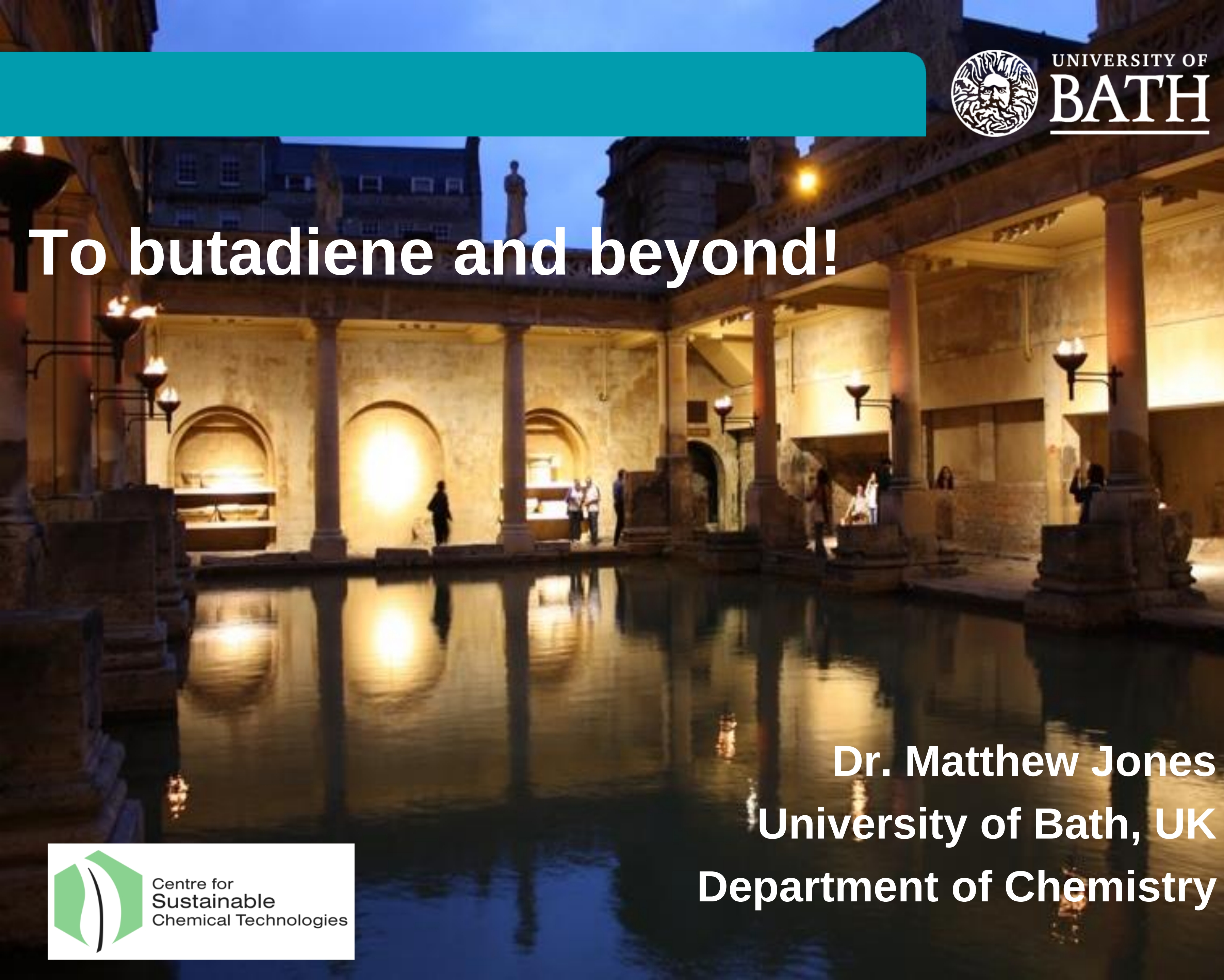

To butadiene and beyond!

Dr. Matthew Jones
University of Bath, UK
Department of Chemistry

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Projects on the go!

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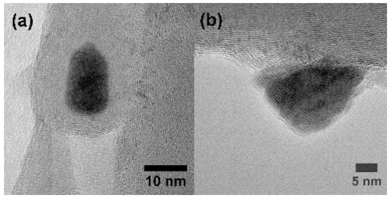
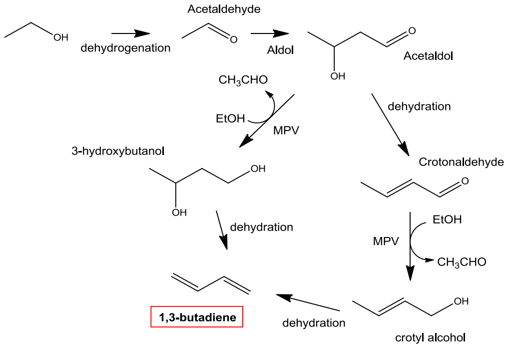
CO_2 conversion



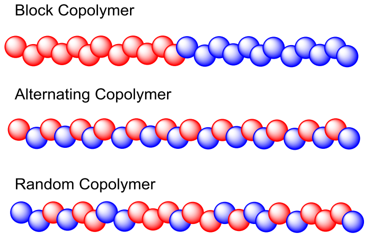
ChemPhysChem 2017, 3211. *ChemSusChem,* 2015, 4064. *Cat. Sci. Technol*., 2014, 3351 *Cat. Sci. Technol*., 2013, 1202.

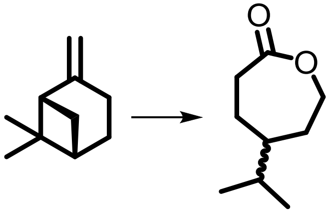
Biorenewables upgrading



ChemSusChem, 2018, 1073. *ChemCatChem* 2016, 2376. *Catal. Today,* 2016, 1232. *Catal*. *Commun,* 2014, 25. WO Patent granted WO/2014/180778 .

Copolymers and new monomers





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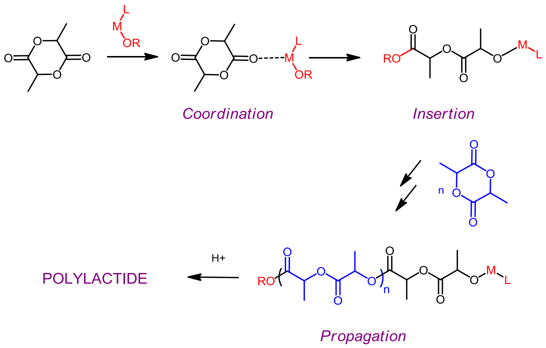
Dalton Trans., 2016, 13846
Poly. Chem., 2017, 833.

Sustainable Polymerisations



Organometallics 2018, 1719. *ChemSusChem,* 2017, 3547. *Dalton Trans*., 2017, 5048. *Chem. Commun.* 2016, 10431.*Organometallics* 2016, 3837. *Chem. Sci.,* 2015, 5034.

Projects on the go!

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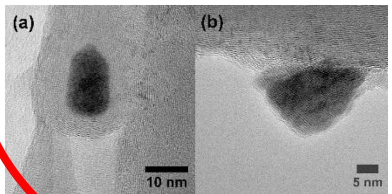
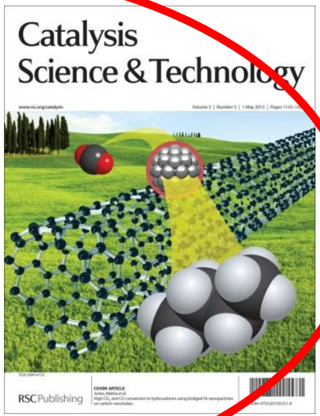
CO_2 conversion





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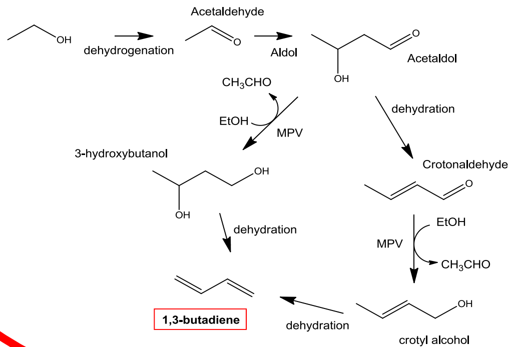
Biorenewables upgrading



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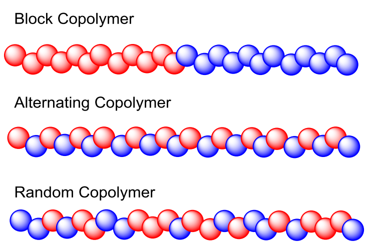

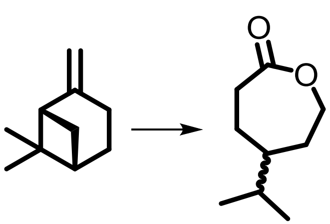

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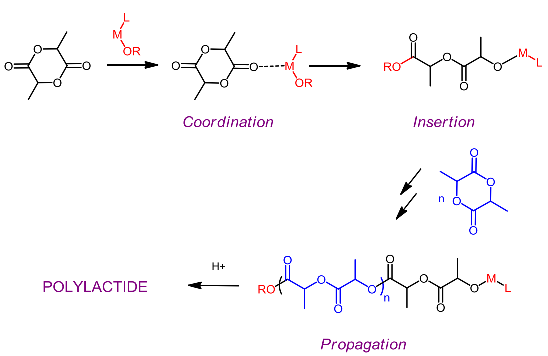
Sustainable Polymerisations



Organometallics 2018, 1719. *ChemSusChem*, 2017, 3547. *Dalton Trans*., 2017, 5048. *Chem. Commun.* 2016, 10431.*Organometallics* 2016, 3837. *Chem. Sci.*, 2015, 5034.

Key stage 3 Science lesson

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How do we make ethanol?

- Biomass?

- How much sugar is in this jar of smarties?

- How much ethanol can we get?

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How do we make ethanol?

- Fermentation of sugar

Is this bad?

$$C_6H_{12}O_6 \xrightarrow{\text{Enzyme}} 2C_2H_5OH + 2CO_2$$

- How much sugar is in this jar of smarties?

- How much ethanol can we get?

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How do we make ethanol?

- Fermentation of sugar

$$C_6H_{12}O_6 \xrightarrow{\text{Enzyme}} 2C_2H_5OH + 2CO_2$$

- How much sugar is in this jar of smarties?
  - 1832 smarties = 430 g of sugar

- How much ethanol can we get?

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How do we make ethanol?

- Fermentation of sugar

$$C_6H_{12}O_6 \xrightarrow{\text{Enzyme}} 2C_2H_5OH + 2CO_2$$

- How much sugar is in this jar of smarties?
  - 1832 smarties = 430 g of sugar

Is this a good assumption?

- How much ethanol can we get?

215 g EtOH (assuming 100% conversion)

130 g ethene (polyethene) ca. 20 plastic bags

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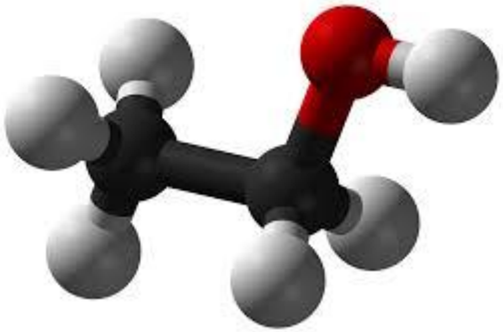
Should we use smarties to make ethanol??



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Ethanol as a platform chemical

- How much ethanol is produced in Brazil annually?

- What can we use ethanol for?

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Ethanol as a platform chemical

- How much ethanol is produced in Brazil annually?

  23.4 billion litres in 2014

  If a car travels 10,000 km/yr it needs ca. 1,000 litres

  234,000,000,000 km ca. 5.8 million times round the world

- What can we use ethanol for?

