Green Chemistry by Nanocatalysis

Fibrous Nano-Silica (KCC-1) Based Catalysts

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**Current Challenges**

**Catalysis for Energy:**
1. Improvement in catalytic processes that will increase resources and energy utilization efficiencies.
2. Green and sustainable utilization of coal and bio-mass.
3. Efficient photocatalysis for water splitting.
4. Carbon dioxide capture, storage and conversion.

**Catalysis for Environment:**
1. Cleaning up emissions, such as VOC, ozone, pesticides, air & water pollution.
2. Development of green catalytic processes, using alternative energy, water as a solvent etc.

**Ways to go: Novel Catalytic Materials**
1. High selectivity (atom economy).
2. Use of cheap and abundant metals.
Nano-Catalysts

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

1. Isolation and Recyclability

2. Stability

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
Fibrous Nano-Silica (KCC-1)

1. Nano-Silica (200 to 1000 nm),
2. High surface area (500-900 m²/g),
3. High thermal stability (up to 800°C),
4. Hydro-thermal stability,
5. Excellent mechanical stability (up to 130 MPa),
6. UNIQUE Fibrous surface morphology (never seen before).
7. Easy to synthesize

V. Polshettiwar* et al.

Angew. Chem. Int. Ed. 2010, 49, 9652,
Angew. Chem. Int. Ed. 2011, 50, 2747,
Chemical Science, 2012, 3, 2224,
ACS Sustainable Chem. Eng. 2013, 1, 1192,
Angew. Chem. Int. Ed. 2015, 54, 2190,

Polshettiwar, US 20110253643
SEM images of KCC-1

3D-Tomography of Silica Nanospheres

Proposed Mechanism of KCC-1 Formation

CPB Micelles → TEOS → CPB → Assembly of silicate → \((\text{SiO}_4)^4-\) → Calcination → KCC-1

50 nm
Proposed Mechanism of KCC-1 Formation
Size and Fiber Density Controlled KCC-1

- High & Accessible Surface Area (1244 m²/gm)
- Controllable Particle Size (170 to 1120 nm)
- Tunable Fiber Density
- High Pore Volume (2.18 cm³/gm)
Possible Applications of KCC-1

- Catalyst
- Chromatography
- Paints
- Drug Delivery
- Cosmetics
- CO₂ Capture
Hydrogenolysis of Alkanes by Ru/KCC-1

\[ C_nH_{2n+2} + H_2 \xrightarrow{\text{Ru/KCC-1, } 175 \, ^\circ C} C_mH_{2m+2} + C_{n-m}H_{2(n-m)+2} \]

\[ \rightarrow CH_4 \]

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

1. Reflux in toluene

   \[ \text{NH}_2(\text{CH}_2)_3\text{Si(OR)}_3, \]

2. RuCl\(_3\), H\(_2\)O, RT

3. H\(_2\), 400 °C

---

(a) \( ^{29}\text{Si} \) CP-MAS NMR

(b) \( ^{13}\text{C} \) CP-MAS NMR

(c) \( ^{29}\text{Si} \) CP-MAS NMR

(d) Weight (mg) vs. Temperature (°C)
Hydrogenolysis of Propane:

\[
\begin{align*}
\text{H}_3\text{C} & \quad \text{KCC-1/Ru} \quad \text{H}_2 \\
\text{CH}_3 & \quad \rightarrow \\
\text{H}_3\text{C} & \quad \text{CH}_3 \quad + \quad \text{CH}_4 \\
\end{align*}
\]

“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”

Bouhrara, Fihri, Saih, Polshettiwar,* *ACS Catalysis, 2012, 2, 1425.*
**Comparison** (for propane hydrogenolysis)

**KCC-1/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>KCC-1/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>

"KCC-1/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 KCC-1/Ru nano-catalyst show elevated catalytic activity?

>>> Accessibility provides the explanation.

Bouhrara, Fihri, Saih, Polshettiwar,*  *ACS Catalysis, 2012, 2, 1425.*
Why does the KCC-1/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 KCC-1/Ru nano-catalyst does not deactivate even after several reactions?

>>> Restricted sintering provides the explanation.

