Supplementary Material (ESI) for Catalysis Science & Technology

SUPPORTING INFORMATION

Investigations into the conversion of ethanol into 1,3-butadiene

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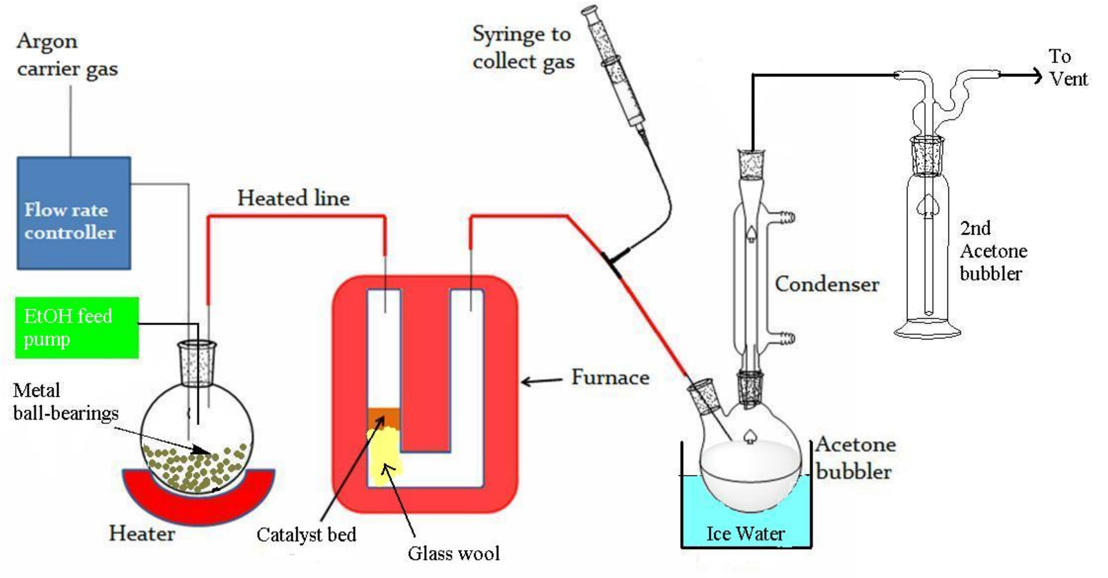
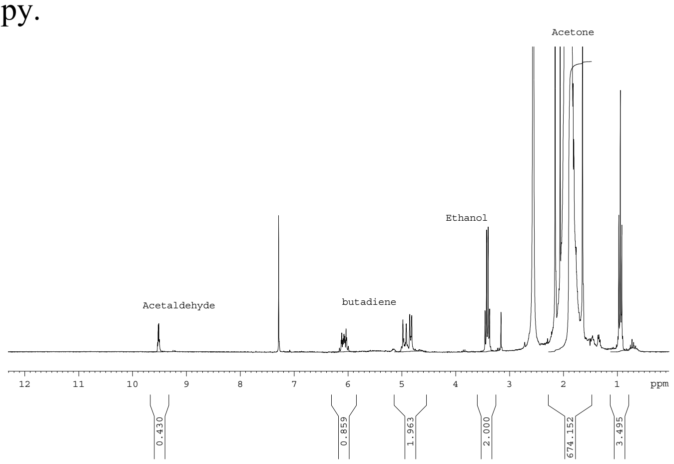
A schematic representation of the rig used is shown below:



Catalyst Test Procedure

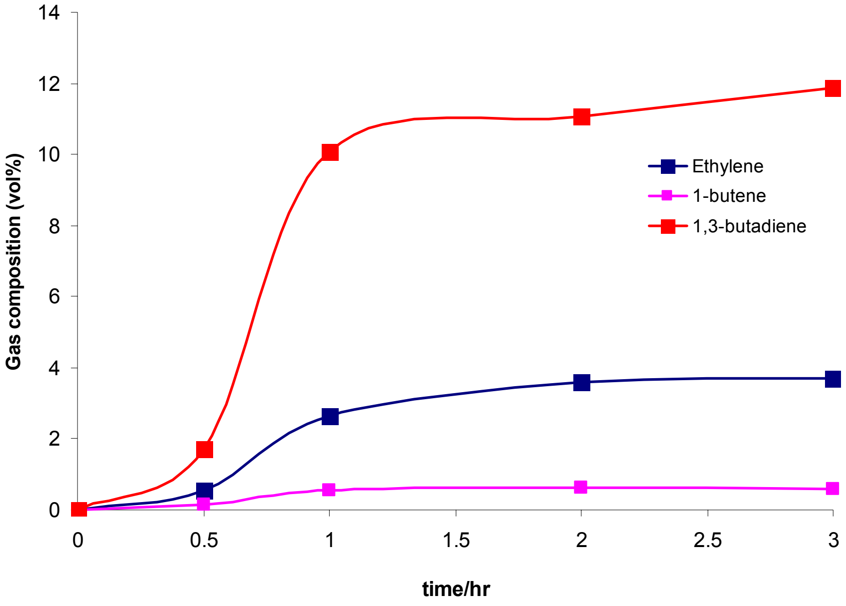
- ✓ Standard procedure is followed for all runs to aid reproducibility and integrity of results. The most promising catalysts were repeated and conversion/selectivities were within 2 %.
- ▪ 1 g of catalyst (Volume measured to calculate LHSV) add to quartz U-tube. The EtOH feed flask is weighed.
- ▪ All heating elements are turned on, and Ar is passed (at a rate of 25 ml/min) over the catalyst to purge the tube, and the apparatus is left in this state until the furnace has reached the desired temperature (~ 15 mins)
- ▪ The cooling system to the condenser is then turned on, and Bubbler 1 immersed in ice.
- ▪ The HPLC pump is switched on, and EtOH added to the feed flask at a rate of 0.1 ml/min. This is time t = 0
- ▪ The apparatus is monitored for the entire run in case of abnormalities.
- ▪ At the end of the run, a sample of the exhaust gas is taken for analysis by Gas Chromatography
- ▪ At the desired end point, all heating elements are turned off and the argon and cooling system remain on and the HPLC pump switched off. It is left in this state for 5 mins.
- ▪ The valves are then adjusted to bypass the reactor, and this is left for 10 minutes, to purge any remaining EtOH
- ▪ All apparatus is switched off, and the trace heating unplugged.
- ▪ The mass of liquid in Bubbler 1 and 2 is determined, and a sample taken for NMR analysis. From the NMR analysis it is possible to determine the mass of EtOH that has come over and the mass of dissolved butadiene, acetaldehyde and diethyl ether to corroborate the GC analysis.
- ▪ The final mass of the EtOH feed flask is determined to account for any EtOH that has not passed over the catalyst

