

Organotextile Catalysis

Lee, J. W.; Gall, T. M.; Opwis, K.; Song, C. E.; Gutmann, J. S.; List, B.*
Science, 2013, 341, 1225

1. Introduction

1.1 Background

- Heterogeneous organocatalysts (Fig. 1A-C)
 - high turnover efficiency
 - preventing leaching
 - recyclability
- Challenges of heterogeneous organocatalysts
 - no general immobilization method for high stability, recyclability, and reactivity
 - complex and time consuming immobilization method
 - narrow range of organocatalyst that can be immobilized.

1.2 How to solve these problems?

- Organotextile (Nylon 6, 6) (Fig. 1D, Fig. 2, and Fig. 3) as a support
 - high durability, broad accessibility
 - Alkylation of glycine derivatives at α -position with olefin through photoirradiation has been reported¹.
- The authors expected that photoirradiation of nylon 6, 6 can immobilize various organocatalysts on the surface.
- Efficient immobilization of organocatalysts on high durable support nylon 6, 6 can be achieved.

This work

- Development of facile immobilization method on the surface of nylon 6, 6 through photoirradiation
- Application of the immobilized organotextile catalyst as acid, base, and chiral catalyst
- High durability, recyclability, and reactivity of organotextile catalyst
- Large scale reaction under simple flow reactor system

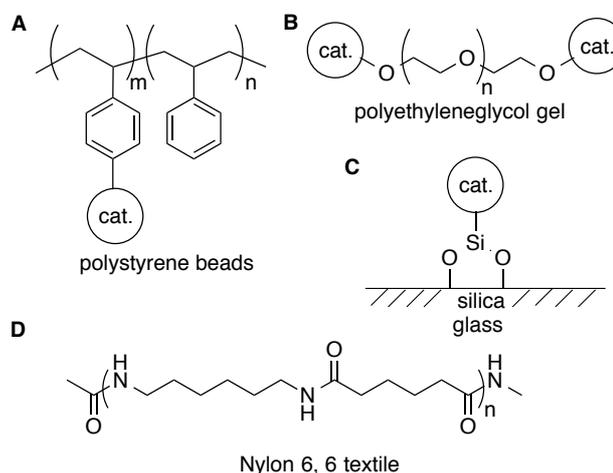


Fig. 1. Examples of heterogeneous organocatalysts



Fig. 2. A photograph of organotextile



Fig. 3. Electron microscopic image of organotextile

2. Results and Discussion

2.1 Immobilization of organocatalysts (Fig. 4)

- Lewis basic catalyst, Brønsted acid catalyst, and bifunctional chiral organocatalyst were successfully functionalized by irradiating the organotextile (Scheme 1).

- Increasing irradiation time slightly decreased the amount of immobilized organocatalyst (Table 1).

→ Degradation of the textile and organic catalysts occurred by long irradiation.

→ Only 5 minutes irradiation were required.

- PETA (penta-erythritol triacrylate) as radical initiator improved the amount of catalyst loading (Table 1).

2.2. Catalytic activity and recyclability

- Acid and base catalyst

- The reactions proceeded in the similar yield even with the same amount of catalyst loading in homogeneous catalyst case (eqs. 1–3).

→ High reactivity of organocatalysts supported by textile, which has large surface area and capillary action caused by the folded shape on the surface.

- Catalysts were easily recovered by decantation, washing with organic solvent, and drying in the air.

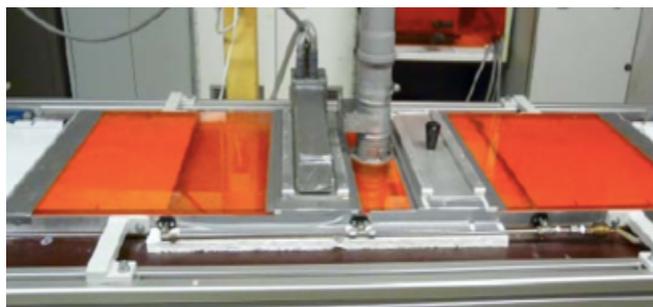


Fig. 4. The irradiation machine

Scheme 1. Reaction conditions for the photochemical immobilization. (A) Lewis basic catalyst (B) Brønsted acid catalyst (C) bifunctional chiral catalyst

