ (RDS-I)} \tag{11}
\]

\[
\text{CH}_3\text{O}^{(1)} + \text{CH}_2\text{O}^{(1)} \xrightarrow{\text{k}_{\text{CH}_2\text{O}}} \text{CH}_3\text{OCH}_2\text{O}^{(1)} + S_1 \tag{12}
\]

\[
\text{CH}_3\text{OCH}_2\text{O}^{(1)} + S_{1a} \xrightarrow{\text{k}_{\text{CH}_3\text{OCH}_2\text{O}}} \text{CH}_3\text{OCHO}^{(1)} + \text{H}^{(1a)} \tag{13}
\]

\[
\text{CH}_3\text{OCHO}^{(1)} + \text{OH}^{(1)} \xrightarrow{\text{k}_{\text{HCOOH}}} \text{HCOOH}^{(1)} + \text{CH}_3\text{O}^{(1)} \tag{14}
\]

\[
\text{HCOOH}^{(1)} + S_{1a} \xrightarrow{\text{k}_{\text{HCOOH}}} \text{H}^{(1a)} + \text{HCOO}^{(1)} \tag{15}
\]

\[
\text{OH}^{(1)} + \text{CO}^{(1)} \xrightarrow{\text{k}_{\text{HCOO}}} \text{HCOO}^{(1)} + S_1 \text{ (RDS-II)} \tag{16}
\]
3.5. Elementary reactions occurring on Type 2 and Type 2a sites

As stated elsewhere, based on the observations from the earlier kinetic studies, it has been shown that the decomposition reaction is occurring on a different type of active site than the methanol–steam reaction and the water–gas shift reaction [18]. The majority of the elementary reactions, however, were assumed to be the same as those on Type 1 sites. The main difference between the Type 1 and Type 2 sites is that the latter do not support the reaction between hydroxyls and methyl formate; hence, a decarbonylation via a formyl occurs instead of hydroxylation as in steam reforming. Furthermore, because this second phase is structurally different from the phase containing Type 1 and Type 1a sites, it is assumed that the entropy and enthalpy for the adsorption of hydrogen will be somewhat different. A Type 2a site for hydrogen adsorption on the second phase involving copper is therefore required for the decomposition reaction mechanism

\[
\text{HCOO}^{(1)} + \text{S}_{1a} \xrightleftharpoons[k_{-\text{CO}^{(1)}}, a]{k_{\text{CO}^{(1)}, a}} \text{H}^{(1a)} + \text{CO}_2^{(1)} \quad (17)
\]

\[
\text{CH}_3\text{OCH}_2\text{O}^{(2)} + \text{S}_{2a} \xrightleftharpoons[k_{-\text{C}_2\text{H}_6\text{O}^{(2)}}, a]{k_{\text{C}_2\text{H}_6\text{O}^{(2)}, a}} \text{CH}_3\text{OCHO}^{(2)} + \text{H}^{(2a)} \quad (23)
\]

\[
\text{CH}_3\text{OCHO}^{(2)} \xrightleftharpoons[k_{-\text{CH}_3\text{OCHO}}]{k_{\text{CH}_3\text{OCHO}}^{(2)}} \text{CH}_3\text{OCHO(g)} + \text{S}_2 \quad (24)
\]

\[
\text{CH}_3\text{OCHO}^{(2)} + \text{S}_{2a} \xrightleftharpoons[k_{-\text{CO}^{(2)}}, a]{k_{\text{CO}^{(2)}, a}} \text{CH}_3\text{O}^{(2)} + \text{CHO}^{(2)} \quad (25)
\]

\[
\text{CHO}^{(2)} + \text{S}_{2a} \xrightleftharpoons[k_{-\text{CO}^{(2)}, a}]{k_{\text{CO}^{(2)}, a}} \text{CO}^{(2)} + \text{H}^{(2a)} \quad (26)
\]

The difference between the Type 1 and Type 2 sites is therefore required for the decomposition reaction mechanism

\[
\text{S}_2 + \text{S}_{2a} + \text{CH}_3\text{OH}^{(g)} \xrightleftharpoons[k_{\text{CH}_3\text{OH}^{(2)}, a}]{k_{\text{CH}_3\text{OH}^{(2)}, a}} \text{CH}_3\text{O}^{(2)} + \text{H}^{(2a)} \quad (18)
\]

\[
\text{S}_2 + \text{CO}^{(g)} \xrightleftharpoons[k_{-\text{CO}^{(2)}}, a]{k_{\text{CO}^{(2)}, a}} \text{CO}^{(2)} \quad (19)
\]

\[
2\text{S}_{2a} + \text{H}_2^{(g)} \xrightleftharpoons[k_{-\text{H}_2^{(2a)}}, a]{k_{\text{H}_2^{(2a)}}, a} 2\text{H}^{(2a)} \quad (20)
\]