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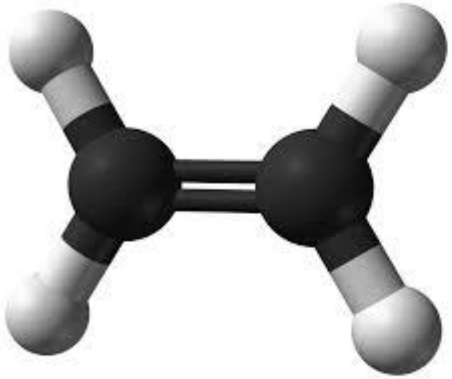

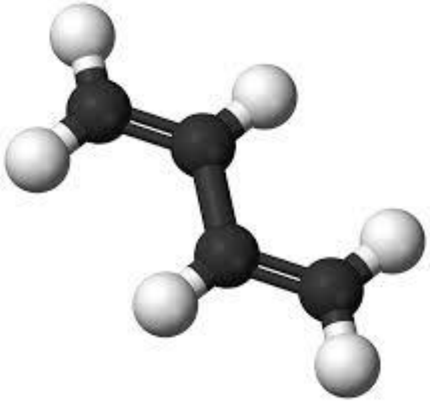

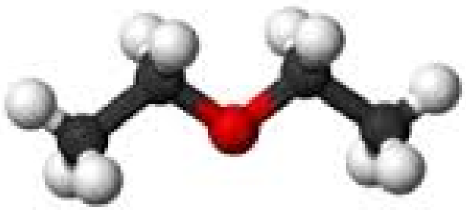

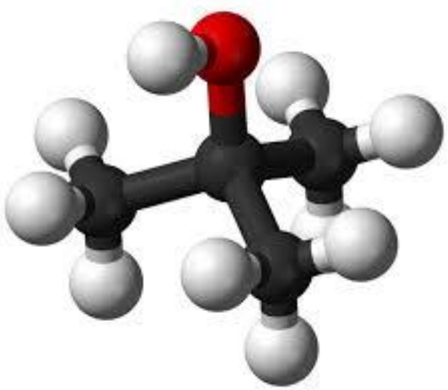

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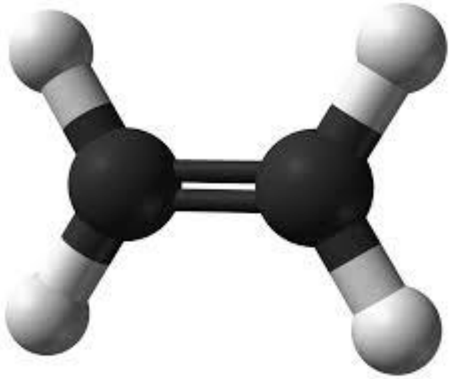

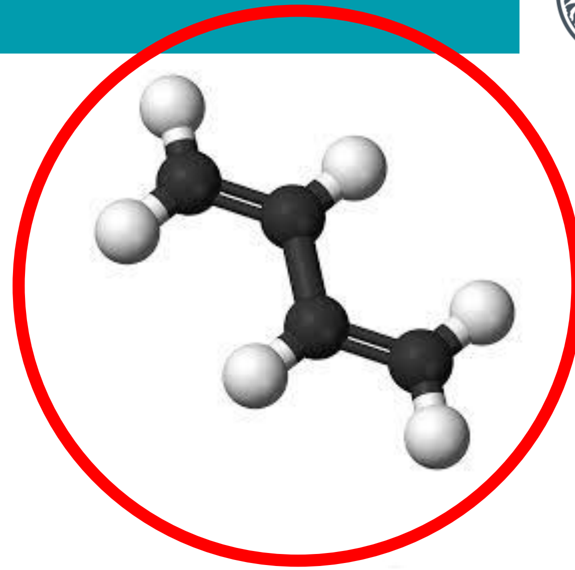

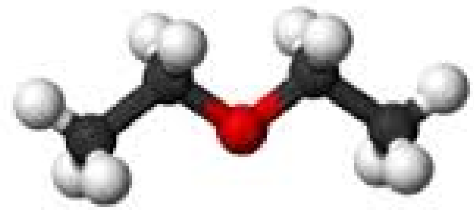

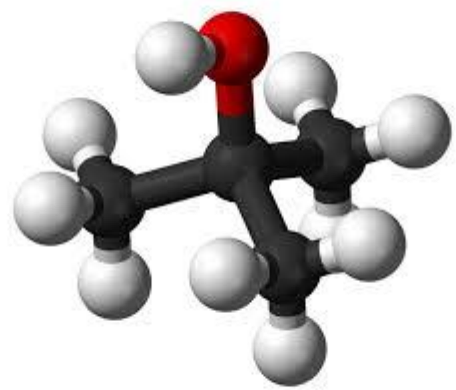

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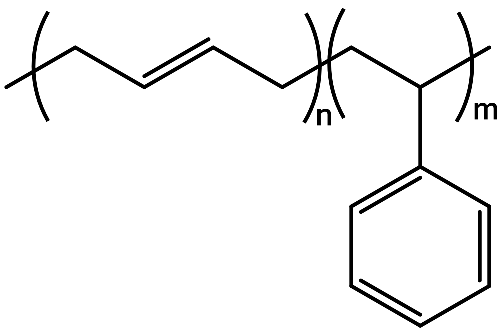
How is butadiene made?

95% is produced as the by-product of ethene production from steam crackers (breaking down of large hydrocarbons into smaller ones)

Uses of butadiene?



SBR – used an alternative to natural rubber

What is shale gas?

Methane ca. 76%, Ethane ca. 16%, Propane 6% (rest butanes)

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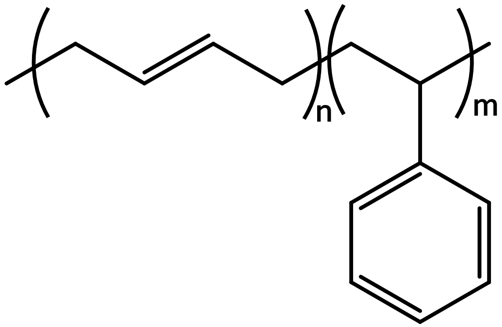

SBR – used an alternative to natural rubber

What is shale gas?

Methane ca. 76%, Ethane ca. 16%, Propane 6% (rest butanes)

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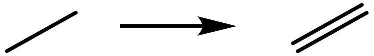
How is ethene made?

1. Steam cracking of higher hydrocarbons

2. 

Ethane Ethene

What are the consequences of a new *cheap* supply of ethane?

What is shale gas?

Methane ca. 75%, Ethane ca. 16%, Propane 6% (rest butanes)

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Initial experiments

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Mn/Zn doped sepiolite systems (*J. Chem. Soc., Chem. Commun.*, 1981, 401-402)

$MgO/Na_2O/SiO_2$ (*Applied Catalysis*, 1988, **43**, 117-131)

Hydroxyapatite (*J. Catal.*, 2008, **259**, 183-189; butanol)

Tantalum oxide on silica (*J. Am. Chem. Soc.*, 1947, **69**, 593-599)

Various metal oxides on silica (*Industrial and Engineering Chemistry Process Design and Development*, 1963, **2**, 45-51)

$MgO/Na_2O/SiO_2$ (*J. Chem. Soc., Chem. Commun.*, 1985, 1613-1614)

One pass system binary, ternary oxides– fluidised bed (Bhattacharyya *I&EC Process design and Dev*., 1963, 45.)

1920s-30s Lebedev's single pass system

vs

Problem reproducing results……..

Experimental sections very vague (if present!)

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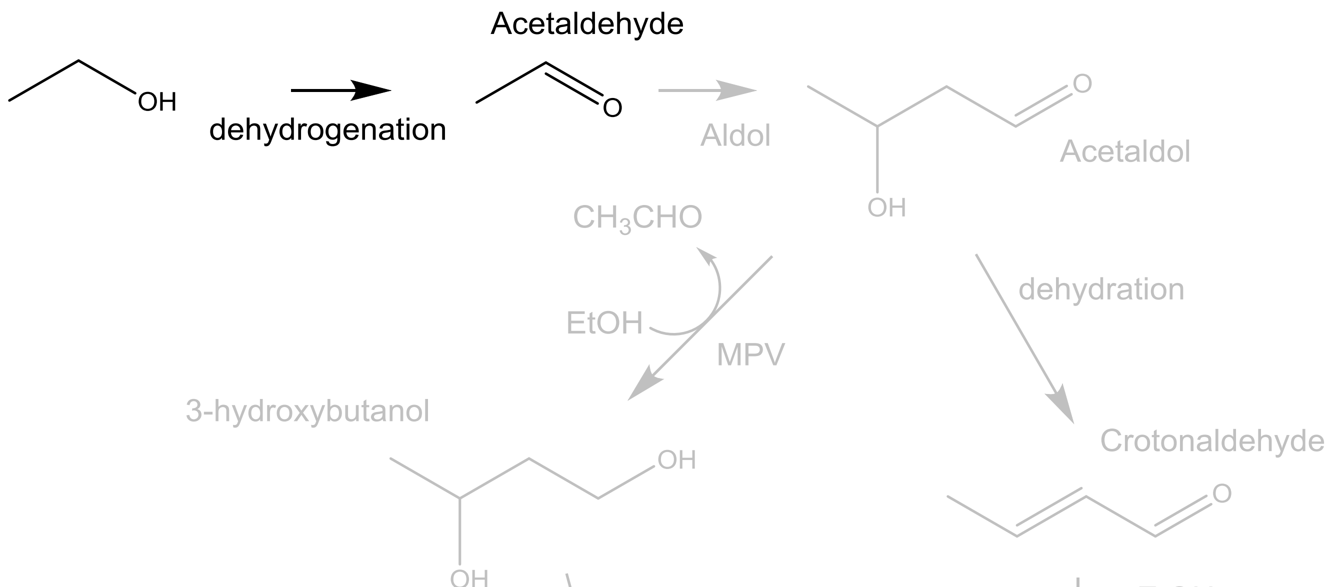
1,3-Butadiene Mechanism



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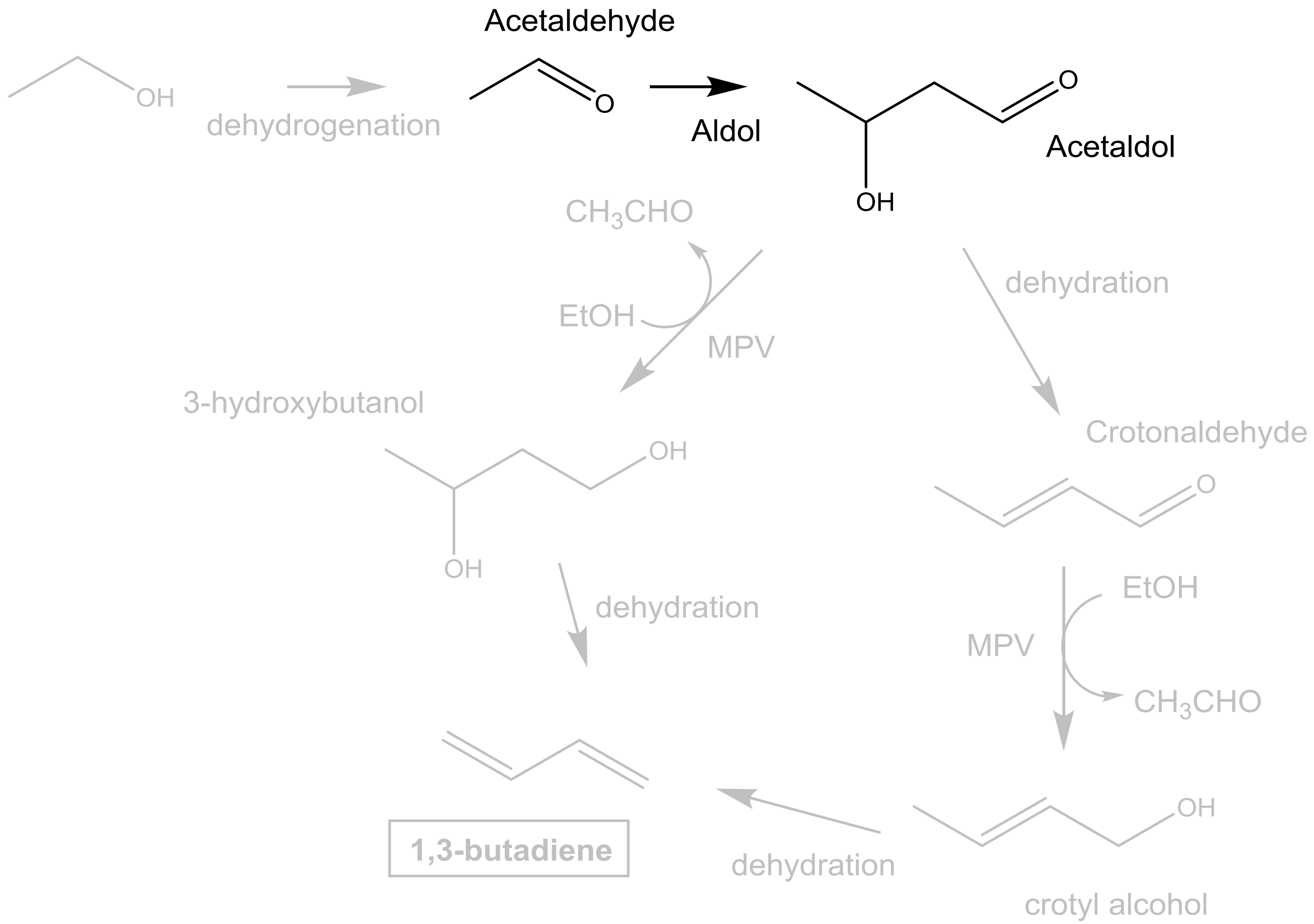