The exhaust gases can be analysed *via* GC with helium at the flow gas. Gas samples were analysed on a Hewlett Packard 5890 GC with a CP-LowOx column (10 m by 0.53 mm) and analysed *via* FID. The GC has been calibrated using a certified BOC 5 blend gas mixture (ethene 1.0 vol%, diethylether 0.25 vol%, 1,3-BD 1.0 vol%, 1-butene 0.5 vol%, acetaldehyde 0.25 vol%). The GC is then calibrated for these gases, which were the main products formed in our process. We observed no evidence for butanols, crotonaldehyde, ethylacetate or acetaldol products. Presumably, crotonaldehyde and acetoldol are formed in-situ but are too short lived to be detected. The retention times were corroborated with authenticated pure samples. For the NMR spectroscopic analysis it is possible to determine the amount of EtOH and dissolved condensables (which is used to corroborate the GC analysis). An example of a typical NMR is shown below. The selectivities for Et_2O/acetaldehyde were determined *via* NMR spectroscopy.

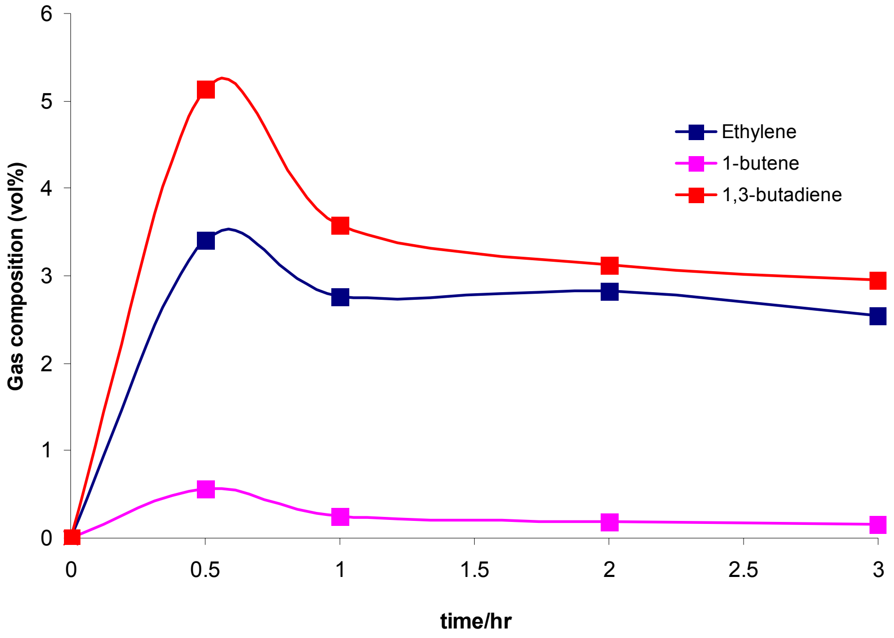


Further selectivity vs time graphs: - all are at an LHSV of 1.5 unless stated.

