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Methanol reforming for fuel-cell applications: development of zirconia-containing Cu–Zn–Al catalysts

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Abstract

The steam reforming of methanol to form mixtures of carbon dioxide and hydrogen, together with traces of carbon monoxide, is considered to be a potential source of hydrogen as the fuel for a fuel-cell to be used in mobile power sources. After outlining some of the constraints inherent in the use of the reaction and the types of catalysts which have been used by other investigators, this paper presents results on the preparation and testing of a series of copper-containing catalysts for this reaction. It is shown that the reaction sequence probably involves the formation of methyl formate which then decomposes to give CO_2 as the primary product; CO is formed by the reverse water–gas shift reaction and this only occurs to an appreciable extent when the methanol is almost completely converted. A number of different copper-containing catalysts are then described and it is shown that of these sequentially precipitated $Cu/ZnO/ZrO_2/Al_2O_3$ materials have the highest activities and stabilities for the steam reforming reaction. © 1999 Elsevier Science B.V. All rights reserved.

Keywords: Steam reforming of methanol; Fuel cell; Zirconia; Catalyst development; Copper-based catalysts; Hydrogen production

1. Introduction

There is currently significant worldwide interest in finding methods to reduce the very significant emissions formed from mobile sources, predominantly internal combustion engines and diesel engines. One possibility is to use a fuel-cell powered vehicle using hydrogen as a fuel. Although hydrogen has a high fuel density, it is difficult to handle. An alternative source of hydrogen which might be utilised, despite its significantly lower energy density, is methanol since this molecule can, in principle, be converted to hydrogen-containing mixtures by steam reforming. The original aim of the work of which this paper represents a part was to try to find active catalysts for the reaction which operate at temperatures low enough that carbon monoxide is not a significant product and which were stable under operating conditions. Preliminary work showed that it was possible to make materials which gave lower than the thermodynamically predicted concentrations of CO and so the aim was to find the most active and stable materials which maintained this low selectivity to CO.

A large variety of catalysts for the steam reforming of methanol have been reported in the literature. The majority of these have been copper based [1–13]; commercial copper-containing water–gas shift and methanol synthesis catalysts [10,11] have also been found to be active for the steam reforming reaction. Shimokawabe et al. [12] and Takezawa et al. [13] have recently reported that highly active Cu/ZrO_2 catalysts

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could be prepared by impregnation of ZrO_2 with an aqueous solution of tetrammine copper (II) nitrate. They found that the Cu/ZrO_2 catalysts had significantly higher activities than the corresponding silica-supported copper catalysts. However, more attention has been given to the use of Cu/ZrO_2 catalysts for the synthesis of methanol, the reverse of the methanol reforming reaction. Since it is likely that catalysts effective for the synthesis of methanol will also be effective for the steam reforming reaction, it is instructive to review briefly the literature on the synthesis reaction using zirconia-based catalysts.

Highly active Cu/ZrO_2 catalysts have been prepared by a variety of different methods, including precipitation of metal salts [14–18], impregnation of copper onto a zirconia support [16,17,19], the formation of amorphous aerogels [20,21] and the in situ activation of amorphous CuZr alloys [22]. The recurring theme in many of these papers is that it is necessary to maintain the amorphous nature of zirconia under calcination and reaction conditions in order to maintain the catalyst in a state of high activity. Crystallisation of the amorphous zirconia results in a drastic decrease in copper and BET surface areas of the catalyst and a subsequent loss in its activity [17]. Maintaining a high copper/zirconia interfacial area has been found to be very important in preventing catalyst deactivation. Tetragonal zirconia can be stabilised by the addition of oxides such as La_2O_3, Y_2O_3 and Al_2O_3 [23,24] and it has been found that phase transformations could be prevented, or at least retarded, by doping zirconia with such oxides.

The main aim of this paper is to describe the development of stable copper-containing catalysts for use for the steam reforming of methanol. A secondary aim is to show that these materials are selective for the production of CO_2, only giving CO as a product at higher operation temperatures, and that the reaction probably involves the production of methyl formate as an intermediate, in agreement with the reaction scheme favoured by Takahashi et al. [8]. The paper first presents typical data for the behaviour of a typical catalyst of the type prepared in this work and shows that CO is probably a secondary product of the reaction. Results are then given for the activities for the methanol reforming reaction of various catalysts prepared by either sequential precipitation (SP) or co-precipitation (CP) of the metal nitrate salts using sodium carbonate as the precipitant; the effect of the addition of ZnO to the Cu/Zr catalysts was also investigated and several of the series of catalysts were doped with Al_2O_3, Y_2O_3 or La_2O_3 in order to elucidate the effect that these additives might have on the activity and stability of the resultant materials under the conditions used for the steam reforming of methanol.

2. Experimental

Table 1 lists the compositions of, and preparation methods used for, the catalysts tested for the steam reforming reaction; the majority of the samples were prepared by sequential precipitation (SP) but some were also prepared by co-precipitation (CP). For example, the Cu/Zn catalysts were prepared by sequential precipitation of first copper and then zinc while the Cu/Zr catalysts were prepared by co-precipitation. The three-component catalysts were prepared sequentially by first precipitating either zirconium or aluminium, following this by that of copper and then of zinc. The Cu/Zn/Zr/Al (SP) catalyst was prepared by co-precipitating initially alumina and zirconia, precipitating copper on top of the precipitate formed from the zirconium and aluminium species and then precipitating zinc. The catalysts containing lanthana or yttria were prepared in a similar manner to that used for the Cu/Zn/Zr/Al (SP) catalyst but aluminium, zirconium and lanthanum or yttrium were first co-precipitated before adding the other components in the same order as before. All the catalysts were prepared using sodium carbonate as precipitant at a constant pH of 7.0 and at a constant temperature of 70°C. After precipitation, the co-precipitates were aged for 15 min in the mother liquor, while the sequentially precipitated materials were aged for 15 min in the mother liquor after each stage in the precipitation procedure outlined above. All the samples were dried in an oven at 120°C and were then calcined in air at 350°C for 6 h.

