Hydrocarbon Selective
Oxidation

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Overview

Commercial large scale oxidation of hydrocarbons:

- VPO: butane; Molybdates: propene
- Gas phase with high temperatures

This presentation will focus on low temperature conditions

1) Alkane oxidation: CH\(_4\) and C\(_2\)H\(_6\)
2) Alkene epoxidation
Methane oxidation
Two approaches adopted
1) Au-Pd with $\text{H}_2\text{O}_2$
2) Zeolite catalysts with $\text{H}_2\text{O}_2$

Selective oxidation of methane is one of the key challenges in catalysis
$\text{CH}_4$, $\text{CO}_2$, $\text{H}_2\text{O}$ very abundant
Thermodynamics versus kinetics
About every 10 years there is a new approach to CH$_4$ oxidation

**Lunsford: Nature** 314, 721 (1985)
- Oxides at 600 C; gas phase radical chemistry

- Pt salts in acid, oxidant (Pt$^{4+}$) is made in situ
- Hydrolysis of the ester formed to produce methanol
- Not a closed catalytic cycle, corrosive system

- Methane to methyl trifluoroacetate (CF$_3$COOCH$_3$) using H$_2$O$_2$ in trifluoroacetic acid anhydride using Pd(II) and Cu(II)
- Not a closed cycle, hydrolysis to obtain methanol

*Is it possible to get a closed catalyst cycle at low temperature?*
methane mono-oxygenase

$O_2 \ 5.05 \text{ mol( CH}_3\text{OH) kg (sMMO)}^{-1} \text{ h}^{-1}$

$H_2O_2 \ 0.076\text{mol (CH}_3\text{OH)h}^{-1} \text{ kg(MMOH) }^{-1}$

sMMO uses a di-iron active site and NADH is required

Cu form of MMO is also found in bacteria

Au containing enzyme analogues have been observed to oxidise methane
Our experimental approach

Liquid phase oxidation of methane

- at low temperature (< 90°C)
- without the use of strong acidic media
- water as solvent
- environmentally benign and economically attractive oxidants e.g. H₂O₂, O₂


**AuPd alloys are active for oxidation so this is the starting point**
METHODS OF PREPARATION

- *Impregnation* (5-25nm, multiply twinned)*
- *Co-precipitation* (1-10 nm, + atoms, clusters)†
- *Deposition precipitation* (1-10 nm + atoms, clusters)*
- *Sol-immobilisation* (2-6 nm)*

* Support is pre-formed
† Support is formed during the preparation
Interaction between Au/support crucial
Synthesis strategy-1: Conventional wet-impregnation (Clm)

Support

HAuCl₄

PdCl₂

Water

Dried at 90°C

“Dried” Catalyst

High Temperature Calcination

400°C / 4h

Supported AuPd Catalysts

Impregnation leads to a bimodel particle size distribution
Comparison for Au, Pd and Au-Pd supported on TiO₂ for Benzyl alcohol oxidation


Benzyl alcohol conversion and selectivity in benzaldehyde with the reaction time at 373 K, 0.2 MPa O₂ pressure: (■) Au/TiO₂, (○)Pd/TiO₂, (▲) Au-Pd/TiO₂; solid symbols – conversion, open symbols – selectivity;

Although very broad particle size range impregnated catalysts are very active

Why no benzoic acid?

*Nature Comm* 2014
Synthesis strategy – 2: Sol immobilization method (Slm) for controlling size

Experimental Set-Up

Used for H₂O₂ addition protocol and ‘in situ’ protocol
Closed system

Typical reaction conditions

- Water solvent (total volume 10mL)
- H₂O₂: 5000 μmol
  - All peroxide added at start
- Catalyst: 1 x 10⁻⁵ moles metal
- CH₄: 440 psi (30.5 bar)
- 2°C - 90°C; (50°C standard)
- 2 min – 4 h (0.5h standard)
- 1500 rpm
Product Analysis & Quantification