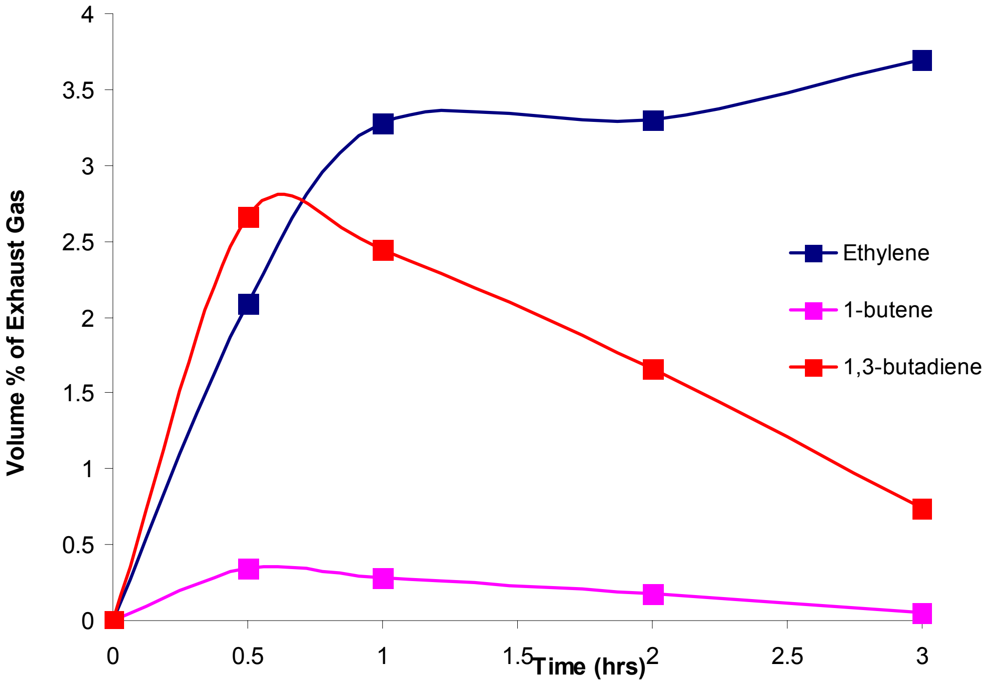
Gas composition over time for 3 hour test of **CuZnZrSi-150**



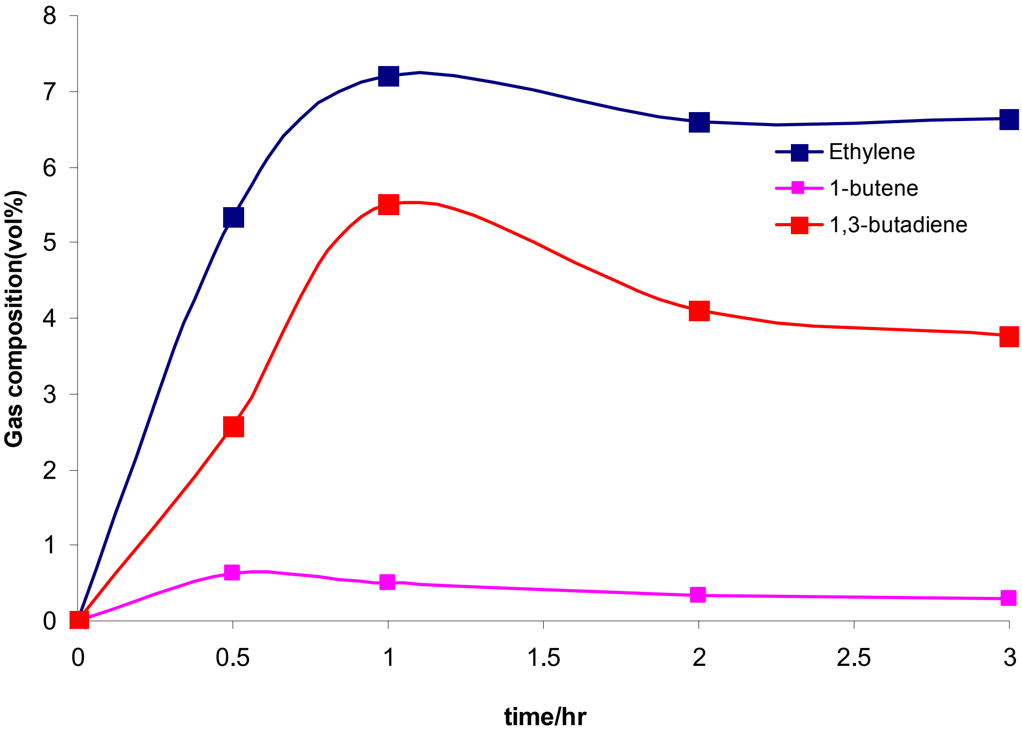
Gas composition over time for 3 hour test of **CuZnZrSi-60**



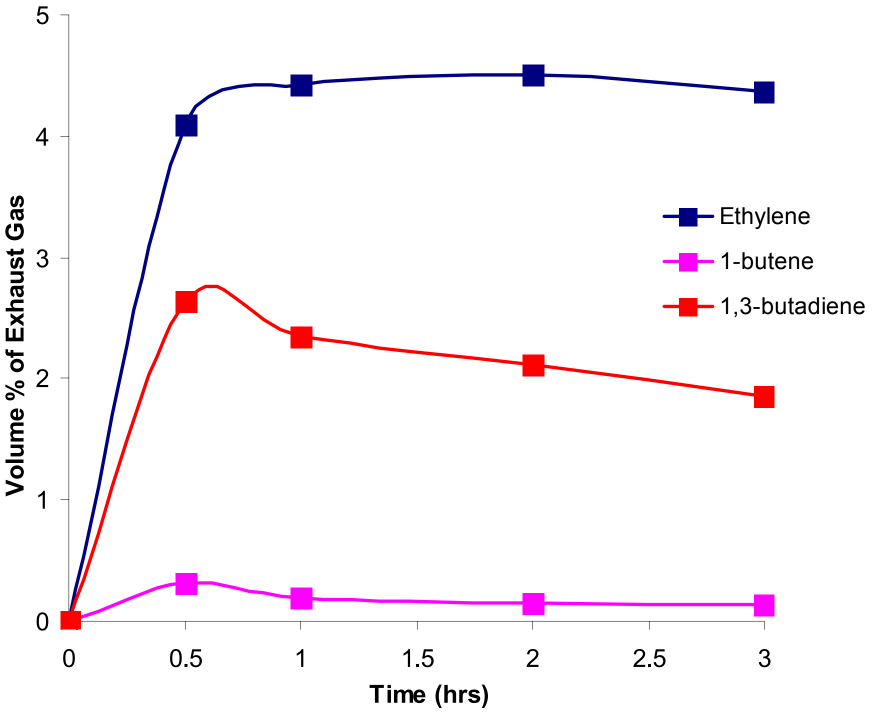
Gas composition over time for 3 hour test of **CuZrSi-60**.



