“Dendritic Fibrous Nanosilica (DFNS) for Catalysis and CO₂ Capture-Conversion”

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Nano-Catalysts

- Nanoscale size
- Control over size, shape & morphology
- Catalyst separation by magnetic attraction
- Utmost exposed active sites
- Easy tailoring of surface functionalities
Challenges of Nano-Catalysts?

1. Stability

2. Isolation and Recyclability

Heterogeneous Nano-Catalysts?

1\textsuperscript{st} Component: \textbf{Active sites}
\textit{E.g. metal nanoparticles}

2\textsuperscript{nd} Component: \textbf{Support}
\textit{e.g. high surface area silica}
High Surface Area of Silica is mostly due to the Pores and therefore NOT always accessible.

Conventional Silica

Fibrous Nano-Silica
Dendritic Fibrous Nano-Silica (DFNS)

1. Nano-Silica (50 to 1200 nm),

2. High surface area (500 to 1200 m²/g),

3. Thermal stability (up to 800°C),

4. Hydro-thermal stability,

5. Mechanical stability (up to 130 MPa),

6. Unique Fibrous surface morphology,

7. Easy to synthesize.

Polshettiwar et al.*
Angew. Chem. Int. Ed. 2010, 49, 9652,
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Chemical Science, 2012, 3, 2224,
ACS Catalysis 2012, 2, 1425
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Angew. Chem. Int. Ed. 2015, 54, 2190,
Angew. Chem. Int. Ed. 2015, 54, 5985,
ACS Catal. 2016, 6, 2770,
J. Mat. Chem. A, 2016, 4, 7005 and 2016, 4, 12416,
Sci. Reports 2016, 6, 24888,
Green Chem. 2016, 18, 5890,
ChemPlusChem 2016, 81, 1142,
ChemSusChem 2017, 10, 2182 and 2017, 10.1002/cssc.201701076
NanoCatalysis Group
Dendritic Fibrous Nanomaterials (DFNM)

- Dendritic Fibrous NanoSilica (DFNS/KCC-1)
- Dendritic Fibrous NanoTitania (DFNT)
- Dendritic Fibrous NanoTantalumOxide (DFNTO)
- Dendritic Fibrous NanoCobaltOxide (DFNCO)
- Dendritic Fibrous NanoCarbon (DFNC)
- Dendritic Fibrous NanoSilicaAluminate (DFNSA)

- Shaped Iron Oxide
- Shaped Cobalt Oxide
- Shaped MOF

Morphology Controlled Nanocatalysts

- Insights into the Catalytic Activity of Nitrated Fibrous Silica
- Tuning the Activity of SBA-15-Oxynitrides
- Sustainable Protocols for Supported Metal Nanocatalysts
- Ultrasmall NPs and Pseudo Single Atoms of Pt and Au based Catalysts with High TON

“Functionalyzed Nanomaterials for CO₂ Capture”

- Design of CO₂ Sorbents & Insights into the Effect of the Morphology
- Tuning the CO₂ Capture Efficiency by Fiber Density of KCC-1
- Silica Nano Sheets for CO₂ Capture

“Hybrid Photocatalysts with Quantized Active Sites”

- Making KCC-1 Photoactive by Coating of TiO₂ on its Fibers using ALD
- Role of Fibrous Morphology in KCC-1 Supported TiO₂ Photocatalysts
- KCC-1 as Hard Template for the Synthesis of High Surface Area Nanostructured Metal Oxides

“Formation Mechanism and Dendritic Fibrous Nanomaterials”

- Shaped Iron Oxide
- Shaped Cobalt Oxide
- Shaped MOF
“After our discovery of DFNS, now more than 75 groups worldwide using DFNS, with around 200 citations and 150 reports of actual use of DFNS in various fields”
Properties of Dendritic Fibrous Nanosilica (DFNS)
SEM Images of DFNS
TEM Images of DFNS
Formation Mechanism of DFNS
Fractalization of Bicontinuous Microemulsion Droplets (BMDs)

