

Hydrogen Peroxide Oxidations catalysed by Metallosilicalite Xerogels

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Metallosilicalite xerogels of the type $\text{MO}_x\text{-SiO}_2$ where M is Ti^{IV} , V^{V} , Mo^{VI} , W^{VI} and Se^{IV} have been prepared by the sol-gel method and used as heterogeneous catalysts for the epoxidation, allylic oxidation and carbon-carbon bond cleavage of alkenes, the hydroxylation of phenols, and the oxidation of alcohols to ketones by hydrogen peroxide.

Emphasis in the manufacture of fine chemicals has in the past mostly been on the use of stoichiometric reagents commonly used by synthetic chemists. For oxidations, often used oxidants are dichromate, permanganate or manganese dioxide. Processes using these oxidants produce enormous amounts of waste.¹ Environmental and the resulting economic concerns now make it essential that new catalytic oxidation processes applicable to fine chemicals be developed. In this context, hydrogen peroxide, owing to its availability, low cost and environmentally safe by-products (water and molecular

oxygen) is the oxidant of choice. An important recent breakthrough in the field of the catalytic activation of hydrogen peroxide has been in the effective use of titanium substituted silicalite zeolite catalysts, TS-1² (MFI or ZSM-5 structure) and TS-2³ (MEL or ZSM-11 structure). The important features of these catalysts are (a) it is active in a variety of oxidations with hydrogen peroxide including the hydroxylation of phenol to a mixture of hydroquinone and catechol,⁴ the epoxidation of ethylene to ethylene oxide,⁵ the hydroxylation of alkanes⁶ and the ammonoxidation of

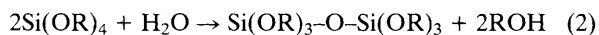
Table 1 Oxidation of alkenes catalysed by metallosilicalite xerogels^a

Substrate	Product ^c	TiO ₂ -SiO ₂ ^b		V ₂ O ₅ -SiO ₂ ^f		MoO ₃ -SiO ₂ ^g		WO ₃ -SiO ₂ ^h		SeO ₂ -SiO ₂ ⁱ	
		Yield ^d	Turnover ^e	Yield ^d	Turnover ^e	Yield ^d	Turnover ^e	Yield ^d	Turnover ^e	Yield ^d	Turnover ^e
Cyclooctene	Cyclooctene oxide	Trace	—	88.9	293	18.7	107	15.9	148	1.6	7
Styrene	Benzaldehyde	3.4	11	21.4	141	19.4	221	17.3	322	1.8	8
	Benzoic acid	—	—	12.0	118	2.1	34	2.1	58	—	—
Cyclohexene	Cyclohexene oxide	Trace	—	1.5	5	Trace	—	13.4	125	—	—
	Cyclohexen-2-ol	0.1	0.3	23.1	76	2.8	16	7.2	67	—	—
	Cyclohexen-2-one	0.4	1.2	25.8	85	4.2	24	8.1	75	—	—
Phenol	Hydroquinone	—	—	15.2	50	<1	—	<1	—	—	—
	Catechol	—	—	7.8	26	<1	—	<1	—	—	—
1-Phenylethanol	Acetophenone	2.1	7	89.9	297	16.8	95	63.4	590	3.4	15

^a Reaction conditions: 1 mmol substrate, 1 mmol 30% hydrogen peroxide, 5 mg catalyst, 1 ml Bu^tOH; 60 °C, 20 h. ^b Ratio TiO₂:substrate 1:320. ^c The reaction mixture was analysed by GLC with reference standards using an SPB-5 25 m 0.25 μ capillary column. All possible products except adipic acid (in the cyclohexene oxidation; not found) can be analysed by this method. The absence of adipic acid was confirmed by methylation of the reaction mixture with diazomethane and analysis of the resulting dimethyl adipate by GLC. ^d (mol product/mol substrate) × 100. ^e mol H₂O₂ required/mol catalyst. ^f Ratio VO_{2.5}:substrate 1:330. ^g Ratio MoO₃:substrate 1:572. ^h Ratio WO₃:substrate 1:930. ⁱ Ratio SeO₂:substrate 1:444.

cyclohexanone;⁷ (b) there is little non-productive hydrogen peroxide decomposition; (c) the catalyst is stable under reaction conditions and easy to recycle. Unfortunately, the synthesis of the zeolite catalysts is quite difficult,⁸ requiring specialized expertise, equipment and use of proprietary knowledge. Also, the small pores of the zeolite limit access to the catalytic site by large organic substrates more prevalent in the synthesis of fine chemicals.

