Available online at www.sciencedirect.com

ScienceDirect

Catalysis Today 127 (2007) 291–294

CATALYSIS TODAY

www.elsevier.com/locate/cattod

The preparation and properties of coprecipitated Cu–Zr–Y and Cu–Zr–La catalysts used for the steam reforming of methanol

Patricia Clancy [a], John P. Breen [b], Julian R.H. Ross [a,*]

[a] *University of Limerick, Limerick, Ireland*
[b] *Queen's University of Belfast, Belfast, Ireland*

Abstract

A series of Cu–zirconia catalysts containing various additives (Y_2O_3, La_2O_3, Al_2O_3 and CeO_2) have been prepared by coprecipitation and their activities and stabilities under operating conditions have been obtained for the steam reforming of methanol. It has been found that an yttria-promoted catalyst containing 30 mol% Cu and 20 mol% of Y_2O_3 is not only very active but is also very stable under reaction conditions. The yttria appears to stabilise a high copper surface area and may also have a slight promotional effect on the copper. The results obtained with this material compare very favourably with data for the best catalysts reported in the literature.

Keywords: Coprecipitated Cu–Zr–Y and Cu–Zr–La catalysts; Steam reforming of methanol

1. Introduction

Much work is currently being carried out on alternative energy sources and fuels for transportation purposes. One energy carrier which has received particular attention is methanol, a molecule which can be transformed into hydrogen by steam reforming:

$$CH_3OH + H_2O \rightarrow CO_2 + 3H_2$$

the hydrogen produced being used as fuel in low temperature fuel cells utilizing polymer membranes. Carbon monoxide may also be formed in the reaction system, either through the direct decomposition of methanol:

$$CH_3OH \rightarrow CO + 2H_2$$

or by the reverse water–gas shift reaction:

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

For use in the low temperature fuel cells, the CO concentration must be kept low in order to avoid poisoning of the fuel cell electrodes and so catalytic materials with high activity at low temperature are required which are also stable for long periods of operation in vehicles.

A wide range of metals supported on, or combined with, various different support materials have been investigated for the steam reforming of methanol, these including iron [1], platinum [2], nickel [3], cobalt [4] and palladium [5,6] with alumina, silica and zirconia. However, the majority of the research on this topic has concentrated on copper-based materials and it has generally been recognised that the presence of copper is a requirement for an active steam reforming catalyst since the copper-based materials show the highest activities and selectivities [7]. We have previously described the preparation and use of a series of Cu–Zn–Al–Zr catalysts made by both coprecipitation and sequential precipitation, the latter materials being the more active and stable of the two types; we also found that the addition of either Y or La ions during the sequential preparation process improved the stabilities of the resultant catalysts [8]. This paper presents the results of an investigation of the properties of a series of coprecipitated Cu–Zr–Ce, Cu–Al–Zr, Cu–Zr–Y and Cu–Zr–La materials for the methanol steam reforming reaction and a comparison of these results with those presented previously.

2. Experimental

The catalysts were prepared by precipitation from the corresponding nitrate precursors using 1 M sodium carbonate

---

* Corresponding author.
E-mail address: julian.ross@ul.ie (J.R.H. Ross).

0920-5861/$ – see front matter © 2007 Published by Elsevier B.V.
doi:10.1016/j.cattod.2007.06.040

Table 1
The physical characteristics and performances of the catalysts prepared for the steam reforming of methanol at 300 °C

Catalyst	Fresh				After 10 h on stream			
	H_2 production rate at 573 K (mmol kg_{cat}^{-1} s^{-1})	BET surface area (m^2 g^{-1})	Copper surface area (m^2 g^{-1})	TOF[a] at 573 K ($\times 10^3$ s^{-1})	H_2 production rate at 573 K (mmol kg_{cat}^{-1} s^{-1})	BET surface area (m^2 g^{-1})	Copper surface area (m^2 g^{-1})	TOF[a] at 573 K ($\times 10^3$ s^{-1})
Cu/ZrO_2 30/70	98	110	8.2	493	61	52	5.0	503
$Cu/La_2O_3/ZrO_2$ 32/5/63	187	104	10.9	708	143	95	8.5	694
$Cu/La_2O_3/ZrO_2$ 30/10/60	214	187	12.1	730	172	162	9.7	732
$Cu/La_2O_3/ZrO_2$ 30/20/50	211	120	11.9	731	173	96	9.6	743
$Cu/Y_2O_3/ZrO_2$ 32/5/63	156	115	11.0	585	106	105	7.8	561
$Cu/Y_2O_3/ZrO_2$ 30/10/60	215	214	12.8	698	190	207	11.2	700
$Cu/Y_2O_3/ZrO_2$ 30/20/50	252	175	15.4	675	249	158	15.0	685
$Cu/CeO/ZrO_2$ 30/10/60	149	177	8.4	732	105	61	5.9	734
$Cu/Al_2O_3/ZrO_2$ 32/5/63	145	158	10.1	592	114	103	7.7	611
$Cu/Al_2O_3/ZrO_2$ 30/10/60	211	205	12.6	635	145	94	8.8	643