CTAB

IV

BMDs

I

II

Lamellar Micelles

III

Alcohol

V
Applications of DFNS
Application of DFNS for Catalysis

Hydrogenolysis of Alkanes by DFNS/Ru

\[
\begin{align*}
C_nH_{2n+2} & \quad n = 2, 3, 4 \\
m = 1, \ldots (n-1) & \\
+ H_2 & \quad \text{DFNS/Ru, 175 } ^\circ \text{C} \\
\rightarrow & \\
C_mH_{2m+2} & \\
+ & \\
C_{n-m}H_{2(n-m)+2} & \\
\rightarrow & \\
CH_4 & 
\end{align*}
\]

Bouhrara, Fihri, Saih, Polshettiwar,* *ACS Catalysis, 2012, 2, 1425.*
Synthesis of Ru/KCC-1:

1. React with \( \text{NH}_2(\text{CH}_2)_3\text{Si(OEt)}_3 \) and reflux in toluene.
2. Reduce with \( \text{H}_2 \) at 400 °C.

Chemical structures and NMR spectra are shown to support the synthesis process.
Hydrogenolysis of Propane:

\[
\begin{align*}
\text{H}_3\text{C} & \quad \text{CH}_3 \\
\text{H}_2 & \quad \text{DFNS/Ru} \\
\text{H}_3\text{C} & \quad \text{CH}_3 \\
\end{align*}
\]

\[
\text{CH}_4
\]

---

“TON was greater than 13,000 and Even after 200 h, no change in conversion or selectivity was observed, and the catalyst worked as efficiently as like a fresh catalyst during this period”

Comparison (for propane hydrogenolysis)

DFNS/Ru, SBA-15/Ru and MCM-41/Ru

<table>
<thead>
<tr>
<th>Catalysts</th>
<th>Reaction Temperature</th>
<th>Conversion (%)</th>
<th>Selectivity for CH₄</th>
<th>Selectivity for C₂H₆</th>
<th>TON after 7 days</th>
</tr>
</thead>
<tbody>
<tr>
<td>DFNS-Ru</td>
<td>175 ºC</td>
<td>84</td>
<td>73</td>
<td>27</td>
<td>11010</td>
</tr>
<tr>
<td>SBA-15/Ru</td>
<td>175 ºC</td>
<td>77</td>
<td>73</td>
<td>27</td>
<td>7210</td>
</tr>
<tr>
<td>MCM-41/Ru</td>
<td>175 ºC</td>
<td>25</td>
<td>86</td>
<td>14</td>
<td>3927</td>
</tr>
</tbody>
</table>

“DFNS/Ru has TON (11010), which is nearly double than SBA-15/Ru (7210) and nearly triple than MCM-41 (3927). Also, it showed better stability compare to SBA-15 or MCM-41 system.”

Why does the DFNS/Ru nano-catalyst show elevated catalytic activity?

>>> Accessibility provides the explanation.

DFNS/Ru

Vs

MCM-41/Ru

Why does the DFNS/Ru nano-catalyst show elevated catalytic activity?

>>> Nanoparticle shape provides the explanation.

“Hexagonal nanoparticles contain several corners and sharp edges and the metal atoms at these sites possess the lowest coordination numbers. More reactive metal atoms at the edges and corners enhances the activity”
Why the DFNS/Ru nano-catalyst does not deactivate even after several reactions? >>> Restricted sintering provides the explanation.
Highly Monodispersed Metal NPs on DFNS

Application of DFNS for Catalysis

Suzuki Coupling of Halo Aromatics by DFNS/Pd

\[
\begin{align*}
R & \text{-} \begin{array}{c}
\text{Br} \\
\end{array} \\
+ & \\
\text{B(OH)}_2 & \\
\text{H}_2\text{O/EtOH} & \\
\text{K}_3\text{PO}_4, \ 100^\circ\text{C} & \\
\rightarrow & \\
R & \text{-} \begin{array}{c}
\text{aryl} \\
\text{aryl} \\
\end{array} \\
\text{Yield} & = 55-85\%
\end{align*}
\]

Application of DFNS for Catalysis - ORGANOMETALLIC

Novel Reaction “Hydro-Metathesis” by DFNS/TaH

\[
\text{DFNS/TaH} \quad \text{H}_2
\]