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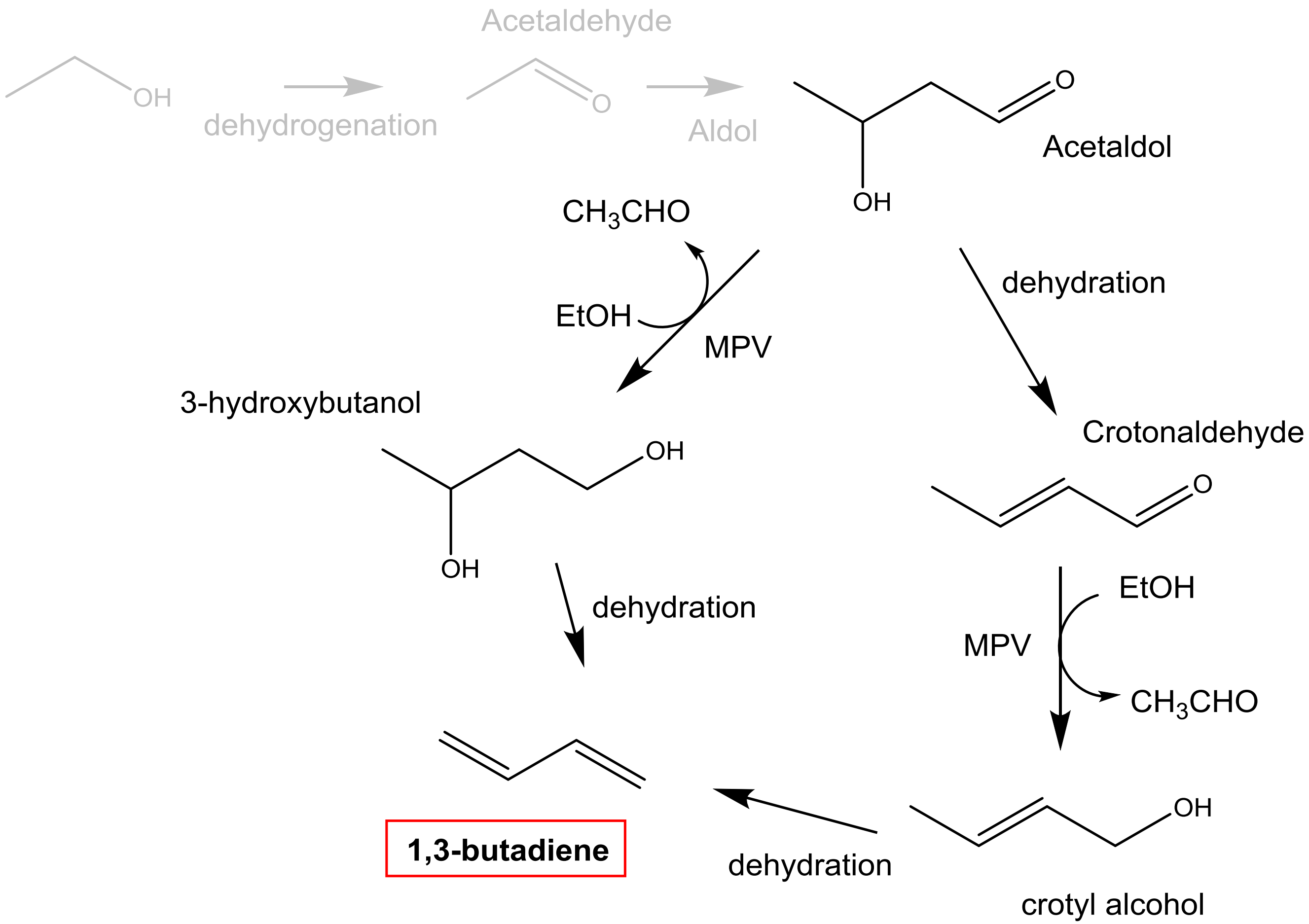
1,3-Butadiene Mechanism



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Back to basics

Catalyst Description	Conversion / %	Selectivity Measurements / %				
		1,3-BD	Ethylene	Acetaldehyde	Ether	1-butene
Co:Zn	17.0	6.5	29.8	47.4	16.1	0.4
Cu:Zn	29.0	20.9	42.1	30.1	4.6	2.2
Co:Zr	20.0	3.9	66.9	5.9	14.1	9.4
Cu:Co	17.0	10.8	39.3	37.6	10.9	1.4
Co:Mn	13.0	23.0	47.0	19.2	9.6	1.3
Ce:Zr	24.0	26.6	40.0	27.8	3.5	2.1
Hf:Zn	15.0	4.9	26.9	57.0	11.0	0.2
Mn:Zr	10.5	28.8	46.4	9.3	15.5	0
Cu:Mn	18.0	10.1	10.6	61.7	15.4	2.1
Mn:Zn	17.0	19.0	28.0	35.5	16.5	1.0
Zr:Zn	46.0	38.9	41.1	10.3	6.7	3.0

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T = 375 ^{o}C, LHSV = 1 h^{-1}

Cat. Sci. Technol. 2011, 267

Back to basics

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Cu:Co	**17.0**	**10.8**	39.3	**37.6**	10.9	1.4
Co:Mn	**13.0**	23.0	**47.0**	19.2	9.6	1.3
Ce:Zr	**24.0**	26.6	**40.0**	27.8	3.5	2.1
Hf:Zn	**15.0**	**4.9**	26.9	**57.0**	**11.0**	0.2
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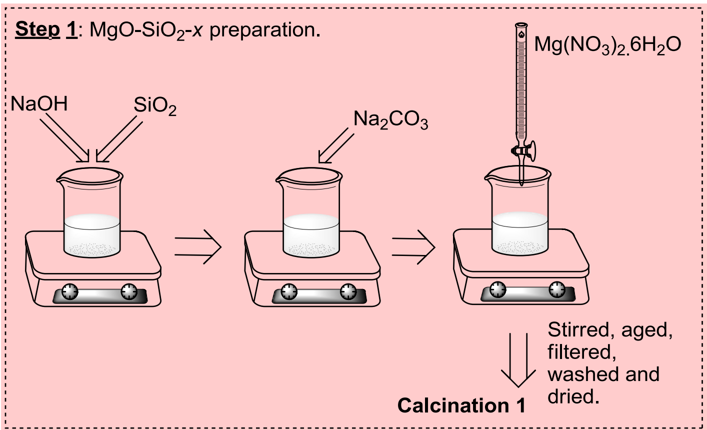
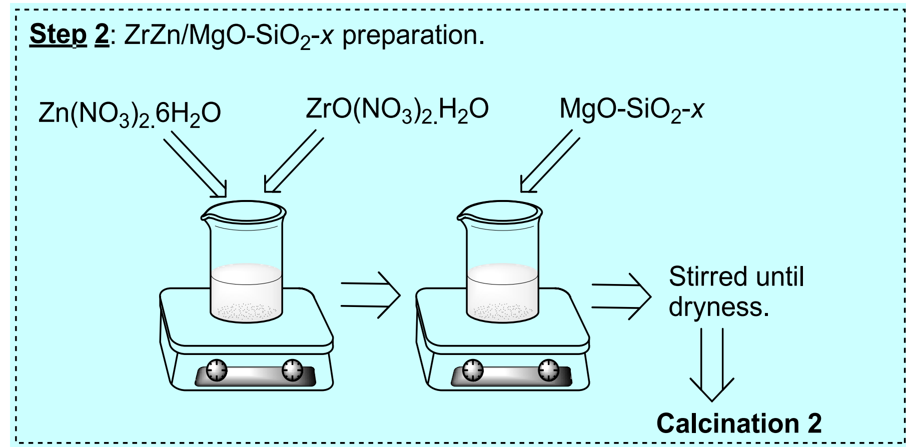
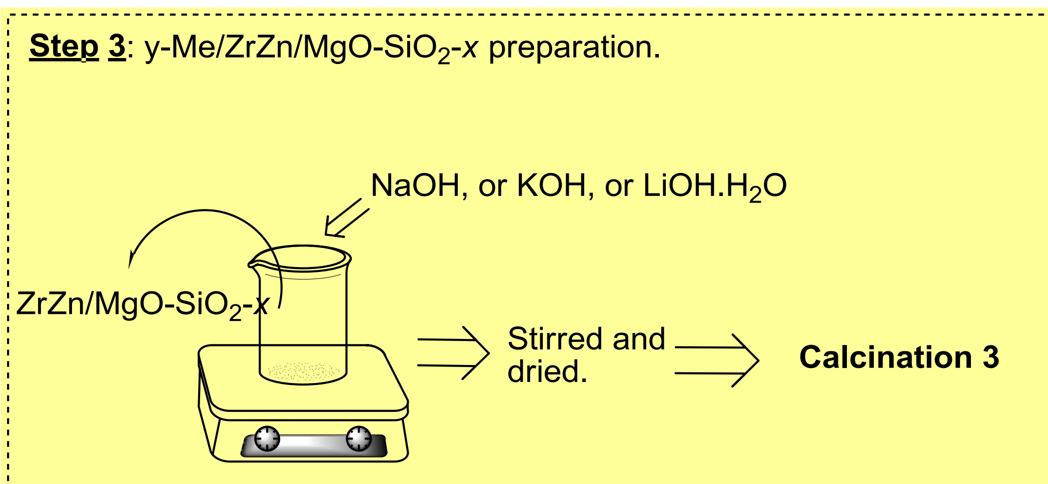
T = 375 ^{o}C, LHSV = 1 h^{-1}

Cat. Sci. Technol. 2011, 267

Water/ZrZn/MgO:SiO$_2$-1 system







Previous systems too much ethene/diethyl ether use MgO.

I do not like when we cannot repeat work in the literature….. systematic

Catal. Commun. 2014, 25.
ChemCatChem 2016, 2376
Chem. Eng. J., 2017, 988
Appl. Catal.-A Gen 2017, 530

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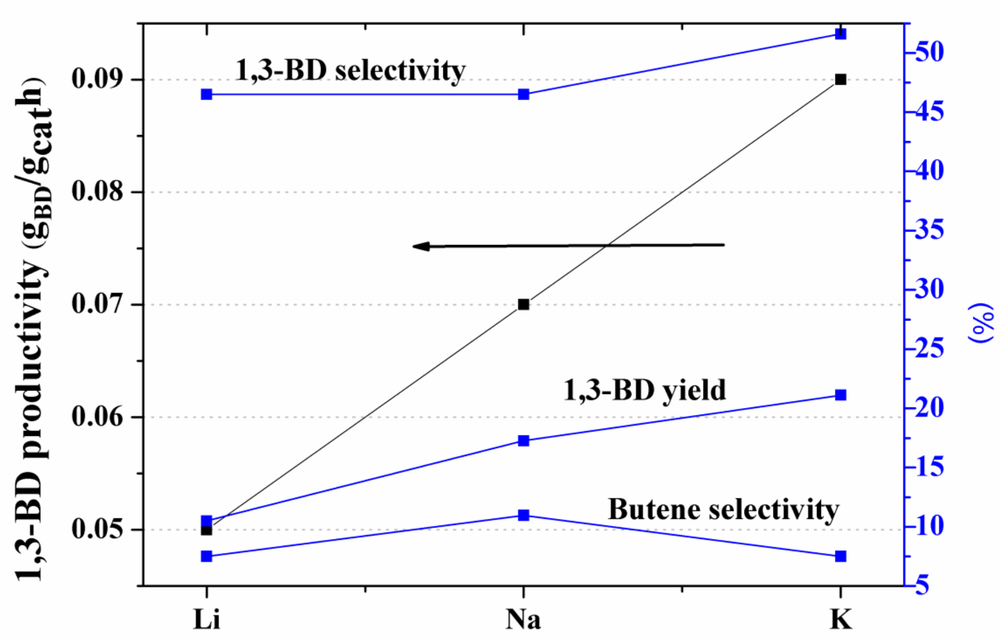
Water/ZrZn/MgOSiO$_2$-1 system

Table 1 Catalytic results for 3 h of time on stream temperature 375 °C and WHSV = 0.62 h^{-1}.

Entry	Catalyst	X (%)	Selectivities (%mol)					1,3-BD yield (%mol)	1,3-BD productivity ($g_{BD}/g_{cat}\cdot h$)
			1,3-BD	AcH	Ethene	DEE	Butene		
1	ZrZn/MgO-SiO$_2$-1	40	35.9	8.3	32.2	9.8	9.2	30.4	0.13
2	1.2-Na/ZrZn/MgO-SiO$_2$-1	24	46.5	13.1	18.7	4.6	10.9	17.3	0.07
3	Water/ZrZn/MgO-SiO$_2$-1	46	32.5	6.6	34.9	10.4	10.6	26.8	0.11

Comparison of NaOH effect with KOH and LiOH



81 m²/g	219 m²/g	243 m²/g

Both systems were effective in the suppression of ethanol dehydration, presenting lower selectivities to ethene and DEE.

The best performance observed for K_2O containing samples may be related to its higher surface area.