[a] Turn-over frequency, number of hydrogen molecules produced per surface copper atom per second.

solution at a pH of 7.0 ± 0.1 at a constant temperature of 343 K. The nomenclature of the samples prepared is illustrated by the following example: CuYZr 32/5/63 denotes a $Cu/Y_2O_3/ZrO_2$ catalyst with metal/cation mole percentages of 32, 5 and 63, respectively. The final catalyst was obtained after calcination at 623 K for 6 h after ramping to that temperature at 5 K min^{-1} and, prior to reaction, was reduced in a flow of 5% H_2 in N_2 at 513 K for 4 h, ramping to that temperature at 2 K min^{-1}. Catalytic tests were carried out either at a constant temperature or in a series of steps over a range of temperatures from 423 to 573 K in a flow microreactor using a catalyst weight of 100 mg, a flow of 77.2 cm^3 min^{-1} which was made up of N_2, 38.6 cm^3 min^{-1}, CH_3OH, 16.6 cm^3 min^{-1} and H_2O, 22 cm^3 min^{-1}. Catalyst stability was tested over a period of reaction of 10 h at 573 K. The metallic Cu areas of reduced samples were determined by N_2O reaction using the method described by Luys et al. [9] in an Intelligent Gravimetric Analyser (IGA, Hiden Analytical) as described previously [8]. X-ray diffraction results were obtained using a Philips X'Pert-MPD diffractometer with nickel-filtered copper Kα radiation. In situ Raman spectra were obtained using a JY Horiba LABRAM no. 1/168 IM Raman Spectrometer equipped with a TS 1500 temperature stage.

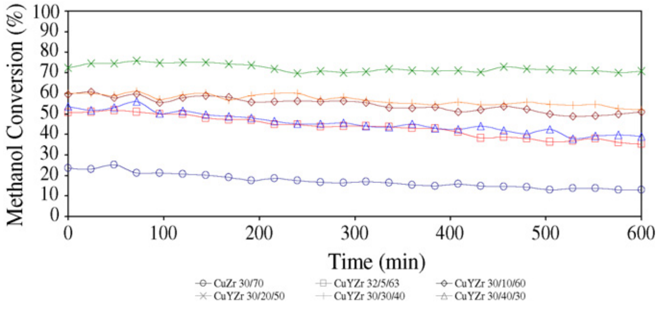

Fig. 1. Catalytic activities of a series of CuYZr catalysts for the steam reforming of methanol. The sample without promoter (CuZr) is shown for comparison purposes. Reaction conditions: N_2, 38.6 cm^3 min^{-1}; CH_3OH, 16.6 cm^3 min^{-1}; H_2O, 22.0 cm^3 min^{-1} and $P = 101$ kPa.

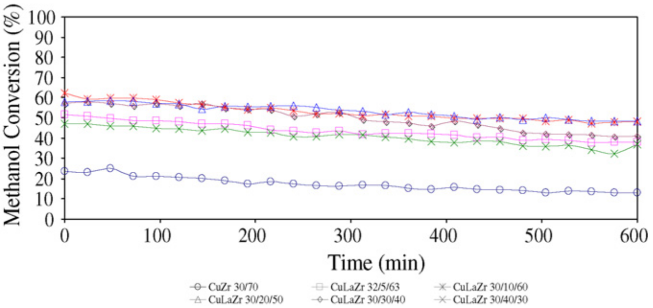

Fig. 2. Catalytic activities of a series of CuLaZr catalysts for the steam reforming of methanol. The sample without promoter (CuZr) is shown for comparison purposes. Reaction conditions: N_2, 38.6 cm^3 min^{-1}; CH_3OH, 16.6 cm^3 min^{-1}; H_2O, 22.0 cm^3 min^{-1} and $P = 101$ kPa.