TON 800 in 60hr

Polshettiwar, Basset et al
### Application of DFNS for ORGANOCATALYSIS

<table>
<thead>
<tr>
<th>Sample Name</th>
<th>Surface Area (m²/g)</th>
<th>Nitrogen Content (wt %)</th>
<th>Conversion (%)</th>
<th>TON</th>
</tr>
</thead>
<tbody>
<tr>
<td>DFNS</td>
<td>669</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>DFNS-N400</td>
<td>650</td>
<td>1.13</td>
<td>62</td>
<td>12258</td>
</tr>
<tr>
<td>DFNS-N500</td>
<td>646</td>
<td>1.60</td>
<td>89</td>
<td>12323</td>
</tr>
<tr>
<td>DFNS-N600</td>
<td>639</td>
<td>1.83</td>
<td>91</td>
<td>11462</td>
</tr>
<tr>
<td>DFNS-N700</td>
<td>633</td>
<td>3.23</td>
<td>88</td>
<td>6148</td>
</tr>
<tr>
<td>DFNS-N800</td>
<td>578</td>
<td>5.63</td>
<td>81</td>
<td>3297</td>
</tr>
<tr>
<td>DFNS-N900</td>
<td>565</td>
<td>7.29</td>
<td>80</td>
<td>2378</td>
</tr>
<tr>
<td>DFNS-N1000</td>
<td>497</td>
<td>14.03</td>
<td>72</td>
<td>1194</td>
</tr>
<tr>
<td>DFNS-N1100</td>
<td>426</td>
<td>20.68</td>
<td>75</td>
<td>822</td>
</tr>
</tbody>
</table>
FT-IR spectra of KCC-1-N series

With increase in nitridation temperature, the intensity of the IR band for silanols at 3741 cm$^{-1}$ decreases, and new bands appeared corresponding to N-H stretching at 3516 and 3444 cm$^{-1}$ and N-H bending at 1552 cm$^{-1}$. 
An X-ray photoelectron spectroscopy (XPS) study showed peaks at binding energies of ca. -103, -and -400 eV for Si 2p and N 1s ionization, respectively. It revealed that with the increase in nitridation temperature, the binding energy for N 1s decreases as amine protons are replaced with silicon atoms. Similarly, the binding energy of the Si 2p electrons also decreases as electronegative oxygen atoms are replaced with comparatively less electronegative nitrogen atoms.
(a) $^1H$ and (b) $^{29}Si$ MAS-NMR spectra of KCC-1-N series

KCC-1: $-94$, $-104$ and $-113$ ppm, for $Q^2$ ($SiO_2(OH)_2$), $Q^3$ ($SiO_3OH$) and $Q^4$ ($SiO_4$), respectively.

KCC-1-N (up to 700 °C) : $-90$ ppm : surface amine groups;
KCC-1-N (above 700 °C) : $-70$ ppm : for silazane (-Si-NH-Si-) species.
Dynamic Nuclear Polarization (DNP) Enhanced $^{15}$N NMR

$^1$H→$^{15}$N CP-MAS of DFNS-N impregnated with 16 mM bis-TEMPO-bisketal in EtCl$_4$ (DFNS-N is moisture sensitive) at 9.4 T and MAS 8 kHz

Solid base Catalysis using SBA-15-Oxynitrides

DFNS- based Photo-Catalysts
DFNS/TiO$_2$ by ALD for Photocatalysis

- High TiO$_2$ loading, with minimum reduction in surface area, and hence more accessibility of active sites.
- Increase in light harvesting property due to fibrous structure of the DFNS, (enhanced scattering and internal reflections of incident light),
- Large adsorption of dye and water molecules during dye degradation and water splitting respectively due to high and accessible surface area of DFNS.

Precursor: Ti(OCH(CH$_3$)$_2$)$_4$ & H$_2$O$_2$, 150 $^\circ$C, 1 Torr

Polshettiwar et al. ACS Catalysis 2016, 6, 2770–2784
STEM and EDS mapping of DFNS/TiO$_2$ series

Distribution of Ti species by Energy-dispersive X-ray spectroscopy (EDS) mapping.