Change 1 variable this has an effect on another

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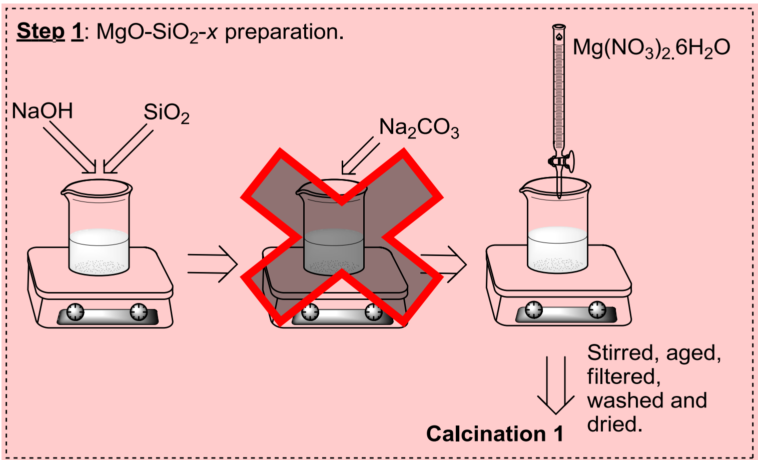
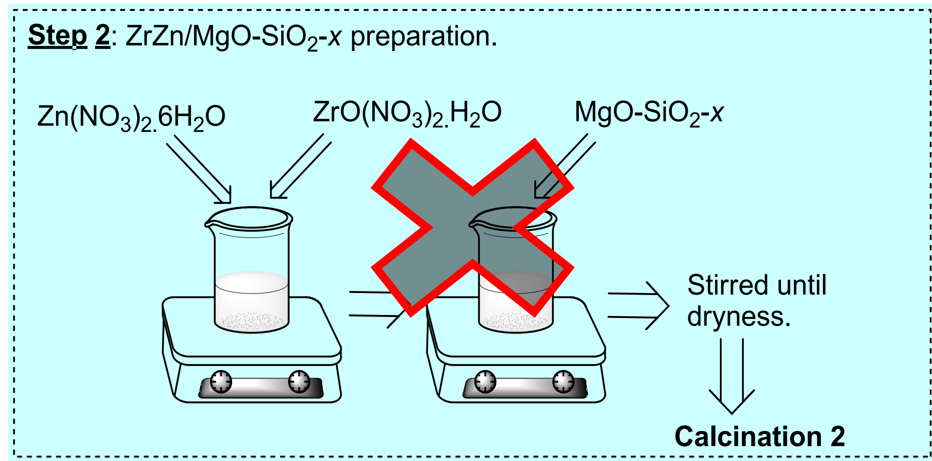
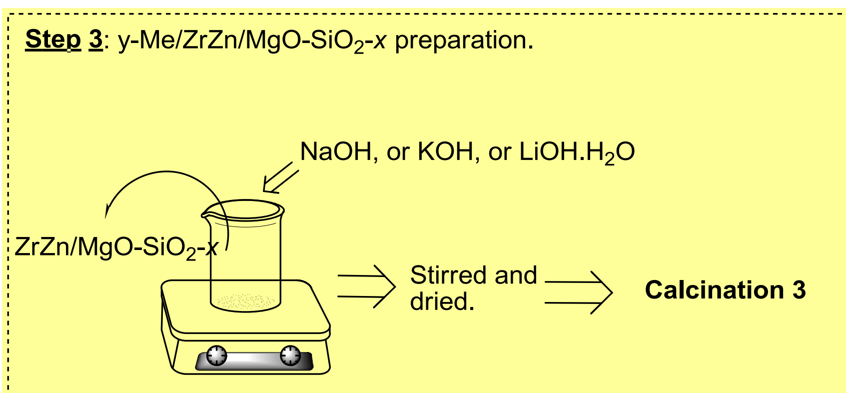
Effect of calcination step removal







Or just one calcination

Typically 3 but more energy intensive

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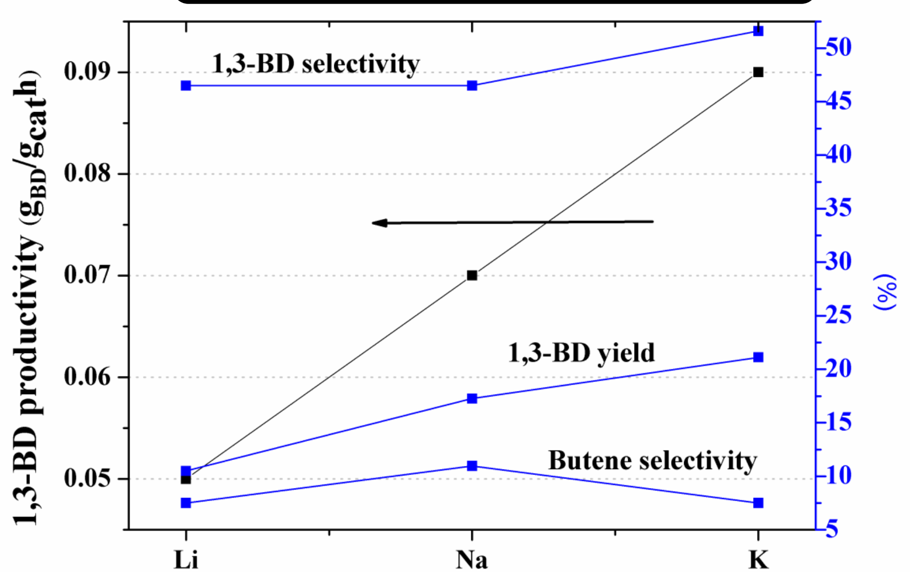
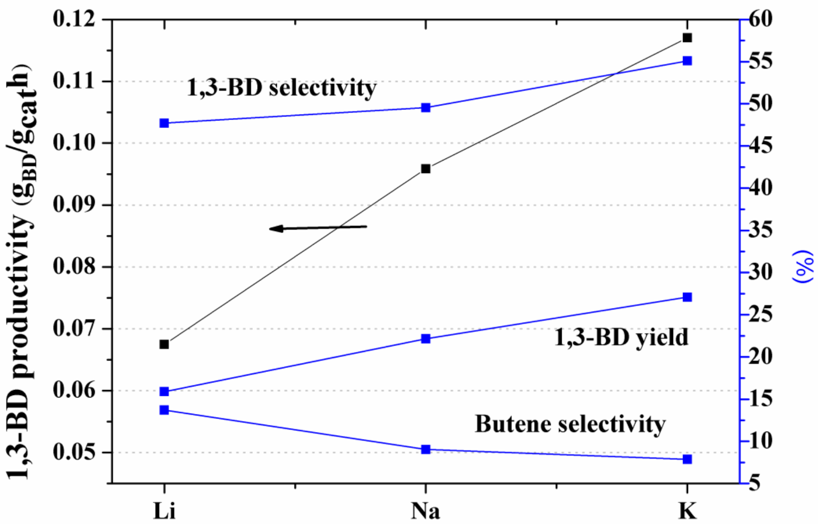
Comparison of NaOH effect with KOH and LiOH

3 calcination steps



1 calcination step



81 m^2/g	219 m^2/g	243 m^2/g	210 m^2/g	290 m^2/g	305 m^2/g

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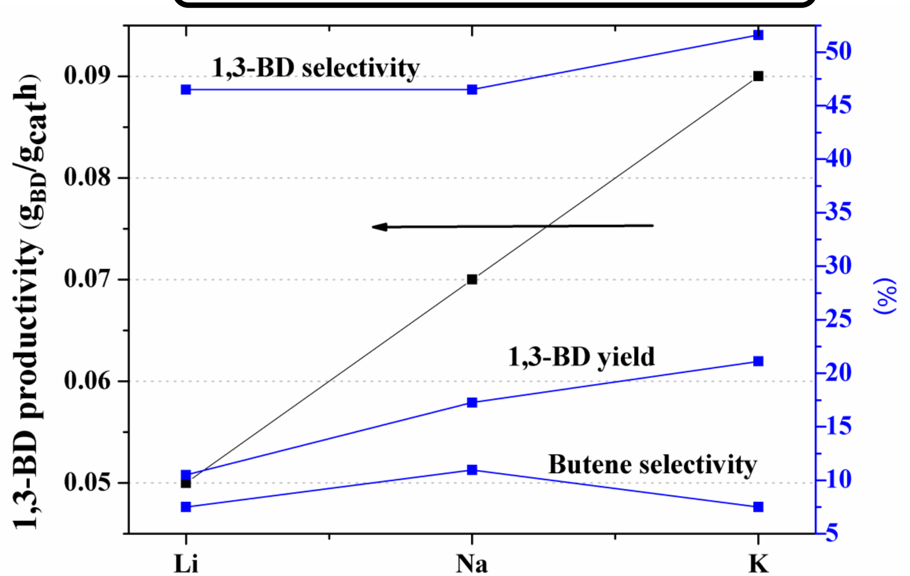
Comparison of NaOH effect with KOH and LiOH

3 calcination steps



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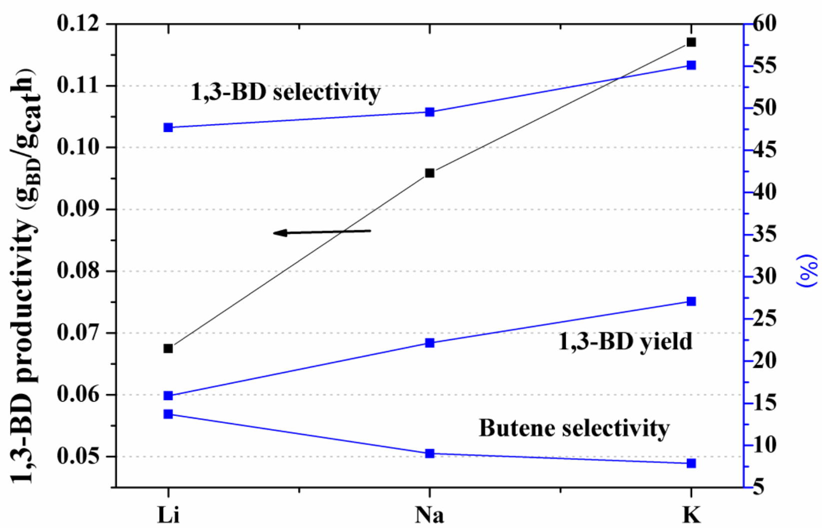

3 calcination steps		
81 m^2/g	219 m^2/g	243 m^2/g

1 calcination step		
210 m^2/g	290 m^2/g	305 m^2/g

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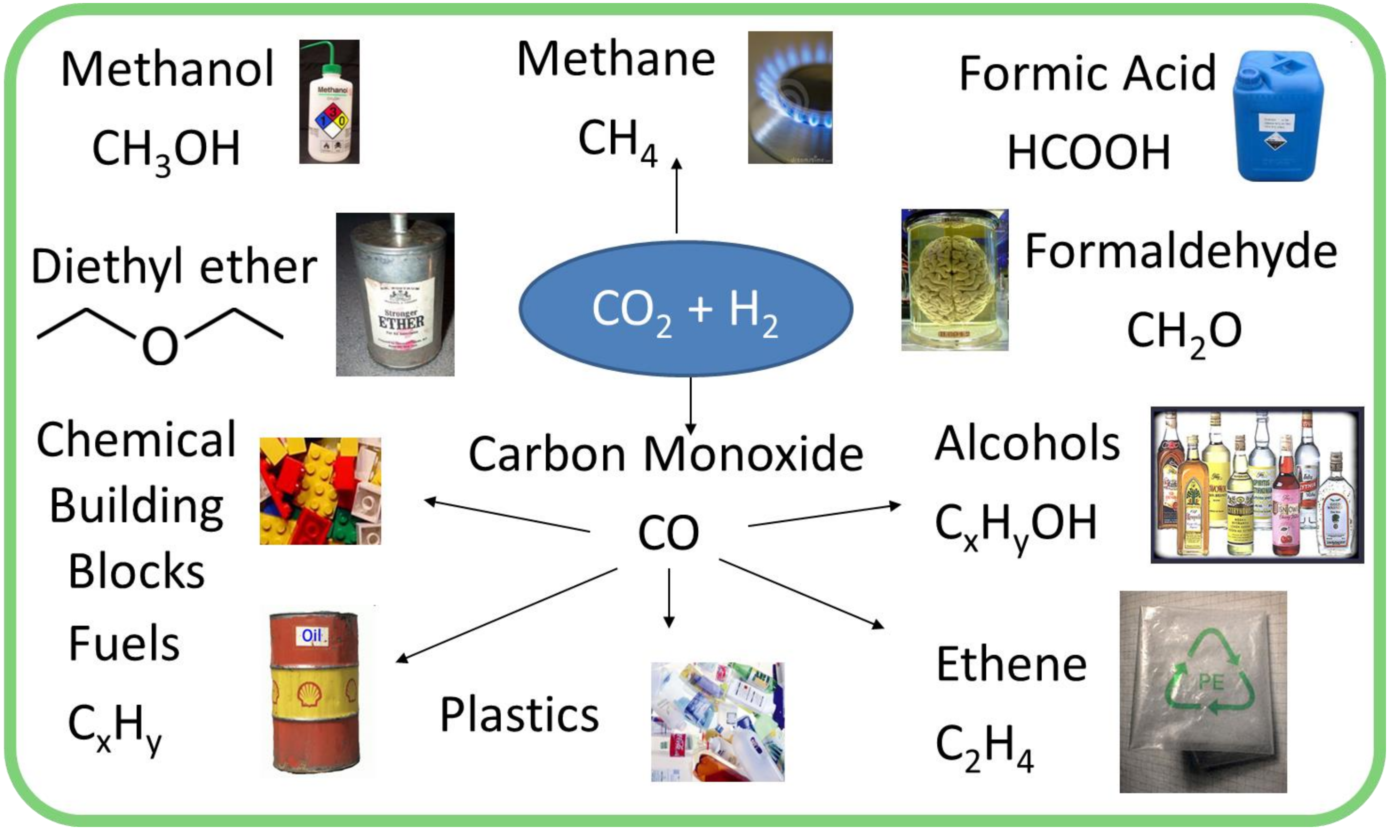
Where are we going with this?