3. Results and discussion

Table 1 shows the compositions of the catalysts prepared and examined in this work and Figs. 1–4 show the results of the catalytic experiments carried out at 573 K over a period of 600 min for each of the samples. The selectivity to CO_2 was in each case 100% as has generally been found for such catalysts at relatively low conversions [8]. (The detection limit for CO

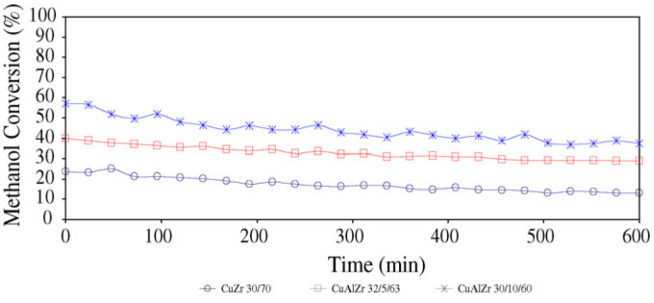

Fig. 3. Catalytic activities of a series of CuAlZr catalysts for the steam reforming of methanol. The sample without promoter (CuZr) is shown for comparison purposes. Reaction conditions: N_2, 38.6 cm^3 min^{-1}; CH_3OH, 16.6 cm^3 min^{-1}; H_2O, 22.0 cm^3 min^{-1} and $P = 101$ kPa.

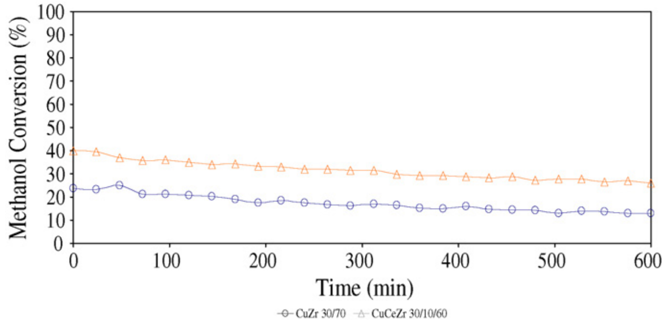

Fig. 4. Catalytic activities of a CuCeZr catalysts for the steam reforming of methanol. The sample without promoter (CuZr) is shown for comparison purposes. Reaction conditions: N_2, 38.6 cm^3 min^{-1}; CH_3OH, 16.6 cm^3 min^{-1}; 1; H_2O, 22.0 cm^3 min^{-1} and $P = 101$ kPa.

was approximately 0.1%.) Table 1 also gives the hydrogen production rates calculated from the data of Figs. 1–4 at the start of the reaction and after reaction for 600 min and also shows the total (BET) and metallic surface areas of each of the samples as well as the turn-over frequencies (TOF—number of hydrogen molecules produced per surface copper atom per second) calculated from the hydrogen production rates using the metal surface area data. Strictly speaking, it is only possible to calculate turn-over frequencies from conversions in experiments such as these if the conversions are low or if the full kinetic expression for each case is known. Hence, the turn-over frequencies are likely to be under-estimates of the true values, especially for the catalysts giving the highest conversions (Figs. 1–4) but the values still show the trends caused by addition of the promoters.