- Liquid products analysed by $^1$H-NMR spectroscopy
  - 1% TMS/CDCl$_3$ internal standard
  - GC-MS and LC-MS used for validation
  - 500 MHz Bruker instrument

- Gaseous products analysed by gas chromatography (GC-FID)
  - Calibration curve for CO$_2$
  - CO$_2$(aq) could also be analysed with GC-FID using liquid injections

- H$_2$O$_2$ quantified by titration vs. Ce$^{4+}$ solution with Ferroin indicator
Time on Line Au-Pd/TiO₂

CH₃OOH is the primary product
CH₃OH and CO₂ secondary products

Reaction Temperature: 50°C, [H₂O₂]: 5000 μmol, Solvent: H₂O, 10 mL.
Catalyst: 1.0 x 10⁻⁵ mol of metal, 28mg 2.5wt% Au-2.5wt% Pd/TiO₂
Au-Pd/TiO$_2$ - effect of temperature

0.2µmoles methanol produced at 2ºC
CO$_2$ selectivity increases at higher temperature
Low oxygenate productivity
CH₄ oxidation using H₂ + O₂ and AuPd/TiO₂ (in situ H₂O₂)

‘in situ’ protocol works
AuPd can synthesise H₂O₂ and perform CH₄ oxidation simultaneously
Considerations

- Low productivity in AuPd system linked to high $\text{H}_2\text{O}_2$ decomposition rates.

- If the reaction mechanism is radical in nature then confinement of the substrate or intermediates may improve the selectivity/conversion.

- Acids are a key part of all the previous approaches to methane oxidation and may be beneficial......Zeolites: acid/confinement.
Au-Pd supported on ZSM-5

**AuPd catalysts (TiO₂ vs ZSM5)**

<table>
<thead>
<tr>
<th>Reference Catalyst</th>
<th>MeOH (μmol)</th>
<th>HCOOH (μmol)</th>
<th>CO₂ (g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>AuPd/TiO₂ IMP</td>
<td>2</td>
<td>1</td>
<td>0.5</td>
</tr>
<tr>
<td>AuPd/TiO₂ DPU</td>
<td>4</td>
<td>2</td>
<td>1.5</td>
</tr>
<tr>
<td>AuPd/ZSM5 (30) DPU</td>
<td>6</td>
<td>3</td>
<td>2.5</td>
</tr>
<tr>
<td>ZSM5 (30)</td>
<td>8</td>
<td>4</td>
<td>3.5</td>
</tr>
</tbody>
</table>

**ACTIVITY COMES FROM THE ZSM5 ALONE!**

With ZSM-5:
- H₂O₂ left >90%
- Oxy. Select. >98%

\( \text{H}_2\text{O}_2: 5000 \mu\text{mol}, 50^\circ\text{C}, 30 \text{ min}, p(\text{CH}_4) = 440 \text{ psi}, \text{mass of catalyst; 27 mg} \)
Activity of other zeolites

Catalytic activity of other zeolite materials

- Other MFI materials exhibit negligible catalytic activity
  - Silicalite-1
  - TS-1

- Confinement effect of MFI alone is not responsible for the catalysis
  - Role of acidity (Al)?
  - Role of trace metal impurities?
Proposed active species in ZSM-5 (contains 0.014wt% Fe)

Based on EXAFS data used for computational modelling

Similar to structures proposed previously (benzene to phenol)

Similar to sMMO active site
Proposed Mechanism

Is the mechanism supported experimentally?