Coating of TiO$_2$ on fibrous nano-silica DFNS was homogeneous and uniform
TiO₂ Loading

Catalysts | TiO₂ loading at C60 cycles (Wt %) | BET Surface Area (m²/g) (standard error ± 4 %) | Reduction in Surface Area (m²/g)
--- | --- | --- | ---
DFNS/TiO₂-C60 | 57 ± 3 | Before TiO₂ loading: 598 | After C60-TiO₂ cycles: 222 | 376
MCM-41/TiO₂-C60 | 39 ± 2 | Before TiO₂ loading: 962 | After C60-TiO₂ cycles: 421 | 541
SBA-15/TiO₂-C60 | 63 ± 3 | Before TiO₂ loading: 1391 | After C60-TiO₂ cycles: 182 | 1209
The diffraction peak at $2\theta = 25$ degree for anatase TiO$_2$ was monitored in PXRD.

Unlike previous reports, even after heat treatment, most of the materials did not show any peaks for crystalline TiO$_2$ in their XRD pattern.

However, we started to observe a weak signal for crystalline TiO$_2$ from C30 samples onwards which indicated that layer thickness is playing crucial role in the TiO$_2$ crystallization.
1\textsuperscript{st} band at 202-230 nm was assigned to ligand to metal charge transfer (LMCT) from O to Ti in isolated TiO$_4$ units with tetrahedral titanium.

2\textsuperscript{nd} band at 250-370 nm was also due to LMCT from O to Ti but with titanium in octahedral environment.

Intensity of band at 250-370 nm increases with ALD cycle, indicating that tetrahedral Ti sites were converting into octahedral Ti-sites.

Red shift in the band at 250-370 nm with increase in ALD cycles, may be due to formation of bigger nanoparticles at higher ALD cycles, forming Ti-sites with increased co-ordination numbers.
Bandgap Measurement

- Band gap value decreased from 3.53 eV to 3.28 eV for as-prepared samples from C1 to C60.
- When samples were heated at 700 °C, the band gap decreased as compared to its as-prepared counterpart, indicating the transformation of amorphous TiO₂ to crystalline TiO₂.
- We also observed blue shift in the band gap within heated samples from C1 to C60.

Quantum confinement effect?

Nano-particle formation?

Bandgap measurement using Kubelka-Munk function $K = (1-R)/2R$, and Tauc plot $(K*\nu)^{1/2} = f(\nu)$
Nanoparticles Formation after Heat Treatment

Heat treatment fragmented the amorphous TiO$_2$ layers and crystalline NPs were formed.

TiO$_2$ NPs particle size increases with increase in ALD cycles as well as with increase in heating temperature.

Since the particle sizes were very small and they were highly dispersed, we did not see their signature peaks in PXRD until C30 cycles.
Photocatalytic dye degradation of Rh-B under UV light
## Catalyst Comparison: DFNS vs SBA-15 vs MCM-41

<table>
<thead>
<tr>
<th>S.No.</th>
<th>Catalysts</th>
<th>Rate Constant (min⁻¹)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>DFNS/TiO₂-C60-700</td>
<td>0.0684 ± 0.0047</td>
<td>This MS</td>
</tr>
<tr>
<td>2</td>
<td>MCM-41/TiO₂-C60-700</td>
<td>0.0254 ± 0.0010</td>
<td>This MS</td>
</tr>
<tr>
<td>3</td>
<td>SBA-15/TiO₂-C60-700</td>
<td>0.0139 ± 0.0001</td>
<td>This MS</td>
</tr>
<tr>
<td>4</td>
<td>P25 nano-powder</td>
<td>0.0414 ± 0.0017</td>
<td>This MS</td>
</tr>
<tr>
<td>6</td>
<td>SiO₂@TiO₂</td>
<td>0.00473</td>
<td>J. Photochem. Photobio. A. Chem 2007, 185, 19</td>
</tr>
<tr>
<td>7</td>
<td>Diatomite@TiO₂</td>
<td>0.034209</td>
<td>App Catal. A Gen 2013, 458, 103</td>
</tr>
<tr>
<td>8</td>
<td>Opal@TiO₂</td>
<td>0.010437</td>
<td>App Catal. A Gen 2013, 458, 103</td>
</tr>
<tr>
<td>9</td>
<td>Porous Silica@TiO₂</td>
<td>0.012529</td>
<td>App Catal. A Gen 2013, 458, 103</td>
</tr>
</tbody>
</table>
TOF: KCC-1 vs SBA-15 vs MCM-41