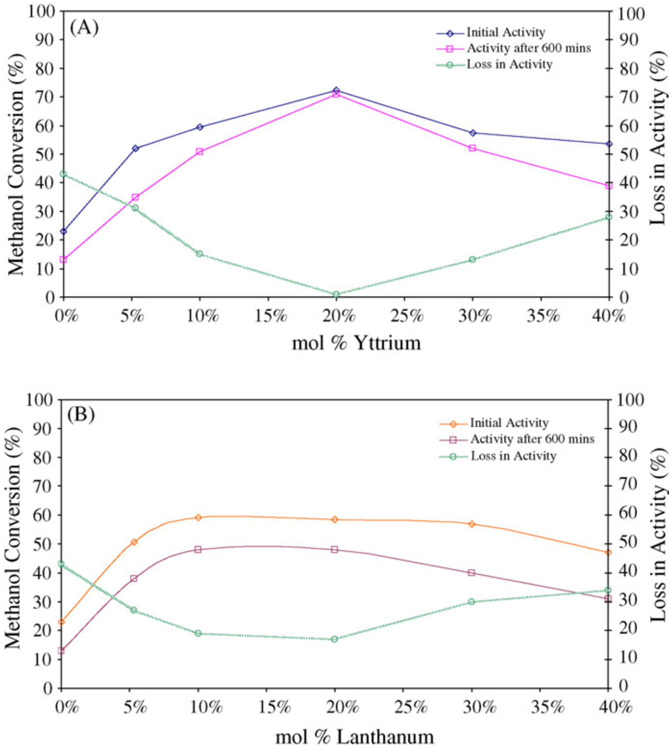

Fig. 5. The initial methanol conversions compared with % loss in activity seen after testing for 600 min at 573 K plotted against increasing additive concentration. (A) $Cu/Y_2O_3/ZrO_2$ and (B) $Cu/La_2O_3/ZrO_2$ (reaction conditions: $CH_3OH = 16.6$ cm^3 min^{-1}, $H_2O = 22.0$ cm^3 min^{-1}, $N_2 = 38.6$ cm^3 $min^{-1}$and $P = 101$ kPa).

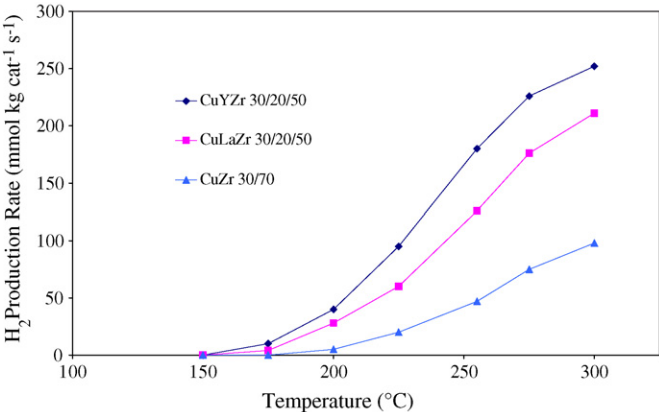

Fig. 6. The influence of temperature on the rate of hydrogen production over Cu/ZrO_2 based catalysts (reaction conditions: $CH_3OH = 16.6$ ml min^{-1}, $H_2O = 22.0$ ml min^{-1}, $N_2 = 38.6$ ml $min^{-1}$and $P = 101$ kPa).

It can be seen from the data of Figs. 1–4 that all the promoted catalysts are more active at 573 K than is the CuZr 30/70 sample. The most active catalyst was the CuYZr 30/20/50 material (Fig. 1) and the other Y-promoted samples were also very active, as were all the La-promoted samples (Fig. 2). Al and Ce were less effective promoters (Figs. 3 and 4).

It can also be seen that all the catalysts (with one exception) lose activity as a function of time on stream. Table 1 gives the activities of all the samples after operation under reaction conditions for 600 min while Fig. 5 shows the initial methanol conversions, the final activities and the loss in conversion at the end of each experiment for the La and Y series as a function of promoter content. It can be seen that with both promoters, the loss of activity is at a minimum for approximately 20 mol% of the promoter. For the sample CuYZr 30/20/50, the level of deactivation was negligible. The very significant promoting action of both La and Y is particularly clear from these plots. It is also clear that the loss of activity is at its lowest for both sets

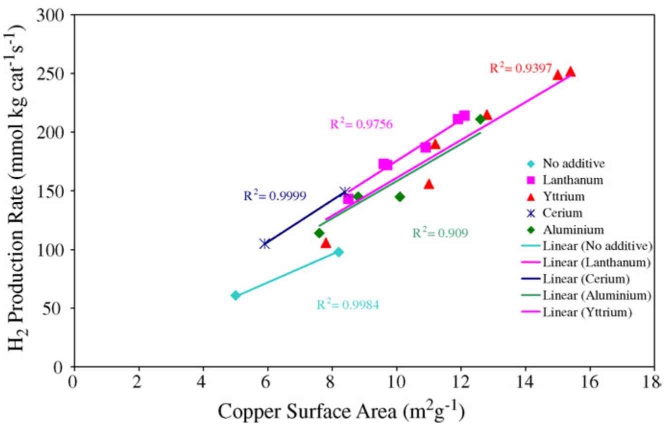

Fig. 7. Plot of the measured hydrogen production rates at the start of reaction and after testing for 600 min against the measured copper.

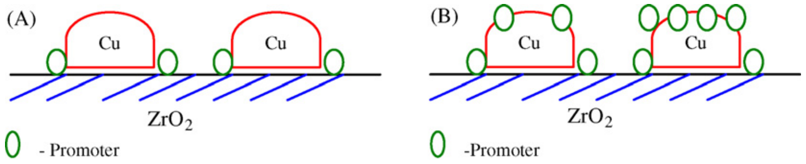

Fig. 8. Schematic representation of the stabilisation mechanism.

of samples at the promoter concentrations which give the highest level of promotion.