The catalyst samples were characterised by temperature programmed reduction (TPR), nitrous oxide decomposition, FTIR and nitrogen physisorption measurements. Nitrous oxide decomposition was used to determine the Cu surface areas of the reduced samples and was carried out using an Intelligent Gravimetric

Analyser from Hiden Analytical, employing a technique similar to that described by Luys et al. [25]. The calculation of Cu surface area was based on the assumption that there are 1.46×10^{19} copper atoms per m^2 [26,27] and that the adsorption stoichiometry $Cu_{(s)}/O_{(ads)}$ is 2. TPR studies were carried out in an apparatus similar to that described by Bhatia et al. [28] using the following conditions: 20 mg of sample, 20 cm^3 min^{-1} flow of 5% H_2/N_2 and a temperature ramp rate of 10°C min^{-1}. BET surface areas were also measured using a standard Micromeritics Gemini II 2370 system.

The reaction of methanol with steam was studied at atmospheric pressure using a conventional flow system. The reactants were introduced into the reactor in the molar ratio $H_2O/CH_3OH=1.3/1$ at a flow rate of 38.6 cm^3 min^{-1}; the mass of catalyst used was 0.1 g. Prior to reaction, each catalyst sample was reduced in situ with a 5% H_2/N_2 mixture; the temperature was increased at a ramp rate of 5°C min^{-1} to 240°C, dwelling at 240°C for 4 h. Reaction products were analysed at reaction temperatures between 140°C and 345°C. Catalyst turnover frequencies (TOF, s^{-1}) were calculated as the number of hydrogen molecules produced per surface copper atom as determined by the nitrous oxide decomposition measurements described above.

Accelerated ageing tests were carried out on the Cu/Zn/Zr/Al (SP), 2 mol% La and Y catalysts by cycling the reactor temperature between 250°C and 400°C as shown in Fig. 1. During the cycles, the reaction products were analysed by GC at intervals of roughly 20 min. As the conversions measured at 400°C were the equilibrium values of ca. 100%, the conversions at 250°C were taken to represent the activity of the catalyst after each period at the upper temperature.

3. Results and discussion

3.1. *Effect of reaction temperature on conversion and selectivity and possible reaction scheme*

Fig. 2 shows results typical of all the catalysts tested in the present work, illustrating the effect of temperature on the methanol conversion and the molar compositions with respect to carbon monoxide, carbon dioxide and hydrogen for a catalyst containing Cu, Zn, Zr and Al prepared by sequential precipitation; the ratio of water to methanol used in the feed was chosen

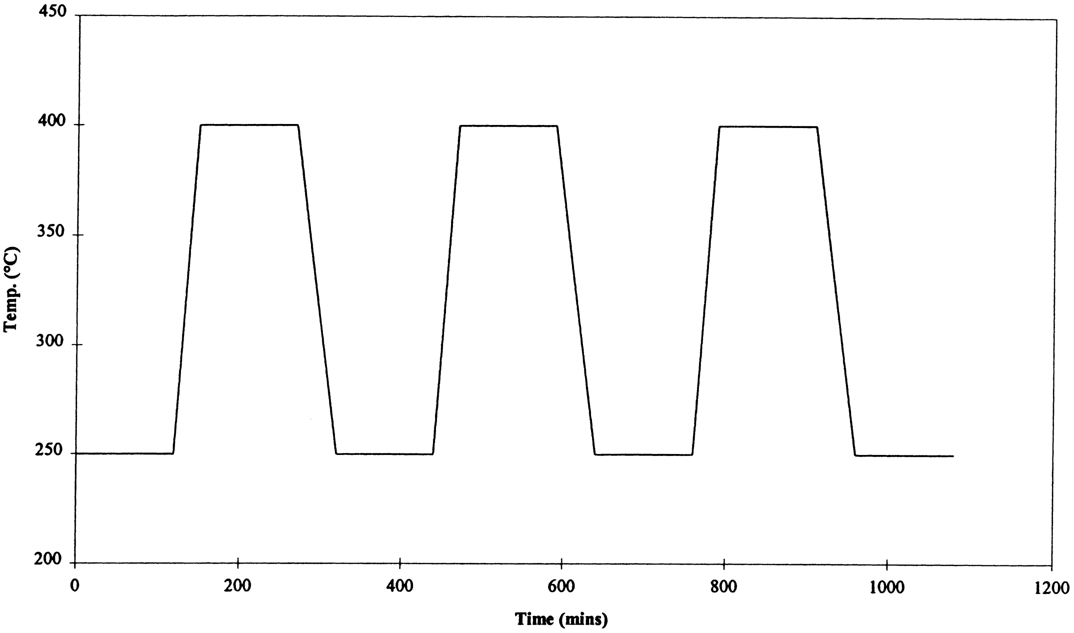

Fig. 1. Reactor temperature profiles during the accelerated ageing tests as a function of time on stream.

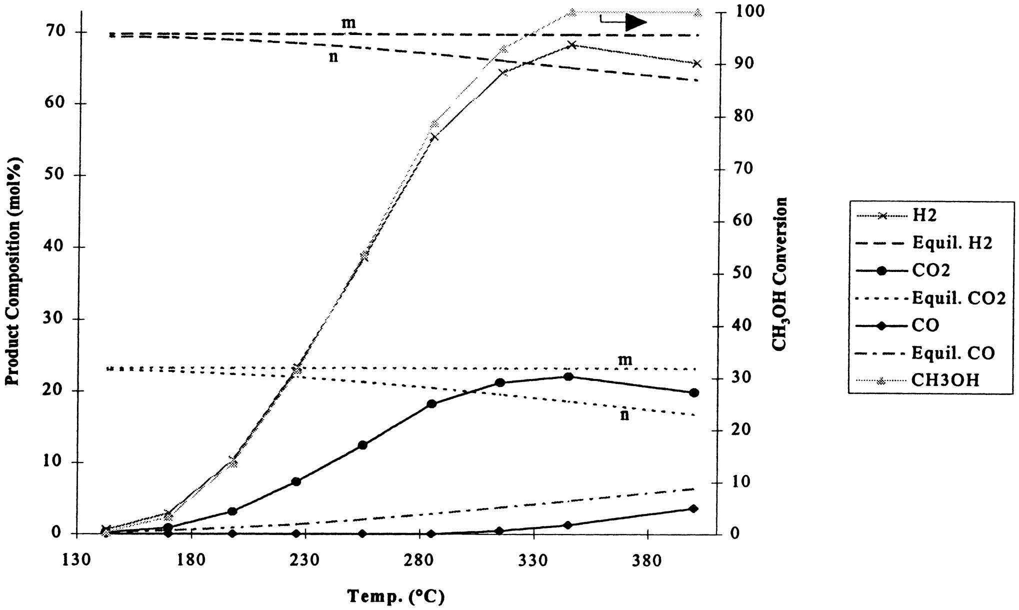

Fig. 2. Influence of temperature on product compositions, m=equilibrium excluding CO from calculations, n=equilibrium including CO in calculations (H_2O/CH_3OH=1.3, P=101 kPa, W/F=0.00259 g min cm^{-3}).