In order to adapt the desirable properties of the TS-1 zeolite catalyst, yet prepare catalysts with large pores of up to 100 Å by a simple synthetic procedure, we synthesized amorphous metallosilicalite xerogels, MO_x-SiO₂, (Ti^{IV}, V^V, Mo^{VI}, W^{VI} and Se^{IV}) by the sol-gel method⁹ and used them as catalysts in the oxidation with hydrogen peroxide of various organic substrates. Silicalite xerogels are easily synthesized by the acid- or base-catalysed combined hydrolysis, eqn. (1), and condensation, eqn. (2), of silicon tetraalkoxides.

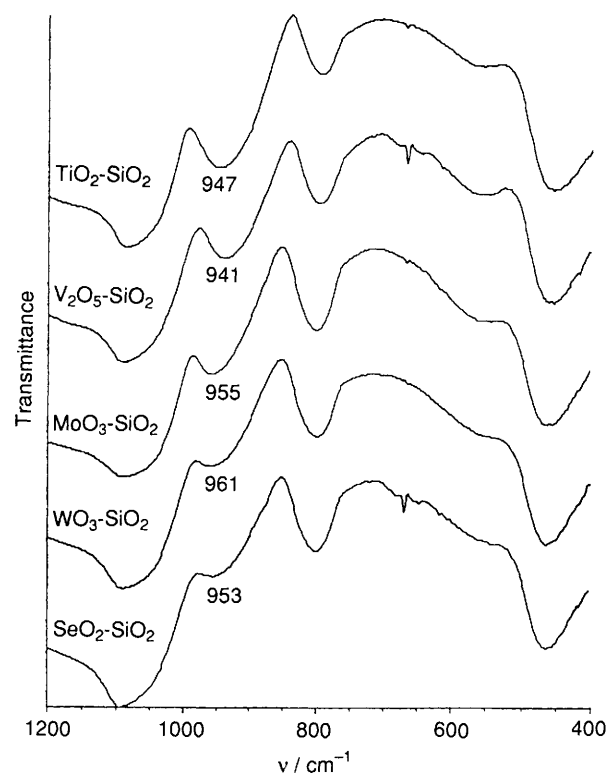


In order to prepare the required metallosilicalites,¹⁰ mixtures of silicon and metal alkoxides are used. The typical procedure for the preparation of the MO_x-SiO₂ xerogels is as follows. Silicon tetraethoxide (57 mmol) was dissolved in absolute ethanol (17 ml) and water (114 mmol) added as a 0.15 mol l⁻¹ HCl solution. The solution was heated to 60 °C for 1.5 h and then cooled to room temperature followed by addition with stirring of 3 mmol of the metal isopropoxide or ethoxide. † The mixture formed a gel almost immediately and was then left in an open beaker allowing slow evaporation of the solvent; within 12–24 h a brittle 5% MO_x-SiO₂ xerogel was formed. ‡ The xerogel was ground and dried in air overnight at 100 °C. The xerogels (those of Mo^{VI}, W^{VI} and Se^{IV} are reported for the first time) were characterized by their IR spectra (Fig. 1). Since the metallosilicalites contain 95% SiO₂, there are as expected no large differences in their spectra except for small variations in the peak attributable¹¹ to the M-O-Si bond vibration at ca. 940–960 cm⁻¹ which changes in both wavelength and intensity.

In the presence of hydrogen peroxide the metal oxides under consideration are known to form inorganic peracids

† Ti(OPrⁱ)₄ and VO(OPrⁱ)₃ were available commercially whereas the MoO(OEt)₄, WO(OEt)₄ and Se(OPrⁱ)₄ compounds were prepared by a known procedure.¹³

‡ TiO₂-SiO₂ formed a slightly yellow sol and a white gel; V₂O₅-SiO₂ formed an orange sol and a green gel; MoO₃-SiO₂ a brownish sol and gel; WO₃-SiO₂ a colourless sol and a white gel; and SeO₂-SiO₂ a colourless sol and a slightly pink gel.

