Mechanistic aspects of the steam reforming of methanol over a $CuO/ZnO/ZrO_2/Al_2O_3$ catalyst

John P. Breen,* Frederic C. Meunier and Julian R. H. Ross

Centre for Environmental Research, University of Limerick, Limerick, Ireland. E-mail: john.paul.breen@ul.ie

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CO is not a primary but is a secondary product of the steam reforming of methanol over a $CuO/ZnO/ZrO_2/Al_2O_3$ catalyst, CO is formed as a secondary product by the reverse WGS reaction only when the methanol has reacted.

The steam reforming of methanol is attracting growing interest as a means of producing hydrogen for use in fuel cells. CO produced in the steam reforming reaction is currently a poison to the promising proton-exchange membrane (PEM) fuel cells and as a result much attention has been focused on the mechanism of CO formation during the reaction. The formation of carbon monoxide as a product and the fact that copper is a good catalyst for the water–gas shift (WGS) reaction[1] has led some workers[2–5] to speculate that a decomposition/WGS reaction sequence is involved [eqn. (1) and (2)]:

$$CH_3OH \rightarrow CO + 2H_2 \quad (1)$$

$$CO + H_2O \rightleftharpoons H_2 + CO_2 \quad (2)$$

$$CH_3OH + H_2O \rightarrow CO_2 + 3H_2 \quad (3)$$

However, Amphlett *et al.*[6,7] have more recently noted that carbon monoxide production is less than that predicted from equilibrium. As a result, they have revised their reaction scheme to one containing parallel reactions, the steam reforming of methanol [eqn. (3)] occurring in parallel to the decomposition of methanol to CO and H_2 [eqn. (1)]; they suggest that adjustment of the CO/CO_2 ratio also occurs as a result of the WGS reaction [eqn. (2)]. Peppley *et al.*[8,9] found that the methanol decomposition reaction is much slower than the steam reforming reaction but argued that it must be included in the overall reaction scheme. Takahashi *et al.*[10] found that methyl formate was formed at low water/methanol ratios and so they incorporated methyl formate into their reaction scheme [eqn. (4)–(6)]:

$$2CH_3OH \rightarrow CH_3OCHO + 2H_2 \quad (4)$$

$$CH_3OCHO + H_2O \rightarrow HCOOH + CH_3OH \quad (5)$$

$$HCOOH \rightarrow CO_2 + H_2 \quad (6)$$

Jiang *et al.*[11,12] carried out a detailed kinetic analysis of the steam reforming reaction and found that the reaction over a $Cu/ZnO/Al_2O_3$ catalyst could also be explained by eqn. (4)–(6), they suggested that the carbon monoxide observed in the product stream is produced *via* the decomposition of methyl formate. Studies of the surface mechanism of the steam reforming reaction have been limited[9] and authors have instead tended to use the large quantity of data published on the methanol synthesis reaction to support their mechanistic surface reaction models.[9,12]

We have previously reported[13] that copper–zirconia containing catalysts are very active for the steam reforming of methanol and that they give good selectivities towards CO_2 production. We have now obtained clear evidence from both kinetic measurements and *in situ* DRIFTS experiments for the formation of CO as a secondary product during the reforming reaction over a $CuO/ZnO/ZrO_2/Al_2O_3$ catalyst and details of the surface species involved in the reaction are given here.

The $CuO/ZnO/ZrO_2/Al_2O_3$ catalyst was prepared by sequential precipitation, the order and method of precipitation having been described elsewhere.[13] The reactants and products of the reaction were analysed by GC equipped with a Porapak Q column. This column gave satisfactory separation of CO and N_2 at a column temperature of 25 °C, the limit of detection for CO was *ca.* 1000 ppm with an accuracy of ±2%. The reaction was carried out in a quartz plug-flow microreactor, the composition of the reactant gases being 28.5% H_2O, 21.5% CH_3OH, with a balance of N_2. Prior to introduction of the reaction mixture, the catalyst was reduced *in situ* in a 5% H_2–N_2 mixture at a temperature of 240 °C for 4 h, ramping to this temperature at a rate of 5 °C min^{-1}. IR measurements were carried out using a Nicolet Magna 550 FTIR fitted with a diffuse reflectance cell and incorporating a high-pressure, high-temperature catalytic chamber.