to be slightly above the stoichiometric value as thermodynamic calculations showed that this ratio would tend to favour optimum hydrogen yields if CO were to be formed in equilibrium quantities. The value of W/F used was chosen experimentally as it gave the optimum selectivity to hydrogen and CO_2. The broken curves shown in Fig. 2 represent the equilibrium compositions of hydrogen (two curves), carbon monoxide (one curve) and carbon dioxide (two curves) which would be formed at equilibrium at the different temperatures; according to thermodynamics, the methanol would be completely converted at all temperatures of the range shown. The values for the curves m were calculated by assuming that carbon monoxide was not a product of the steam reforming reaction, whereas the values for the curves n included carbon monoxide in the calculations.

The experimental results shown in Fig. 2 demonstrate that the methanol conversion started above about 150°C and that its production was kinetically controlled over almost the whole range of temperature. Hydrogen and CO_2 were the only products over a relatively wide range of temperature. The conversion of methanol was 100% at temperatures $\geq$345°C and the percentages of hydrogen and carbon dioxide also peaked at this temperature. The molar compositions of the carbon dioxide and hydrogen exceeded the equilibrium line n and approached line m at a temperature of 345°C. At 400°C, the hydrogen and carbon dioxide percentages decreased from the optimum compositions found at 345°C and approached but did not reach the equilibrium line n. It is of significance that CO only started to form at about 300°C even though it is permitted thermodynamically at much lower temperatures. These results indicate that the reaction sequence is such that CO_2 and H_2 are the primary products of the reaction and that the CO is formed at higher temperatures by the reverse water–gas shift reaction:

$$CO_2 + H_2 \rightarrow CO + H_2O$$

Additional experiments, to be reported elsewhere, indicated, that CO was not formed at low contact times and that its concentration only became significant when the methanol was almost consumed at higher contact times. It was also shown that when methanol alone was used as a feed, small quantities of methyl formate were formed at temperatures above about 200°C. Although we found no evidence for the formation of formic acid as an intermediate, we suggest, in agreement with the results of Takahashi et al. [8], that the following sequence of reactions may occur over our catalysts:

$$2CH_3OH \rightarrow CH_3OCHO + 2H_2$$

$$CH_3OCHO + H_2O \rightarrow HCOOH + CH_3OH$$

$$HCOOH \rightarrow CO_2 + H_2$$

A significant consequence of our results is that it is possible to operate a catalyst of the type which we have tested above under conditions when the CO concentration is much lower than that predicted by thermodynamics; as long as the temperature is low enough and the space velocity high enough to prevent complete conversion of the methanol, the production of CO by the reverse water–gas shift reaction is relatively insignificant. The use of a more sensitive detector for the GC would be required to establish whether or not the CO concentrations are sufficiently low to enable such catalysts to produce gases suitable as feedstock for fuel-cell application without further treatment to remove the CO present. Typical PEMFC stacks require CO concentrations to be less than 50 ppm.

3.2. Preparation and characterisation of novel catalysts

Table 1 summarises the hydrogen production rates, copper and BET surface areas and turnover frequencies (TOFs) for the steam reforming of methanol of the various catalysts prepared in this work. The temperature chosen for the comparisons was 255°C since, as shown in Fig. 2, the conversion of methanol was well below 100% at this temperature; the selectivities to hydrogen and carbon dioxide at this temperature were also 100% for the majority of the catalysts, exceptions being the Cu/Zn (80/20) and Cu/Zn (90/10) materials which also produced carbon monoxide at this temperature (3% and 4%, respectively). The behaviours of the various catalysts will now be described in turn.

3.2.1. Sequentially precipitated Cu/Zn catalysts

Three Cu/Zn catalysts were prepared by sequential precipitation (first copper, then zinc) with molar Cu/Zn ratios of 70/30, 80/20 and 90/10 (Table 1). The

Table 1
The characteristics and performance of methanol reforming catalysts at 255°C

Catalyst	Composition (mol%)	Preparation method[a]	Copper surface area ($m^2 g^{-1}$)	BET surface area ($m^2 g^{-1}$)	Hydrogen production rate at 255°C (mmol $kg_{cat}^{-1} s^{-1}$)	TOF[b] at 255°C ($10^3 s^{-1}$)
Cu/Zn	70/30	SP	12.9	34.5	117	375
Cu/Zn	80/20	SP	14.2	44.2	123	355
Cu/Zn	90/10	SP	8.5	38.3	62	302
Zr	–	–	0	173.8	0	0
Cu/Zr	30/70	CP	3	116.9	25	341
Cu/Zr	70/30	CP	3.7	60.8	44	488
Cu/Zn/Zr	70/18/12	CP	16.3	57.0	108	272
Cu/Zn/Zr	70/18/12	SP	15.6	94.7	165	436
Cu/Zn/Al	70/18/12	CP	16.8	49.6	106	259
Cu/Zn/Al	70/18/12	SP	11.9	94.0	127	436
Cu/Zn/Zr/Al	70/18/10/2	CP	25.7	78.0	161	257
Cu/Zn/Zr/Al	70/18/10/2	SP	24.0	103.3	186	318
Cu/Zn/Zr/Al/La	70/17/10/2/1	SP	13.6	63.9	138	418
Cu/Zn/Zr/Al/La	69/17/10/2/2	SP	16.7	67.1	144	356
Cu/Zn/Zr/Al/La	68/17/10/2/4	SP	14.0	69.3	102	300
Cu/Zn/Zr/Al/Y	70/17/10/2/1	SP	21.8	90.3	154	290
Cu/Zn/Zr/Al/Y	69/17/10/2/2	SP	19.5	91.5	162	341
Cu/Zn/Zr/Al/Y	68/17/10/2/4	SP	25.6	119.9	145	233

[a] SP=sequential precipitation, CP=co-precipitation.

[b] Hydrogen molecules produced per surface copper atom per second.