- Predicted:
  - \( \text{H}_2\text{O}_2 \): Products = 2:1
  - \( \text{CH}_3\text{OOH} \) as the primary product
  - \( \text{CH}_3\text{OH} \) formation accompanied by \( \cdot\text{OH} \) formation
  - Free \( \cdot\text{CH}_3 \) not formed
  - Both oxidant and substrate are activated

- ALL OF THE ABOVE OBSERVED
Tuning the product distribution

Cu/ZSM-5 produces $\text{CH}_3\text{OH} + \text{CO}_2$

$\text{H}_2\text{O}_2$: Products better for Cu vs. Fe

Fe-Cu combination leads to high $\text{CH}_3\text{OH}$ productivity and selectivity

System is now selective to $\text{CH}_3\text{OH}$

BUT has high $\text{H}_2\text{O}_2$ decomposition

For appreciable conversion we need a catalyst which has high productivity but low peroxide decomposition rate
Catalytic activity of Fe/ZSM-5 with homogeneous Cu present in solution

Cu²⁺ (aq) shuts off over-oxidation to formic acid and catalyst productivity is not diminished

This is also seen for any physical mixture of Cu and Fe catalysts
Fe and Cu Silicalite-1

Cu-silicalite-1 behaves like homogeneous Cu
- Methanol oxidation switched off

Fe-silicalite-1 (no Cu)
- 10% conversion
- 96% selectivity (oxy)
- 8% selectivity (MeOH)

Fe-silicalite-1 (with Cu)
- 9.5% conversion
- 93% selectivity (MeOH)

In presence of Cu$^{2+}$ OH radicals no longer present

*Reaction conditions:* cat: various; $P(\text{CH}_4)$: 3 bar; $[\text{H}_2\text{O}_2]$: 1.0M; temp: 70$^\circ$C; time: 30 min; rpm: 1500;
Ethane oxidation with zeolite catalysts
ZSM5 (30) (27mg), Temp = 50°C, [H2O2] = 1M, Volume 20ml, P(C2H6) = 20bars, 1500 rpm

Primary Products
- Acetaldehyde
- Ethanol

Major Products
- Acetic Acid (38%)
- Formic Acid (13%)
- 4h
2.5% FeZSM5 reaction of ethane

Time on line plot for 2.5% Fe/ZSM5 catalysed C₂H₆ oxidation with stirring during ramp

- CH3OOH
- CH3OH
- HCOOH
- C2H5OH
- CH3COOH
- CH3CHO
- COx
- CH4
- C2H4

At 50°C
- 5% conversion
- 50% Acetic acid selectivity
- 22.5% formic acid selectivity

2.5% FeZSM5 (30) CVI (27mg), Temp = 50°C, [H2O2] = 0.5 M, Volume 10 ml, P(C₂H₆) = 20bars, 1500 rpm
2.5% CuZSM5 reaction of ethane

Time on line plot for 2.5% Cu/ZSM5 catalysed \( \text{C}_2\text{H}_6 \) oxidation

- **Primary Products**
  - Ethene
  - Ethanol
  - Ethyl-hydroperoxide

- **Major Products**
  - Ethene (41%)
  - Acetaldehyde (22%)
  - Ethanol (15%)

2.5% CuZSM5 (30) CVI (27mg), Temp = 50°C, \([\text{H}_2\text{O}_2] = 1\text{M}\), Volume 20ml, \(P(\text{C}_2\text{H}_6) = 20\text{bars}\), 1500 rpm
oxidation of ethane

- **Ethene**
  - Selectivity $> 38\%$

- **Acetic Acid**
  - At 70°C
  - $> 50\%$ conversion
  - $70\%$ selectivity
Product distribution as a function of reaction temperature in the oxidation of ethane using hydrogen peroxide and 1.1wt% Fe/ZSM-5(30) under different test conditions;

(a) 28mg catalyst; \( \text{H}_2\text{O}_2 : 0.5\text{M} \); reaction volume: 10ml; \( \text{C}_2\text{H}_6 : 0.02\text{mol} \); stirring rate: 1500rpm; and

(b) 54 mg catalyst; \( \text{H}_2\text{O}_2 : 1\text{M} \); reaction volume: 20ml; \( \text{C}_2\text{H}_6 : 0.0032\text{mol} \); stirring rate: 1500rpm.