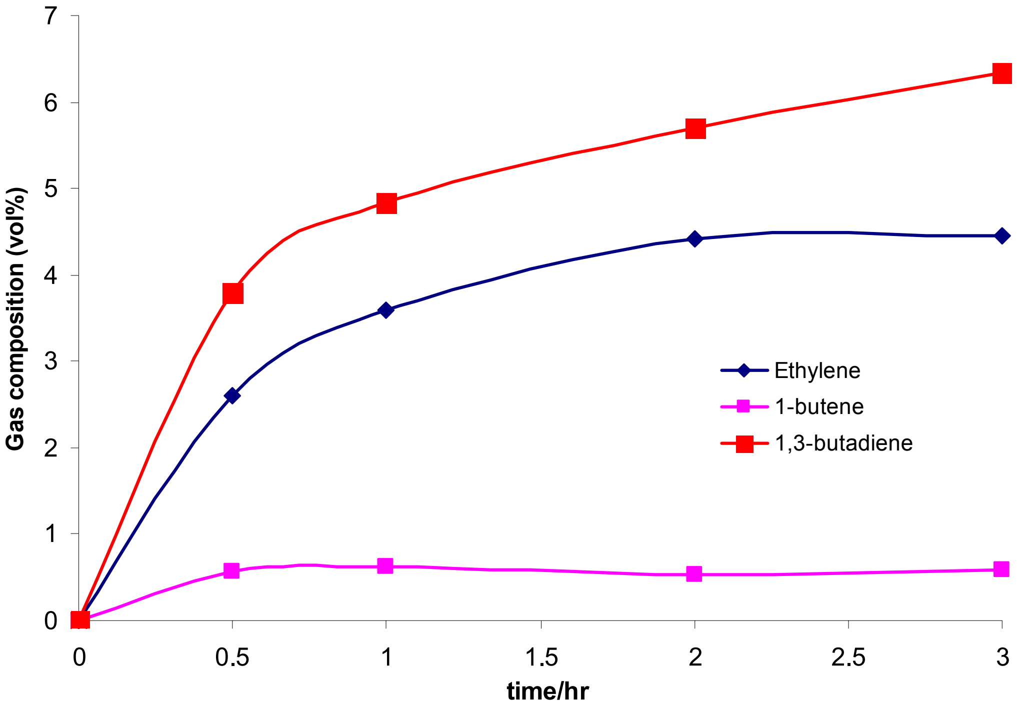
Gas composition over time for the 3 hour test of **ZnZrSi-60**