CO_2 UTILISATION



We do need a sustainable source of H_2

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CO_2 conversion – it's not that simple

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Reverse water-gas shift reaction

$$CO_2 + H_2 \rightleftharpoons CO + H_2O$$

thermodynamically unfavorable:

$$\Delta G_r^o = 20.6\ kJ\ mol^{-1}$$

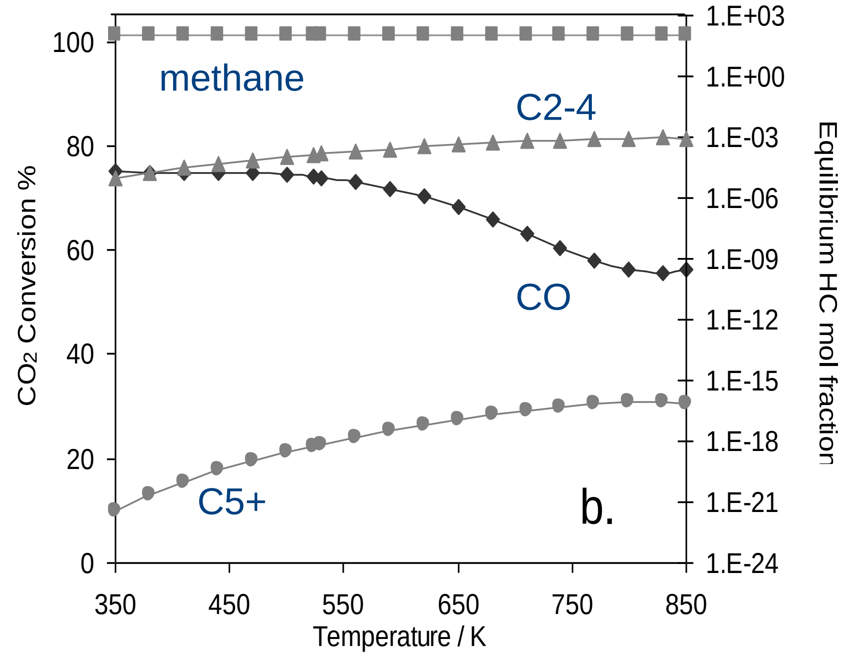
So it would be best to work with CO rather than CO_2. But CO_2 is what we are emitting in the atmosphere!

Fischer-Tropsch reactions

$$nCO + (2n+1)H_2 \longrightarrow C_nH_{2n+2} + nH_2O$$

$$nCO + 2nH_2 \longrightarrow C_nH_{2n} + nH_2O$$

$$nCO + 2nH_2 \longrightarrow C_nH_{2n+2}O + (n-1)H_2O$$



the most thermodynamically stable product is methane

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Journal of CO_2 Utilisation 2014, 34

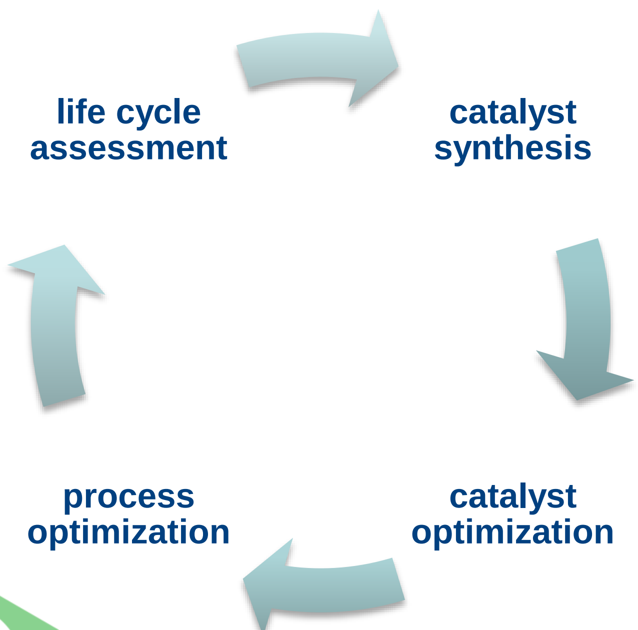
Our approach

Reverse water-gas shift reaction

$$CO_2 + H_2 \rightleftharpoons CO + H_2O$$

thermodynamically unfavorable:

$$\Delta G_r^o = 20.6\ kJ\ mol^{-1}$$



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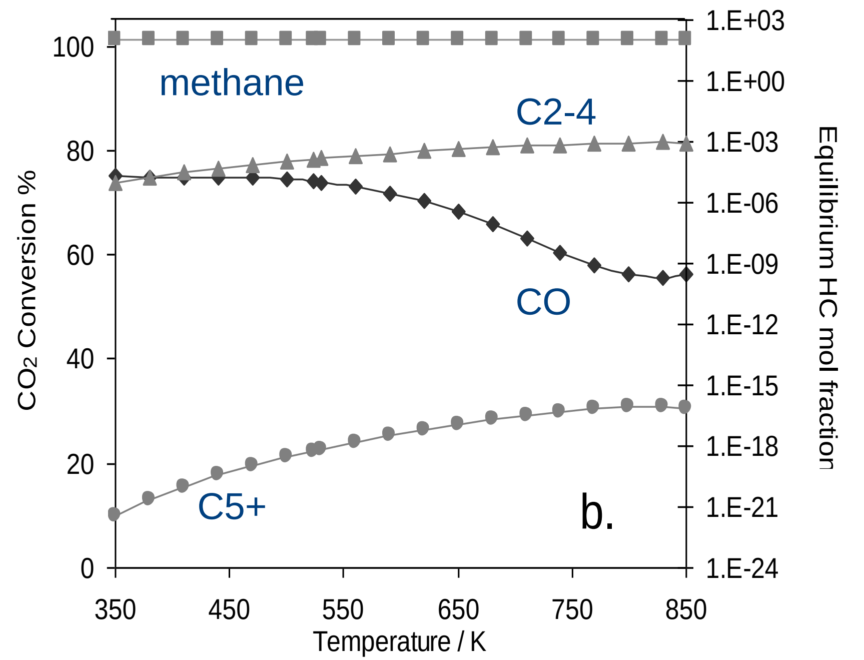
$$nCO + 2nH_2 \longrightarrow C_nH_{2n+2}O + (n-1)H_2O$$



the most thermodynamically stable product is methane

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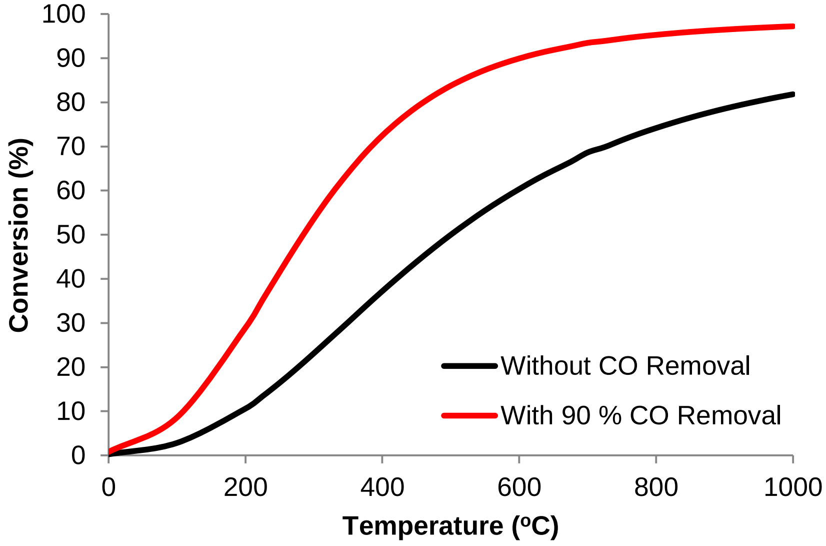
Journal of CO_2 Utilisation 2014, 34

CO removal

Reverse water-gas shift reaction

$$CO_2 + H_2 \rightleftharpoons CO + H_2O$$

The reverse water-gas shift reaction is an equilibrium process and as such CO_2 conversion is limited by thermodynamics



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CO_2 to hydrocarbons

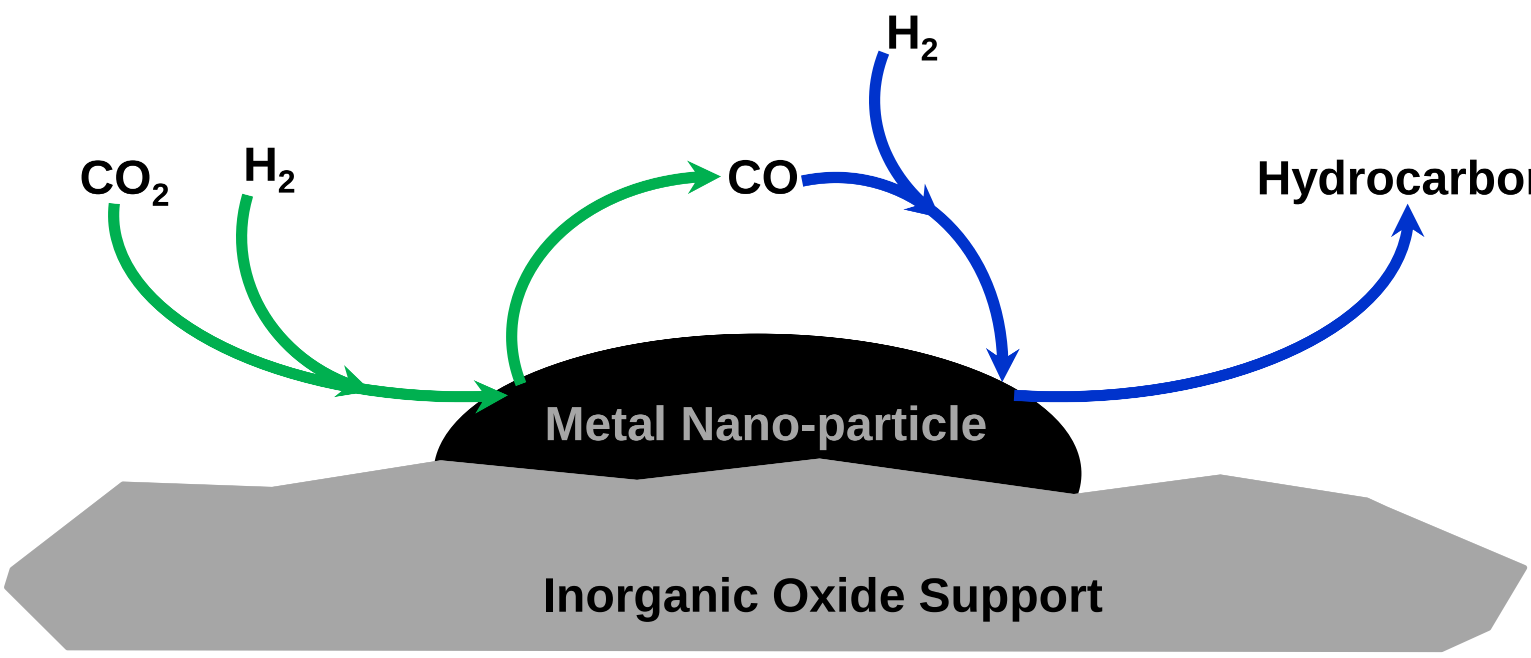
CO_2 can be converted to hydrocarbons through a two-step process

RWGS

$$CO_2 + H_2 \underset{}{\overset{[cat]}{\rightleftarrows}} CO + H_2O$$

Fischer-Tropsch

$$(2n+1)H_2 + nCO \xrightarrow{[cat]} C_nH_{(2n+2)} + nH_2O$$



Catalyst Design

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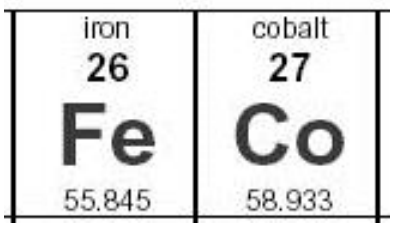
The majority of previous work has been conducted using ‘traditional’ Fischer-Tropsch catalysts based on iron and cobalt