\[
\text{CH}_3\text{O}^{(2)} + \text{S}_{2a} \xrightleftharpoons[k_{-\text{CH}_2\text{O}^{(2)}}, a]{k_{\text{CH}_2\text{O}^{(2)}, a}} \text{CH}_2\text{O}^{(2)} + \text{H}^{(2a)} \quad \text{(RDS-III)} \quad (21)
\]

\[
\text{CH}_3\text{O}^{(2)} + \text{CH}_2\text{O}^{(2)} \xrightleftharpoons[k_{-\text{C}_2\text{H}_6\text{O}^{(2)}}, a]{k_{\text{C}_2\text{H}_6\text{O}^{(2)}, a}} \text{CH}_3\text{OCH}_2\text{O}^{(2)} + \text{S}_2 \quad (22)
\]

\[
\text{HCOO}^{(1)} + \text{S}_{1a} \xrightleftharpoons[k_{-\text{CO}^{(1)}}, a]{k_{\text{CO}^{(1)}, a}} \text{H}^{(1a)} + \text{CO}_2^{(1)} \quad (17)
\]

\[
\text{CH}_3\text{OCHO}^{(2)} \xrightleftharpoons[k_{-\text{CH}_3\text{OCHO}}]{k_{\text{CH}_3\text{OCHO}}^{(2)}} \text{CH}_3\text{OCHO(g)} + \text{S}_2 \quad (24)
\]

\[
\text{CH}_3\text{OCHO}^{(2)} + \text{S}_{2a} \xrightleftharpoons[k_{-\text{CO}^{(2)}}, a]{k_{\text{CO}^{(2)}, a}} \text{CH}_3\text{O}^{(2)} + \text{CHO}^{(2)} \quad (25)
\]

\[
\text{CHO}^{(2)} + \text{S}_{2a} \xrightleftharpoons[k_{-\text{CO}^{(2)}, a}]{k_{\text{CO}^{(2)}, a}} \text{CO}^{(2)} + \text{H}^{(2a)} \quad (26)
\]

3.6. Rate expressions and adsorption terms

A kinetic analysis of the surface reaction mechanisms was done to eliminate the unknown surface concentrations. The overall equilibrium constants for each reaction were also factored in and a site balance for each type of active site was done. Details of these derivations are reported elsewhere [25]. The following are the rate expressions and the adsorption terms for each reaction.

\[
\text{Rate expression for methanol–steam reforming:}
\]

\[
r_R = \left( \frac{k_R K_{\text{CH}_3\text{OH}^{(1)}} / K_{\text{H}^{(1a)}}^{1/2}}{\phi_1 \phi_1} \right) \left( \frac{p_{\text{CH}_3\text{OH}} / p_{\text{H}_2}^{1/2}}{1 - (1 / K_R)} \left( \frac{p_{\text{H}_2} p_{\text{CO}_2}}{p_{\text{CH}_3\text{OH}} p_{\text{H}_2}} \right) \right) C_{S_1}^{\text{T}} e^{-S_{1a}^{\text{T}}} \quad (30)
\]
Eq. (30) is derived directly from the rate expression for the RDS for the methanol–steam reaction. However, it is now written as the rate of the overall methanol–steam reaction, \( r_R \), instead of \( r_{\text{CH}_3\text{O}(i)} \), while the rate constant \( k_{\text{CH}_3\text{O}(i)} \) is now written as \( k_R \). \( \phi_1 \) and \( \phi_{1a} \) in Eq. (30) are given by the following expressions:

\[
\phi_1 = 1 + \frac{K_{\text{CH}_3\text{O}(i)} P_{\text{CH}_3\text{OH}}}{K_{\text{H}(i)}^{1/2} P_{\text{H}_2}^{1/2}} \left( \text{methoxy} \right) + \frac{K_{\text{CO}_2(i)}^{1/2} P_{\text{CO}_2} P_{\text{H}_2}}{K_{\text{H}(i)}^{1/2} P_{\text{H}_2}^{1/2}} \left( \text{methanol} \right) + \frac{K_{\text{CH}_3\text{O}(i)}^{1/2} P_{\text{CH}_3\text{OH}} P_{\text{H}_2}^{1/2}}{K_{\text{H}(i)}^{1/2} P_{\text{H}_2}^{1/2}} \left( \text{methoxy} \right) + \frac{K_{\text{CO}_2(i)}^{1/2} P_{\text{CO}_2} P_{\text{H}_2}}{K_{\text{H}(i)}^{1/2} P_{\text{H}_2}^{1/2}} \left( \text{methanol} \right)
\]

\[
\phi_{1a} = \left( 1 + K_{\text{H}(i)}^{1/2} P_{\text{H}_2}^{1/2} \right).
\]

Similarly, for the WGS reaction and the decomposition reaction the following rate expressions were derived.