The question now is: what is the effect of the promoter in each of these examples? Does the promoter just increase the total and/or metallic surface areas of the samples or is there an effect on the specific activity of the Cu in the samples? Table 1 shows the total and Cu metal surface areas for all the samples, both fresh and after reaction. It can be seen that each promoter stabilises a higher total surface area, presumably by stabilising the structure of the zirconia. The magnitude of the drop in surface area after operation for 10 h at 573 K is an indication of the all-over stability of the catalysts; although the catalysts were calcined at 623 K in the preparation step, there was clearly further structural change during operation under reducing conditions but that this was reduced by the presence of the promoters, especially Y and La oxides. However, the metal surface areas of the promoted samples were also higher and so it appears that the promoter also has some effect on the dispersion of the Cu. The values of the turnover frequencies were therefore calculated for the activity data at 573 K and the values are also given in Table 1. The values of the TOF's for all the promoted samples are higher than that of the unpromoted material, indicating that the active site must be affected in some way by the presence of the promoter and that the promoter does not just have the structural promotion effect shown by the total surface are results. It is also significant difference for any sample between the initial and final TOF values, this indicating that any metallic sintering occurring does not change the promoting effect to any significant degree.

Fig. 6 shows plots of rate of production of hydrogen as a function of catalyst temperature for the most active of the CuYZr and CuLaZr series together with comparable data for the CuZr sample. The Y-promoted material is the most active over the whole range of temperature while the La-promoted material is also very active.

Fig. 7 shows plots of the rates of production of hydrogen for the various sets of catalysts as a function of Cu surface area. The data for the fresh catalysts as well as those for the catalysts after use for 600 min are shown. It can be seen that there is a good linear relationship between activity and Cu metal area for each series and there are slight differences between each series. Whether or not these differences are really significant would require more detailed examination but, if they are real, they indicate that there is some small effect of the promoters on the activity of the Cu active sites.

It is clear from the data presented here that the promoters added to the co-precipitated Cu–zirconia catalysts have a significant effect on their behaviour and that the greatest effect seems to be in stabilising a higher surface area. It therefore appears that the promoters are in close proximity with the active sites, perhaps as shown schematically in Fig. 8A and B. In (A), the promoter sits only on the surface of the support and prevents sintering; in (B), the promoter also decorates the copper surface and therefore is likely also to affect the nature of the active site. As indicated above, further detailed kinetic work would be necessary to probe the differences.

It is clear from the data presented here that the promoters added to the co-precipitated Cu–zirconia catalysts have a significant effect on their behaviour and that the greatest effect seems to be in stabilising a higher surface area. It therefore appears that the promoters are in close proximity with the active sites, perhaps as shown schematically in Fig. 8A and B. In (A), the promoter sits only on the surface of the support and prevents sintering; in (B), the promoter also decorates the copper surface and therefore is likely also to affect the nature of the active site. As indicated above, further detailed kinetic work would be necessary to probe the differences.

4. Conclusions

A catalyst containing Cu, Y and Zr in the molar ratio 30:20:50 was found to be very active for the steam reforming of methanol over a range of temperatures up to 573 K and was found to be very stable under the reaction conditions used.

References

[1] F. Domka, M. Laniecki, React. Kinet. Catal. Lett. 8 (1978) 507.
[2] K. Takahashi, H. Kobayashi, N. Takezawa, Chem. Lett. (1985) 759.
[3] K. Mizumo, K. Yoshikawa, N. Wakejima, Y. Takeuchi, A. Watanabe, Chem. Lett. (1986) 1969.
[4] N. Iwasa, S. Kudo, H. Takahashi, S. Masuda, N. Takezawa, Catal. Lett. 19 (1993) 211.
[5] N. Iwasa, S. Masuda, N. Takezawa, React. Kinet. Catal. Lett. 55 (1995) 349.
[6] Y. Chin, R. Dagle, J. Hu, A.C. Dohnalkova, Y. Wang, Catal. Today 77 (1–2) (2002) 79.
[7] J.C. Amphlett, R.F. Mann, R.D. Weir, Can. J. Chem. Eng. 59 (1981) 720.
[8] J.P. Breen, J.R.H. Ross, Catal. Today 51 (1999) 521.
[9] M.J. Luys, P.H. van Oeffelt, W.G.J. Brouwer, A.J. Pijpers, J.J.F. Scholten, Appl. Catal. 46 (1989) 161.