Iron

-Active for both the RWGS reaction and FT

-Relatively high selectivity towards higher hydrocarbons and olefins

-lower conversions observed when CO_2 is used as a carbon feedstock

Cobalt

-High activity for the FT process

-Higher chain growth probability than iron for FT

-Not RWGS active

-Generally high (>75%) selectivity to methane with CO_2 hydrogenation

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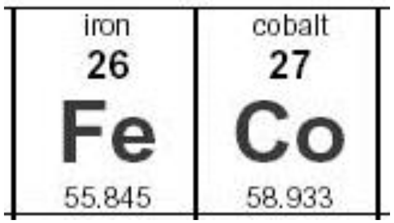

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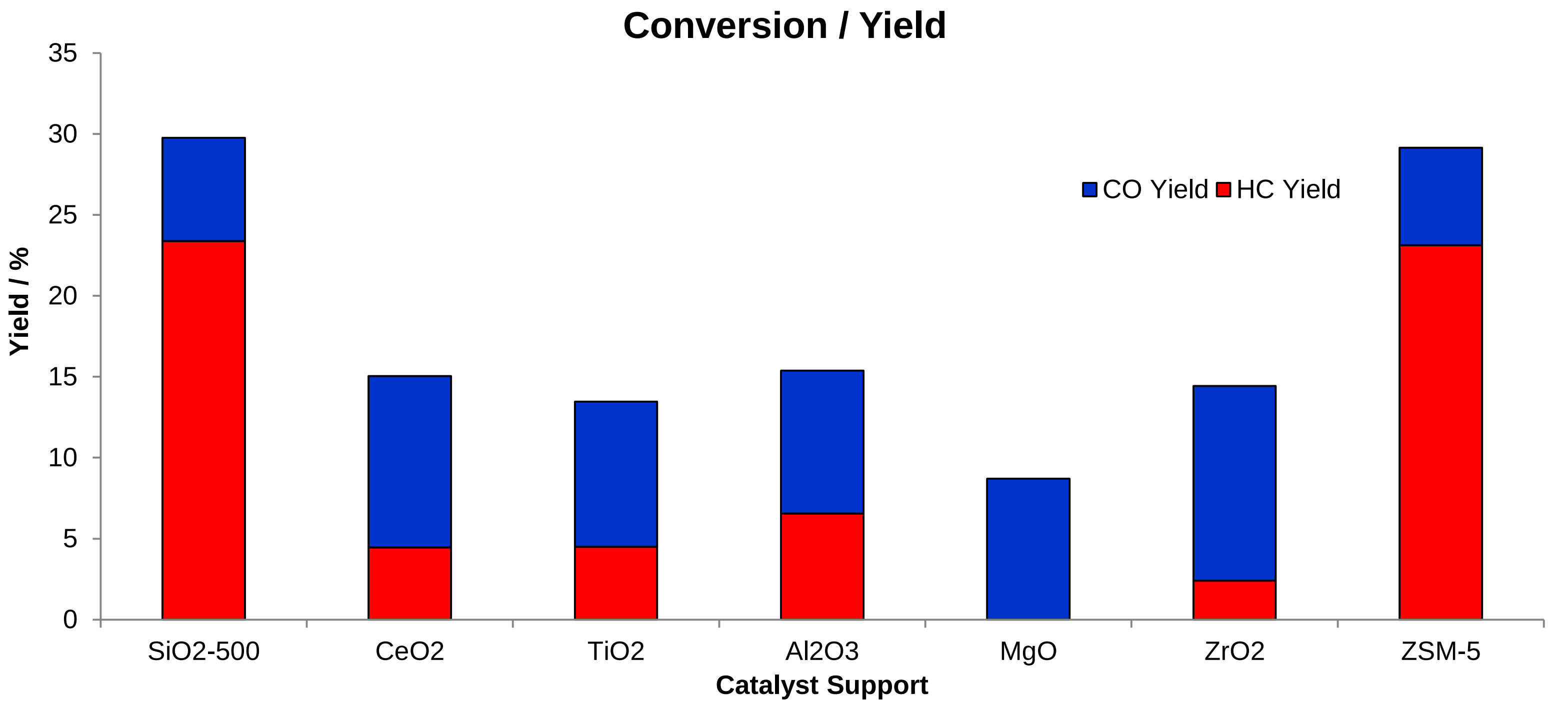
Support Variation (Cobalt Catalysts

Cobalt-based catalysts have also been shown to give high CO selectivities. Variation of the catalyst support can play an important role in directing selectivity away from hydrocarbon products.

Catalyst:

20wt%Co/3wt%Mo/1wt%Na



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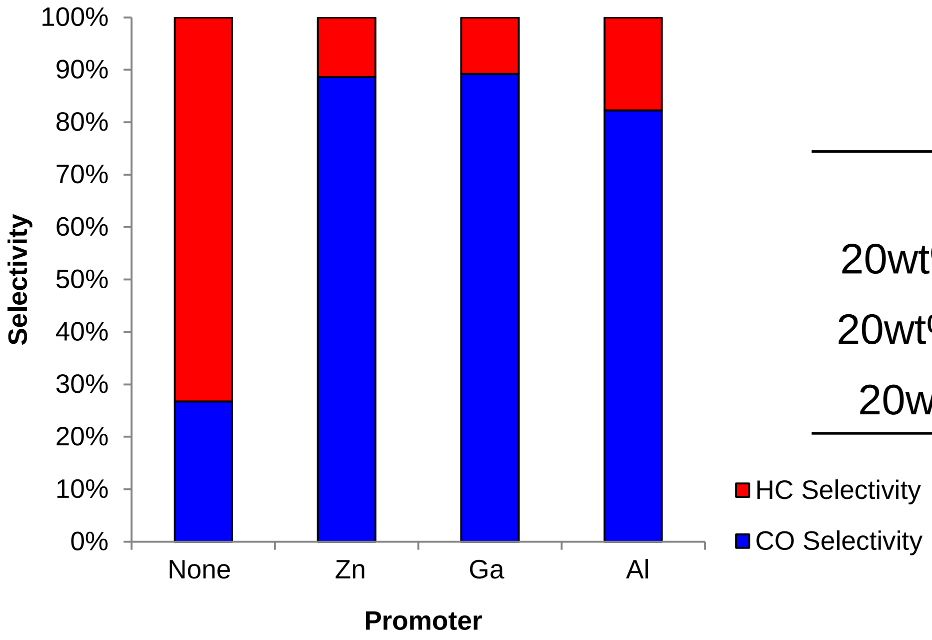
J. CO_2 Utilisation 2016, 97

Promoter Addition (SiO_2 supported)

The addition of the appropriate promoters can greatly improve selectivity towards CO or HCs.



Catalyst Composition	CO_2 Conversion (%)
20wt%Fe/SiO_2-250Å	35
20wt%Fe/10wt%Zn/SiO_2-250Å	8
20wt%Fe/10wt%Ga/SiO_2-250Å	7
20wt%Fe/1wt%Al/SiO_2-250Å	28

T = 370 °C

HC selectivity of Fe/SiO_2 catalyst can be improved by the addition of promoters.

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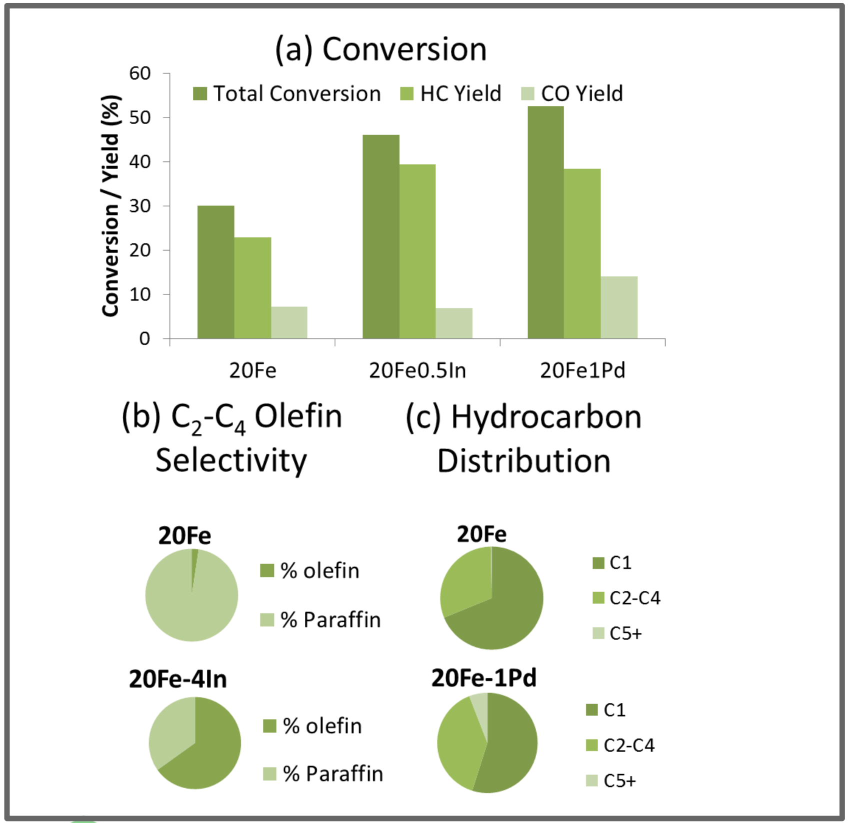
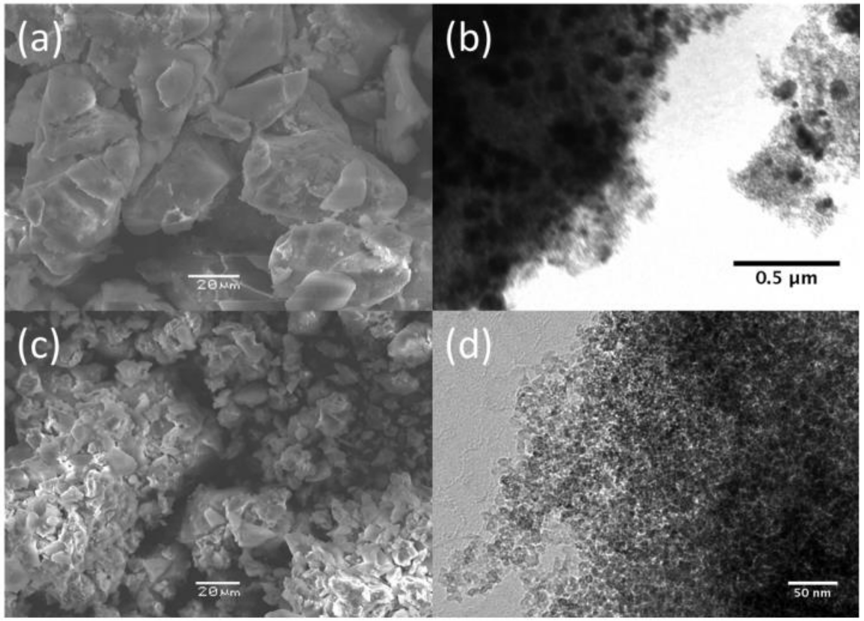
Iron Catalysts: Palladium Promotion

The addition of palladium was found to improve the performance of an iron-silica catalyst system





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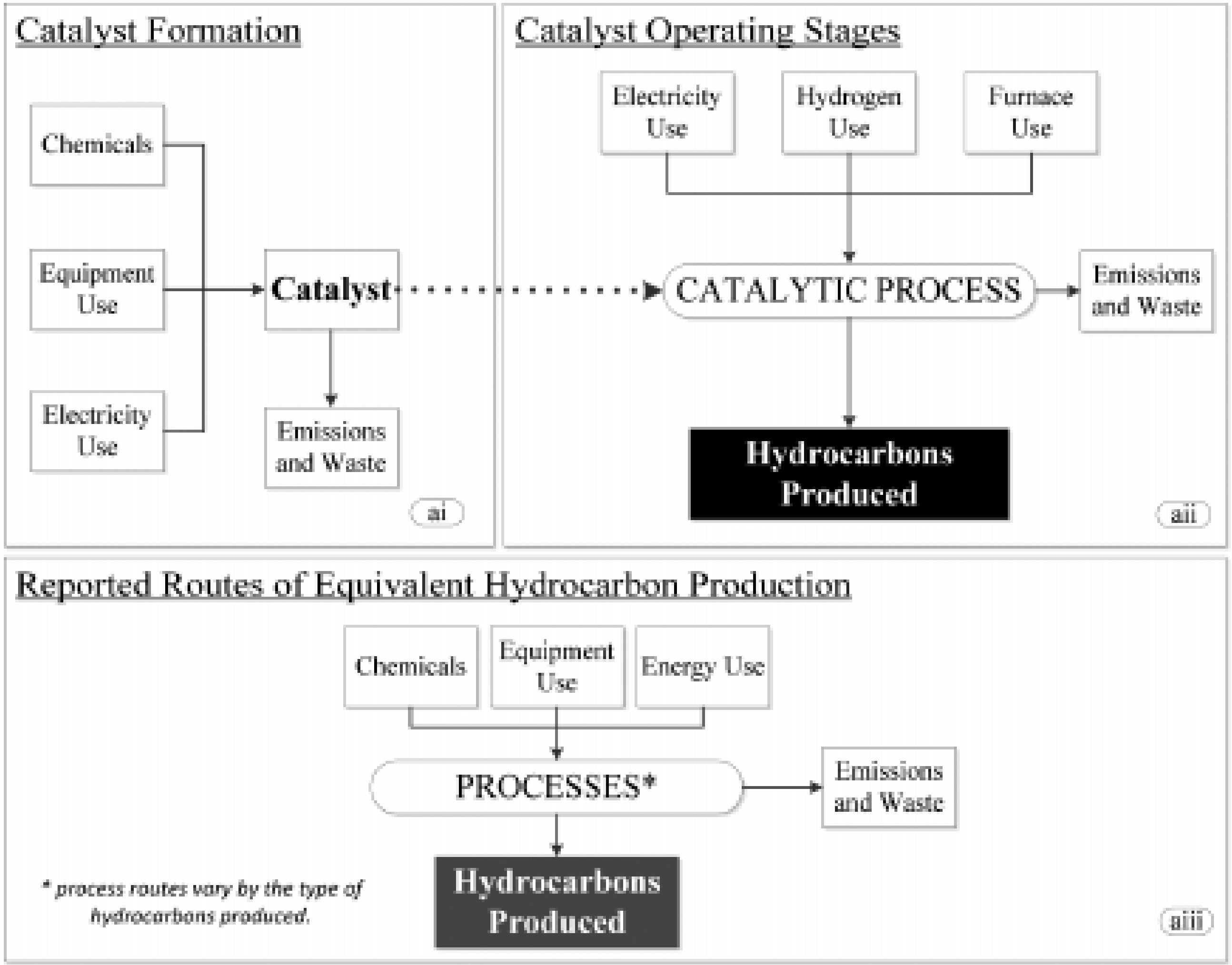
ChemPlusChem 2013, 1536

Iron Catalysts: Palladium Promotion



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Marcelle McManus
Glyn Griffiths

Why iron and carbon?