Catalysts

TOF (min\(^{-1}\)) \times 10^{-7}

- KCC-1/TiO\(_2\)-C60-700
- MCM-41/TiO\(_2\)-C60-700
- SBA-15/TiO\(_2\)-C60-700
- P-25
Solution Phase TiO$_2$ Coating on DFNS

**Photocatalytic \( \text{H}_2 \) Production**

<table>
<thead>
<tr>
<th>Entry</th>
<th>Catalyst</th>
<th>Light Region</th>
<th>Light Source</th>
<th>Reaction Conditions</th>
<th>( \text{H}_2 ) yield (( \mu \text{mol h}^{-1} \ \text{g}^{-1} \text{TiO}_2 ))</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>DFNS-Ti-2.5-750</td>
<td>UV</td>
<td>300-W Xe lamp (250&lt; ( \lambda ) &lt;385 nm), 111 mw/cm(^2)</td>
<td>5 mg of catalyst, 2.5 mL of ethanol, 50 mL of H(_2)O</td>
<td>26398</td>
<td>This Work</td>
</tr>
<tr>
<td>2</td>
<td>( \text{TiO}_2/\text{SiO}_2 ) (Ti-MCM-48-1-200.)</td>
<td>UV</td>
<td>A 500-W Xe lamp optical transmission filter (230 nm &lt; ( \lambda ) &lt; 380 nm)</td>
<td>2.0 mg of catalyst, 1.6 mL of H(_2)O, 0.4 mL of methanol in a 5-mL quartz reactor.</td>
<td>12750</td>
<td>69</td>
</tr>
<tr>
<td>3</td>
<td>( \text{SiO}_2/\text{TiO}_2 )</td>
<td>UV</td>
<td>300-W Xe lamp</td>
<td>0.1 g of catalyst, water:CH(_3)OH (80:20), 0.5 % Pt</td>
<td>12487</td>
<td>73</td>
</tr>
<tr>
<td>4</td>
<td>( \text{TiO}_2/\text{MCM-48-im-200} )</td>
<td>UV</td>
<td>300-W Xe lamp equipped with an optical cut-off filter (230 nm &lt; ( \lambda ) &lt; 380 nm).</td>
<td>2.0 mg of catalyst, 1.6 mL of deionized water, 0.4 mL of methanol in a 5-mL quartz reactor.</td>
<td>3830</td>
<td>70</td>
</tr>
<tr>
<td>5</td>
<td>Mesoporous ( \text{TiO}_2/\text{SiO}_2 )</td>
<td>UV</td>
<td>300-W Xe lamp</td>
<td>0.1 g of catalyst, 10 mL of water and 5 mL of CH(_3)OH, 1% Pt</td>
<td>3108</td>
<td>65</td>
</tr>
<tr>
<td>6</td>
<td>1.2 wt % Pt/TiO(_2)</td>
<td>UV</td>
<td>350-W Hg lamp</td>
<td>0.1 g of catalyst, 54 mL of water and 6 mL of CH(_3)OH</td>
<td>2700</td>
<td>82</td>
</tr>
<tr>
<td>7</td>
<td>0.5% Pt/TiO(_2/)KIT-6-1.75</td>
<td>UV</td>
<td>300_W Xe</td>
<td>100 mg of catalyst suspended in 270 mL of a 20% methanol aqueous solution</td>
<td>2179</td>
<td>83</td>
</tr>
</tbody>
</table>

*Visible light catalysis is in good progress*
DFNS- based Pseudo Single Atom Catalysts
“Nanocatalysis is no more field of just academic curiosity but can be practically used by industries to develop sustainable processes”
Gold Nanocatalysts with Half Million TON using DFNS

Gold Nanocatalysts with Half Million TON using DFNS

DFNS/Au (10%)  DFNS/Au (5%)  DFNS/Au (1%)  DFNS/Au (0.5%)  DFNS/Au (0.05%)
STEM Image of Pseudo Single Atoms of DFNS/Au (0.05%)
Silane to Silanols by DFNS/Au

\[ \text{H-Si-Ph} \xrightarrow{\text{DFNS/Au}} \text{Si-OH-Ph} \]