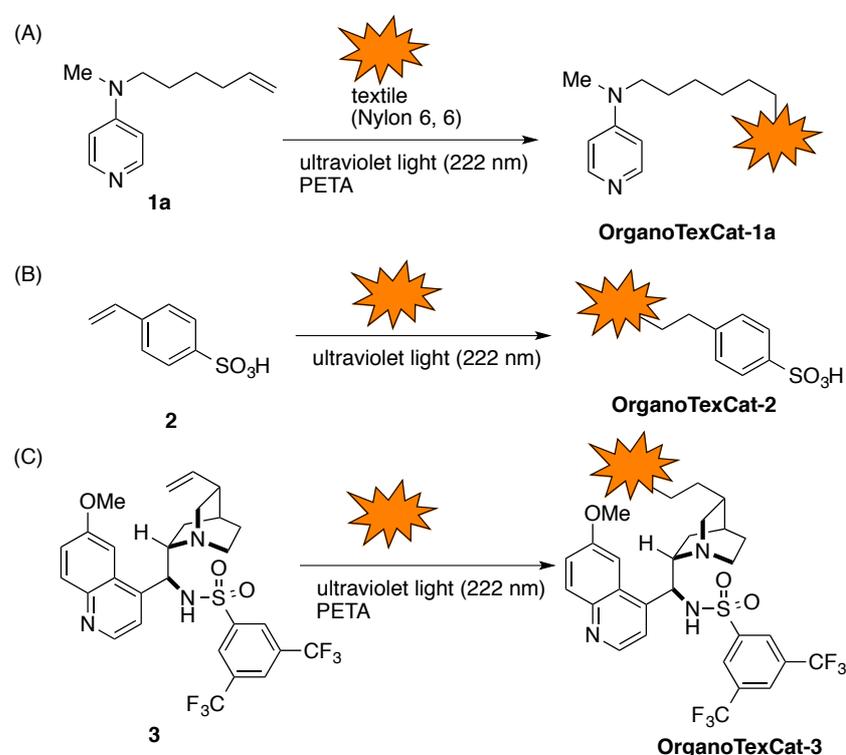


Table 1. Optimization of the immobilization conditions for 1a on textile

entry	1a (mmol/sheet)	Irradiation time (repeat N x min)	PETA (mmol/sheet)	Catalyst loading ^a (mmol/g)
1	0.3	2 x 5	0	0.00744
2	0.3	2 x 5	0.17	0.01136
3	0.3	2 x 10	0	0.00731
4	0.3	2 x 10	0.17	0.01126

^a The amount of catalyst loading to the organotextile (mmol)/organotextile (g), organotextile is 1.25 (g)

- Catalysts showed good recyclability without erosion (Fig. 5).

→ The deactivation due to the formation of acid-base salt was recovered by washing the surface with triethylamine

- Catalysts could work and recycled under the harsh reaction requiring high pressure and temperature (eq. 2).

→ The amount of leaching of organocatalyst from textile is small, which suggested the high stability and durability of organotextile.

- The conversion of the substrate was dependent on the organocatalysts' substituents on the olefin (Table 2).

→ Higher substitution on the olefin (entries 1-3) might prevent side reaction during photochemical reaction.

→ Poor conversion of styrene derivatives (entry 4) might be due to the polymerization.

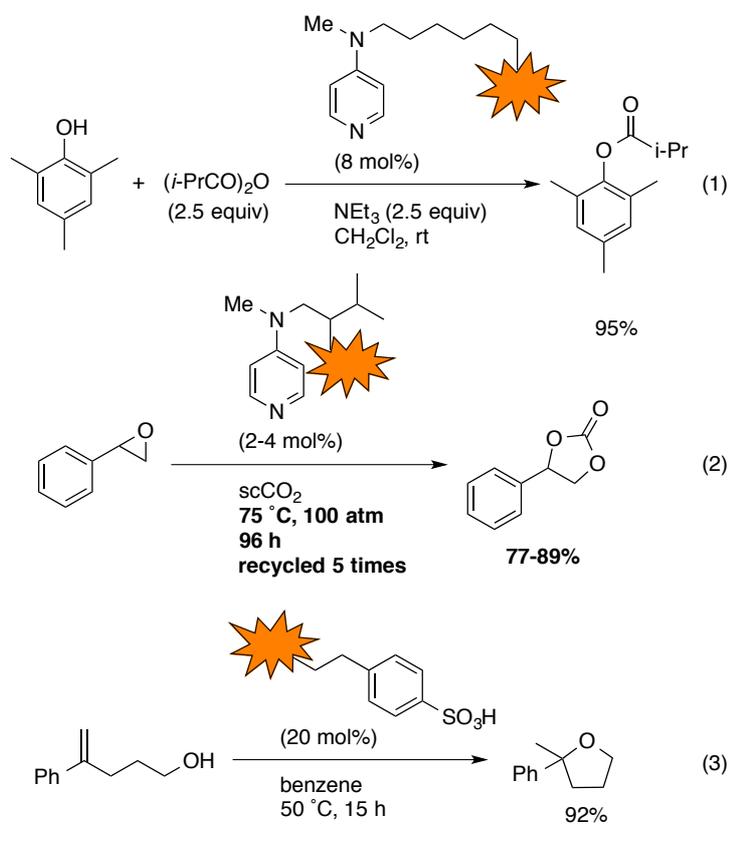


Table 2. Catalytic activity of 1a derivatives

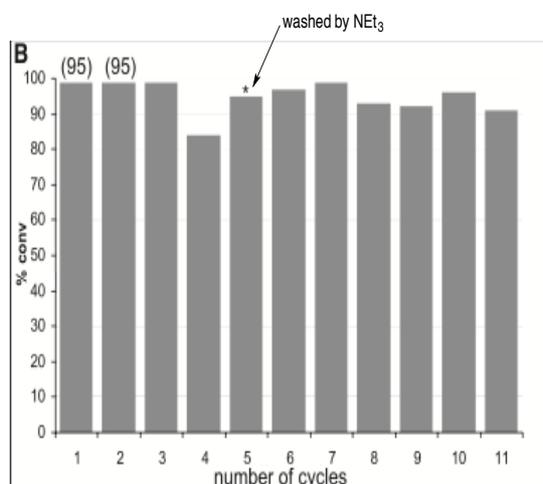


Fig. 5. Recycling experiments of OrganoTexCat-1a (eq. 1). *After the 4th cycle, OrganoTexCat was washed by NEt₃.