Gas composition over time for the 3 hour test of **ZnZrSi-60 + $Ba(OH)_2$**



Gas composition over time for 3 hour test of **CuZnZrSi-150 (LHSV 0.75)**

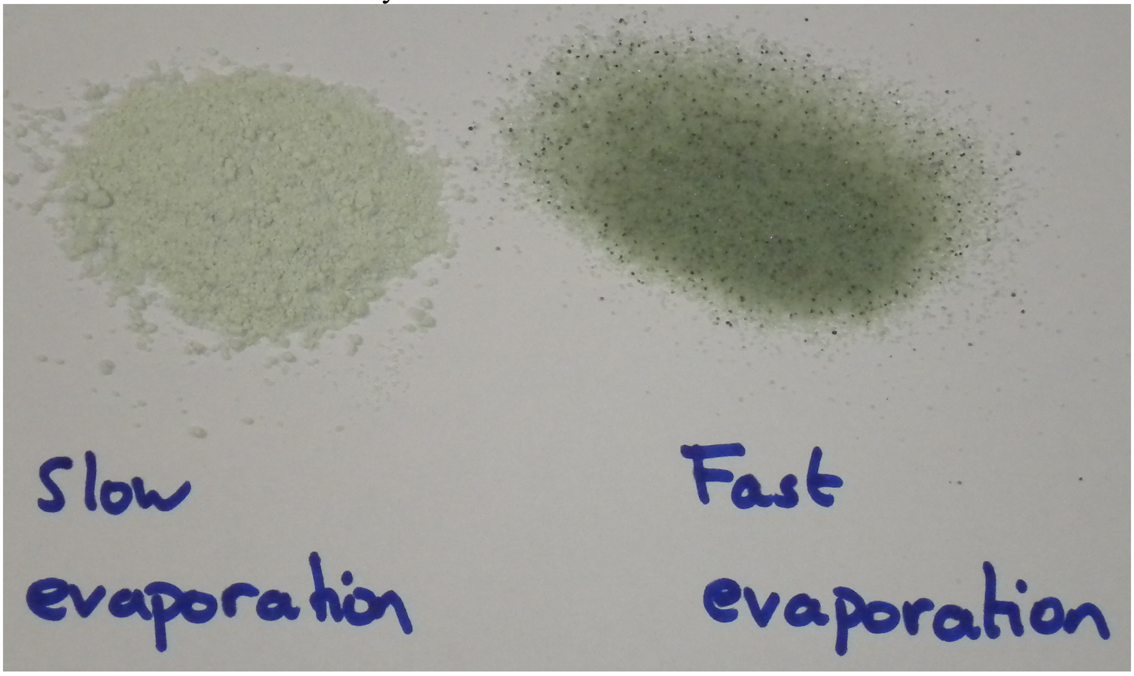


Typical Catalyst Preparation Procedure:

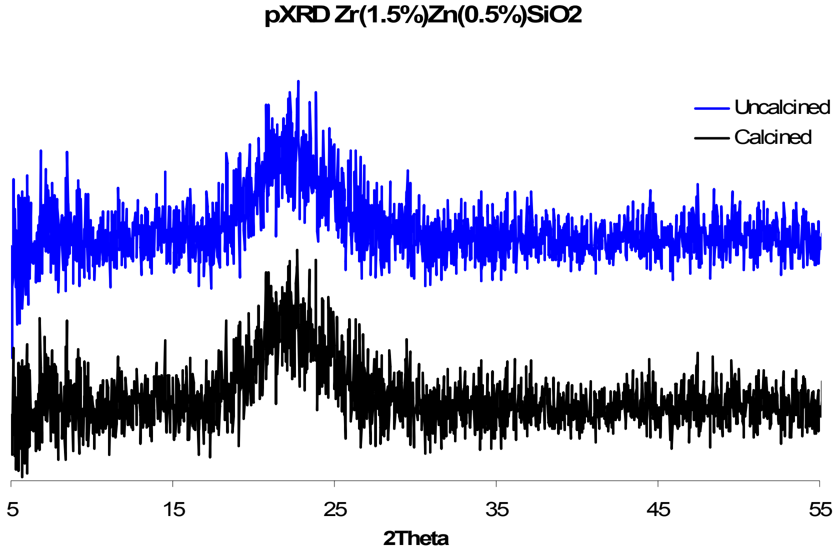
The appropriate amount of each metal salt (salts used were $Cu(OAc_2)_2.H_2O$ $Co(NO_3)_3.6H_2O$, $Mn(OAc)_2.4H_2O$, $Zn(NO_3)_2.6H_2O$, $Ce(NO_3)_3.6H_2O$ $ZrO(NO_3).6H_2O$, HfO_2 – target 1 wt% of each metal in the final catalyst) was dissolved in water (200 ml) and silica (10 g) was added, this was stirred in a beaker until all the water had evaporated, typically 72 hrs.

For example, for the Zn/Cu catalyst: $Cu(OAc)_2.H_2O$ (0.31 g) and $Zn(NO_3)_2.6H_2O$ (0.41 g) were dissolved in water (200 ml) and silica added (10 g). Mn/Zn $Mn(OAc)_2.4H_2O$ (0.45 g) and $Zn(NO_3)_2.6H_2O$ (0.41 g) were dissolved in water (200 ml) and silica added (10 g). Zn/Zr $ZrO(NO_3)_2.6H_2O$ (0.55 g) and $Zn(NO_3)_2.6H_2O$ (0.20 g) were dissolved in water (200 ml) and silica added (10 g). Co/Zn $Co(NO_3)_2.6H_2O$ (0.49 g) and $Zn(NO_3)_2.6H_2O$ (0.41 g) were dissolved in water (200 ml) and silica added (10 g). Cu/ZrZn $ZrO(NO_3)_2.6H_2O$ (0.375 g), $Cu(OAc)_2.H_2O$ (0.31 g) and $Zn(NO_3)_2.6H_2O$ (0.20 g) were dissolved in water (200 ml) and silica added (10 g), Cu/Zn $Cu(OAc)_2.H_2O$ (0.31 g) and $Zn(NO_3)_2.6H_2O$ (0.41 g) were dissolved in water (200 ml) and silica added (10 g). Co/Mn $Co(NO_3)_2.6H_2O$ (0.49 g) and $Mn(CH_3CO_2)_2.6H_2O$ (0.45 g) were dissolved in water (200 ml) and silica added (10 g). Cu/Co $Cu(OAc)_2.H_2O$ (0.31 g) and $Co(NO_3)_2.6H_2O$ (0.49 g) were dissolved in water (200 ml) and silica added (10 g). The powder was then dried in an oven at 80 °C for three hours before being calcined. The materials were calcined by heating at 5 °C per minute until at 300 or 500 °C at which point the sample was held at this temperature for a further 5 hours before being cooled to room temperature.