The effect of contact time on the distribution of reaction products was studied by varying the *W*/*F* ratio while using a constant feed composition at two different temperatures (200 and 300 °C). Fig. 1 shows the methanol conversions and the percentages of hydrogen, carbon dioxide and carbon monoxide in the product stream as a function of the (pseudo-)contact time, *W*/*F* (g min cm^{-3}), at 300 °C. Two equilibrium lines for the carbon dioxide and hydrogen production are also shown as dotted lines; the top line (line '*m*') in each case represents the equilibrium values obtained by excluding carbon monoxide from the calculations whereas the bottom line (line '*n*') shows calculated equilibrium values with the inclusion of carbon monoxide as a product. It must be noted that the equilibrium lines '*m*' and '*n*' correspond to the situation when complete conversion of methanol is assumed; the equilibrium values shown in Fig. 1 are the results of thermodynamic calculations carried out using the HSC Chemistry for Windows software package (Outokumpu Research Oy). This software uses the Gibbs Free Minimisation Method to calculate equilibrium compositions.[14]

At 200 °C, 100% conversion of methanol was not attained and carbon monoxide was not detected in the product stream at any of the pseudo-contact times.

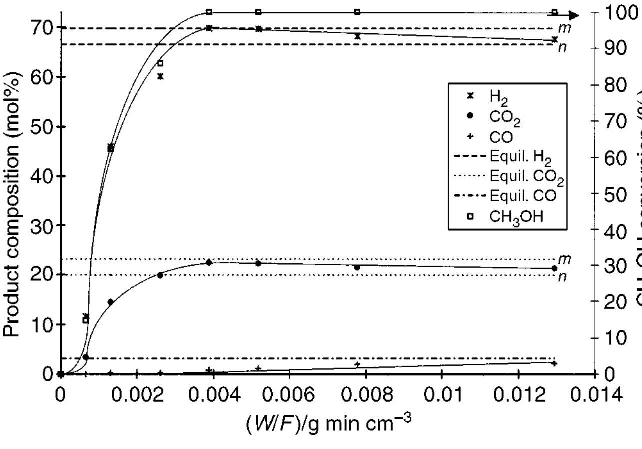

Fig. 1 The influence of *W*/*F* on the product compositions at $T = 300$ °C over a $CuO/ZnO/ZrO_2/Al_2O_3$ catalyst, *m* = equilibrium excluding CO from calculations, *n* = equilibrium including CO in calculations (H_2O/CH_3OH = 1.3, $P = 101$ kPa).

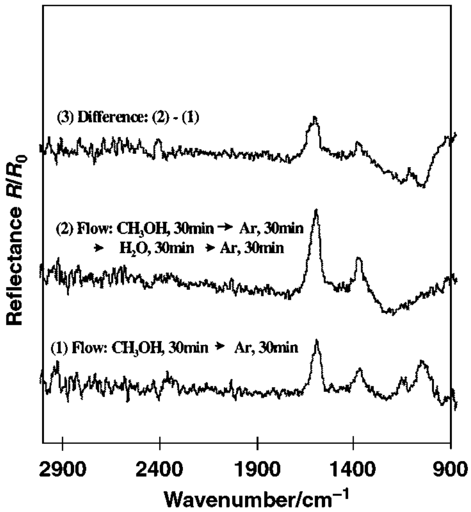

Fig. 2 FTIR spectra of surface species generated by methanol adsorption followed by water adsorption on a $CuO/ZnO/ZrO_2/Al_2O_3$ catalyst at 240 °C.

