

# SiliaCat<sup>®</sup>: Novel Silica-Supported Catalysts

Lynda Tremblay\*, Valerica Pandarus, Geneviève Gingras, Annie Michaud, and François Béland  
SiliCycle<sup>®</sup> Inc. (www.silicycle.com) 114-1200 St-Jean-Baptiste Avenue, Quebec City, Quebec, G2E 5E8, Canada

\*(lyndatremblay@silicycle.com)

Si

## Introduction

Supported catalysts are available on different supports such as polymer, charcoal, alumina, and silica. Silica presents many other advantages such as no swelling, good mechanical and thermal stabilities, and ease of scalability.

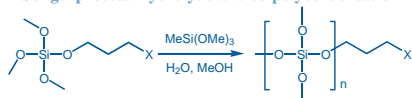
SiliCycle<sup>®</sup> has developed innovative heterogeneous silica-based catalysts made of leach-proof organoceramic matrix. SiliaCat catalysts are highly efficient and selective. They provide high turnover number (TON) in oxidation and coupling reactions such as Heck, Suzuki, etc.

## The SiliaCat Matrix

SiliaCat are made from an innovative technology:

- Organically modified silica
- Sol-gel hybrid organic-inorganic material

Sol-gel process: hydrolysis and co-polycondensation



## SiliaCat Properties

Sol-Gel Properties:

- High thermal stability
- Inertness within entrapped molecules
- Reagent concentrated at the surface of the material
- Robust

Catalyst Properties:

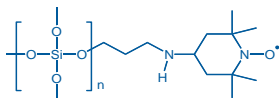
- High catalyst loading
- High surface area
- High turnover number (TON)
- Recyclable (multi-uses)
- Leach-proof organoceramic matrix
- Easy purification

## The SiliaCat TEMPO

SiliaCat TEMPO is an effective and useful oxidizing catalyst for delicate primary and secondary alcohol substrates into valued carbonyl derivatives.

SiliaCat TEMPO Characteristics:

- Loading: 0.8-0.85 mmol/g
- Surface: 450-550 m<sup>2</sup>/g
- Particle size: 100-150 microns



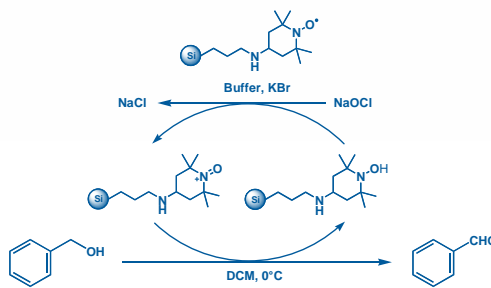
SiliaCat TEMPO [R723-100]

## Highly Recyclable

Recycle	Time (min)	Yield (%)
1 <sup>st</sup> to 6 <sup>th</sup>	30	100
7 <sup>th</sup>	30 / 60	88 / 96
8 <sup>th</sup>	30 / 60	95 / 100
9 <sup>th</sup>	30 / 60	97 / 100
10 <sup>th</sup>	30 / 60	90 / 100

SiliaCat TEMPO (1 mol%) for BnOH oxidation to PhCHO

## SiliaCat TEMPO Catalytic Cycle



## Catalytic Performance



Entry	Mol %	Time (h)	Yield (%)	TON	Si (ppm)*
1	0.1	1	95	950	-
2	0.02	2	96	4800	-
3	0.02	3	100	5000	2
4	0.01	2	83	8300	3
5	0.01	3	95	9500	1.6
6	0.01	4	96.5	9650	1.5

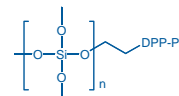
\* leaching

## The SiliaCat DPP-Pd

SiliaCat DPP-Pd is an effective and useful catalyst for coupling reactions such as Suzuki and Heck.

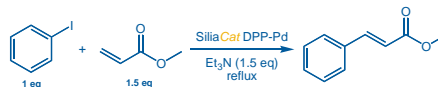
SiliaCat DPP-Pd Characteristics:

- Loading: 0.14 mmol/g
- Surface: 180-292 m<sup>2</sup>/g
- Particle size: 60-120 microns

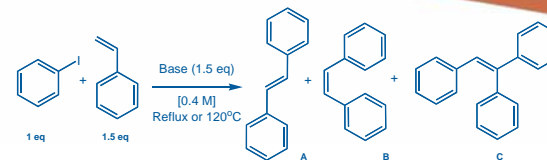


SiliaCat DPP-Pd

## Heck Coupling



MeCN	Time (h)	Yield (%)	Si-DPP-Pd (mol%)
0.4 M	24	100	0.5
0.4 M	24	80	0.1
(neat)	24	80	0.1
0.8 M	8	93	0.1
(neat)	20	100	0.1



Base	Solvent	Time (h)	Yield (%) A / B / C	Si-DPP-Pd (mol%)
KOAc	DMF	24	100 (90 / 9.5 / 0.5)	0.5
Na <sub>2</sub> CO <sub>3</sub>	DMF	24	67 (62 / 47 / 0)	0.5
Et <sub>3</sub> N	MeCN	24	93 (77 / 6 / 11)	0.1
Et <sub>3</sub> N	H <sub>2</sub> O	24	75 (70 / 5 / 0)	0.1
Et <sub>3</sub> N	(neat)	20	100 (95 / 5 / 0)	0.1

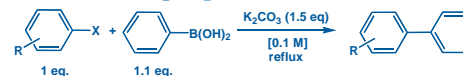
## Heterogeneous vs Homogeneous Catalyst

SiliaCat DPP-Pd: - Higher selectivity  
- No phosphine contamination

	Yield (%)	P (ppm)
SiliaCat DPP-Pd (0.1 mol %)	98 (A) / 2 (B)	0*
Pd(OAc) <sub>2</sub> , TPP (1 mol %)	70 (A) / 22 (B) / 8 (C)	6030

\* leaching

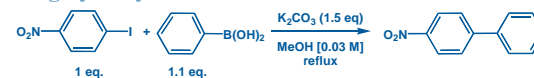
## Suzuki Cross-Coupling



SiliaCat DPP-Pd (0.01 mol%)

X	R	Solvent (10 / 1)	Time (h)	Yield (%)	TON
I	NO <sub>2</sub>	EtOH/H <sub>2</sub> O	2	100	10 000
I	H	EtOH/H <sub>2</sub> O	2	100	10 000
Br	H	PrOH/H <sub>2</sub> O	4	100	10 000

## Highly Recyclable



Recycle	Time (min)	Yield (%)
1 <sup>st</sup> to 7 <sup>th</sup>	30	100

## Conclusion

SiliaCat are innovative heterogeneous catalysts. They are selective and useful for various organic reactions. SiliaCat offer an attractive alternative to expensive catalysts. They present many advantages such as high TON, can be recycled many time (without loss of activity), ease of purification, etc. SiliaCat are convenient tools for green chemistry.

Acknowledgements to Prof. Mario Pagliaro (Institute of Chemistry and Technology of Natural Products, CNR, Italy)

**SILICYCLE** Inc.