**Rate expression for the water-gas shift reaction:**

\[
r_{\text{W}} = \frac{K_{\text{CO}(i)}^{1/2} K_{\text{OH}(i)}^{1/2} \left( P_{\text{CO}P_{\text{H}_2}^{1/2}} \right)}{K_{\text{H}(i)}^{1/2} P_{\text{H}_2}^{1/2}} \left( 1 - (1/K_{\text{W}}) \left( P_{\text{CO}P_{\text{H}_2}^{1/2}} \right) \right) \left( c_{S_i}^{T} \right)^2.
\]

**Rate expression for the methanol decomposition reaction:**

\[
r_{\text{D}} = \frac{K_{\text{CH}_3\text{O}(i)}^{1/2} \left( P_{\text{CH}_3\text{OH}} P_{\text{H}_2}^{1/2} \right)}{K_{\text{H}(2a)}^{1/2} P_{\text{H}_2}^{1/2}} \left( 1 - (1/K_{\text{D}}) \left( P_{\text{CO}P_{\text{CH}_3\text{OH}}} \right) \right) \left( c_{S_i}^{T} \right)^2 c_{S_{h(i)}}^{T}.
\]

where \( \phi_2 \) and \( \phi_{2a} \) are defined as

\[
\phi_2 = 1 + \frac{K_{\text{CH}_3\text{O}(i)}^{1/2} P_{\text{CH}_3\text{OH}}}{K_{\text{H}(i)}^{1/2} P_{\text{H}_2}^{1/2}} \left( \text{methoxy} \right) + \frac{K_{\text{CO}_2^{(i)} K_{\text{CH}_3\text{O}(i)}^{1/2} P_{\text{CO}P_{\text{H}_2}^{1/2}}}}{K_{\text{H}(2a)}^{1/2} P_{\text{H}_2}^{1/2}} \left( \text{formyl biformate} \right) + \frac{K_{\text{CH}_3\text{O}(i)} K_{\text{CO}_2^{(i)}}^{1/2} K_{\text{CHO}_2^{(i)}}^{1/2}}{K_{\text{H}(2a)}^{1/2} P_{\text{CH}_3\text{OH}P_{\text{CO}P_{\text{H}_2}^{1/2}}}} \left( \text{ethoxy} \right) + \frac{K_{\text{CO}_2^{(i)} P_{\text{CO}_2} K_{\text{CO}_2^{(i)}}^{1/2}}}{K_{\text{H}(2a)}^{1/2} P_{\text{CO}P_{\text{H}_2}^{1/2}}^{1/2}} \left( \text{formate} \right). \tag{35}
\]

\[
\phi_{2a} = \left( 1 + K_{\text{H}(2a)}^{1/2} P_{\text{H}_2}^{1/2} \right). \tag{36}
\]

Referring Eqs. (33) and (34) back to the rate expression for the RDS of the water-gas shift mechanism and the decomposition reaction, respectively, it is seen that \( r_{\text{W}} \) and \( k_{\text{W}} \) have been substituted for \( r_{\text{HCOO}(i)}^{1/2} \) and \( k_{\text{HCOO}(i)}^{1/2}, \) and \( r_{\text{D}} \) and \( k_{\text{D}} \) have been substituted for \( r_{\text{CH}_3\text{O}(i)}^{1/2} \) and \( k_{\text{CH}_3\text{O}(i)}^{1/2} \).

### 3.7 Summary

Reversible Langmuir–Hinshelwood rate expressions for each of the overall reactions involved in
the process of methanol–steam reforming on Cu/ZnO/Al₂O₃ catalysts have been derived by a kinetic analysis of the elementary surface reactions occurring on the catalyst. Parallel reaction mechanisms occurring on two different phases of the catalyst were developed. For both reaction mechanisms involving methanol, the dehydrogenation of the adsorbed methoxy intermediate was considered to be the RDS. The reaction path for the water-gas shift reaction occurs on the same phase as the methanol–steam reaction. The RDS for the water-gas shift reaction was taken to be the formation of an adsorbed formate from adsorbed hydroxyls and adsorbed CO according to the mechanism of Dümpelmann [12].

Eqs. (30), (33) and (34) are general forms of the rate expressions based on the surface mechanisms which have been proposed. There are terms for every intermediate surface species and there is an equilibrium constant for the concentration of each of these species on the catalyst surface. Terms have also been included for adsorbed species which are not involved in the reaction mechanism but could occupy a significant number of active sites under certain conditions.

4. Development of a comprehensive model of the kinetics of methanol–steam reforming on Cu/ZnO/Al₂O₃

4.1. Formulation of a kinetic model from reaction rate expressions

In each kinetic experiment the rates of production of CO₂ and of CO per mass of catalyst were determined for a given gas composition and reactor temperature. In order to model these experimental responses, it was necessary to combine the rate expressions for each individual reaction and multiply by the surface area per unit mass of fresh catalyst $S_A$ (m² kg⁻¹):

$$r_{CO_2} = (r_R + r_W)S_A \quad (mol s^{-1} kg^{-1}),$$

$$r_{CO} = (r_D - r_W)S_A \quad (mol s^{-1} kg^{-1}).$$

Because the rate measurements were done by operating the reactor in differential mode, Eqs. (37) and (38) could be used directly and did not need to be integrated in a design equation. This greatly simplified the analysis.