![Image](before_after_reaction_images.png)

**Before Reaction**

**After Reaction**
Application of KCC-1 for Catalysis

Suzuki Coupling of Halo Aromatics- by Pd/KCC-1

\[ \begin{align*}
R & \quad \text{Br} \\
+ & \\
\text{B(OH)}_2 & \\
\text{H}_2\text{O/EtOH} & \quad 0.06 \text{ mol} \% \\
\text{K}_3\text{PO}_4, 100^\circ\text{C} & \quad \text{Pd/KCC-1} \\
R & \quad \text{R} \\
\text{Yield} & = 55-85\% 
\end{align*} \]

Highly Monodispersed Metal NPs on KCC-1

Engineering Selectivity in Nanocatalysis
By KCC-1/Pt
Pseudo Single Atom Catalysis by KCC-1/Au

Acetalization Reaction with TON of 40000
Application of KCC-1 for Catalysis - ORGANOMETALLIC

Novel Reaction “Hydro-Metathesis” by TaH/KCC-1

\[ \text{TaH/KCC-1, } \text{H}_2 \]

TON 800 in 60hr

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# Nitridation of KCC-1

<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>KCC-1</td>
<td>669</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>KCC-1-N400</td>
<td>650</td>
<td>1.13</td>
<td>62</td>
<td>12258</td>
</tr>
<tr>
<td>KCC-1-N500</td>
<td>646</td>
<td>1.60</td>
<td>89</td>
<td>12323</td>
</tr>
<tr>
<td>KCC-1-N600</td>
<td>639</td>
<td>1.83</td>
<td>91</td>
<td>11462</td>
</tr>
<tr>
<td>KCC-1-N700</td>
<td>633</td>
<td>3.23</td>
<td>88</td>
<td>6148</td>
</tr>
<tr>
<td>KCC-1-N800</td>
<td>578</td>
<td>5.63</td>
<td>81</td>
<td>3297</td>
</tr>
<tr>
<td>KCC-1-N900</td>
<td>565</td>
<td>7.29</td>
<td>80</td>
<td>2378</td>
</tr>
<tr>
<td>KCC-1-N1000</td>
<td>497</td>
<td>14.03</td>
<td>72</td>
<td>1194</td>
</tr>
<tr>
<td>KCC-1-N1100</td>
<td>426</td>
<td>20.68</td>
<td>75</td>
<td>822</td>
</tr>
</tbody>
</table>

NH₃ (300 ml/min)
400-1100°C
Dynamic Nuclear Polarization (DNP) Enhanced $^{15}$N NMR

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

**KCC-1/TiO₂ by ALD for Photocatalysis**

- High TiO₂ 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 KCC-1, (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 KCC-1.

Precursor: Ti(OCH(CH₃)₂)₄ & H₂O₂, 150 °C, 1 Torr
Formation mechanism of TiO$_2$ coated KCC-1 by atomic layer deposition (ALD)

(Collaborator: Prof. Hao Feng)

$^{29}$Si CP-MAS three main signals at $\delta = -96$, -105 and -115 ppm, attributed to $Q^2$ [SiO$_2$(OH)$_2$], $Q^3$ [SiO$_3$OH], and $Q^4$ [SiO$_4$] sites, respectively.

From C1 to C30, a decrease in the ratio of $Q^3$ to $Q^4$ indicates that more $Q^4$ sites are forming, due to the formation of more and more Si-O-Ti bonds.

$^1$H MAS-NMR spectrum shows the signals at $\delta = 1.2$ and 4.1 ppm for surface silanols and tilanols respectively.

$H_2O = H_2O/H_2O_2$
STEM and EDS mapping of KCC-1/TiO$_2$ series

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

Coating of TiO$_2$ on fibrous nano-silica KCC-1 was homogeneous and uniform
TiO\textsubscript{2} Loading

<table>
<thead>
<tr>
<th>Catalysts</th>
<th>TiO\textsubscript{2} loading at C60 cycles (Wt %)</th>
<th>BET Surface Area (m\textsuperscript{2}/g) (standard error ± 4 %)</th>
<th>Reduction in Surface Area (m\textsuperscript{2}/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>KCC-1/TiO\textsubscript{2}-C60</td>
<td>57 ± 3</td>
<td>598</td>
<td>222</td>
</tr>
<tr>
<td>MCM-41/TiO\textsubscript{2}-C60</td>
<td>39 ± 2</td>
<td>962</td>
<td>421</td>
</tr>
<tr>
<td>SBA-15/TiO\textsubscript{2}-C60</td>
<td>63 ± 3</td>
<td>1391</td>
<td>182</td>
</tr>
</tbody>
</table>
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 TiO$_2$ to crystalline TiO$_2$.
- 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 $K = (1-R)2/2R$, and Tauc plot $(K*\text{hv})^{1/2} = f(\text{hv})$
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.
Catalysis by KCC-1/TiO$_2$ series