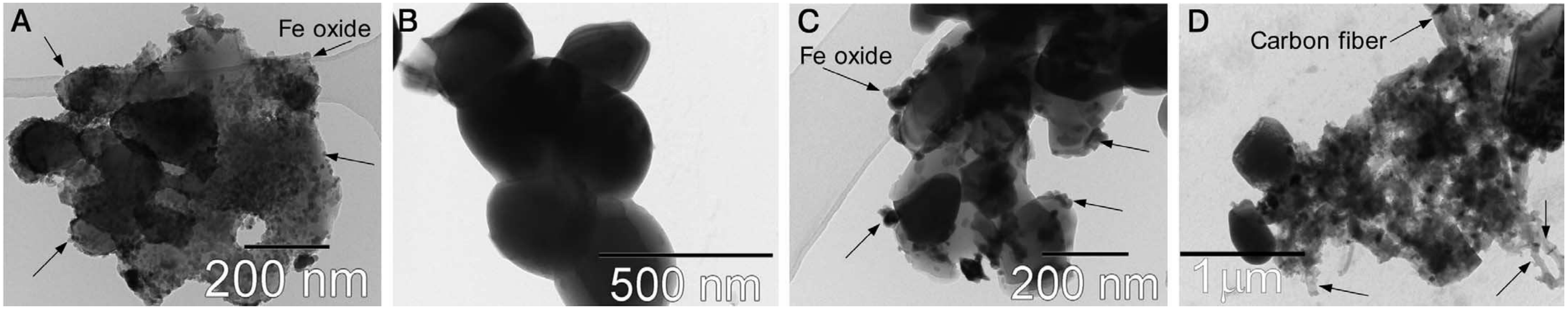

Table 1. Product selectivity and catalytic activity at 1 bar. Catalytic tests were performed at 350°C and a H_2/CO ratio of 1; results after 15 hours on stream are shown (CO conversion: 0.5 to 1.0%). The product mixture that was analyzed consisted of C_1 to C_{16} hydrocarbons. Iron time yield (FTY) represents moles of CO converted to hydrocarbons per mol of Fe per second; %C is defined as carbon atoms in a product with respect to the total number of C atoms in the hydrocarbon mixture. CO_2 was not measured.

Sample	FTY (10^{-6} $mol_{CO}/g_{Fe}.s$)	Selectivity (%C)			
		CH_4	C_2–C_4 olefins	C_2–C_4 paraffins	C_{5+}
Fe/CNF	1.41	23	61	4	12
Fe/α-Al_2O_3 (12 wt % Fe)	0.65	22	61	4	13
Fe/β-SiC	6.52	31	58	4	7
Fe/SiO_2	0.14	38	56	5	1
Fe/γ-Al_2O_3	0.07	54	44	2	0
Fe-Ti-Zn-K	0.13	83	16	1	0
Fe-Cu-K-SiO_2	0.20	43	46	2	9
Bulk Fe	0.08	76	21	2	1

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Torres Galvis, H. M., et al., *Science* **2012,** *335* (6070), 835-838.

Fe-nanoparticle – CNT catalysts for CO_2 conversion

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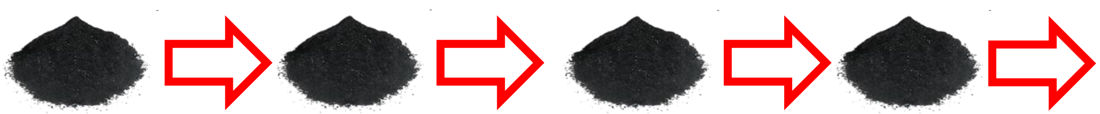
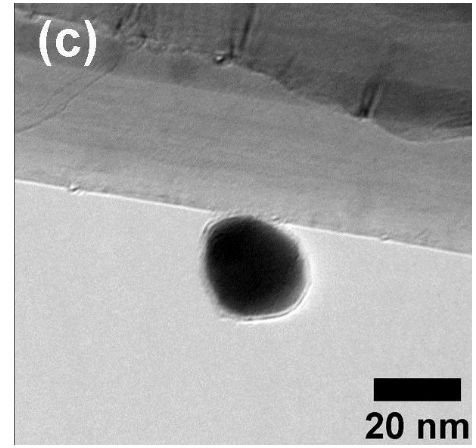
Conventional process:
complex, inefficient, expensive

CNT synthesis | removal of residual iron | impregnation of Fe catalyst | drying and calcination

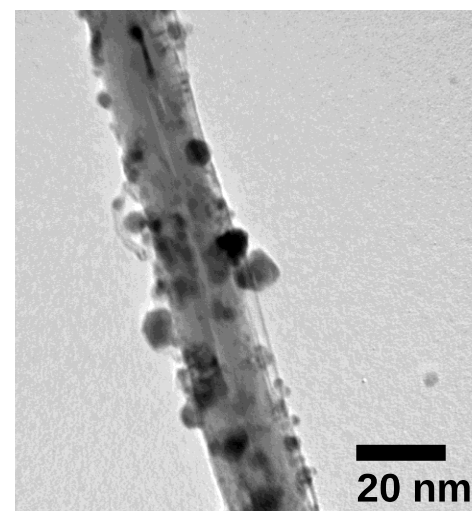


catalyst activation



One-step process:

Fe@CNT
synthesis



Fe nanoparticles used to synthesize the CNTs are re-used as catalysts for CO_2 conversion

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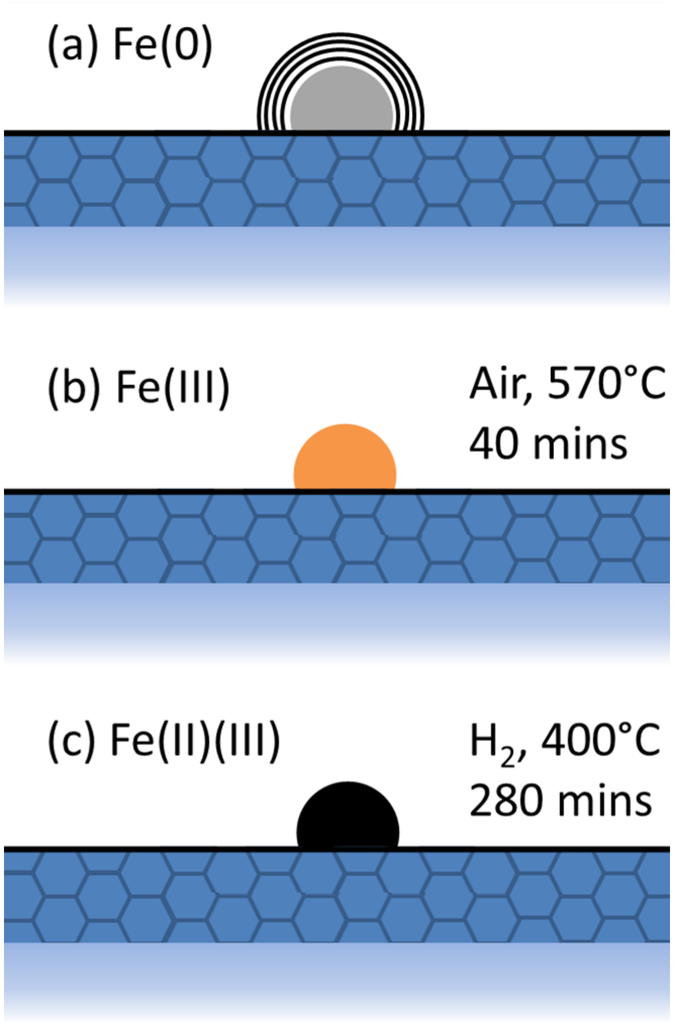
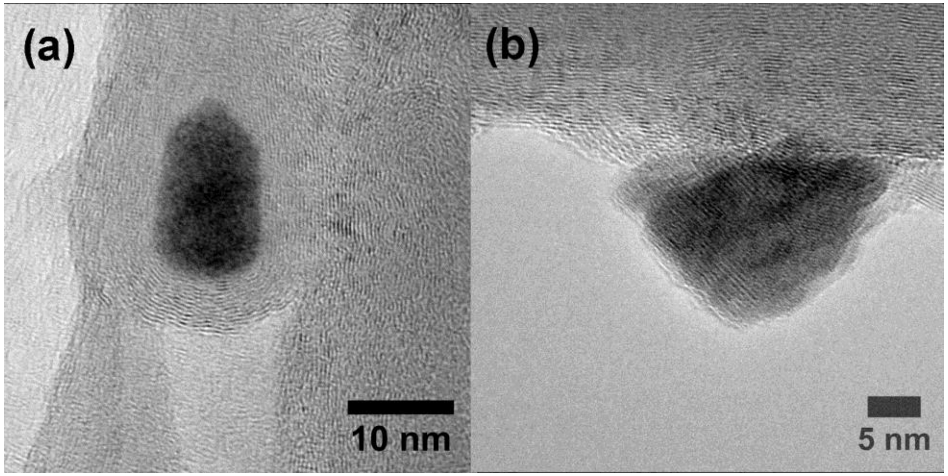
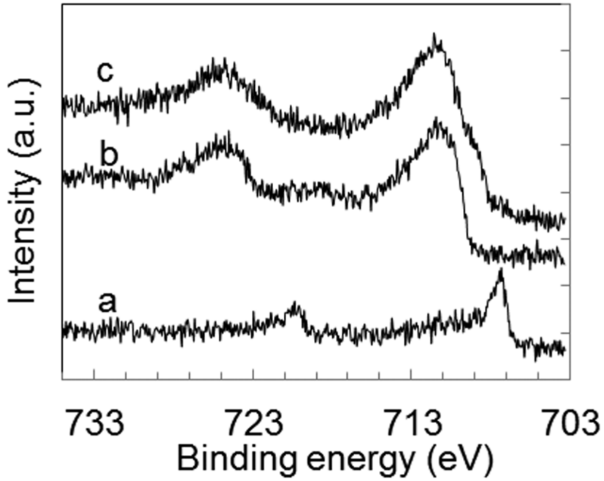
Cat. Sci. Technol. 2013, 1153

Fe@CNT: Fe nanocatalyst activation







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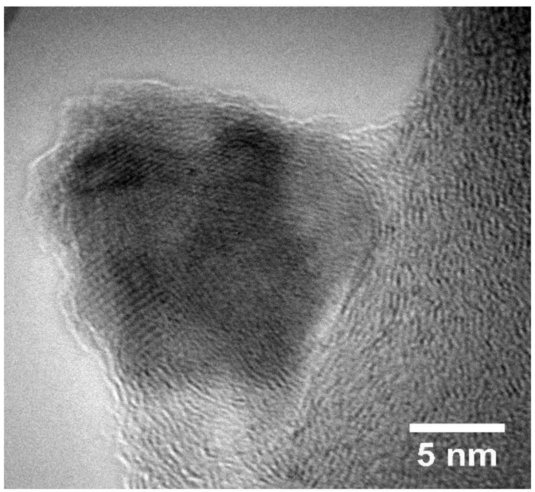
Oxidation and reduction are all done on-line and *in situ*, no additional process steps