**DFNS/Au (5%)**

- 1.5 mmol
- 3 mmol
- 5 mmol
- 7 mmol
- 10 mmol

**DFNS/Au (1%)**

- 1.5 mmol
- 3 mmol
- 5 mmol
- 7 mmol

**DFNS/Au (0.5%)**

- 1.5 mmol
- 3 mmol
- 5 mmol
- 7 mmol

**DFNS/Au (0.05%)**

- 1 mmol
- 1.5 mmol
- 3 mmol

Turnover Number vs. Time (h)
DFNS/Au vs Best Reported Catalysts  
(for DMPS oxidation)

<table>
<thead>
<tr>
<th>Entry</th>
<th>Catalysts</th>
<th>TON</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>DFNS/Au (0.05%)</td>
<td>5,91,000</td>
<td>This Work</td>
</tr>
<tr>
<td>2</td>
<td>MnO₂-Au</td>
<td>98,333</td>
<td>Applied Catalysis B: Environmental, 2016, 184, 35.</td>
</tr>
<tr>
<td>7</td>
<td>Au-SiO₂</td>
<td>983</td>
<td>Applied Catalysis B: Environmental, 2016, 184, 35.</td>
</tr>
<tr>
<td>8</td>
<td>Bentonite/Au</td>
<td>245</td>
<td>ChemComm. 2016, 52, 10625.</td>
</tr>
</tbody>
</table>
For fair comparison, catalysts need to be compared on the basis of multiple parameters such as,

- Turnover Number (TON)
- Turnover Frequencies (TOF)
- Reaction Temperature (Energy)
- Scale of Reaction (Upscalability)
- Recyclability of Catalysts (Stability)

**Figure of Merit (FOM)**

$$FOM = \frac{(TOF) \times N \times S}{298 + \Delta T}$$

- N - Number of Cycles
- S - Scale of Reaction
- $\Delta T$ - Deviation in the reaction temperature from the ambient (taken as 298 K).

However, generally maximum number of reaction cycles carried out to study the stability of the catalysts varies in various reports, and to minimize this inconsistency, we have chosen five cycles as maximum number required to confirm the stability and recyclability of the catalysts.
Comparison of the DFNS/Au (0.05%) catalyst with various reported catalysts for DMPS oxidation. Single-digit FOM values were scaled to 20 for visualization in the figure.
**Reaction Mechanism**

*Mechanism for silane to silanols by DFNS/Au*

\[
\text{DFNS-APTS + DMPS} \rightarrow \text{DFNS/Au(10%) + DMPS}
\]
Substrate Scope

\[
\begin{align*}
R_1 \quad & \quad \text{KCC-1-APTS/Au (0.05\%)} \quad \text{THF-H}_2\text{O, 45 \degree C, 22 h} \\
R_2-Si-H & \quad \rightarrow \quad R_1 \quad \text{R}_2-Si-OH \\
\end{align*}
\]

- \( \text{Ar-Si-OH} \) 100\% (100\%), 591000
- \( \text{Pr-Si-OH} \) 62\% (100\%), 366420
- \( \text{Ar-CH}_2\text{-Si-OH} \) 95\% (100\%), 561450
- \( \text{5-norbornene-Si-OH} \) 56\% (100\%), 330960
- \( \text{Ph-Si-OH} \) 98\% (100\%), 579180
- \( \text{Ph-Si-OH} \) 75\% (100\%), 443250
- \( \text{Ph-Si-OH} \) 50\% (100\%), 295500
Reaction Scope - Alcoholysis of silane

\[
\text{Si-H} + \text{R-OH} \xrightarrow{\text{KCC-1-APTS/Au (0.05%)}} \text{Si-O-R}
\]

