

Electrooxidation of Alcohols in an Aqueous *N*-Oxyl-Immobilized Silica Gel Disperse System

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N-Oxyl-mediated electrooxidation of alcohols has been intensively investigated and well recognized as a prominent procedure for oxidation of various 1° and 2°-alcohols. In a preceding paper,¹⁾ we reported the first example of a silica gel-disperse electrolysis which can offer an organic solvent-free-electrooxidation system. In our continuing studies on electrooxidation of alcohols in the silica gel-disperse system, we found an *N*-oxyl-immobilized silica gel disperse system in which the disperse phase as well as the disperse media could be repeatedly used for the oxidation of alcohols to the corresponding carbonyl compounds, offering a totally closed system.

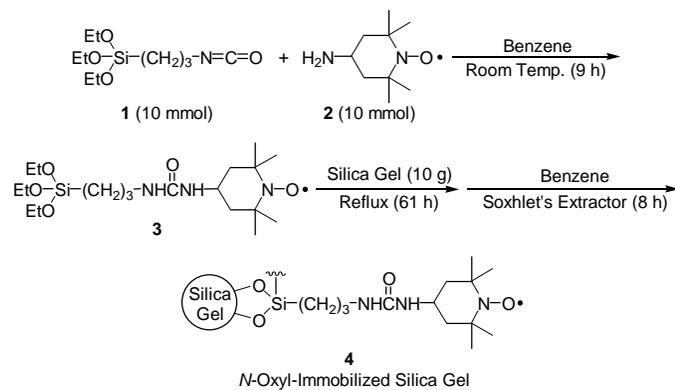
Immobilization of *N*-oxyl on the silica gel surface was performed by reaction of 3-(triethoxysilyl)propyl ester **1** with 4-amino-2,2,6,6-tetramethylpiperidine-1-oxyl **2** in benzene for 9 h, affording the corresponding urea **3** which was dissolve in benzene and heated to reflux with silica gel (Merck, Silica Gel 60, 43-60 μm) for 61 h, yielding pale orange solids (Scheme 1). The content of *N*-oxyl moiety was estimated 0.6 mmol/g by elemental analysis (C, 11.90; H, 1.78; N, 2.60).

A typical procedure of the electrolysis is as follows: In a beaker-type undivided cell were placed 1-(4-chlorophenyl)ethyl alcohol (**5a**, 1 mmol), *N*-oxyl-immobilized silica gel **4** (500 mg), and an aqueous saturated sodium hydrogencarbonate containing sodium bromide (20 w%) (6.0 mL). Two platinum electrodes were immersed into the mixture, and a constant current (30 mA, 2.23 h, 2.5 F/mol) was supplied at 0 °C under vigorous stirring to afford 4-chloroacetophenone (**6a**) in 83% yield (Scheme 2).

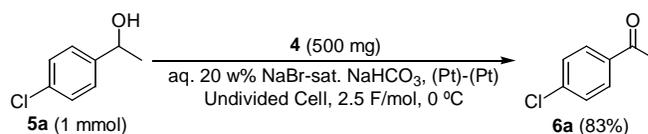
The *N*-oxyl-immobilized silica gel **4** as well as the disperse media (aq. 20w% NaBr-sat. NaHCO₃) could be repeatedly used without significant change of the product (Table 1), indicating that the newly devised silica gel-disperse electrolysis system offers a totally closed system without any waste materials.

The *N*-oxyl-immobilized silica gel disperse electrolysis system was successfully applied to the electrooxidation of various alcohols. The representative results are summarized in Table 2.

1) Tanaka, H.; Kawakami, Y.; Goto, K.; Kuroboshi, M.
Tetrahedron Lett. **2001**, 42, 445.



Scheme 1



Scheme 2

Table 1. Recycling Use of the *N*-Oxyl Mediator and the Aqueous Media^{a)}

Entry	Yield 6a (%) ^{b)}	Recovered 5a (%) ^{b)}
1	94 (83) ^{c)}	- (-) ^{c)}
2	92	-
3	95	-
4	92	-
5	93	-

^{a)} *N*-Oxyl mediator and the aqueous media were recovered and repeatedly used.

^{b)} Yields were determined by GC analysis using acetophenone as an internal standard.

^{c)} Isolated yield.

Table 2. Electrooxidation of Alcohols

Substrate	Electricity (F/mol)	Products	Yield (%) ^{a)}
5a	2.5	6a	83 (82) ^{b)}
5b	2.5	6b	84 (84) ^{b)}
5c	2.5	6c	84 (82) ^{b)}
5d	2.5	6d	76 (41) ^{b)}
5e	2.5	6e	86 (86) ^{b)}
7a	4.5	8a	88 (92) ^{b)}
7b	4.5	8b	48 (74) ^{b)}
7c	4.5	8c	59 (84) ^{b)}

^{a)} Isolated yield.

^{b)} *N*-Oxyl-adsorbed silica gel disperse system.