



Selective epoxidation of olefins by hydrogen peroxide in water using a polyoxometalate catalyst supported on chemically modified hydrophobic mesoporous silica gel

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Abstract

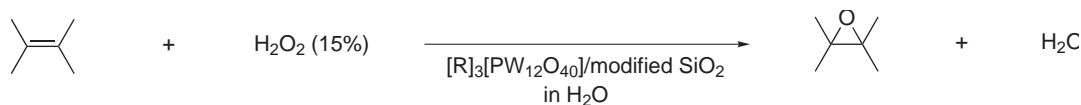
A new heterogeneous catalyst prepared by immobilisation of polyoxometalates on chemically modified hydrophobic mesoporous silica gel has been successfully applied to the selective epoxidation of olefins with 15% aqueous H_2O_2 without the use of organic solvent. © 2000 Elsevier Science Ltd. All rights reserved.

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The catalytic epoxidation of olefins using environmentally benign oxidants, typically H_2O_2 , instead of stoichiometric reagents common in the field of synthetic organic chemistry has received significant research attention in recent years, particularly from viewpoints of green chemistry.¹ Recently, Newmann and his coworkers reported interesting prototypical systems for heterogeneous catalysis of olefin epoxidation in aqueous H_2O_2 without the use of organic solvent.^{2,3} They prepared a polyoxometalate catalyst fixed on a polyether-modified silica surface, which can catalyse the epoxidation of cyclooctene in 30% aqueous H_2O_2 .² However, this catalyst has a crucial drawback in its synthetic application, since a relatively long reaction time is required for the completion of the reaction. Moreover, no information has been given on the applicability of this catalyst to various olefins other than cyclooctene. Another solid catalyst reported by them is a silicate xerosol prepared by a sol–gel method, the reaction centre of which is a quaternary ammonium/polyoxometalate ion pair covalently fixed on the silica surface.³ With this catalyst, however, the olefin epoxidation in 30% aqueous H_2O_2 is not selective or efficient except for a few particular olefins. While the Newmann's catalysts have certainly opened up a new route to heterogeneous catalysis of olefin epoxidation, there still remain crucial problems to be explored for designing more efficient catalysts of synthetic significance. An essential factor is

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to control chemical features of the silica surfaces, since heterogeneous reaction rates should be determined by such surface processes as the access of the reactants to the catalysis centre and adsorption/desorption of the reactants and products, as well as by microscopic environments surrounding the catalysis centre. From these viewpoints, we have been investigating surface modifications of silica particles to explore the possible effects of hydrophobicity on the catalytic efficiencies. In this paper, we wish to report a novel type of solid catalyst that has been prepared by non-covalent fixing of the tungstophosphate anion on chemically modified hydrophobic mesoporous silica gel. This catalyst has been found to catalyse the selective epoxidation of various olefins by 15% aqueous H_2O_2 without the use of organic solvent (Scheme 1).



Scheme 1.

A typical example for the preparation of the catalyst is as follows. Mesoporous silica gel with an average pore diameter of 100 Å (Kieselgel 100, 2 g) was activated with hot concentrated hydrochloric acid⁴ and then added to a dry toluene solution (10 cm³) containing either or both ethoxytriphenylsilane (0.153 g, 0.5 mmol) and *N,N*-dimethylformamide dibenzylacetal⁵ (0.136 g, 0.5 mmol). After refluxing the mixture for 7 h under nitrogen, the resulting solid was collected by filtration, washed thoroughly with toluene and acetone and then dried overnight in a vacuum oven at room temperature. To a suspension of the solid (2.22 g) in dry acetone (10 cm³) was added tris(cetylpyridinium)-12-tungstophosphate⁶ (TCPTP, [$\pi\text{-C}_5\text{H}_5\text{N}^+(\text{CH}_2)_{15}\text{CH}_3$]₃(PW₁₂O₄₀)) (0.91 g, 0.24 mmol) in dry acetone (40 cm³). The mixture was refluxed for 5 h under nitrogen, evaporated slowly at room temperature, carefully washed twice with water and acetone, and then dried under vacuum at 80°C for 7 h to give the catalyst.