entry	monomers	Catalyst loading (mmol/g)	conversion (%) ^a
1	1b	0.0088	29
2	1c	0.0065	35
3	1d	0.0087	64
4	1e	0.0059	26

^a Conversion of phenol 4 to acylated product 5 as shown eq. 1

- Bifunctional chiral catalyst

- Chiral catalyst supported by textile showed similar enantioselectivity to the homogeneous catalyst (Scheme 2).

- Organotextile catalyst showed robustness by recycling experiments (Fig. 6).

→ The desired products were obtained without erosion of enantioselectivities for more than 220 cycles.

→ Deactivation of the catalyst after 231st cycle was recovered by increasing the catalyst amount, which suggests detachment of catalytically active species from textile.

- Organotextile catalyst could be easily applicable to the flow system in large scale (Fig. 7).

→ Textile material showed good absorption ability for organic solvents via capillary action.

→ Textile material is superior in large surface area and uniform catalyst immobilization thanks to the capillary action.

Scheme 2. Desymmetrization of anhydrides catalyzed by OrganoTexCat 3.

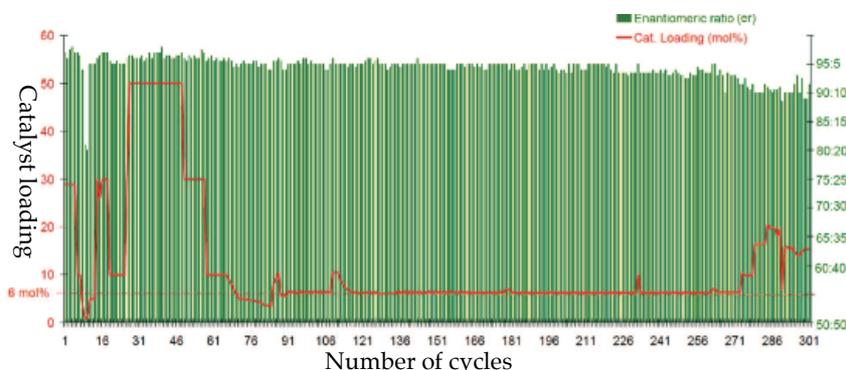
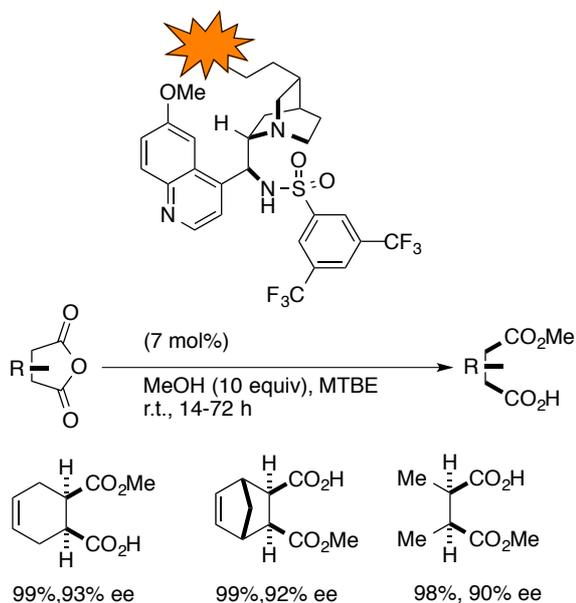


Fig. 6. Recycling experiments. Identical organotextile was used, and catalytic loading was controlled by changing the amount of the substrate.

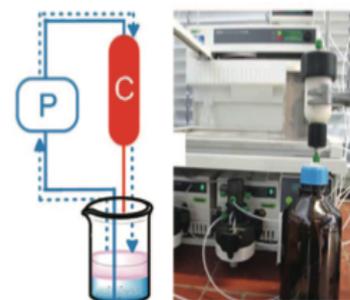


Fig. 7. Schematic illustration of the continuous circle reactor

3. Conclusion

- first example of using organotextile as a robust solid support for organocatalysts
- Organotextile catalysts were easily prepared through photoirradiation.
- Organotextile catalysts showed excellent stability, activity, and recyclability thanks to the large surface area and capillary action.

4. Reference

¹ M. Y. Mel'nikov; N. V. Fok, *Russ. Chem. Rev.* **1980**, 49, 131.

Abbreviation