Based on the stoichiometry of Reactions (I)–(III) the rates of the other three components in the reaction mixture can also be modelled as follows:

$$r_H = (3r_R + 2r_D + r_W)S_A = 3r_{CO_2} + 2r_{CO}$$

$$-r_{CH_3OH} = (r_R + r_D)S_A = r_{CO_2} + r_{CO}$$

$$-r_{H_2O} = (r_R + r_W)S_A = r_{CO_2}$$

However, as was stated above, only two of the three reactions are linearly independent and there is, therefore, no justification in using more than two responses in the non-linear regression.

In many kinetic modelling studies the surface site concentrations are either combined with the rate constants or conversely the rate is expressed as a per site turnover number. In this work, however, the site concentrations were kept separate and explicit in the rate expressions. There are several reasons for this approach. Firstly, it is hoped that eventually the variation in site concentrations can be used to explain the variation in the catalyst selectivity with time-on-stream. Secondly, at this point there is no way to adequately distinguish between the site concentrations for Type 1 sites versus Type 2 sites and therefore a turnover number cannot be calculated for each reaction.

In order to allow for these future objectives and to obtain reasonable parameter estimates for the model, total site concentrations were set at 7.5×10⁻⁶ mol m⁻² for Type 1 and Type 2 and 1.5×10⁻⁵ mol m⁻² for Type 1a and Type 2a sites based on the ab initio model for the water-gas shift reaction on the (1 1 1) face of metallic copper developed by Oveson et al. [26]. Since, statistically, the parameter for the site concentration and the rate constant are perfectly correlated the least squares estimate of the rate constant will simply vary to compensate for any error in the estimate of the site concentration and hence will not effect the quality-of-fit of the model.

4.2. Simplification of the expressions for fractional surface coverages

The adsorption term for Type 1 sites, $\phi_1$, is given by Eq. (31) and for Type 2 sites, $\phi_2$ is given by Eq. (35).
\( \Phi_1 \) and \( \Phi_2 \) are the inverses of the fractions of vacant sites of Types 1 and 2, respectively. \( \Phi_{1a} \) and \( \Phi_{2a} \) are the analogous adsorption terms for hydrogen on Type 1a and Type 2a sites. The more strongly an intermediate or a spectator species adsorbs on an active site, the fewer the number of sites available for reaction, and hence slower the rate of reaction when all else is constant. Each term in Eqs. (31) and (35) has been labelled according to the adsorbed surface species which it represents. As a first step in simplifying the rate expressions, a number of the terms in Eqs. (31) and (35) will be eliminated based on observations from surface studies.

4.2.1. DRIFTS studies of surface processes on Cu/ZnO/Al₂O₃ catalysts

DRIFTS measures the wavelength and intensity of IR radiation absorption by various chemical bonds associated with specific chemical species. By taking into account the absorption coefficient, the relative surface concentrations of the adsorbed species can be estimated by an analysis of the spectra. Fig. 2 shows a typical spectrum for the adsorption of methanol and steam on a Cu/ZnO/Al₂O₃ catalyst. As can be seen, there are large bands for methoxy groups and formate groups. Bands for methyl formate and methyl bifor- 

mate (expected at 1674 cm⁻¹), however, are absent, as are bands for adsorbed CO (expected at 2150 cm⁻¹).

A significant simplification in Eqs. (31) and (35) is obtained by eliminating the site concentrations for the species which do not appear in the FTIR spectra. The adsorption terms for Site 1 and Site 2 can then be reduced to

\[
\phi_1 = \left( 1 + \frac{K_{\text{CH}_3\text{O}(1)}P_{\text{CH}_3\text{OH}}}{K_{1/2}^{1/2}P_{\text{H}_2}^{1/2}} \right) + \frac{K_{\text{OH}(1)}P_{\text{H}_2}^{1/2}}{K_{1/2}^{1/2}P_{\text{H}_2}^{1/2}} + \frac{K_{\text{CO}(1)}^{1/2}P_{\text{CO}_2}^{1/2}}{K_{1/2}^{1/2}P_{\text{H}_2}^{1/2}} + \frac{K_{\text{CO}_2}^{1/2}P_{\text{CO}_2}^{1/2}}{K_{1/2}^{1/2}P_{\text{H}_2}^{1/2}} \right),
\]

\[
\phi_2 = \left( 1 + \frac{K_{\text{CH}_3\text{O}(2)}P_{\text{CH}_3\text{OH}}}{K_{1/2}^{1/2}P_{\text{H}_2}^{1/2}} \right) + \frac{K_{\text{OH}(2)}P_{\text{H}_2}^{1/2}}{K_{1/2}^{1/2}P_{\text{H}_2}^{1/2}} + \frac{K_{\text{CO}(2)}^{1/2}P_{\text{CO}_2}^{1/2}}{K_{1/2}^{1/2}P_{\text{H}_2}^{1/2}} + \frac{K_{\text{CO}_2}^{1/2}P_{\text{CO}_2}^{1/2}}{K_{1/2}^{1/2}P_{\text{H}_2}^{1/2}} \right). \]

The adsorption terms for hydrogen adsorption, \( \phi_{1a} \) and \( \phi_{2a} \) remain unchanged.

