

Silica sulfuric acid/KClO₃/wet SiO₂ as an efficient heterogeneous method for the oxidation of alcohols under mild conditions[†]

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Abstract: A combination of silica sulfuric acid and potassium chlorate in the presence of wet SiO₂ was used as an effective oxidising agent for the oxidation of alcohols to their corresponding aldehyde or ketone derivatives in acetonitrile or toluene with good yields.

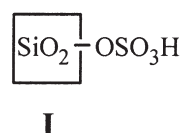
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For oxidation of organic functionalities, one turns often to high-valent metal oxides or their mineral salts.¹ Classic reagents of this type are manganese dioxide (MnO₂), potassium permanganate (KMnO₄), chromium trioxide (CrO₃), potassium chromate (K₂CrO₄), and potassium dichromate (K₂Cr₂O₇).² These are all frequently-used reagents, whether in the laboratory or in industry, and yet they are beset with problems. For satisfactory and reproducible results, these oxidants demand vigorous control of the experimental conditions. The other drawbacks against such oxidants and their use in multistage organic synthesis, in spite of their power, are their lack of selectivity, strong protic and aqueous conditions, low yields of the products, and tedious work-up.³ For instance, overoxidation of aldehydes to carboxylic acids or formation an ester is often an unavoidable side reaction.⁴ Very recently, three excellent procedures have been reported for the oxidation of alcohols, two of them using buthyl triphenyl phosphonium periodate, the Nafion-cerium (IV) and Nafion chromium (III) systems for oxidation of alcohols.^{5,6} The third one, is a microwave irradiation method for the oxidation of alcohols under solvent free conditions.⁷

In continuation of our studies on the application of inorganic acidic salts and silica chloride,⁸ we found that silica gel reacts with chlorosulfonic acid to give silica sulfuric acid (I) which is an excellent candidate for sulfuric acid replacement in organic reactions without any limitations such as sulfonation of activated aromatic rings and destruction of acid-sensitive functional groups.⁹⁻¹⁴ Such heterogeneous reagent systems have many advantages, such as simple experimental procedures, mild reaction conditions and minimisation of chemical wastes as compared to their liquid phase counterparts.⁸⁻¹⁴ The above fact encouraged us to seek a completely heterogeneous system for the oxidation various alcohols, and we have investigated a number of different reaction conditions based upon the *in situ* generation of HClO₃ at the surface of SiO₂ in low concentration by inorganic acidic resin i.e. silica sulfuric acid and potassium chlorate. We now report a simple and convenient method for the effective conversion of alcohols (1) to their corresponding aldehyde or ketone derivatives (2) under heterogeneous conditions (Scheme 1).

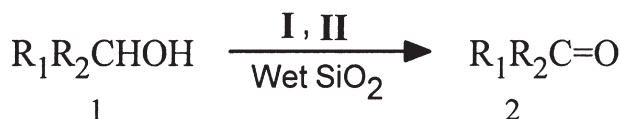
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[†] This is a Short Paper, there is therefore no corresponding material in *J Chem. Research (M)*.



Different types of alcohols (1) were subjected to oxidation reaction in the presence of silica sulfuric acid (I), KClO₃ (II), and wet SiO₂ in acetonitrile or toluene. The oxidation reactions were performed under completely heterogeneous conditions with good to excellent yields (Table 1). It was also observed that the oxidation of primary alcohols (1) gives only aldehydes.

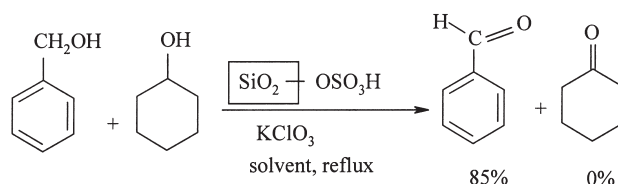
The present oxidation reaction can be readily carried out by placing silica sulfuric acid (I), KClO₃ (II), and wet SiO₂ in acetonitrile or toluene in a reaction vessel and efficiently stirring the resulting heterogeneous mixture under reflux conditions. The results and reaction conditions are given in Table 1.



Scheme 1

In order to show the chemoselectivity of the method we have carried out the successful oxidation of benzyl alcohol in the presence of cyclohexanol (Scheme 2 and Entry 11).

In conclusion, the cheapness and the availability of the reagents, and excellent yields make this method attractive for the large-scale operations. This procedure is very simple and contamination by over oxidation of side-products is avoided. Moreover, the new element here is that the oxidation reaction



Scheme 2

Table 1 Oxidation of various alcohols(2.5mmole) to aldehydes and ketones by silica sulfuric acid (I)(0.2g), KClO₃ (II)(1mmole, 0.122g), and wet SiO₂(60%w/w)(0.2g) in organic solvent under heterogeneous conditions

Entry	Substrate	Product	Solvent	Condition	Time/min	Yield/%
1	Benzyl alcohol	Benzaldehyde	Acetonitrile	Reflux	35	90
2	Cyclohexanol	Cyclohexanone	Acetonitrile	Reflux	70	82
3	<i>m</i> -Methoxy benzylalcohol	<i>m</i> -Methoxy benzaldehyde	Toluene	Reflux	60	50
4	Hydroquinone	<i>p</i> -Benzoquinone	Acetonitrile	Reflux	30	90
5	Benzhydrol	Benzophenone	Toluene	Reflux	30	60
6	1-Hexanol	Hexanal	Acetonitrile	Reflux	60	80
7	Benzoin	Benzil	Toluene	Reflux	60	50
8	<i>p</i> -Chloro benzylalcohol	<i>p</i> -Chloro benzaldehyde	Acetonitrile	Reflux	45	88
9	2-Pentanol	2-Pentanone	Acetonitrile	Reflux	60	70
10	1-Butanol	Butanal	Acetonitrile	Reflux	60	82
11	Benzylalcohol + Cyclohexanol	Benzaldehyde	Acetonitrile	Reflux	35	85

occurred under heterogeneous conditions. We believe that the present methodology would be an important addition to existing methodologies.

Experimental

General: Chemicals such as alcohols, potassium chlorate, toluene, acetonitrile and silica gel were purchased from Fluka, Merck and Aldrich chemical companies. Silica sulfuric acid was synthesised according to the our previously reported procedure.⁹⁻¹² The oxidation products were characterised by comparison of their spectral (IR, ¹H-NMR), TLC and physical data with authentic samples.

Oxidation of hydroquinone to *p*-benzoquinone; a typical procedure: A mixture of hydroquinone (0.275 g, 2.5 mmole,), potassium chlorate (0.122 g, 1 mmole), silica sulfuric acid (0.2 g) and wet SiO₂ (60% w/w, 0.2 g) in acetonitrile (5 ml) was stirred at in reflux for 30 minutes. The heterogeneous mixture was filtered and the solvent was removed *in a vacuum*. The solid was crystallised from *n*-hexane. The *p*-benzoquinone was obtained in good yield (Table 1).

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