NANOSTRUCTURED CARBON AS HETEROGENEOUS CATALYSTS
FUNDAMENTALS
The function of a catalyst: The single crystal approach

Bulk is “irrelevant”, no chemical transformations sub-surface

Reactivity?
Di-oxygen as oxidant

- Atomic chemisorbed oxygen (created typically in UHV) is amphoteric in redox properties: at “virtual pressure” → sub-surface
- Sub-surface oxygen is not reactive but
  - Polarizes the surface for adsorption
  - Restructures the surface by incorporation (autocatalytic)
  - Segregates to the surface as O nucleo
  - Polarizes atomic oxygen into O electro
- Electrophilic oxygen
  - Oxidizes functional substrates (CO, olefines)
  - Creates all oxygenate organic molecules
- Nucleophilic oxygen
  - Activates C-H bonds into functional substrates
  - Creates basicity and binds water (OH)

With metals
Need for novel materials

Traditional:
- Gas $[O_2]$
- Solid $[O_2]$
- Cat structure controlled by $[\square O_2]$ gas
- Examples: VPO, MoVTe, Ag, Cu, Pd

New:
- Gas $[O_2]$
- Solid $[O_2]$
- Cat structure independent of $[O_2]$
- Cat metastable, surface controlled by bulk
- Example: nanocarbon
Some Facts about “Carbon”
Anisotropy

There is no other material than graphitic carbon showing such pronounced electronic structural anisotropy resulting from the anisotropy of the sp$^2$ bonding: only the (blue) prism face is reactive, the (red) basal plane is inert.
Nanostructured anisotropy

Nanostructures allow flexibility in controlling anisotropy
Graphitic CNT with high surface area

Enhancement of surface area from 16 m²/g to 347 m²/g
Graphene

100 x 100 nm

Wintterlin et al, PRB, 76, 2007
Graphite oxidation

F. Atamny
Acid-base groups
Surface functional groups
Carbon as Catalyst
metal-free heterogeneous catalysis
Concept: carbon as oxidation catalyst

- Advantage over metals and oxides: only required oxygen present: selectivity control
- Design
  - Avoid burning of surface by suitable ordering of the oxygen-activating surface.
  - Create terminations for bonding covalently oxygen species (acid-base-functions).
  - Bend the surface to control bond localization and to tune C-O interaction.
  - Assume that oxygen sites can activate additional oxygen (catalytically active).
- Defects become essential.
Insufficient electronic localization at elevated temperature

Forced localization by bending the graphene: CNT/CNF
Styrene synthesis from Ethylbenzene

Dehydrogenation (non oxidative)

\[ \Delta H = +124.9 \text{ KJ/mol} \]

\[ \text{Dehydrogenation (non oxidative)} \]

Industrial Process:

- Reaction temperature \( T_{\text{reaction}} = 600 - 650 \text{ °C} \)
- Excess of overheated steam \( \text{H}_2\text{O}/\text{EB} = 10-15/1 \)
- Conversion 50-60 %
- Selectivity 90-95 %

\[ \text{Target process: ODH; Today not possible technologically} \]

\[ \text{Styrene synthesis from Ethylbenzene} \]

\[ \Delta H = -116 \text{ KJ/mol} \]

\[ \text{C} + 1/2 \text{O}_2 + \text{H}_2 \text{O} \]
How it may work

\[ \Delta E_{\text{ODH}} = 0.28 \text{ eV} \]

\[ \Delta E_{\text{H}_2\text{O}} = -1.92 \text{ eV/molecule} \]

At 673 K and O:EB 1:1 clear stability of nanoC, activated carbon is instable, hence unreliable kinetic data.
Variants: Immobilized, molecular

\[
\text{C}_6\text{H}_5 - \text{C}_2\text{H}_5 + 0.5\text{O}_2 \xrightarrow{400^\circ \text{C}} \text{C}_6\text{H}_5 - \text{C}_2\text{H}_3 + \text{H}_2\text{O} \quad -124 \text{ kJ/mol}
\]

Collab: FHI TH, MPI Mainz, FHI AC
Butane ODH: another challenge

Homogeneous reaction and thermal cracking were negligible
Structure function relation in butane ODH

- Prism face CNF
- Basal plane CNT
- Palm shell AC
The function of OH groups in metal-free catalysis
How metal free?