**Fig. 1** IR spectra of the various metallosilicalite xerogels

which may oxidize organic substrates by a heterolytic or homolytic mechanism.¹² Thus, some simple model compounds including alkenes, alcohols and phenol were reacted to test the catalytic activity of the metallosilicalite xerogels. In a typical reaction, substrate (1.0 mmol) and 30% hydrogen peroxide (1.0 mmol) were reacted in Bu^tOH (0.5 ml) in the presence of 5% MO_x-SiO₂ (5 mg) at 60 °C in a sealed 3 ml vial. The results of some reactions are summarized in Table 1. The specific substrates were chosen to represent various possible oxidation reactions. Thus, for alkenes one may distinguish between epoxidation, allylic oxidation and carbon-carbon bond cleavage reaction pathways. Although reaction conditions were not optimized the results show interesting trends. Thus, the TiO₂-SiO₂ compound is the poorest catalyst having almost no activity for epoxidation of cyclooctene and hydroxylation of phenol, and only slight activity for carbon-carbon bond cleavage in styrene, allylic oxidation in cyclohexene and oxidation of 1-phenylethanol to acetophenone. The SeO₂-SiO₂ xerogel was a somewhat better catalyst showing low but

significant catalytic activity for all reactions. On the other hand the V_2O_5 - SiO_2 , MoO_3 - SiO_2 and WO_3 - SiO_2 xerogels are the preferred catalysts, all three having high catalytic activity (in general V_2O_5 - $SiO_2 \geq WO_3$ - $SiO_2 > MoO_3$ - SiO_2). Thus, activated alkenes such as cyclooctene are efficiently epoxidised to cyclooctene oxide. Cyclohexene which is very susceptible to allylic oxidation yielded mostly cyclohexen-2-ol and cyclohexen-2-one in ca. 1:1 ratio although with WO_3 - SiO_2 considerable epoxidation was also observed. The more nucleophilic styrene shows high activity for carbon-carbon bond cleavage with formation of both benzaldehyde as primary product and benzoic acid. No styrene oxide was observed. 1-Phenylethanol is efficiently oxidised to acetophenone. Phenol was hydroxylated to a significant extent only with V_2O_5 - SiO_2 as catalyst. Surprisingly, only hydroquinone and catechol were formed with no formation of benzoquinone or tars.

Several preliminary experiments tested the integrity of the heterogeneous catalyst, the effect of different solvents on the reaction and the yield based on hydrogen peroxide. First, we demonstrated that we have a truly heterogeneous catalyst, *i.e.* the metal oxides are not leached into solution. A reaction mixture as described above without the organic substrate was stirred and heated at 60 °C for two hours and then filtered. Cyclooctene was added to the filtrate and the mixture heated overnight. No cyclooctene oxide was observable in the GLC analysis. On the other hand, the filtered catalyst in a new reaction mixture showed the usual activity. Other solvents could be used in the catalytic oxidation. Thus, methanol gave somewhat inferior results, whereas acetonitrile was generally as effective as Bu^tOH . Acetonitrile, however, caused considerable leaching of V_2O_5 , MoO_3 and WO_3 so that in this solvent the catalyst is not heterogeneous but is composed of soluble metal oxides.¹² Finally, the decomposition of hydrogen peroxide was investigated under reaction conditions in the presence of cyclooctene as substrate by the iodide-thiosulfate titration method. After 18 h, ca. 15, 15, 98, 25 and 35% of the original hydrogen peroxide had been used for TiO_2 - SiO_2 , SeO_2 - SiO_2 , V_2O_5 - SiO_2 , MoO_3 - SiO_2 and WO_3 -

SiO_2 xerogels respectively indicating relatively slow non-productive dioxygen formation and fair utilisation of hydrogen peroxide.

Received, 29th June 1993; Com. 3103726F

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