It was found that the catalytic epoxidation of various olefins in 15% aqueous H_2O_2 using the solid catalyst does occur in various efficiencies and selectivities depending on different modifications of silica gel as well as on the organic counter cations of tungstophosphate. Table 1 summarises the catalytic epoxidation of 1-octene in 15% aqueous H_2O_2 using the various catalysts prepared (Cat. 1–13). As a typical run, a mixture of 1-octene (3 mmol), Cat. 1 (0.5 mol%) and 15% H_2O_2 (6 mmol) was heated at 90°C for 10 h. GLC analysis showed the quantitative formation of 1,2-epoxyoctane at the complete consumption of 1-octene. Prominent features are as follows: (1) Modification of silica gel with both Ph_3SiOEt and $\text{Me}_3\text{NCH}(\text{OCH}_2\text{Ph})_2$ in a 1:1 ratio generally gave effective catalysts, i.e. Cat. 1, 10 and 11 among which the first is the most effective. In contrast, the starting silica gel without surface modification gave a poor catalyst (Cat. 4). (2) Catalytic activities were significantly or considerably low when silica gel had been modified only with either Ph_3SiOEt or $\text{Me}_2\text{NCH}(\text{OCH}_2\text{Ph})_2$ (Cat. 2 and 3) or with a 1:3 or 3:1 mixture of them (Cat. 5 and 6). (3) The less the hydrophobicity of the organic counter cation [R], the lower the catalytic activities become; the reaction conversions decrease in the order Cat. 10 ~ Cat. 11 > Cat. 12 > Cat. 13. (4) IR analysis of Cat. 1 showed the complete disappearance of the silanol absorption of the starting silica gel at 3745 cm⁻¹, whereas the silanol absorption still occurred significantly in the cases of Cat. 2 and 3. This implies that different types of silanol groups on the silica gel surface⁷ have different reactivities with either Ph_3SiOEt or $\text{Me}_2\text{NCH}(\text{OCH}_2\text{Ph})_2$. As a consequence, the high hydropho-

bic modification of silica gel surface can be achieved by the treatment with both of the agents. All these features strongly suggest that the hydrophobic environment on the catalyst surface should play essential roles in the efficient and selective epoxidation. Presumably, high hydrophobicity of both the silica gel surface and the counter cation [R] might favour strong binding of the catalysis centre $[\text{PW}_{12}\text{O}_{40}]^{3-}$ on the silica gel surface and also easy access of the hydrophobic reactant 1-octene to the catalysis centre.

Table 1
Epoxidation of 1-octene with 15% aqueous H_2O_2^a

Cat.	Catalyst ^b			Conversion of 1-octene (%) ^c	Selectivity of epoxide (%) ^c
	Polyoxometalate $[\text{R}]_3(\text{PW}_{12}\text{O}_{40})^{3-}$	Silane coupling agent (SA)	Alkylating agent (AA) $(\text{CH}_3)_2\text{NCH}(\text{OX})_2$		
1	$\text{R} = \pi\text{-C}_5\text{H}_5\text{N}^+(\text{CH}_2)_{15}\text{CH}_3$	$\text{Ph}_3\text{SiOC}_2\text{H}_5$	X = benzyl	100	> 98
2	$\text{R} = \pi\text{-C}_5\text{H}_5\text{N}^+(\text{CH}_2)_{15}\text{CH}_3$	$\text{Ph}_3\text{SiOC}_2\text{H}_5$	None	59	97
3	$\text{R} = \pi\text{-C}_5\text{H}_5\text{N}^+(\text{CH}_2)_{15}\text{CH}_3$	None	X = benzyl	45	97
4	$\text{R} = \pi\text{-C}_5\text{H}_5\text{N}^+(\text{CH}_2)_{15}\text{CH}_3$	None	None	18	96
5 ^d	$\text{R} = \pi\text{-C}_5\text{H}_5\text{N}^+(\text{CH}_2)_{15}\text{CH}_3$	$\text{Ph}_3\text{SiOC}_2\text{H}_5$	X = benzyl	72	> 98
6 ^e	$\text{R} = \pi\text{-C}_5\text{H}_5\text{N}^+(\text{CH}_2)_{15}\text{CH}_3$	$\text{Ph}_3\text{SiOC}_2\text{H}_5$	X = benzyl	47	> 98
7	$\text{R} = \pi\text{-C}_5\text{H}_5\text{N}^+(\text{CH}_2)_{15}\text{CH}_3$	$\text{Ph}_2\text{Si}(\text{OC}_2\text{H}_5)_2$	X = benzyl	79	> 98
8	$\text{R} = \pi\text{-C}_5\text{H}_5\text{N}^+(\text{CH}_2)_{15}\text{CH}_3$	$\text{Ph}_3\text{SiOC}_2\text{H}_5$	X = <i>n</i> -butyl	81	97
9	$\text{R} = \pi\text{-C}_5\text{H}_5\text{N}^+(\text{CH}_2)_{15}\text{CH}_3$	$\text{Ph}_3\text{SiOC}_2\text{H}_5$	X = cyclohexyl	78	97
10	$\text{R} = \text{C}_{12}\text{H}_{25}(\text{CH}_3)_3\text{N}^+$	$\text{Ph}_3\text{SiOC}_2\text{H}_5$	X = benzyl	90	97
11	$\text{R} = \text{CH}_3(\text{C}_8\text{H}_{17})_3\text{N}^+$	$\text{Ph}_3\text{SiOC}_2\text{H}_5$	X = benzyl	88	97
12	$\text{R} = (\text{C}_4\text{H}_9)_4\text{N}^+$	$\text{Ph}_3\text{SiOC}_2\text{H}_5$	X = benzyl	41	97
13	R = H	$\text{Ph}_3\text{SiOC}_2\text{H}_5$	X = benzyl	21	96