<table>
<thead>
<tr>
<th>Reaction</th>
<th>Product</th>
<th>Yield</th>
<th>MW</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \text{Si-O-CH}_2-\text{CH}_2 )</td>
<td>( \text{Si-O-CH}_2-\text{CH}_2 )</td>
<td>100% (56%), 221000</td>
<td></td>
</tr>
<tr>
<td>( \text{Si-O-CH}_2-\text{CH}_2-\text{CH}_2 )</td>
<td>( \text{Si-O-CH}_2-\text{CH}_2-\text{C}_2 )</td>
<td>100% (72%), 284000</td>
<td></td>
</tr>
<tr>
<td>( \text{Si-O-CH}_2-\text{C}=\text{C} )</td>
<td>( \text{Si-O-CH}_2-\text{C}=\text{C} )</td>
<td>91% (78%), 280000</td>
<td></td>
</tr>
<tr>
<td>( \text{Si-O-CH} )</td>
<td>( \text{Si-O-CH} )</td>
<td>88% (74%), 257000</td>
<td></td>
</tr>
</tbody>
</table>
Reaction Scope - Hydrosilylation of aldehydes

\[
\text{Si-H} + \text{R-CHO} \xrightarrow{\text{KCC-1-APTS/Au (0.05\%)}} \text{Si-O-R}
\]

\[
\text{Si-O-CH}_3 \quad \text{Si-O-Cl} \quad \text{Si-O-F}
\]

- 70% (72%), 199000
- 70% (71%), 257000
- 100% (56%), 221000
- 98% (65%), 359000

THF, 75°C, 24 h
Pseudo Single Atoms of Platinum on DFNS
DFNS based CO$_2$ Capture & Conversion
DNFS based Sorbents for CO\textsubscript{2} Capture

- Capture Good Amount of CO\textsubscript{2}
- At Moderate Temperature and Atmospheric Pressure
- Faster Kinetics
- Stable and Recyclable
- Selectivity

## KCC-1- Silicon Oxynitrides for CO₂ capture

![Image of KCC-1 and KCC-1-N with NH₃ and temperature indications]

### Properties

<table>
<thead>
<tr>
<th>Properties</th>
<th>KCC1-N700</th>
<th>SBA15-N700</th>
<th>MCM41-N700</th>
</tr>
</thead>
<tbody>
<tr>
<td>Surface Area (m² g⁻¹)</td>
<td>418</td>
<td>728</td>
<td>935</td>
</tr>
<tr>
<td>Pore Volume (cm³ g⁻¹)</td>
<td>0.65</td>
<td>1.05</td>
<td>0.87</td>
</tr>
<tr>
<td>N₂ Contents (%)</td>
<td>6.8</td>
<td>7.89</td>
<td>8.38</td>
</tr>
<tr>
<td>CO₂ Capture Capacity (mmol g⁻¹)</td>
<td><strong>1.86</strong></td>
<td><strong>2.22</strong></td>
<td><strong>2.72</strong></td>
</tr>
<tr>
<td>at 1 bar, 25 °C</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>% Wt. Loss up to 800 °C</td>
<td>2.90</td>
<td>1.95</td>
<td>3.53</td>
</tr>
</tbody>
</table>

1) Good CO$_2$ capture capacity,

2) Faster kinetics, which will have a shorter adsorption/desorption cycle time and cause more gas to be absorbed in a shorter amount of time;

3) Easy regeneration and efficient reuse of sorbents;

4) Excellent mechanical strength, which will help to sustain the overall CO$_2$ capture process;

5) High thermal stability in an inert and oxidative environment, which will help these materials retain a good capture capacity even after several temperature swing regeneration cycles in an industrial environment; and
DFNS- Amine for CO$_2$ capture

B. Singh and V. Polshettiwar,
*J. Mat. Chem. A*, 2016, 4, 7005.

“Emerging Investigators themed issue”
DFNS-Amines for CO$_2$ Capture

Conclusions

“Morphology Makes the Difference”

“unique textural properties of DFNS seems to the reason behind remarkable activity of DFNS based nanocatalysts, photocatalysts and CO$_2$ sorbents”
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Mr. B. Singh
Mr. M. Dhiman
Mr. A. Maity
Mr. Krishna Kant
Mr. Amit Mishra
“CO₂ Is The Most Serious Problem Mankind Has Ever Faced”

“I alone absorb 22 KG of CO₂ in a year. All I ask in return is that "you let me live"

saytrees.org

“Nanotechnology can help Combat Climate Change”