Reaction conditions – CH_3OH: 16.6 $cm^3 min^{-1}$; H_2O: 22.0 $cm^3 min^{-1}$, N_2: 38.6 $cm^3 min^{-1}$; p=101 kPa, H_2O/CH_3OH=1.3/1.

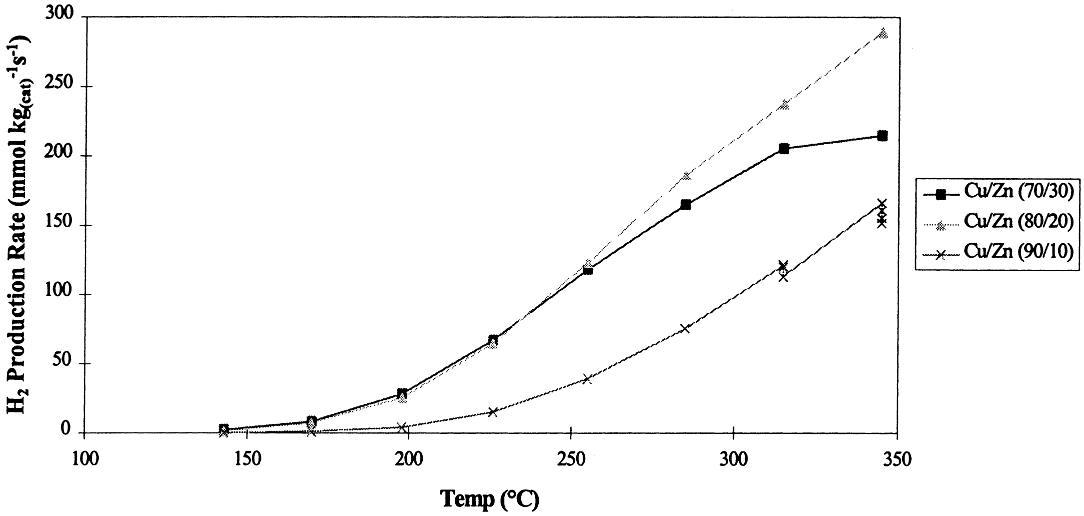

Fig. 3. The influence of reaction temperature on the rate of hydrogen production for a series of Cu/Zn (SP) catalysts. (Conditions: CH_3OH, 16.6 cm^3 min^{-1}; H_2O, 22.0 cm^3 min^{-1}; N_2, 38.6 cm^3 min^{-1}; p=101 kPa, H_2O/CH_3OH=1.3/1).

influence of temperature on the activities of these catalysts is shown in Fig. 3. The 60/40, 70/30 and 80/20 catalysts all had similar activities over the low temperature range, 143–255°C. In the higher temperature range (255–345°C), the 80/20 catalyst had a higher activity for the production of hydrogen than did the others. Fig. 3 shows that the hydrogen production rate over the Cu/Zn (70/30) catalyst was limited at high temperatures (315–345°C); this was probably due to deactivation of the catalyst as a result of sintering of copper at high temperatures. Due to the fact that there was no apparent deactivation at temperatures 315°C and 345°C, the deactivation is likely to have occurred during the ramping of temperature. The 90/10 catalyst was less active than the other Cu/Zn catalysts at all temperatures and there was noticeable deactivation of this material with time at 315°C and 345°C, probably due to the fact that there was insufficient ZnO to stabilise copper against sintering.

3.2.2. Co-precipitated Cu/Zr catalysts

Fig. 4 compares the activities of two co-precipitated Cu/Zr catalysts. The Cu/Zr (70/30) material was more active than was the Cu/Zr (30/70) material at all temperatures. Both of the Cu/Zr catalysts deactivated at temperatures ≥285°C and there was severe deactivation at 345°C; the hydrogen production rate over the Cu/Zr(70/30) catalyst at the latter temperature fell from 138.3 to 109.8 mmol kg_{cat}^{-1} s^{-1} over the 2 h period of measurement at the highest temperature and there was an equally dramatic decrease from 88.3 to 70.0 mmol kg_{cat}^{-1} s^{-1} over the Cu/Zr (30/70) catalyst. The Cu/Zr catalysts were less active than the Cu/Zn catalysts between 143°C and 345°C. ZrO_2 on its own was found not to catalyse the reaction.

Table 1 shows that both the Cu/Zr co-precipitated catalysts had low copper surface areas: 3.0 m^2 g^{-1} for the Cu/Zr (30/70) catalyst and 3.7 m^2 g^{-1} for the Cu/Zr (70/30). The binary Cu/Zn catalysts however showed considerably greater copper dispersions (12.9, 14.2 and 8.5 m^2 g^{-1}) than the Cu/Zr catalysts. This is in agreement with the data of Nitta et al. [15] who also found an increase in the dispersions of Cu/Zn catalysts compared to those of Cu/Zr catalysts. The increased activities of the Cu/Zn catalysts can be attributed partially to the increased copper surface areas of these materials (Table 1). Rasmussen et al. [29] showed that the addition of ZnO to CuO induces a reduction of the CuO crystallite size.

Despite the low activities of the Cu/Zr catalysts, these materials had high turnover frequencies at 255°C which were comparable to those of the Cu/Zn catalysts at the same temperature. This suggests that copper was promoted to a similar extent by both zinc and zirconia.