4.3. Simplification by definition of composite parameters

Further simplification to the algebraic form of the model can be achieved by converting ratios and products of parameters into lumped parameters. This can be justified based on the reduction of the total number of parameters in the model. The degree of correlation between parameters in Langmuir–Hinshelwood kinetic models is well known and reducing the number of parameters finally results in a more reliable model [27].

The following substitutions were made in Eqs. (30), (33), (34) and (43):

\[
K_{\text{CH}_3\text{O}(1)}^* = \frac{K_{\text{CH}_3\text{O}(1)}}{K_{1/2}^{1/2}},
\]

\[
K_{\text{OH}(1)}^* = \frac{K_{\text{OH}(1)}}{K_{1/2}^{1/2}},
\]

\[
K_{\text{CO}(1)}^* = \frac{K_{\text{CO}(1)}^{1/2}K_{1/2}^{1/2}}{K_{1/2}^{1/2}},
\]

\[
K_{\text{HCOO}(1)}^* = \frac{K_{\text{CO}_2}^{1/2}K_{1/2}^{1/2}}{K_{1/2}^{1/2}},
\]

\[
k_{W} = k_{W}K_{\text{CO}(1)},
\]

\[
K_{\text{CH}_3\text{O}(2)}^* = \frac{K_{\text{CH}_3\text{O}(2)}}{K_{1/2}^{1/2}},
\]

\[
K_{\text{OH}(2)}^* = \frac{K_{\text{OH}(2)}}{K_{1/2}^{1/2}},
\]

\[
K_{\text{HCOO}(2)}^* = \frac{K_{\text{CO}_2}^{1/2}K_{1/2}^{1/2}}{K_{1/2}^{1/2}}.
\]

With these substitutions the forms of \( r_R, r_W \) and \( r_D \), described previously as Eqs. (30), (33) and (34),
become considerably simpler.

\[
r_r = k_R K_{CH_3O} (p_{CH_3OH} / p_{H_2}) \left( 1 - \left( \frac{p_{H_2} p_{CO} / k_R p_{CH_3OH} p_{H_2}}{k_R K_{CH_3O}} \right) C_{S1}^T C_{S1a}^T \right) \left( 1 + K_{CH_3O}^* (p_{CH_3OH} / p_{H_2}) + K_{HCCHOO}^* p_{CO} p_{H_2}^{1/2} + K_{OH}^* (p_{H_2} / p_{H_2}) + K_{CO}^* p_{CO} \right) \left( 1 + K_{H_2a}^{1/2} / p_{H_2}^{1/2} \right),
\]

(51)

\[
r_w = \frac{k_w K_{OH}^* (p_{CO} p_{H_2} / p_{H_2}) (1 - p_{H_2} p_{CO} / k_w p_{CO} p_{H_2}) C_{S1}^T}{\left( 1 + K_{CH_3O}^* (p_{CH_3OH} / p_{H_2}) + K_{HCCHOO}^* p_{CO} p_{H_2}^{1/2} + K_{OH}^* (p_{H_2} / p_{H_2}) + K_{CO}^* p_{CO} \right)^2},
\]

(52)

\[
r_d = \frac{k_d K_{CH_3O} (p_{CH_3OH} / p_{H_2}) (1 - p_{H_2}^2 p_{CO} / k_d p_{CO} p_{H_2}) C_{S1}^T C_{S2a}^T}{\left( 1 + K_{CH_3O}^* (p_{CH_3OH} / p_{H_2}) + K_{HCCHOO}^* p_{CO} p_{H_2}^{1/2} + K_{OH}^* (p_{H_2} / p_{H_2}) + K_{CO}^* p_{CO} \right) \left( 1 + K_{H_2a}^{1/2} / p_{H_2}^{1/2} \right)},
\]

(53)

The units of \( r_r, r_w \) and \( r_d \) are still (mol s\(^{-1}\) m\(^{-2}\)). The adsorption terms \( \phi_1, \phi_2, \phi_{1a} \) and \( \phi_{2a} \) have now been written out in full in the equations. There are three rate constants and 10 equilibrium constants in Eqs. (51)–(53). The temperature dependence of each of these constants can be expressed either using the Arrhenius expression or the van’t Hoff expression:

\[
k_R = k_R^\infty \exp \left( \frac{-E_R}{RT} \right),
\]

(54)

\[
k_d = k_d^\infty \exp \left( \frac{-E_D}{RT} \right),
\]

(55)

\[
k_w = k_w^\infty \exp \left( \frac{-E_w}{RT} \right),
\]

(56)

\[
K_{CH_3O}^* = \exp \left( \frac{\Delta S_{CH_3O}^*}{R} - \frac{\Delta H_{CH_3O}^*}{RT} \right),
\]