CO_2 conversion using Fe@CNTs

Ambient pressure, 370 °C, 4 hours

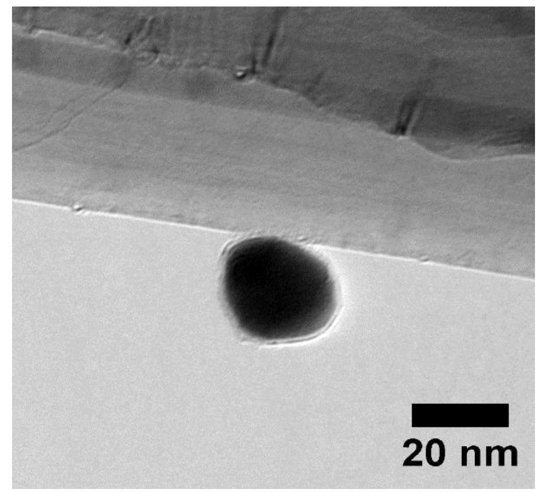
Catalyst	FTY (10^{-5}) mol/g s	CO	CH_4	C_{2-4}	C_{5+}
Fe@CNT	11	45.1	29.3	24.3	1.3
Fe decorated CNT	3.0	82.4	12.4	5.2	0

Fe@CNT



in-situ Fe deposition ✓

Fe decorated CNT



ex-situ Fe deposition ✗

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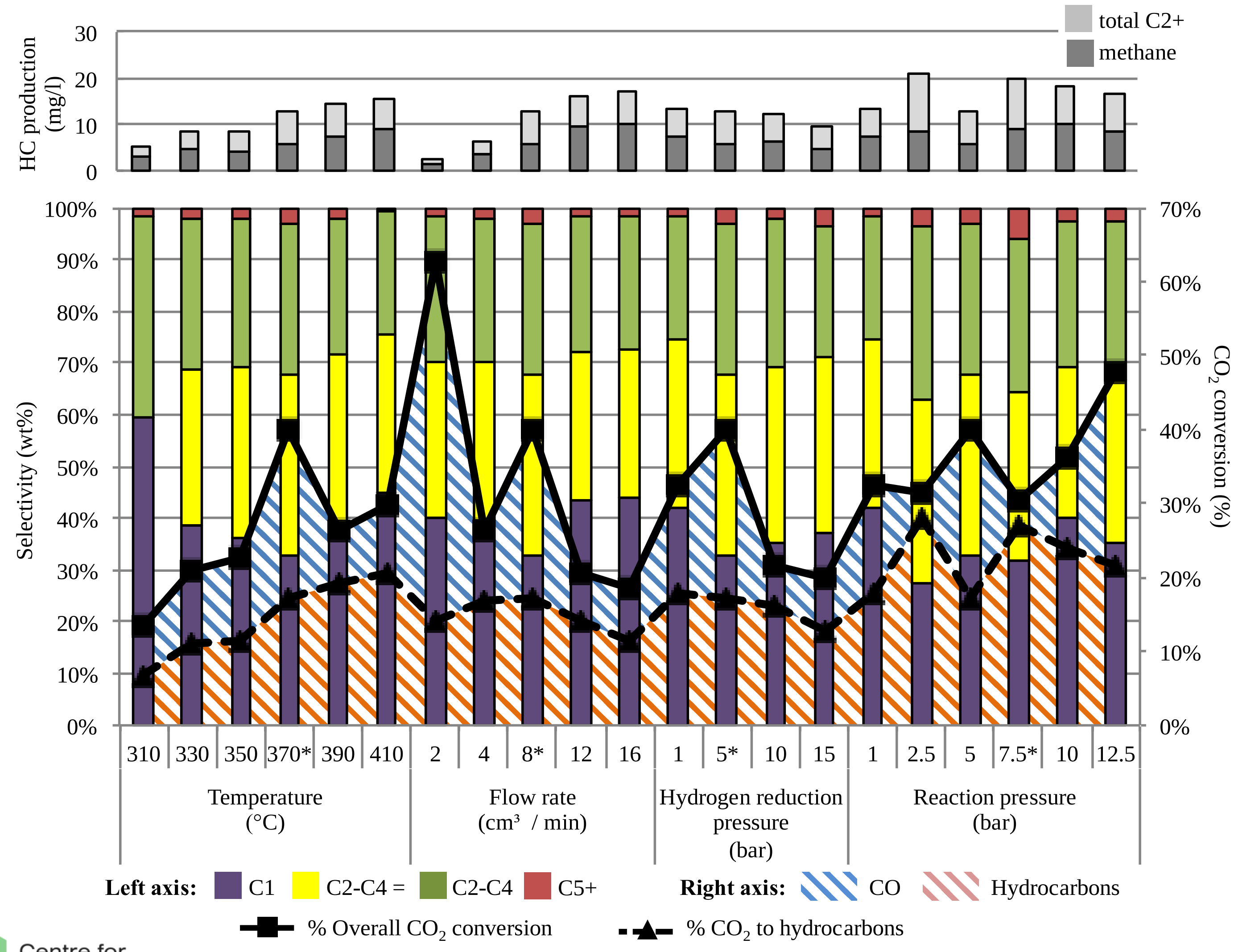
Cat. Sci. Technol. 2013, 1153

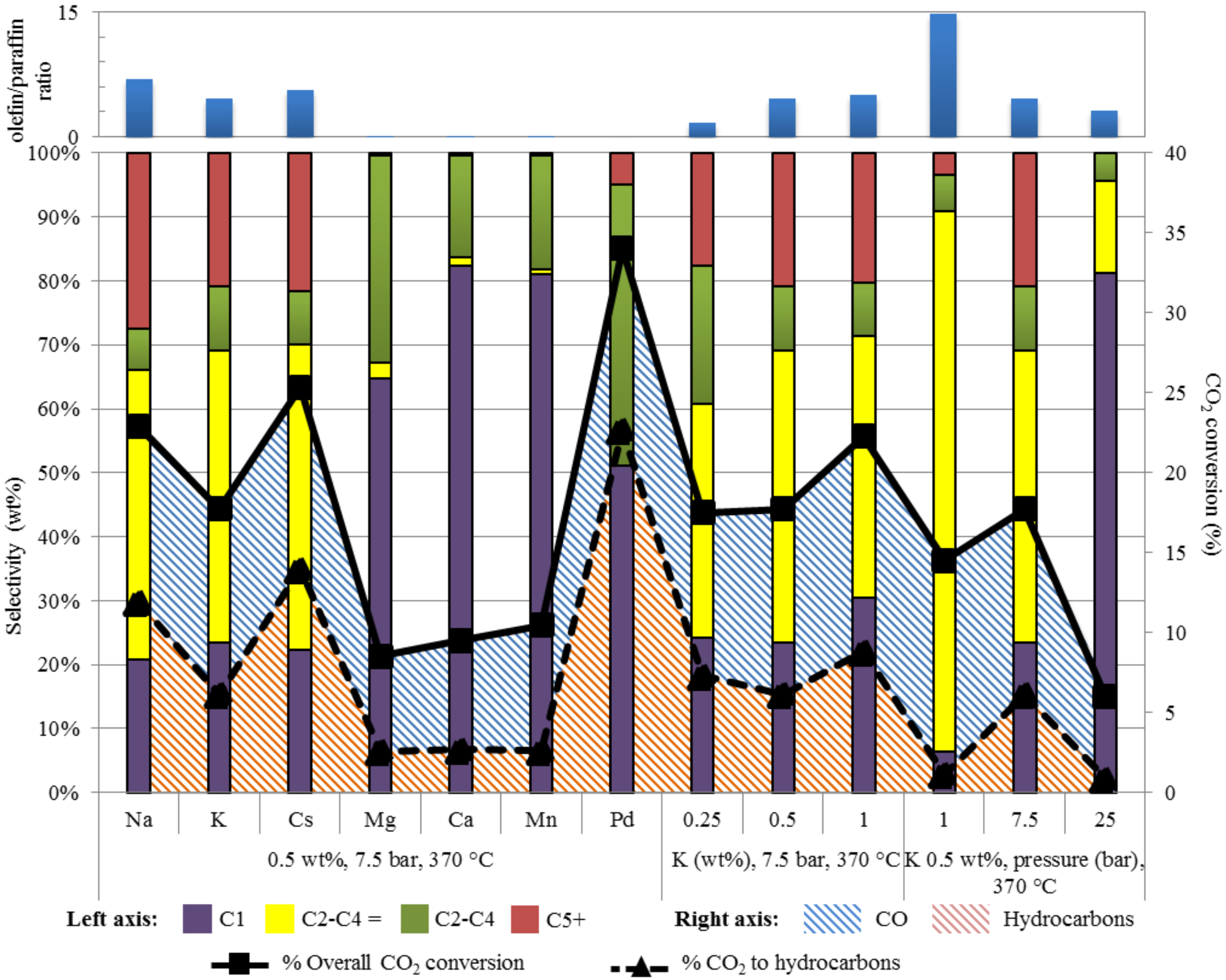
Patent filed

Catalytic variable optimisation



ChemSusChem 2015, 4064

Promoter investigation



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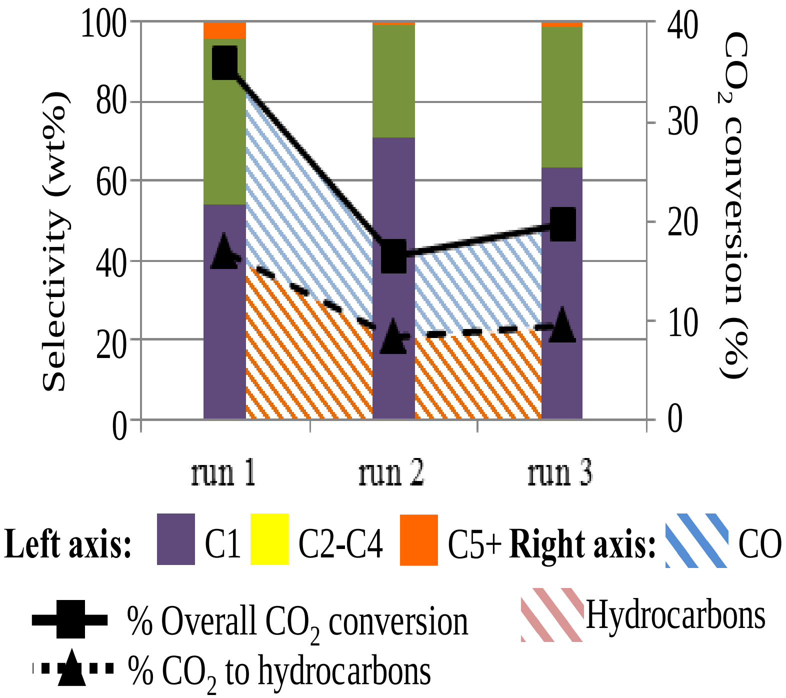
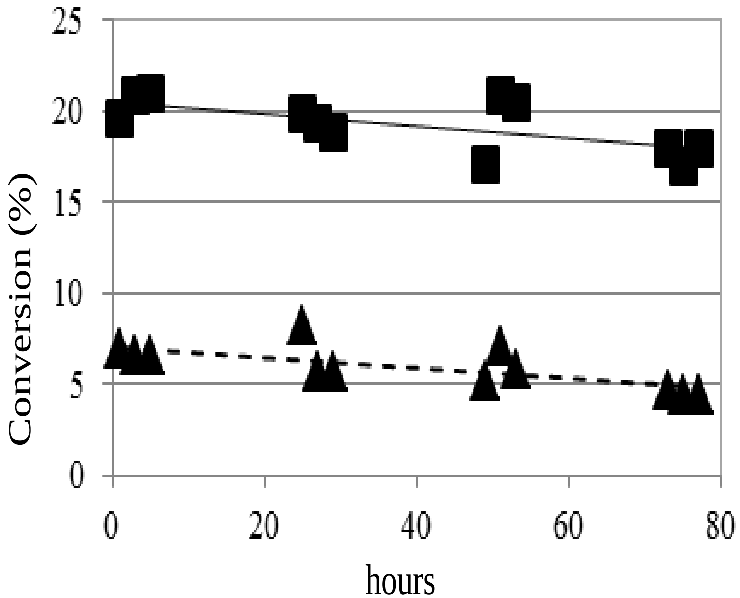
ChemSusChem 2015, 4064

Longevity and recyclability





Area for improvement

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Conclusions

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- Industrial relevant catalysts prepared and tested. Selectivity very sensitive to preparation conditions and operational parameters

- We have prepared highly efficient iron and cobalt nanoparticle catalysts using a one-step method for the conversion of CO_2 to hydrocarbons, with high conversion and selectivity to long hydrocarbons using promoters.

- Life Cycle Assessment was used to optimise catalyst preparation, promoters and process parameters to minimise embodied impacts and maximise hydrocarbon offsets. We have shown there is a credible route towards carbon neutral carbon dioxide utilisation.

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Acknowledgements

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Butadiene: Dr Simoni Da Ros and Prof Jose Carlos Pinto (Rio De Janeiro)

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Any questions?

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