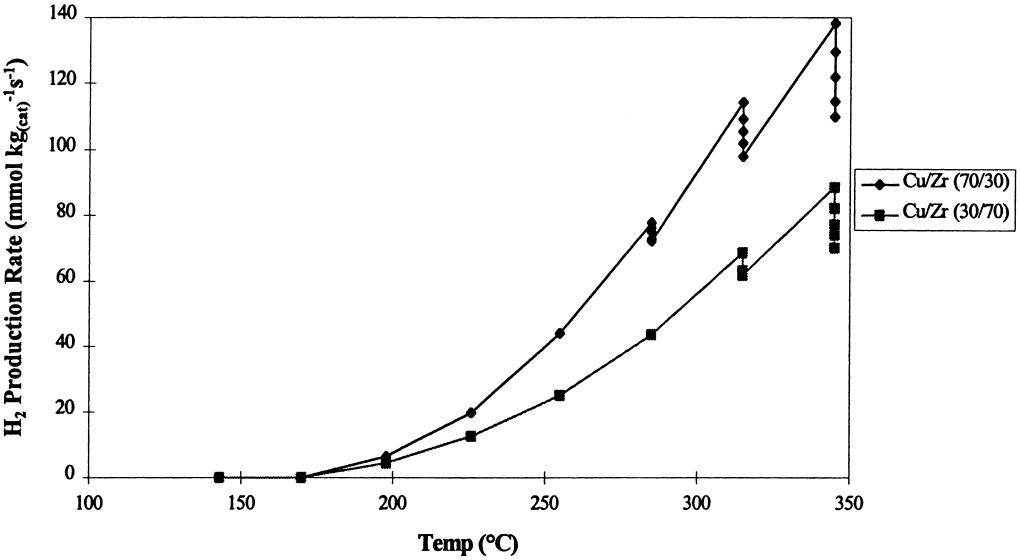

Fig. 4. The influence of temperature on the rate of hydrogen production over Cu/Zr (CP) catalysts. (Conditions: CH_3OH, 16.6 $cm^3\ min^{-1}$; H_2O, 22.0 $cm^3\ min^{-1}$; N_2, 38.6 $cm^3\ min^{-1}$; p=101 kPa, H_2O/CH_3CH=1.3/1).

3.2.3. *The effect of the addition of zirconium and/or aluminium to the Cu/Zn catalyst formulation*

Fig. 5 compares the catalytic activities of the Cu/Zn (70/30), Cu/Zr (70/30), Cu/Zn/Zr (SP), Cu/Zn/Al (SP) and Cu/Zn/Zr/Al (SP) catalysts. The Cu/Zn/Zr/Al (SP) material was the most active at all the temperatures tested and it fully converted all the methanol at 345°C. The Cu/Zn/Zr (SP) catalyst was slightly less active than the Cu/Zn/Zr/Al (SP) sample for the reaction at all temperatures but again it fully converted the

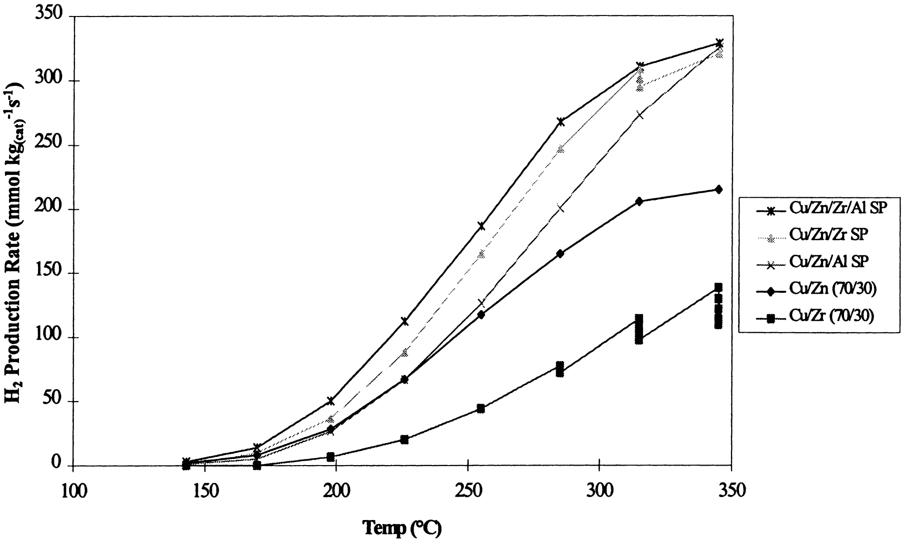

Fig. 5. The influence of temperature on the rate of hydrogen production in the steam reforming of methanol reaction over copper catalysts. (Conditions: CH_3OH, 16.6 $cm^3\ min^{-1}$; H_2O, 22.0 $cm^3\ min^{-1}$; N_2, 38.6 $cm^3\ min^{-1}$; p=101 kPa, H_2O/CH_3OH=1.3/1).

methanol at 345°C. There was, however, noticeable deactivation of the Cu/Zn/Zr (SP) catalyst at a temperature of 315°C and the hydrogen production rate fell from 309 to 295 mmol $\mathrm{kg_{cat}}^{-1}\ \mathrm{s}^{-1}$ over a period of 2 h at this temperature. The addition of alumina to zirconia appeared to bring about the stabilisation of the Cu/Zn/Zr/Al (SP) catalyst and there was no noticeable deactivation at any temperature during the reaction over this sample.

From the results of Table 1, it can be seen that the Cu/Zn/Zr (SP) catalyst combined the beneficial dispersion effects on copper of the added ZnO and the beneficial catalytic synergy between copper and zirconia to give a catalyst with a higher copper dispersion than the Cu/Zr catalysts, a higher turnover frequency than the Cu/Zr catalysts and a higher methanol conversion rate at all temperatures than the Cu/Zn catalysts. The increased activity of the Cu/Zn/Zr (SP) catalyst compared to the Cu/Zr catalyst is probably related to the increased quantity of methanol that can be adsorbed on the higher copper surface area of the Cu/Zn/Zr (SP) material. Bianchi et al. [30] carried out experiments involving TPD of methanol from both copper–zirconia and copper–zinc–zirconia catalysts and found that more methanol could be adsorbed on the zinc-containing catalyst.

3.2.4. *The role of alumina in stabilising zirconia*

Although the Cu/Zn/Zr catalysts were active at low temperatures (170°C), they did show a tendency to deactivate quite severely at higher temperatures (>315°C). However, the materials containing alumina as well as zirconia did not show any noticeable deactivation at any of the temperatures tested. The deactivation of the former samples may be explained by the occurrence of the transformation of zirconia from an initially amorphous form to the crystalline form (probably metastable tetragonal). Koeppel et al. [17] found that their copper/zirconia catalysts changed from amorphous to crystalline at ~470°C under reducing conditions and that catalysts which had been calcined above that temperature showed a large loss in surface area and activity for the methanol synthesis reaction. However, Mercera et al. [31] have shown that the temperature of crystallisation of zirconia can be reduced considerably in the presence of steam which accelerated the process of crystallite growth and hence the presence of steam under the reaction conditions of the experiments described here would also be expected to lower the temperature of the phase transition. The present results show that the stabilities of the Cu/Zn/Zr catalysts were greatly improved by the addition of alumina to zirconia (Fig. 5); there was no noticeable deactivation of these catalysts at any of the temperatures tested, the characteristic stability of the alumina catalysts at higher temperatures being imparted to the zirconia materials. The alumina probably helps to increase the temperature of crystallisation of the zirconia of the catalysts and hence to stabilise their structures. The addition of alumina also had the effect of increasing the BET and copper areas of the catalysts. These effects also imparted improved and more stable catalytic activities. The sequentially precipitated Cu/Zn/Zr/Al catalyst was more active at all temperatures than all the other materials shown in Table 1.