(57)

\[
K_{HCCHOO}^* = \exp \left( \frac{\Delta S_{HCCHOO}^*}{R} - \frac{\Delta H_{HCCHOO}^*}{RT} \right),
\]

(58)

\[
K_{OH}^* = \exp \left( \frac{\Delta S_{OH}^*}{R} - \frac{\Delta H_{OH}^*}{RT} \right),
\]

(59)

\[
K_{CO}^* = \exp \left( \frac{\Delta S_{CO}^*}{R} - \frac{\Delta H_{CO}^*}{RT} \right),
\]

(60)

\[
K_{H_2a} = \exp \left( \frac{\Delta S_{H_2a}}{R} - \frac{\Delta H_{H_2a}}{RT} \right).
\]

(61)

At this point, after considerable simplification, the kinetic model still contained 26 adjustable parameters. Obtaining models with large numbers of parameters is a regrettable characteristic of the Langmuir–Hinshelwood method of analysis. The high degree of correlation between many of the parameters means that there will be a large uncertainty associated with many of the parameter estimates [28]. The correlation between least squares estimates of heats of adsorption and entropies of adsorption is known to be particularly bad [27], therefore it was decided to arbitrarily set the heats of adsorption at values consistent with values reported in the literature from independent adsorption surface studies rather than including them in the regression.
4.4. Experimental planning and results

An extensive experimental program was conducted to collect sufficient kinetic data to obtain parameter estimates for the final rate model. Rate measurements were obtained by the differential method using a fixed-bed plug flow reactor. The change in the partial pressure of any gaseous component was never more than 5–10% and the average partial pressure of each component was used in the kinetic analysis. The catalyst used for these experiments was BASF K3-110 low temperature shift catalyst. Details of the properties of this catalyst, the experimental equipment and the experimental procedure used have been described elsewhere [18,25].

Five different components are involved in Reactions (I)–(III) and the partial pressure of each could be varied independently during differential rate measurements. Temperature could also be varied resulting in a total of six experimental variables. The maximum operating pressure of the apparatus was 35 bar and the maximum recommended operating temperature of the catalyst is 533 K. Six inequalities:

\[

t (433 \text{ K} \leq \text{reactor temperature} \leq 533 \text{ K})
\]

\[
\text{1 bar} \leq \text{reactor pressure} \leq 35 \text{ bar}
\]

\[
\text{0 bar} < \text{partial pressure of CO} \leq 0.5 \text{ bar}
\]

\[
\text{0.29} \leq \text{ratio of partial pressure of CO}_2 \text{ to } \text{H}_2 \leq 0.370,
\]

\[
\text{0} < \text{ratio of partial pressure of CH}_3\text{OH to H}_2\text{O} \leq 1.2,
\]

\[
\text{0.6} \leq \text{ratio partial pressure of } \text{H}_2 \text{ to } \text{H}_2\text{O} \leq 130,
\]

were used to define the experimental operating region and based on these constraints, experiments were designed using the D-optimal criterion for a multi-response model [29]. This criterion chooses the experimental conditions that result in the greatest improvement in the accuracy of the parameter estimates for the model that is being tested.

Fifty-eight experiments were designed and performed. Each data set for the non-linear regression consisted of the rates of formation of CO and CO2, the temperature and the gas composition. In addition, after each kinetic experiment, a baseline conversion versus \(W/F_{\text{CH}_3\text{OH}}\) measurement was done to ensure that the catalyst activity and selectivity had remained stable during the experiment. The baseline conditions were arbitrarily defined as 513 K, S/M ratio of 1, and total pressure of 1.01 bar. Fifteen runs were eliminated due to significant changes in baseline activity leaving a total of 43 usable runs for parameter estimation. A complete listing of the rate data used for the non-linear regression, with experimental conditions, can be obtained by contacting the principal author (pepley-b@rmc.ca).

4.5. Parameter estimation

Eqs. (51)–(66) were substituted into Eqs. (37) and (38) and parameter estimates were obtained by non-linear regression using a multi-response Bayesian criterion [29]. Preliminary regressions revealed that the parameters for the adsorption of CO2 on both the Type 1 and Type 2 sites were not statistically different from zero and hence could be removed from the regression with no loss in goodness-in-fit. Also, the adsorption term for the formate species on Type 2 sites was not statistically different from zero and was removed from the model. In the case of Type 1 sites the CO2 surface concentration is negligible because CO2 either desorbs or is converted to formate, hence the term for CO2 in the site balance can be removed. The CO2 surface concentration term for Type 2 sites is negligible because CO2 neither readily adsorbs on these sites nor readily forms intermediate formate. The final form of the model therefore contained 20 parameters of which seven were fixed and 13 were determined by non-linear regression.

The values and the confidence intervals for all the parameters are presented in Table 2. The confidence intervals were obtained using a simple method based on the concept of the profile \(t\)-plot proposed by Bates and Watts [28]. The confidence interval for each parameter was determined by finding the high and low value which resulted in the sum of squared residuals being \(1+P/(N–P)F(P, N–P, 0.05)\) times the minimum value of the least squares while the remaining parameters were kept at their least-squares values. Fig. 3 and 4 are the parity plots for the rates of CO and CO2 production, respectively.