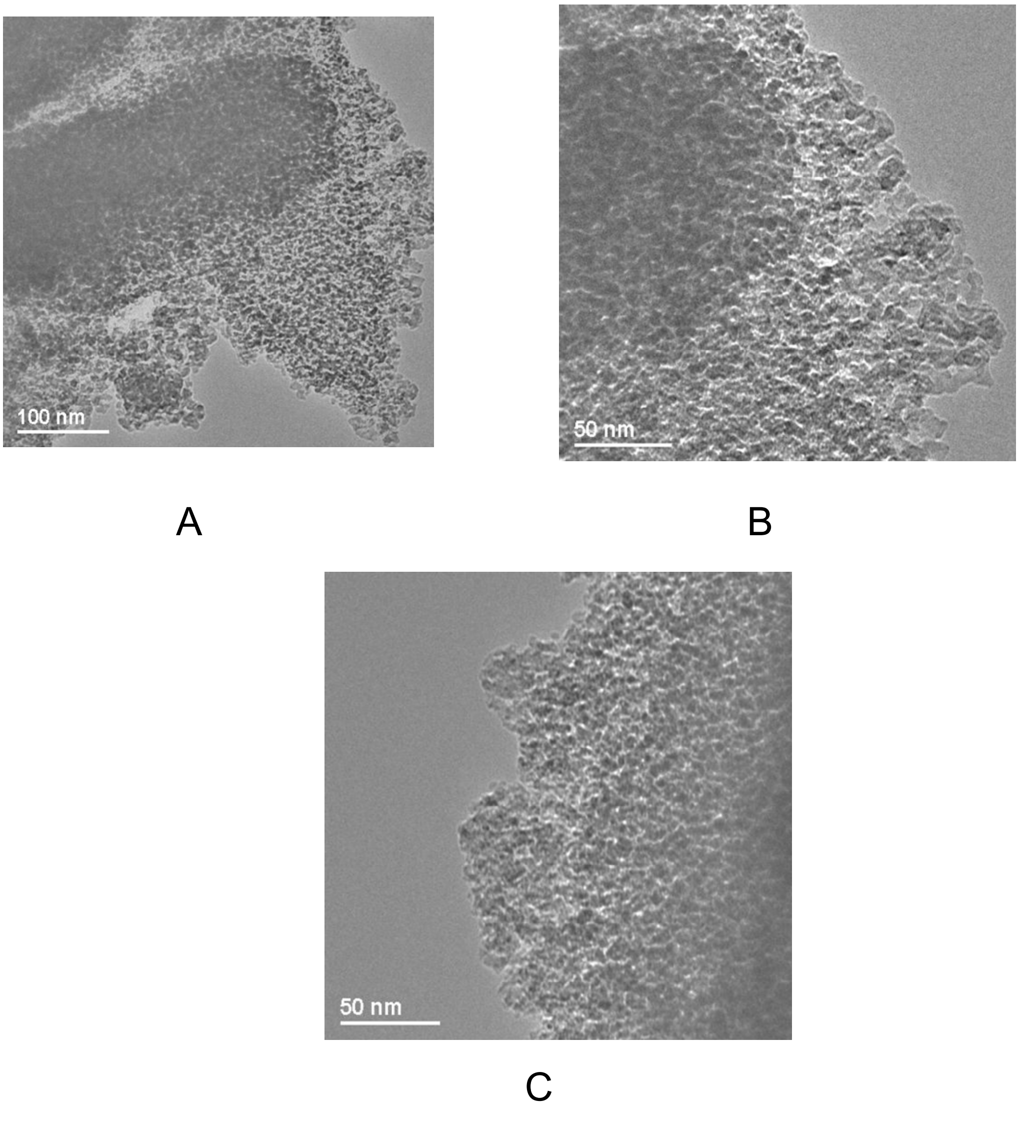
It was observed that if the catalysts were prepared by fast evaporation of the water (rotary evaporation) then a very "speckled" catalyst was observed, which was not observed with the slow method and thus this was preferred. The following pictures are for the calcined CuZrZn catalyst on 60 Å silica:



pXRD of ZrZn on 60 Å catalysts before and after calcination indicating no appreciable ordering in the oxide phase.



TEM images: **A** + **B** CuZrZn on 60 Å SiO_2 calcined at 500 °C **C** ZrZn on 60 Å SiO_2 calcined at 500 °C. Recorded on a Jeol JEM 2001 HRTEM by Dr Zhou using the EPSRC national service.



Equations Used to calculate Conversion/Selectivity/Carbon balance and LHSV:

Carbon balance was determined using the following:

$$Balance = \frac{Total\ \ carbon\ accounted\ in\ products\ and\ unreacted\ EtOH}{Total\ amount\ of\ carbon\ added} \times 100\%$$

The conversion was determined from the following:

$$Conversion = \frac{Mass\ of\ \ EtOH\ \ Added\ \ - Mass\ EtOH\ re\mathrm{cov}ered}{Mass\ EtOH\ \ Added} \times 100\%$$

Selectivities were determined from the following:

$$Selectivity = \frac{Moles\ of\ \ product}{Total\ moles\ of\ \ all\ \ products} \times 100\%$$

Liquid Hour Space Velocity (LHSV) is defined as follows, time in hours and volume both in cm^3.

$$LHSV = \frac{Volume\ of\ \ liquid\ ethanol\ \ passed\ over\ catalyst}{Volume\ of\ \ the\ catalyst \times time}$$

XPS analysis:

These experiments were performed at the EPSRC's facilities in Cardiff or Daresbury respectively.