^a For reactions of 3 mmol 1-octene, 0.015 mmol of catalyst (0.5 mol%) and 6 mmol 15% H_2O_2 at 90°C for 10 h.

^b Unless otherwise stated, SA:AA = 1:1.

^c By GC analysis using Bu_2O as internal standard.

^d SA:AA = 3:1.

^e SA:AA = 1:3.

It was confirmed that Cat. 1 can be successfully applied to the epoxidation of different types of olefins, i.e. terminal, cyclic, highly substituted and aromatic olefins. The corresponding epoxides were produced in >97% (Table 2). In the cases of cyclohexene, cycloheptene, cyclooctene, 1-methyl-1-cyclohexene, 2,3-dimethyl-2-butene, α -pinene, *trans*-stilbene and *cis*-stilbene, the epoxidation was completed in ≤ 6 h at 70°C and the reactions of 1-octene, 1-decene, allyl phenyl ether and styrene occurred quantitatively in 8–10 h at 90°C. Large-scale reactions of olefins can be easily achieved. As a typical run, a mixture of cyclohexene (24.7 g, 0.3 mol), Cat. 1 (13.6 g, 1.5 mmol) and 15% aqueous H_2O_2 (136 g, 0.6 mol) was heated at 70°C for 6 h under N_2 to give pure cyclohexene oxide (27.1 g, 92% yield) after conventional workup followed by simple distillation of the crude product.

Table 2
High yield (>97%) epoxidation of various olefins with 15% aqueous H₂O₂^a

Olefin	<i>T</i> (°C)	<i>t</i> (h) ^b	Olefin	<i>T</i> (°C)	<i>t</i> (h) ^b
Cyclohexene	70	3	2,3-Dimethyl-2-butene	70	3
Cycloheptene	70	3	Allyl phenyl ether	90	10
Cyclooctene	70	2	α-Pinene	70	2
1-Methyl-1-cyclohexene	70	4	Styrene	90	8
1-Octene	90	10	<i>trans</i> -Stilbene	70	6 ^c
1-Decene	90	10	<i>cis</i> -Stilbene	70	6

^a For reactions of 3 mmol olefin, 0.015 mmol of catalyst (0.5 mol%) and 6 mmol 15% H₂O₂.

^b Approximate time required for the disappearance of the starting olefin analysed by GC.

^c Toluene (0.5 g) was added.

The present investigation has provided an effective methodology for designing efficient solid catalysts for olefin epoxidation in water using a low concentration of H₂O₂. Further improvements of the solid catalyst could be achieved by fine tuning both the silica-surface morphology (e.g. porosity) and the surface-modification agents.

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