4.6. Summary – final form of the model

The final forms of the rate expressions for the overall reactions involved in the process of methanol–steam are, therefore, as follows:
steam can also be predicted.

By substituting these expressions into Eqs. (37) and (38) a comprehensive model of methanol–steam reforming is obtained which predicts the rates of production of both CO and CO₂. Furthermore, by using Eqs. (39)–(41) the rate of production of hydrogen and the rates of disappearance of methanol and steam can also be predicted.

5. Validation of the final model

The surface area and copper dispersion of Cu/Zn/Al₂O₃ catalysts are known to vary with both operating atmosphere and time-on-line [5,16,18] and therefore the validation of the final model for “real operating conditions” was not a trivial task. Accumulating sufficient data for which the variation in the activity of the catalyst did not confound the validation test was difficult. Conversely, developing a method of correcting data from a “real reactor” so that the catalyst behaviour could be normalised also presented problems. Several methods were, however, developed for testing the model that minimised the effect of changes in the state of the catalyst.

Fig. 5 shows the variation in the parameter $\Phi_W$ with conversion. $\Phi_W$, which is defined as

\[
\Phi_W = \frac{W}{W_{\text{max}}}
\]

where $W$ is the measured conversion and $W_{\text{max}}$ is the maximum conversion. The data for the final model were then compared with the data for the model that included only the methanol–steam reaction.

### Table 2

<table>
<thead>
<tr>
<th>Rate constant or equilibrium constant</th>
<th>$\Delta S_i$ (J mol⁻¹ K⁻¹) or $S_0$ (% conversion)</th>
<th>$S_{0.95%}$</th>
<th>$S_{0.95%}$</th>
<th>$\Delta H_i$ or $E$ (kJ mol⁻¹)</th>
<th>$S_{0.95%}$</th>
<th>$S_{0.95%}$</th>
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<tbody>
<tr>
<td>$k_R$ (m² s⁻¹ mol⁻¹⁻¹)</td>
<td>7.4E+14</td>
<td>6.8E+14</td>
<td>8.0E+14</td>
<td>102.8</td>
<td>102.4</td>
<td>103.1</td>
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<tr>
<td>$K^*_{\text{CH}_3\text{OH}^{(i)}}$ (bar⁻¹)</td>
<td>-41.8</td>
<td>-42.7</td>
<td>-40.9</td>
<td>-20.0</td>
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<td>-</td>
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<td>$K^*_{\text{CO}_2^{(i)}}$ (bar⁻¹)</td>
<td>-44.5</td>
<td>-47.0</td>
<td>-42.1</td>
<td>-20.0</td>
<td>-</td>
<td>-</td>
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<tr>
<td>$K^*_{\text{H}_2\text{O}^{(i)}}$ (bar⁻¹)</td>
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<tr>
<td>$K^*_{\text{CH}_3\text{O}^{(i)}}$ (m² s⁻¹ mol⁻¹⁻¹)</td>
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<td>174.4</td>
<td>182.9</td>
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<td>-</td>
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<td>$k_D$ (m² s⁻¹ mol⁻¹⁻¹)</td>
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<td>1.6E+20</td>
<td>6.1E+20</td>
<td>170.0</td>
<td>168.0</td>
<td>173.9</td>
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<td>-20.0</td>
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<td>$k_W$ (m² s⁻¹ mol⁻¹⁻¹)</td>
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<td>88.1</td>
</tr>
</tbody>
</table>

Note: Italicised values were set at the values indicated based on published data on the heats of adsorption. They were not included in the non-linear regression.
Fig. 3. Parity plot for rate of CO₂ production after terms involving negligible surface coverages were removed. The slope is 0.98 and the intercept is 890 μmol s⁻¹ kg⁻¹. These values are not statistically different from unity and zero, respectively. The correlation coefficient $r^2=0.97$.

Fig. 4. Parity plot for rate of CO production after terms involving negligible surface coverages were removed. The slope is 1.0 and the intercept is 6.7 μmol s⁻¹ kg⁻¹. The value of the intercept is not statistically different from zero. Correlation coefficient $r^2=0.97$. 
is a measure of the product composition relative to the water-gas shift reaction equilibrium (i.e. when the WGS reaction is at equilibrium \( \Phi_W = 1 \)). The line in Fig. 5 is the value of \( \Phi_W \) predicted by the final model based on Eqs. (67)–(69) using the parameter estimates from Table 2. This curve uses an average value for the catalyst surface area, as used in Eqs. (37) and (38), to model data which were collected from various beds of the BASF catalyst used in the experimental program. Fig. 5 shows that the model was able to accurately predict the product composition for a wide range of methanol conversions. No previous models for methanol–steam reforming on Cu/ZnO/Al\(_2\)O\(_3\) catalysts would have been able to generate this curve. Fig. 5 also demonstrates that the model achieved the key objective of being able to predict the variation in the CO content of the product stream for methanol–steam reforming on Cu/ZnO/Al\(_2\)O\(_3\) catalysts.