Photocatalytic dye degradation of Rh-B under UV light
Photocatalytic dye degradation of Rh-B under UV light
## Catalyst Comparison: KCC-1 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>KCC-1/TiO(_2)-C60-700</td>
<td>0.0684 ± 0.0047</td>
<td>This MS</td>
</tr>
<tr>
<td>2</td>
<td>MCM-41/TiO(_2)-C60-700</td>
<td>0.0254 ± 0.0010</td>
<td>This MS</td>
</tr>
<tr>
<td>3</td>
<td>SBA-15/TiO(_2)-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>7</td>
<td>Diatomite@TiO(_2)</td>
<td>0.034209</td>
<td>App Catal. A Gen 2013, 458, 103</td>
</tr>
<tr>
<td>8</td>
<td>Opal@TiO(_2)</td>
<td>0.010437</td>
<td>App Catal. A Gen 2013, 458, 103</td>
</tr>
<tr>
<td>9</td>
<td>Porous Silica@TiO(_2)</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
**Catalyst Comparison: KCC-1 vs SBA-15 vs MCM-41**

**Water Splitting under UV light**

KCC-1/TiO$_2$-C60-700 exhibited better performance than its MCM-41 and SBA-15 counterparts (Fig. a). Moreover, this catalyst showed a constant hydrogen evolution rate throughout photocatalytic reactions (Fig. b), suggesting its robust nature and stability in water splitting also.
Nanomaterials for CO$_2$ Capture

- Capture Good Amount of CO$_2$
- At Moderate Temperature and Atmospheric Pressure
- Faster Kinetics
- Stable and Recyclable
- Selectivity

## KCC-1- Silicon Oxynitrides for CO$_2$ capture

![Diagram showing the conversion of KCC-1 to KCC-1-N](image)

<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 (m$^2$ g$^{-1}$)</td>
<td>418</td>
<td>728</td>
<td>935</td>
</tr>
<tr>
<td>Pore Volume (cm$^3$ g$^{-1}$)</td>
<td>0.65</td>
<td>1.05</td>
<td>0.87</td>
</tr>
<tr>
<td>N$_2$ Contents (%)</td>
<td>6.8</td>
<td>7.89</td>
<td>8.38</td>
</tr>
<tr>
<td>CO$_2$ Capture Capacity (mmol g$^{-1}$) at 1 bar, 25 °C</td>
<td><strong>1.86</strong></td>
<td><strong>2.22</strong></td>
<td><strong>2.72</strong></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,
3) Easy regeneration and efficient reuse,
4) Excellent mechanical strength,
5) High thermal stability,

*Unstable in presence of water/moisture.*
Due to their unique dendritic, fibrous, extensive large pore structures, the KCC-1-based materials are generally found to have higher adsorption capacity for salmon DNA than the corresponding MCM-41 materials.

KCC-1-based materials are also more effective in transporting and delivering genes in cellular environments than their MCM-41 counterparts.

Magnetic Nano-Catalysts

Because of the super-paramagnetic nature of these nano-catalysts, it can be recovered by simply using external magnets.

“Magnetic Attraction Not Filtration”

Not only SIZE but SHAPE also makes the difference
Low-temperature oxidation of CO catalysed by $\text{Co}_3\text{O}_4$ nanorods

Xiaowei Xie$^{1,*}$, Yong Li$^{1,*}$, Zhi-Quan Liu$^2$, Masatake Haruta$^{3,4}$ & Wenjie Shen$^1$
Use of 3D-Nano-Metal Oxide as a CATALYST

V. Polshettiwar * et al.

Sci. Report, 2015, 5, 9733;
ChemSusChem, 2014, 7, 529;
ACS Sus. Chem. Eng. 2013, 1, 66;
ChemSusChem 2012, 5, 1241;
Nanoscale, 2012, 4, 5202;
RSC Advance, 2012, 2, 7048;
ACS Nano 2009, 3, 728;
Chem. Commun. 2008, 6318;
Conclusions

Due to fibrous morphology of KCC-1, increase in the accessibility of active sites and then the overall catalytic or capture efficiency was observed.
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