“Alcohols” - \( \text{CH}_3\text{OH} + \text{CH}_3\text{CH}_2\text{OH} \) and “Acids”- \( \text{HCOOH} + \text{CH}_3\text{COOH} \).
EPR shows; •OH ✓ •C ✗

ZSM5 catalysed Ethane Oxidation reaction scheme

EPR shows: •OH ✔ •C ✔

* Product identified and quantified via ¹H-NMR
** Product identified and quantified via GC-FID

Regular Pathway

Catalytic cracking
• H abstraction

Radical recombination

Pathway promoted by Cu

Not observed with Cu
<table>
<thead>
<tr>
<th>CH₄</th>
<th>C₂H₆</th>
</tr>
</thead>
<tbody>
<tr>
<td>No carbon centred radicals</td>
<td>Carbon centred radicals present</td>
</tr>
<tr>
<td>Primary product C₁ alkyl</td>
<td>Primary products: ethanol and</td>
</tr>
<tr>
<td>hydroperoxide</td>
<td>ethene</td>
</tr>
<tr>
<td>10% conversion</td>
<td>56% conversion</td>
</tr>
<tr>
<td>&gt; 90% methanol selectivity (2.5% Fe 2.5% Cu ZSM5)</td>
<td>Selectivity can be directed to acetic acid (ca 70% with 2.5% FeZSM5 CVI) or ethene (ca 38% with 2.5% Fe 2.5% Cu ZSM5 CVI)</td>
</tr>
</tbody>
</table>
Custom built three phase trickle bed reactor
Steady State operation – 1.5% Fe 1.5% Cu/ ZSM-5 (30)

Test conditions; **0.25 g catalyst**, flow (CH₄) = 10 ml min⁻¹, 0.25 ml min⁻¹ of 0.123 M H₂O₂/H₂O, 50 °C.

Steady State achieved – in conversion and selectivity.

Catalyst stable over 9 h on line.

High MeOH selectivity – with CO₂ the only other product.

No MeOOH observed – consistent with previous studies on EtOOH which show rapid conversion over Fe/ZSM-5 catalysts.
FURTHER CONSIDERATIONS

- CH$_4$ oxidation using H$_2$O$_2$ is effective but direct O$_2$ activation is preferred
  - Why? H$_2$O$_2$ more expensive than CH$_3$OH!
    (but for C$_2$ and higher H$_2$O$_2$ is possible)
- Also, temperature of $\geq$140 °C preferred
- Why? Oxidation is exothermic and we want to recover the heat
- Catalytic turnover of O$_2$ is required for this reaction
  - Truly Green process - mild conditions
  - Selective- low HCOOH + CO$_x$ formation
  - Stable catalyst
- How do we do this? Is it possible? Not yet with methane. But........
Selective toluene oxidation with Au-Pd/C

- Solvent free toluene oxidation, 40 ml toluene in stirred autoclave with O_2
- 97% Conversion
- Reaction temperature = 160°C

Science 331 (2011) 195

Benzyl benzoate selectivity

conversion
High selectivity to benzylbenzoate is explained by formation and subsequent oxidation of the hemi-acetal (paths $3 \rightarrow 5 \rightarrow 6$)

Catalyst design for methane to methyl formate?
Concluding comments

- Zeolites with Fe and Cu are very effective for methane and ethane activation with $\text{H}_2\text{O}_2$
- Reaction products can be fine-tuned by catalyst design
- Supported AuPd catalysts can activate $\text{O}_2$ and can be active selective oxidation catalysts for hydrocarbons
ALKENE EPOXIDATION
Epoxidation of cyclic alkenes using Au/C with air

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>TBHP g</th>
<th>Con</th>
<th>Selectivity (%)</th>
<th>( \Sigma \text{yield } C_8 )</th>
</tr>
</thead>
<tbody>
<tr>
<td>1%Au/G</td>
<td>0.12g</td>
<td>7.9</td>
<td>81.2 9.3 4.1 0.5</td>
<td>95.1</td>
</tr>
<tr>
<td>1%Au/G</td>
<td>0.02g</td>
<td>7.1</td>
<td>79.2 6.8 3.0 0.5</td>
<td>89.5</td>
</tr>
<tr>
<td>1%Au/G*</td>
<td>0.002g</td>
<td>1.3</td>
<td>82.6 7.4 2.1 0.6</td>
<td>92.7</td>
</tr>
</tbody>
</table>