High-resolution X-ray photoemission spectra (XPS) were measured in a Scienta ESCA 300 spectrometer. This incorporates a rotating anode Al Kα (hν = 1486.6 eV) X-ray source, a 7 crystal X-ray monochromator and a 300 mm mean radius spherical sector electron energy analyser with parallel electron detection system. The X-ray source was run with 100 mA emission current and 14 kV anode bias, whilst the analyser operated at 150 eV pass energy with 0.8 mm slits. Gaussian convolution of the analyser resolution with a linewidth of 260 meV for the X-ray source gives an effective instrument resolution of 350 meV. Sample charging was problematic and it was necessary to stabilise the surface charge with an electron flood gun delivering 3-4 eV electrons. Binding energies were referenced to the residual C 1s peak. Samples were mounted on steel stubs.

	State	**Binding Energy**			**Composition (atom %)**			
		Zr 3p	Zn 2p½	Cu 2p	Zr	Zn	Cu	C
ZrZn	Uncalcined 60Å	333.7	1045.1	-	0.44	0.22	-	6.30
ZrZn	Calcined 500 °C 60Å	334.0	1044.4	-	0.37	0.09	-	3.01
ZrZn	Spent 60Å	333.7	1042.1	-	0.33	0.05	-	33.20
ZrZn	Calcined 500 °C 150Å	334.2	1045.3	-	0.14	0.07	-	2.71
ZrZn	Spent 150Å	334.2	1046.0	-	0.12	0.07	-	10.43
ZrZn	Calcined 500 °C 40Å	334.4	1046.2	-	0.32	0.10	-	0.98
ZrCu	Uncalcined 60Å	333.7	-	933.1	0.37	-	0.54	6.06
ZrCu	Calcined 500 °C 60Å	333.7	-	933.3	0.35	-	0.51	5.09
ZrCu	Spent	333.9	-	932.8	0.31	-	0.25	21.00
CuZrZn	Calcined 500 °C 60Å	333.8	1045.2	933.0	0.38	0.39	0.39	5.33
CuZrZn	Spent 60Å	333.7	1045.9	932.2	0.14	0.23	0.23	35.68
CuZrZn	Calcined 500 °C 150Å	333.9	1044.7	933.6	0.18	0.22	0.12	4.44
CuZrZn	Spent 150Å	334.5	1045.8	933.3	0.12	0.21	0.07	13.36

BET analysis

BET measurements were carried out on a BELSORP Mini-II gas adsorption instrument. Samples were pretreated at 300°C for 420 minutes under vacuum prior to N_2 adsorption. The data was analysed over a P/Po range 0.05 – 0.3.

Pore size/Å	**State**	**BET area/m^2g^{-1}**	**Pore size/nm**	**C**
40	ZrZn fresh	492.3	4.4	46.7
60	ZrZn fresh	500.7	6.9	87.1
150	ZrZn fresh	269.3	14.0	162
60	CuZrZn fresh	457.4	7.7	60.2
150	CuZrZn fresh	250.0	15.2	174
40	ZrZn cal @500 °C	484.7	4.9	90.0
60	ZrZn cal @500 °C	475.2	7.0	130
60	CuZrZn cal @500 °C	450.3	7.5	129
150	CuZrZn cal @500 °C	246.2	15.5	177
150	ZrZn cal @500 °C	272.3	18.8	161
150	CuZrZn cal @300 °C	261.5	15.0	167
60	CuZrZn Spent – last entry table 3	476.9	7.4	139
150	CuZrZn spent – penultimate entry table 3	289.8	14.9	186