There is residual catalyst in CNT/CNF

Metals are intentionally or autogenously passivated by low T carbon deposition
EB dehydrogenation: oxygenated groups as active sites

Carrier gas (20% O₂ / 80% N₂), 1.2 % Eb (v), 40 ml/min,

In-situ PES experiment; two steady states by different residence times: difference in yield reflected in difference in oxygen functional groups.

kinetic verification
Synthesis of oxygen functional groups

The combination of fluid phase oxidation followed by calcination to 600 – 900 K generates a specific set of OH-groups

High resolution TPO through slow heating rate and back-mixing-free operation

The combination of fluid phase oxidation followed by calcination to 600 – 900 K generates a specific set of OH-groups
Active species during butane ODH

$^{18}\text{O}_2$ isotope labelling during in-situ reaction decorates only active sites and shows that basic functional groups are regenerated by gas phase oxygen.

XPS (high resolution) before and after reaction (bottom) show the preferred formation of basic functional groups and higher hydrophilicity in-situ reaction.
OH group modification by reaction

Strong change of OH distribution

Loss of most OH groups

Loss of acidity

(5%P) nanocyl
P modification: auto-inhibition of acidity

Inhibition of catalytic oxidation of carbon/carbon composites by phosphorus

Xianxian Wu *, Ljubisa R. Radovic

Department of Energy and Geo-Environmental Engineering, The Pennsylvania State University, University Park, PA 16802, USA

Received 18 March 2004; accepted 28 June 2005
Available online 15 August 2005

Carbon 2006
Conclusion

- The control of carbon nanostructure is now possible to a sufficient extent for directed experimentation.
- The effect of functional groups and reaction pathways was studied without interference of bulk oxides.
- The concept of “true surface catalysis” without sub-surface chemistry was demonstrated for selective oxidation:
  - EB, butane and propane were activated with promising results.
  - Bulk quantities of catalysts available.
How good is metal-free catalysis in ODH?

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Reactant</th>
<th>Conversion %</th>
<th>Selectivity %</th>
<th>Remarks</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mg$_x$VO$_y$</td>
<td>butane</td>
<td>9</td>
<td>70</td>
<td>H.H. Kung</td>
</tr>
<tr>
<td></td>
<td>propane</td>
<td>6</td>
<td>64</td>
<td>et al.</td>
</tr>
<tr>
<td>EB</td>
<td></td>
<td>25</td>
<td>80</td>
<td>1997</td>
</tr>
<tr>
<td>VMgO</td>
<td>butane</td>
<td>27</td>
<td>60</td>
<td>B.L. Yang</td>
</tr>
<tr>
<td>EB</td>
<td></td>
<td>30</td>
<td>55</td>
<td>1995</td>
</tr>
<tr>
<td>Palm Shell</td>
<td>butane</td>
<td>16</td>
<td>46</td>
<td>X. Liu</td>
</tr>
<tr>
<td>AC</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>CNT/P</td>
<td>butane</td>
<td>19</td>
<td>60</td>
<td>J. Zhang</td>
</tr>
<tr>
<td></td>
<td>propane</td>
<td>10</td>
<td>50</td>
<td>B. Frank</td>
</tr>
<tr>
<td>CNT</td>
<td>EB</td>
<td>65</td>
<td>95</td>
<td>J. Zhang</td>
</tr>
<tr>
<td>CNT Immob.</td>
<td>EB</td>
<td>35</td>
<td>80</td>
<td></td>
</tr>
</tbody>
</table>
Designed supports: Pd/Au on oxidized CNT
Liquid phase oxidation of benzyl alkohol:

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Conversion</th>
<th>Selectivity benzaldehyde</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pd@Au AC X40S</td>
<td>30</td>
<td>&gt;99</td>
</tr>
<tr>
<td>Pd@Au PR-24</td>
<td>5</td>
<td>&gt;99</td>
</tr>
<tr>
<td>Pd@Au PR-24 ox 4430</td>
<td>29</td>
<td>&gt;99</td>
</tr>
<tr>
<td>Pd@Au [N-PR-24 (4441)]</td>
<td>59</td>
<td>&gt;99</td>
</tr>
<tr>
<td>Pd@Au baytubes</td>
<td>68</td>
<td>&gt;99</td>
</tr>
<tr>
<td>Pd@Au [baytubes ox (5028)]</td>
<td>67</td>
<td>98</td>
</tr>
<tr>
<td>Pd@Au [N-baytubes (5027)]</td>
<td>87 (30 min)</td>
<td>96 92</td>
</tr>
<tr>
<td>Pd@Au [N-baytubes (5053)]</td>
<td>57 (30 min)</td>
<td>&gt;99</td>
</tr>
</tbody>
</table>
Nanocarbons represent an attractive family of catalytic materials: metal-free and as supports.

Thank You
Improvement by tuning surface properties

SN 4505: 5wt%P₂O₅ loading oxidized nanocyl CNTs
reaction conditions: 180mg, 1.32%O₂, O₂:C₄=0.5, 10ml/min, 450 °C

<table>
<thead>
<tr>
<th></th>
<th>SN4505</th>
<th>5%FePO₄/nanocyl (4517)</th>
<th>Palmshell AC</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bu Conv (%)</td>
<td>19</td>
<td>15</td>
<td>16</td>
</tr>
<tr>
<td>C₄ Seleç(%)</td>
<td>59</td>
<td>41</td>
<td>46</td>
</tr>
</tbody>
</table>
Ammonia is an excellent choice as storage molecule for hydrogen in a carbon-free chemical energy cycle: challenge is the effective decomposition (no microscopic reversibility!)
Concept: nanocarbon supporting nano-metal

- In contrast to bulk carbon being a weak anchor for metals, nanocarbon is an excellent support.
- Its curvature-related electronic structure allows metal-carbon bonds to form.
- Its curvature allows for localized restructuring around metal nanoparticles.
- Its dense functionalisation allows for metal-heterobonds and for local nanostructures (polymers) to form.
A stable and active metal

Co is a “good” component, Fe is poor as nitridation reduces activity
MoC (N): a stable solution

Much better than supported Mo

Collab: MPI Golm (M. Antonietti)
Ammonia decomposition (fuel cell?)

Not the reverse of synthesis as different masi ($N_2$ vs NH)

Collab: FHI AC, MPI Mülheim, MPI Golm
Present state: activity and stability

Addition of Mo stabilizes, but no synergistic effect on activity

Nanostructured Co is the best system in T, rate slower than Ru

CNT as support is vital for obtaining stable nanostructures on non-reactive support
Highly functionalized nanocarbons: “blacks”

Fullerenoid soot

Probe D 9 C-K-Kanten

$\sigma^*$

$\pi^*$

Energieverlust [eV]

265 285 305 325 345

5 nm

1 nm
Surface functional groups

- carboxyl, COOR, COOH
- carbonyl, C=O
- alcohol, ether, C-OH
- C-O-C
- graphitic carbon
- isolated carbon
- ketone, esters C=O
- ether, C-OH, C-O-C

Binding Energy [eV]

- O1s
- C1s
Structure-function relations

The quantification can be used together with a determination of the average graphene size in a nanocarbon to derive structure-reactivity correlations.
TPO
: stabilizing effect of P addition
XPS analysis

Beware of oversimplification
Reaction pathway