At 300 °C, the percentages of hydrogen and carbon dioxide produced were higher than those at 200 °C for all values of contact time. Carbon monoxide was not detected at the shorter contact times; however, as the value of W/F was increased, carbon monoxide was detected and its molar percentage increased steadily with increasing contact time, approaching, but not attaining, the predicted equilibrium value at higher values of W/F. It is evident from Fig. 1 that carbon monoxide was a secondary product; this effectively rules out the possibility of the occurrence of a mechanism involving methanol decomposition followed by the water–gas shift reaction as proposed by several authors over their catalysts.[2–5].

When 100% methanol conversion was achieved at 300 °C (Fig. 1), the hydrogen and carbon dioxide molar compositions exceeded the equilibrium line '*n*'; at a value of $W/F = 0.00389$ g min cm^{-3}, there was very little carbon monoxide production and the hydrogen and carbon dioxide compositions were very close to the equilibrium values calculated for the steam reforming reaction when carbon monoxide was excluded from the product stream (line '*m*'). At values of $W/F > 0.00389$ g min cm^{-3}, the proportions of hydrogen and carbon dioxide decreased and that of carbon monoxide increased with increasing contact time, approaching equilibrium '*n*' values (a sequence including CO formation) with high contact times. At 100% methanol conversion and a reaction temperature of 300 °C, the carbon dioxide and hydrogen percentages were greater than those predicted by equilibrium (n) whereas the carbon monoxide percentages were less than equilibrium predictions by a similar amount at the different values of W/F.

These results provide evidence of a consecutive reaction scheme in which methanol and water react first to produce carbon dioxide and hydrogen [eqn. (3)] and the carbon dioxide and hydrogen then react *via* the reverse WGS reaction [eqn. (2)] to produce CO. There was no evidence of the occurrence of the methanol decomposition reaction [eqn. (1)].

In order to investigate the nature of the surface species involved in the steam reforming reaction over the $CuO/ZnO/ZrO_2/Al_2O_3$ catalyst, *in situ* IR measurements were carried out. Fig. 2 [spectrum (1)] shows the surface species generated on the surface of the catalyst at 240 °C after passing methanol over the catalyst and then flushing through with Ar. The peaks at 1590 and 1380 cm^{-1} can be attributed to a formate species, the peak at 1150 cm^{-1} to π bonded formaldehyde and the peak centred around 1050 cm^{-1} to a methoxy species.[15] Water was then introduced and the spectrum [Fig. 2, spectrum (2)] taken after the introduction of the water showed that neither the methoxy nor the formaldehyde peaks were evident but that the intensity of the formate peaks had increased. This is illustrated in spectrum (3) of Fig. 2 which shows the difference between spectra (2) and (1). This indicates that the methoxy and/or the formaldehyde species were readily converted to formates by reaction either with gas phase water or more probably with OH groups generated by the dissociative adsorption of water. *In situ* DRIFTS analysis of species during the steam reforming reaction showed that in addition to surface formates, there was an absorption centred at 1033 cm^{-1} which can probably be attributed to gas phase methanol in addition to some adsorbed methoxy species. Gas phase CO_2 (2364 cm^{-1}), was also detected but there was no evidence of either gas phase CO or adsorbed CO species. Formates are known to decompose on $CuO/ZnO/ZrO_2$ aerogels[16] according to eqn. (7) to give either CO and surface OH groups or CO_2 and H_2:

$$OH_{(s)} + CO_{(g)} \leftarrow HCOO^{-}_{(s)} \rightarrow CO_{2(g)} + 1/2H_{2(g)} \qquad (7)$$

The results of the kinetic study, however, showed that CO did not form when methanol was present and that CO_2 and H_2 were the primary products, but that when methanol was fully converted, CO was evident in the gas stream. This points to a mechanism whereby the decomposition of formates to CO is either inhibited in the presence of methanol, or more probably, by the methoxy and/or formaldehyde species formed from the adsorption of methanol on the catalyst. The mechanism of the inhibition of the formation of CO by methanol is the subject of further research.

Notes and references

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