Euler’s method was used to integrate Eqs. (37) and (38) over the length of an isothermal catalyst bed to generate predictions of integral methanol conversion (e.g. greater than 10% conversion). Fig. 6 shows predicted methanol conversion versus \( W/F_{\text{CH}_3\text{OH},0} \) for pressures ranging from 1.16 to 15.9 bar. This figure shows that the comprehensive model developed in this work is valid for pressures considerably higher than previous models. Furthermore, in Fig. 7 we see that the model accurately predicted the decrease in the total conversion as the pressure was increased from 1 to 39 bar. This indicates that the effects of the reverse reaction and the reaction equilibrium are represented well by the model.

Fig. 8 shows the effect of temperature on the fractional conversion versus \( W/F_{\text{CH}_3\text{OH},0} \). The data at 513 K were collected at baseline conditions. The temperature was then increased to 533 K and a second set of data was collected. Again the predictions of the model are in good agreement with the experimental observations.

6. Conclusions

6.1. Surface mechanisms for overall reactions

The elementary reactions which occur on the surface of Cu/ZnO/Al\(_2\)O\(_3\) catalysts during methanol–steam reforming were thoroughly reviewed and surface mechanisms for all three overall reactions were proposed. The mechanisms were progressively improved based on results from an extensive experimental program.
Kinetic analyses of these reaction mechanisms were done to yield reversible Langmuir–Hinshelwood rate expressions for each of the overall reactions. The RDS chosen for both the methanol–steam reaction and the decomposition reaction was the dehydrogenation of adsorbed methoxy. As proposed by Dümpelmann [12], the production of a surface formate from adsorbed hydroxyl and CO was used as the RDS for the water-gas shift reaction.

6.2. Comprehensive kinetic model

A differential fixed-bed reactor was used to accumulate a significant amount of rate data for methanol–steam reforming on a BASF low temperature shift catalyst. Estimates of 13 adjustable parameters were obtained using a multi-response non-linear regression. The result is a comprehensive kinetic model which is able to predict both the rate of hydrogen production
and the composition of the product gas for the process of methanol–steam reforming on a commercial Cu/ZnO/Al2O3 catalyst. In particular the rate of production of CO is successfully modelled. This kinetic model is referred to as comprehensive because it is the first model of methanol–steam reforming which simultaneously takes into account all three reversible overall reactions.

7. Nomenclature

- $C_{S_i}^T$: total surface concentration of site $i$ (mol m\(^{-2}\))
- $E_i$: activation energy for rate constant of reaction $i$ (kJ mol\(^{-1}\))
- $F_{CH_3OH}$: molar flow rate of methanol in feed to reactor (mol s\(^{-1}\))
- $F$: Fisher’s statistic for $P$ parameters and $P$, 0.05
- $N$: number of experimental runs included in the regression
- $p_i$: partial pressure of component $i$ (bar)
- $P$: number of parameters in model
- $r_i$: rate of reaction $i$ (mol s\(^{-1}\) m\(^{-2}\)) or rate of formation of component $i$ (mol s\(^{-1}\) (kg of catalyst)\(^{-1}\))
- $r^2$: correlation coefficient of linear fit to parity plots (Figs. 3 and 4)
- $\Delta S_i$: entropy of adsorption for species $i$ (J mol\(^{-1}\) K\(^{-1}\))
- $S_A$: surface area of fresh catalyst (m\(^2\) kg\(^{-1}\))
- $S_{i\,(r,\pm95\%)}$: the parameter value which produces an excess sum of squared residuals corresponding to the Fisher’s $F$ statistic at the 95% confidence level; columns 3, 4, 6 and 7 of Table 2
- $S/M$: molar ratio of steam to methanol in feed to reactor
- $W$: mass of catalyst (kg)
- $x_{CH_3OH}$: conversion of methanol

Greek symbols

- $\phi_W$: parameter relating composition of reactor effluent to the WGS equilibrium
- $\phi_k$: adsorption term for active site $k$
\( \theta \) fractional coverage; used in Table 1
\( \Theta \) fraction of active sites which are available; used in Eq. (4)

**Subscripts**

- **R** direct-reforming; Reaction (I)
- **W** water-gas shift; Reaction (II)
- **D** decomposition; Reaction (III)
- **1** active site 1 when on variable \( S \)
- **1a** active site 1a when on variable \( S \)
- **2** active site 2 when on variable \( S \)
- **2a** active site 2a when on variable \( S \)
- \( a, b \) indicates an alternate route to a surface intermediate (as in Eqs. (16) and (17))

**Superscripts**

- \( (i) \) species adsorbed on active site \( i \) where \( i \) is 1, 1a, 2 or 2a
- \( * \) composite parameter as defined in Eqs. (44)–(50)
- **T** indicating total concentration of active sites

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**References**