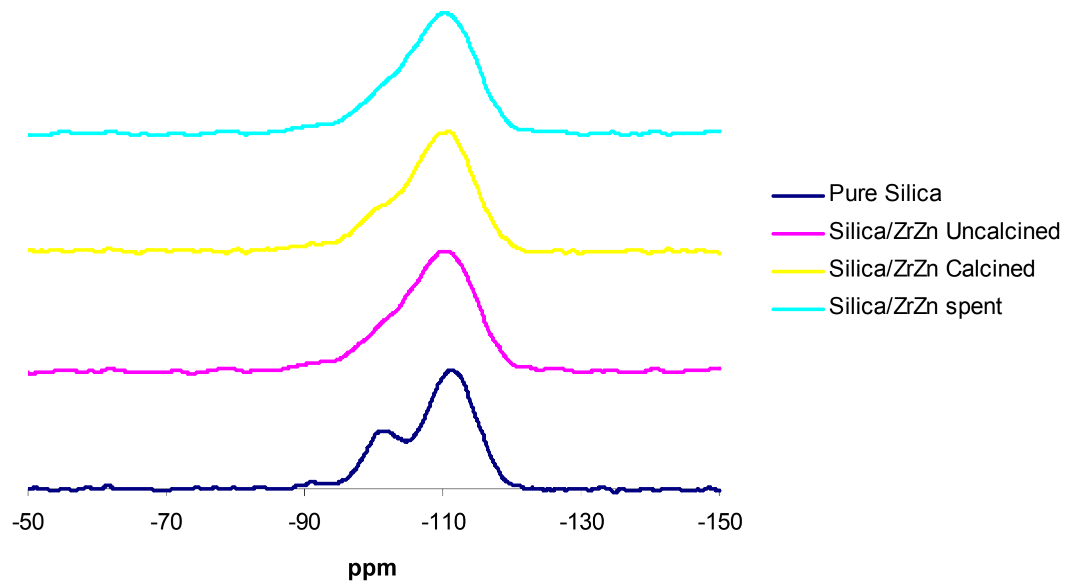
Solid-state NMR spectroscopic analysis

All spectra were recorded at the EPSRC National Solid-state NMR service centre, Durham. ^{29}Si MAS NMR spectra were recorded on a Varian VNMRS 400 MHz spectrometer and referenced to TMS, a pulse delay of 60 s was used. The spectra were deconvoluted to determine the relative proportion of each silicon environment. The materials were all calcined at 500 °C

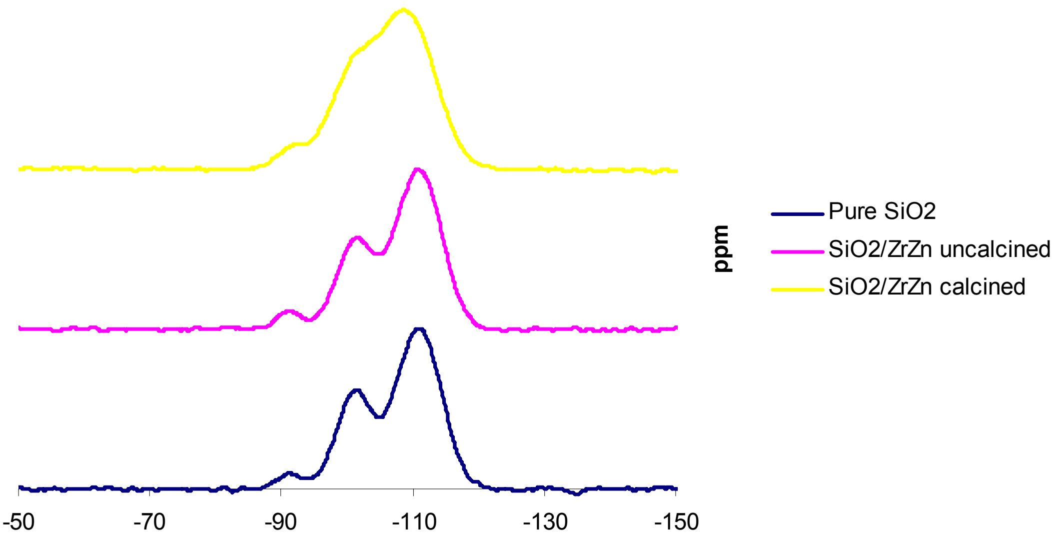
Sample	State	Proportion of sites		
		Q^2	Q^3	Q^4
60 SiO_2	Pure silica	3.8	30.7	65.5
150 SiO_2	Pure silica	2.1	25.8	72.1
40 SiO_2 ZrZn	Uncalcined catalyst	2.5	27.8	69.8
60 SiO_2 ZrZn	Uncalcined catalyst	4.0	30.2	65.8
150 SiO_2 ZrZn	Uncalcined catalyst	2.2	21.8	75.9
40 SiO_2 ZrZn	Calcined	4.9	31.4	63.6
60 SiO_2 ZrZn	Calcined	3.4	26.7	69.9
150 SiO_2 ZrZn	Calcined	2.6	21.7	75.7
150 SiO_2 ZrZn	Spent	2.5	25.7	71.8

Below are the spectra for the silica samples. The data in table was determined from lineshape analysis of the deconvoluted spectra.

150 Å



60 Å


ppm
Pure SiO2
SiO2/ZrZn uncalcined
SiO2/ZrZn calcined
-50
-70
-90
-110
-130
-150

TPD analysis was performed on the pure silica and the trimetallic system:

To a known mass of sample (typically 0.25g) at room temperature, in a vial, the probe molecule (pyridine) was added (typically 3 drops). The vial was placed in an oven at 60 °C until required with the lid securely closed.
A section of stainless steel tubing (¼ inch diameter, 8 cm long) connected to a stainless steel filter was loaded with the sample via use of a large metal fitting serving as a funnel. Once the funnel was removed, the tubing was connected to the GC inlet and the FID (filter in line to protect from particulates) *via* a short length of wide bore capillary column (0.53 mm). After establishing gas flow from the inlet, the installation was checked for leaks with soap solution and any leaks were tightened up with a spanner.

The temperature ramp program for all testing was:

Oven Ramp		
Temp	Rate °C/min	hold time (mins)
40	0	2
120	10	30
300	10	10
50	20	0.5

Results:

	Pyridine	
Catalyst	No OHs	Temp. Max
SiO_2 60 Å	1.55×10^{20}	198
SiO_2 60 Å ZrZn	1.56×10^{20}	200
SiO_2 150 Å	1.45×10^{19}	174
SiO_2 60 Å CuZrZn	8.73×10^{19}	187
SiO_2 150 Å CuZrZn	3.03×10^{19}	198