Reaction conditions: 0.12g catalyst, TBHP, cis cyclooctene (10 ml, 0.066 mol), 80°C, 24 h
Catalysts prepared by impregnation

Tuneable gold catalysts for selective hydrocarbon oxidation under mild conditions Nature 2005
Cycloalkene oxidation

- Cyclopentene (26 °C), cyclohexene (50 °C), cycloheptene (60 °C), cyclooctene (80 °C) and cyclododecene (120 °C).

- 0.12g 1% Au/Graphite catalyst, 10 ml substrate, TBHP 0.064 x 10^{-3} mol, glass reactor, air, 24h.

Cat Sci Tech 2013
Cycloalkene oxidation

- Calculated potential energy surface for the formation of intermediate 5 and ring closure to form the epoxide product, 9 for C5(black) and C8(blue) systems.
- Calculated at the B3LYP/6-31G(d,p) level. For the molecular graphic
- C = grey, O = red and H = white.

- There is a significant trend in the selectivity to the epoxide when the gold catalyst is present.

- The reaction is initiated by cleavage of the tBuO-OH bond over the surface of an Au particle to form surface bound radicals.

- These surface radicals can abstract hydrogen from one of the allylic positions to give the radical, 2. In turn 2 will capture molecular oxygen to form a peroxy radical, 3, which can then abstract hydrogen from another molecule of substrate to produce the hydroperoxide, 4, and further carbon centred radical, 2.

- Invoking the RO-OH cleavage reaction over the surface of Au particles the radical, 5, is generated. At this point there are three possibilities
  - 5 can react with further substrate with H abstraction from an allylic position to produce alcohol, 7, and a further allylic radical.
  - Secondly, interaction between 5 and the double bond of the cycloalkene will result in the intermediate, 8, which can ring close to form the epoxide product, 9, and a further allylic radical.
  - The third alternative involves the reaction of two molecules of 5 via H abstraction to produce the allylic ketone, 6 and the alcohol, 7. In this case radical species are lost and so this can be thought of as the termination step of the process.
Cyclic alkene oxidation

Stabiliser removed by KOH washing, separation and drying
(a) The addition of radical initiator to cyclopentene containing BHT (3 x 10^{-5} M)

(b) the addition of BHT to stabiliser free cyclopentene
2-hexene-1-ol oxidation

Oxidation

Isomerisation

Disproportionation

trans-3-hexen-1-ol

trans-2-hexenal

2-hexenal

4-hexen-1-ol

trans-2-hexenoic acid

2-hexene-1-ol oxidation

Metal composition (Pd %)

Yield (%)

0.0 0.2 0.4 0.6 0.8 1.0

0 1 2 3 4 5 6 7

100% 100% 100%
1-hexene-3-ol oxidation

Oxidation  Isomerisation  Disproportionation  Hydrogenation

1-hexene-3-ol oxidation

1-hexene-3-one
3-hexanone
3-hexanol

Yield (%) vs. Metal composition (Pd %)

100% 100%
SUMMARY ALKENE OXIDATION

- Epoxidation for cyclic alkenes dependent on ring size
- Radical initiator only required to counteract stabilisers added to commercial alkenes
- Internal linear alkenes do not require initiator but α-alkenes only oxidised with peroxide initiators
- Suitable catalysts can be made using all 4 methods
- When C=C and C-OH present only C-OH oxidised
Alkane Oxidation

- Cardiff University
- Ceri Hammond
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- Dr Nikolaos Dimitratos
- Dr Jose A. Lopez-Sanchez
- Dr. Albert Carley
- Dr Robert L. Jenkins
- Prof Stuart H. Taylor
- Prof. David W. Knight
- Dr David Willock

Dow
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