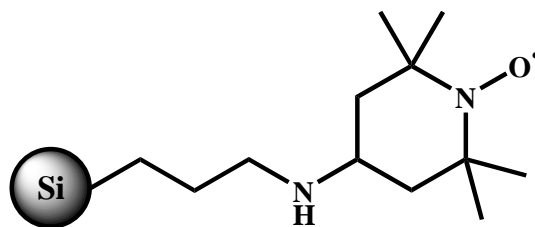


Use of *SiliaCat*TM TEMPO


Carbonyl groups are among the most important functional groups in organic chemistry and their introduction by the oxidation of alcohols is a process of major importance. *SiliaCat*TM TEMPO is a catalyst for selective oxidation of primary and secondary alcohols to aldehydes and ketones respectively. The major advantage of this reagent is the possibility to obtain good yields under mild conditions in the absence of toxic heavy metals. *SiliaCat*TM TEMPO can be used in stoichiometric amount as well as catalytically with a terminal oxidant allowing the closure of the catalytic cycle. *SiliaCat*TM TEMPO is provided under its nitroxyl form and must be transformed to its active form, the oxoammonium ion, prior to use.

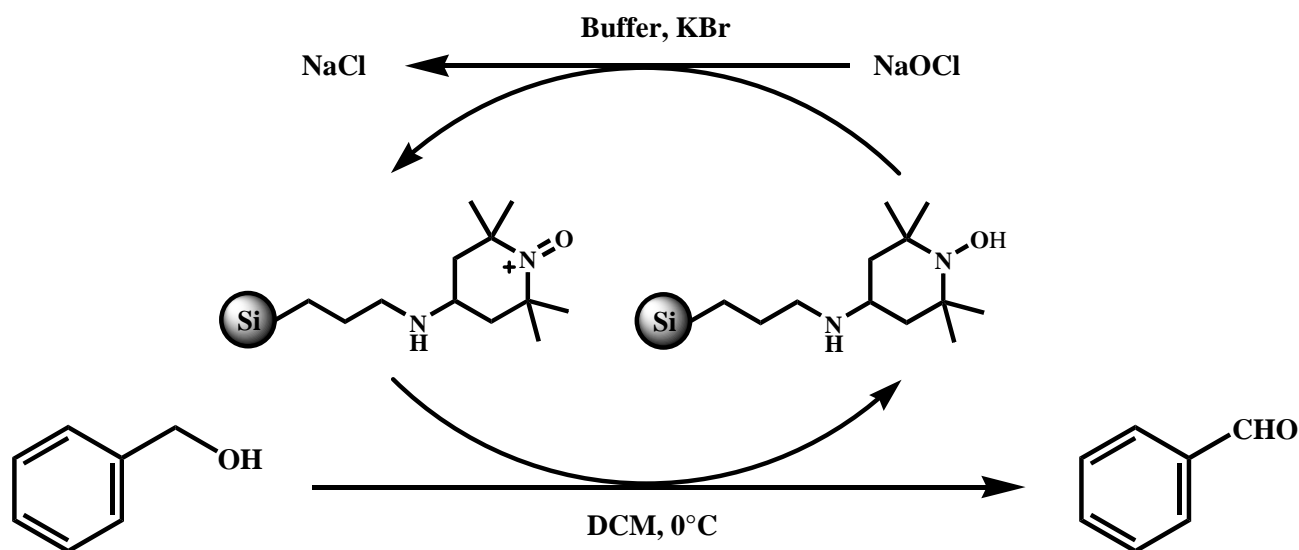


Figure 1: Catalytic oxidation of benzaldehyde in biphasic system

Catalytic oxidation of benzaldehyde

Benzaldehyde (1.00 eq.) was mixed with *SiliaCat*TM TEMPO (0.01 eq.) in DCM to which 0.35 M NaOCl (1.25 eq.) buffered with NaHCO₃ is added. The addition of 0.10 eq. of KBr permits to form the most reactive co-oxidant, BrOCl. The reaction is carried out at 0°C and is complete after 5 minutes. After filtration, the organic phase was separated, dried over MgSO₄, evaporated, and purified by column chromatography. Yield and purity were determined by GC-FID.

Table 1: Catalytic oxidation of benzyl alcohol with SiliaCat™ TEMPO

pH	Time (min)	% Yield (% Purity) ^a
8.6	5	71 (99.4)
9	5	75 (99.7)

A: Determined by GC-FID

Activation method (stoichiometric oxidation)

Add 4 M HCl (6 eq.) in dioxane to a stirred 0.5 M solution of *N*-chlorosuccinimide (5 eq.) in DCM. Stir for 5 min. before adding **SiliaCat™ TEMPO** (1 eq.), stir for 15 min., filter, wash with anhydrous dioxane and DCM, and dry under vacuum.

General oxidation procedure

Mix the alcohol (1 eq.) with freshly activated **SiliaCat™ TEMPO** (4 eq.) in anhydrous DCM. For the oxidation of primary alcohols, stir for 1 h and for secondary alcohols, for 2 h.

All solvents must be HPLC grade.

Efficiency of the **SiliaCat™ TEMPO** has been compared to its polymer-supported equivalent. Our product proved to be equal or superior in most cases with fewer equivalents. Results are presented in table 2. It is also interesting to note the fast kinetics imparted by the silica support: for the oxidation of benzyl alcohol to benzaldehyde, the conversion was over 95 % after only 5 minutes.

Table 2 : Efficiency of supported TEMPO for the oxidation of alcohols

Alcohol	Final product	Yield, PS-TEMPO (%) 5 eq.	Yield, Si-TEMPO (%)		
			4 eq.	2 eq.	1 eq.
Benzyl alcohol	Benzaldehyde	>95	>95	>95	80
3-Phenyl 1-propanol	3-phenylpropanal	90	>95	58	26
1-Phenyl 1-propanol	Phenylpropanone	>95	>95	90	55
Piperonyl alcohol	Piperonal	>95	90	90	50
1,4-butanediol	γ -butyrolactone	65	76	33	5