3.2.5. *TPR of the calcined catalysts*

TPR results were obtained for each of the calcined catalysts. The reduction profiles of samples of copper oxide alone and of copper oxide with one or more of the components ZnO, ZrO_2 and Al_2O_3 are shown in Fig. 6. All the profiles revealed one main reduction peak, presumably due to the reduction of crystalline Cu(II)O, with a shoulder to the main peak visible at a lower temperature for the Cu/Zn and Cu/Zr catalysts. This shoulder may be due to the reduction of amorphous or highly dispersed copper oxide [12] or alternatively to the reduction of hydroxycarbonate species which remain in the catalyst structure after calcination.

The Cu/Zn/Zr and Cu/Zn/Zr/Al catalysts each had reduction peaks at 235°C, 10°C lower than for the Cu/Zn catalyst. The Cu/Zr sample had a reduction peak at 255°C and the Cu/Zn/Al sample required a higher temperature of 265°C to attain a maximum copper (II) oxide reduction rate. Pure copper (II) oxide reduced at a considerably higher temperature (342°C) than did the catalyst samples, indicating that there is a copper/support interaction in the latter which facilitates the reduction of copper (II) oxide. Both bulk and supported CuO become reduced by a process involving nucleation or autocatalytic reduction and it is well documented that supported CuO reduces more easily than does bulk CuO [33]. The higher area beneath the CuO peak compared to the other catalysts was due to

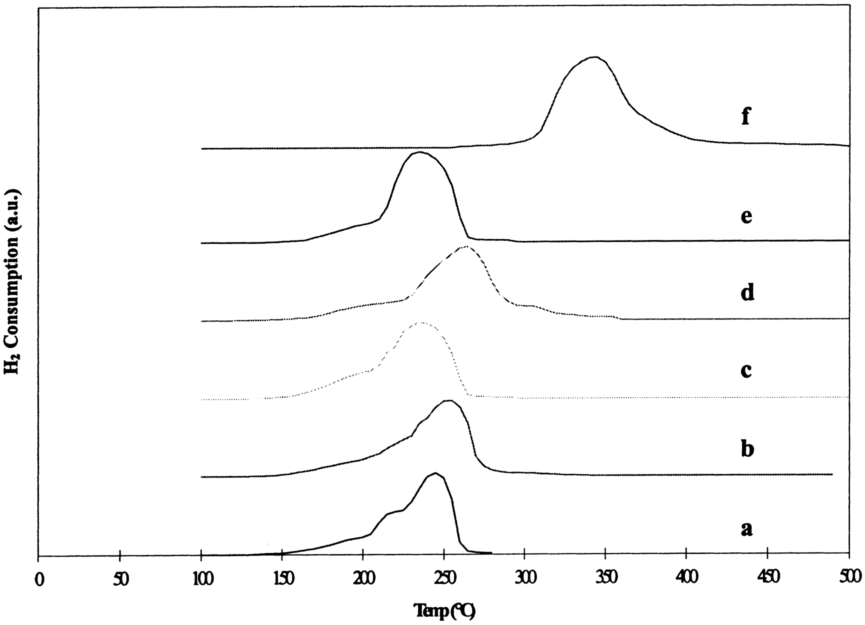

Fig. 6. TPR profiles of the calcined catalysts: (a) Cu/Zn (70/30), (b) Cu/Zr (70/30), (c) Cu/Zn/Zr (SP), (d) Cu/Zn/Al (SP), (e) Cu/Zn/Zr/Al (SP), (f) CuO.

the fact that the copper-containing catalysts contained only 70 mol% CuO. Measurement of the TPR peak areas showed that slightly more hydrogen was consumed for the reduction of the 70 mol% CuO in each of the catalysts than would be expected from the stoichiometric reduction reaction. This excess hydrogen consumption can be attributed to the reduction of undecomposed hydroxycarbonate species in the catalysts. TG analysis of the catalysts after the TPR experiments showed that peaks attributable to hydroxycarbonate species which were present in the catalyst before the TPR experiments were not present after TPR analysis.

The two most active catalysts, Cu/Zn/Zr (SP) and Cu/Zn/Zr/Al (SP), had the lowest temperature reduction peaks of all the catalysts. There is evidence that a Cu^{o}/Cu_{ox} redox mechanism may occur at the boundary layers of metallic copper in intimate contact with ZnO during methanol synthesis [32]; the ease of reducibility is therefore likely to be an important factor in determining the activity of the catalyst.

The Cu/Zr (70/30) catalyst had a reduction peak at a similar temperature to the Cu/Zn (70/30) catalyst, providing further evidence that, in addition to a synergy between Cu and ZnO, there is also a Cu/Zr synergism. There is evidence in the literature of a catalytic synergy between copper and amorphous zirconia for the methanol synthesis reaction [15,18,21,22,34] and that the dispersion of copper and also of zirconia are important in determining the activity of a Cu/Zr catalyst [14].

It is interesting to note that the addition of alumina to the Cu/Zn/Zr catalyst did not have any effect on the temperature of maximum rate of reduction (Fig. 6). This shows that the presence of alumina in the zirconia-containing catalyst did not aid the reduction of the CuO and that the primary importance of alumina in the catalyst most probably lies in its ability to prevent or retard crystallisation of the amorphous zirconia under reaction conditions.

It is apparent from the data presented in Table 1 that there were noticeable differences in the activities and textural and structural properties of those catalysts which had the same molar compositions but which were prepared by different methods (i.e. either by coprecipitation or sequential precipitation). The reasons for these differences will be discussed elsewhere.

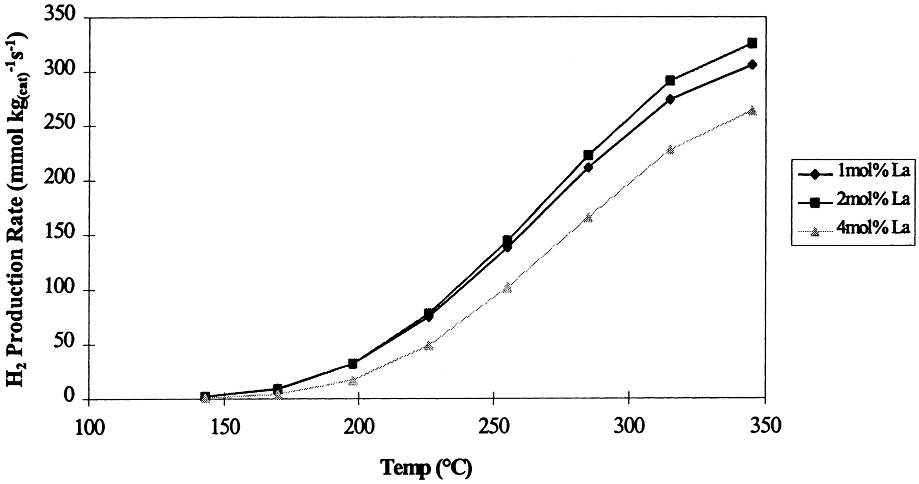

Fig. 7. The influence of temperature on the rate of hydrogen production in the steam reforming of methanol reaction over catalysts containing 1–4 mol% La. (Conditions: CH_3OH, 16.6 cm^3 min^{-1}; H_2O, 22.0 cm^3 min^{-1}; N_2, 38.6 cm^3 min^{-1}; p=101 kPa, H_2O/CH_3OH=1.3/1).

3.2.6. The effect of the addition of La and Y on the activity and stability of the Cu/Zn/Zr/Al SP catalyst

Fig. 7 shows the activities, at temperatures ranging from 143 to 345°C, of the catalysts containing 1, 2 and 4 mol% La. (The full formulations of the samples examined are given in Table 1). The 2 mol% La catalyst gave the highest hydrogen production rate of the three materials at each temperature and the 4 mol% La catalyst was the least active. Fig. 8 shows that the sample containing 2 mol% Y was the most active of the yttria-containing materials at temperatures greater than 225°C; below this temperature, the 1 mol% Y catalyst was most active. The catalysts with 2 and 4 mol% Y both converted the methanol fully at 345°C. The relative activity of the sample containing 1 mol% Y compared to those of the samples containing 2 and 4 mol% Y declined with increasing temperature. This may be due to the fact that there was insufficient Y_2O_3 available to stabilise the catalyst thermally against the ageing effects encountered at increased reaction temperatures.

It must be noted that the La- and Y-containing materials were less active than the Cu/Zn/Zr/Al (SP) sample at all temperatures; see the data of Table 1. The 2 mol% Y catalyst had a hydrogen production rate of 162 mmol kg_{cat}^{-1} s^{-1} and the La catalyst had a production rate of 144 mmol kg_{cat}^{-1} s^{-1} and this should be compared to a rate of 186 mmol kg_{cat}^{-1} s^{-1} for the Cu/Zn/Zr/Al (SP) catalyst.

3.2.7. Catalyst stability under accelerated ageing test conditions

Having prepared catalysts which were highly active for the steam reforming reaction, the next stage in their development was to examine their likely long-term behaviour under reaction conditions. Due to limitations on the volume of liquid that can be delivered using the syringe pump used in this work and hence of the duration of any single experiment, an accelerated ageing process (described in more detail in Section 2) was carried out whereby the methanol conversion was first monitored at 250°C before raising the temperature to 400°C; the reactor was then cooled to 250°C again at which temperature any change in the behaviour of the catalysts due to the period at 400°C could be observed. For each sample, this cycle was repeated 3 times. Fig. 9 shows the results of such experiments using the most active La (2 mol%) and Y (2 mol%) catalysts and also using the Cu/Zn/Zr/Al (SP) catalyst.

Comparing the abilities of the 2 mol% La and Y catalysts to withstand the effects of ageing at 400°C, it is clear that the Y-containing catalyst deactivated to a lesser extent than did the La-containing sample. The yttria catalyst deactivated from an initial conversion rate of methanol of 48% at 250°C to 32% after three cycles at a temperature of 400°C, this corresponding to

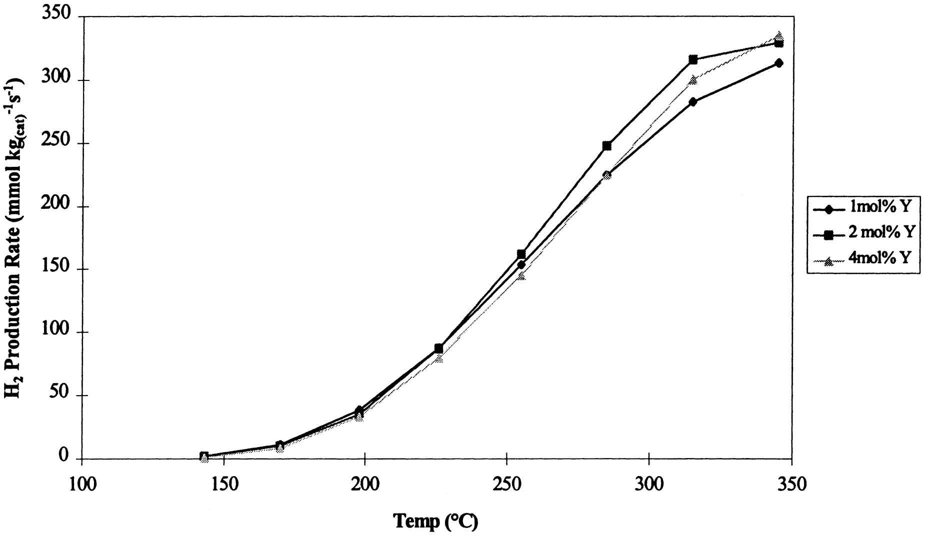

Fig. 8. The influence of temperature on the rate of hydrogen production in the steam reforming of methanol reaction over catalysts containing 1–4 mol% Y. (Conditions: CH_3OH, 16.6 cm^3 min^{-1}; H_2O, 22.0 cm^3 min^{-1}; N_2, 38.6 cm^3 min^{-1}; p=101 kPa, H_2O/CH_3OH=1.3/1).

a loss in activity of 33%. This loss of activity compared favourably with that for the lanthana-containing catalyst which gave an initial conversion of 44% but a conversion of 23% after completing the cycling process, a decrease of 47%. Compared to the yttria-containing catalyst, the Cu/Zn/Zr/Al (SP) catalyst exhibited relatively poor ageing properties, despite being more stable than the Cu/Zn/Zr (SP) catalyst which deactivated noticeably even during the activity tests at temperatures up to 345°C (Section 3.2.3). The initial methanol conversion given by the Cu/Zn/Zr/Al (SP) catalyst was 46% and the conversion declined to 28% after three temperature cycles, a decrease of 39%.

The Cu/Zn/Zr/Al (SP) catalyst did not give full conversion of the methanol at 400°C during the second and third cycles. It is interesting to note that the initial activity of this catalyst of 46% was slightly lower than that of the sample containing 2 mol% yttria (48%), even though it had been 14% more active than the yttria catalyst in the screening tests (Sections 3.2.4 and 3.2.6). In order to investigate why this difference

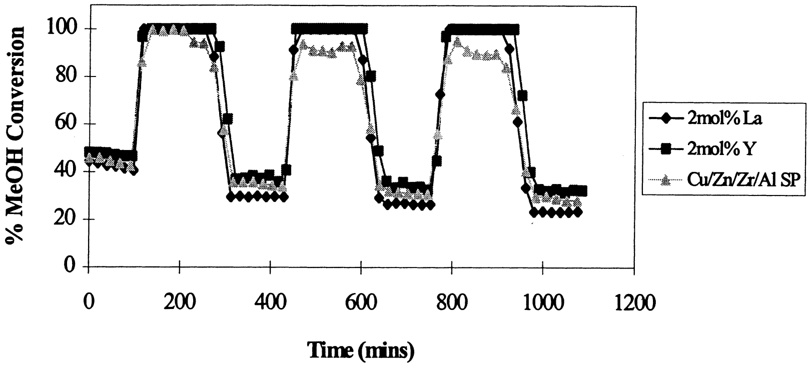

Fig. 9. Influence of accelerated ageing on the methanol conversion rates of catalysts for the steam reforming of methanol. (Conditions – CH_3OH: 16.6 cm^3 min^{-1}; H_2O: 22.0 cm^3 min^{-1}, N_2: 38.6 cm^3 min^{-1}, p=101 kPa, H_2O/CH_3OH=1.3/1).

had occurred, the BET surface area of the Cu/Zn/Zr/Al (SP) was re-tested and was found to have decreased while in storage, for a period of 1 year, from 103 to 89 m^2/g. The copper surface area was also found to have decreased during this period in storage, from 24.0 to 21.2 m^2/g. Catalysts of the same composition as the Cu/Zn/Zr/Al materials presented here prepared by co-precipitation were also examined and it was found that their activities and copper surface areas also decreased with time in storage. Possible explanations for this occurrence will be discussed in greater detail elsewhere; it appears to be related to the formation of carbonate or hydroxycarbonate species on the catalyst material during storage.

The yttria-containing catalysts were thus found to be more active and more stable than their lanthana-containing counterparts. From the data of Table 1, it can be seen that the yttria-containing materials had higher BET and copper surface areas than the lanthana-containing materials. For example, the 2 mol% Y catalyst had a BET surface area of 91.5 $m^2\,g^{-1}$ and a copper surface area of 19.5 $m^2\,g^{-1}$ compared to a BET surface area of 67.1 $m^2\,g^{-1}$ and a copper surface area of 16.7 m^2/g for the 2 mol% La catalyst. It is possible that the yttria-doped catalysts provided a larger and more stable surface area on which the active copper component could reside. Turlier et al. [24] and Mercera et al. [23] found that yttria-doped zirconia supports had higher BET surface areas than their lanthana doped counterparts after calcination at 400°C. Turlier et al. [24] suggested that yttria was a better structural and textural promoter of zirconia than was lanthana because the ionic radii of Y^{3+} (0.9 Å) and Zr^{4+} (0.8 Å) are more similar in size than those of La^{3+} (1.1 Å) and Zr^{4+} (0.8 Å), this having the consequence that there is easier substitution of the yttria into zirconia. The presence of the yttria probably retards the phase transformations of zirconia from initially amorphous zirconia to the tetragonal phase and hence therefore probably also hinders the sintering associated with the phase transformation.

4. Conclusions

A number of conclusions can be drawn from the results presented here:

1. Carbon monoxide appears to be a secondary product of the steam reforming reaction and significant formation of this molecule can be avoided by working at relatively low temperatures and at relatively high space velocities.
2. The addition of zinc to the Cu/Zr catalyst formulation resulted in catalysts with considerably higher copper dispersions than those of the Cu/Zr catalysts and it also improved the activity at temperatures ranging from 143 to 345°C.
3. The Cu/Zn/Zr catalysts were more catalytically active than the Cu/Zn/Al materials prepared by the same method and having the same copper and zinc contents; the values of the TOF of the Cu/Zn/Zr catalysts were also higher than those of the Cu/Zn/Al materials. This suggests that zirconia is a more effective support for Cu and ZnO than alumina. The values of the TOFs and the TPR profiles of the Cu/Zr materials point to the existence of a synergy between copper and zirconia which is not present to the same extent in the Cu/Al materials.
4. The addition of alumina to the Cu/Zn/Zr materials was found to increase the stability of these catalysts; this was probably due to the stabilisation of the active amorphous zirconia phase. The addition of alumina also increased the activity of the catalysts. The increased activity was found to be correlated with an increase in both the copper and BET surface areas imparted to the catalysts by the addition of alumina.
5. Sequential precipitation of the catalyst components resulted in catalysts with higher activities than of those with the same composition prepared by co-precipitation.
6. TPR analysis of the catalysts revealed that the most active materials (Cu/Zn/Zr (SP) and Cu/Zn/Zr/Al (SP)) had reduction peaks at the lowest temperature. There is evidence in the literature of the involvement of a Cu^o/Cu_{ox} redox mechanism in methanol synthesis; the ease of reducibility is therefore likely to be an important factor in determining the activities of the catalysts.
7. The stability of the Cu/Zn/Zr/Al (SP) catalyst was further improved by the addition of yttria to the formulation. The 2 mol% yttria catalyst was the most active of the yttria-promoted materials prepared. The yttria-containing catalysts were found

to be more active and more stable than their lanthana-containing counterparts.

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