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FACTORS INFLUENCING THE CATALYTIC ACTIVITY OF TITANIUM SILICALITES IN SELECTIVE OXIDATIONS

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Titanium silicalites synthesized via different procedures are tested in the oxidation of phenol, 1-octene and n-hexane by aqueous H_2O_2. It is shown that the presence of titanyl groups, on which H_2O_2 is activated by formation of titanium peroxo complexes, is a prerequisite for oxygenation activity. Furthermore, in order to afford high selectivities, titanium silicalites should be free of impurities which cause acid catalyzed side reactions or H_2O_2 decomposition.

Keywords: Titanium silicalite, oxidation catalyst, hydrogen peroxide adsorption, IR, DRS

1. Introduction

In 1983, Taramasso et al. reported on the hydrothermal synthesis of a titanium containing derivative of high silica ZSM-5, denoted as titanium silicalite-1 or TS-1 [1]. TS-1 is assumed to contain isolated titanium atoms, which would be responsible for its catalytic activity in the selective oxidation of organic substrates with aqueous hydrogen peroxide [2–5]. Examples of TS-1 catalyzed reactions are the hydroxylation of aromatics [6], the epoxidation of olefins [7], and the oxyfunctionalization of alkanes [8,9]. Kraushaar et al. described a new method for the preparation of TS-1, consisting of a $TiCl_4$ treatment of acid leached ZSM-5 [10,11]. It is supposed that titanium atoms are inserted into lattice vacancies which were created by the acid dealumination. Treatment of NH_4-ZSM-5 with $(NH_4)_2TiF_6$ is claimed to be able to replace Al in the framework by tetrahedral Ti [12].

In the present study titanium silicalites are prepared by hydrothermal syntheses and by modification of ZSM-5 with titanium compounds, and the obtained materials are used as catalysts in the oxidation of phenol, 1-octene and n-hexane with aqueous hydrogen peroxide. Some critical factors determining the observed catalytic behavior will be discussed and a model for H_2O_2 activation will be proposed based on H_2O_2 chemisorption experiments.

2. Experimental

Preparation of samples 1 to 4 was performed by hydrothermal treatment of a mixture containing a titanium compound, a silicon compound, an organic template and water, according to procedures described in literature. The molar compositions of the synthesis mixtures are given in table 1.

Samples 5 and 6 were prepared via treatment of H-ZSM-5 (Si/Al = 50) with $TiCl_4$ [10,11] and $(NH_4)_2TiF_6$ [12] (both purchased from Aldrich) respectively. According to X-ray diffraction analysis, the treatments did not destroy the crystallinity of the samples.

Infrared analysis of the samples was performed on a PE 580B spectrometer in the lattice vibration region using the KBr wafer technique.

Diffuse reflectance spectroscopy was carried out on a Cary-17 double beam spectrometer with $BaSO_4$ as standard.

The experimental conditions used in the *catalytic oxidations* of phenol, 1-octene and n-hexane are listed to table 2. Analysis of the products was performed by gas chromatography after completion of the reaction and addition of an

Table 1
Molar reagent ratios used for the hydrothermal syntheses of titanium silicalites.

	Molar reagent ratios [a]	Procedure (Ref.)
Sample 1	TEOS; 0.03 TEOT; 0.44 TPAOH; 20 H_2O	[2]
Sample 2	SiO_2 [b]; 0.20 TEOT; 0.90 TPAOH; 4.7 H_2O_2; 97 H_2O	[2]
Sample 3	SiO_2 [b]; 0.14 TiPOT; 0.10 TPAOH; 0.18 NaOH; 49 H_2O	[13]
Sample 4	SiO_2 [c]; 0.20 $(NH_4)_3Ti(O_2)F_5$ [d]; 0.24 TPABr; 1.1 NH_4F; 71 H_2O	[14]

[a] TEOS: TetraEthylOrthoSilicate (Aldrich); TEOT: TetraEthylOrthoTitanate (Aldrich); TPAOH: TetraPropylAmmoniumHydroxide (Alfa); TiPOT: TetraisoPropylOrthoTitanate (Aldrich); TPABr: TetraPropylAmmoniumBromide (Fluka);
[b] Ludox AS 40, ammonium stabilized 40% silica sol (DuPont);
[c] Aerosil 200 (Degussa);
[d] prepared following the procedure given in [15].

Table 2
Experimental conditions used in the oxidation of phenol, 1-octene and n-hexane.

Substrate	phenol	1-octene	n-hexane
Catalyst (mg)	500	500	500
Substrate (mmoles)	175	102	115
H_2O_2 (mmoles) [a]	35	34	230
Acetone (mls)	35	45	45
Temperature (° C)	80	80	100
Reaction time (hrs)	2	2	1

[a] 35% solution in water, added continuously over a 1 hour period for phenol oxidation and batchwize for 1-octene and n-hexane oxidation.

Table 3
Average crystallite length and titanium content of hydrothermally synthesized titanium silicalites.

	Average crystallite length (μm)	Ti/(Si+Ti) [a]
Sample 1	3	0.030
Sample 2	3	0.016
Sample 3	7	0.039
Sample 4	25	0.014

[a] Determined by chemical analysis.

internal standard (2,4-xylenol for phenol oxidation, toluene for 1-octene and n-hexane oxidation).

3. Results

X-ray diffraction was performed on all as synthesized samples and confirmed the presence of a crystalline orthorhombic MFI-phase. Electron microscopy

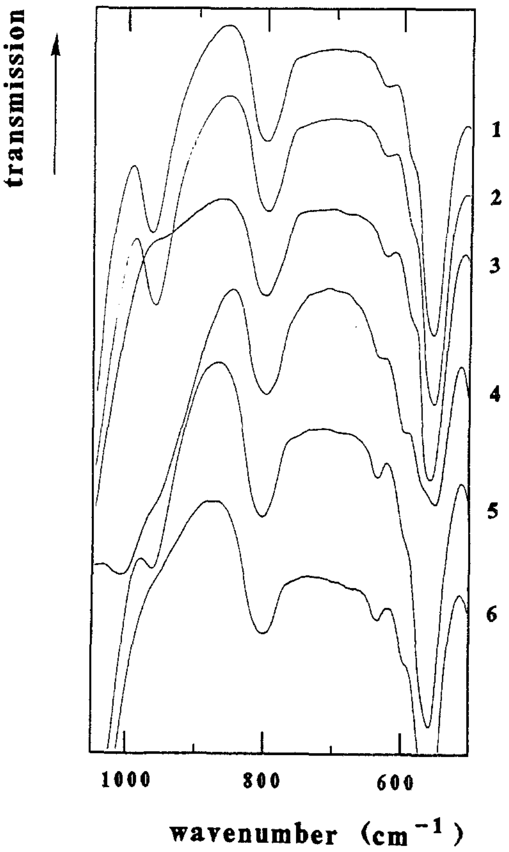


Fig. 1. IR spectra of samples 1 to 6.

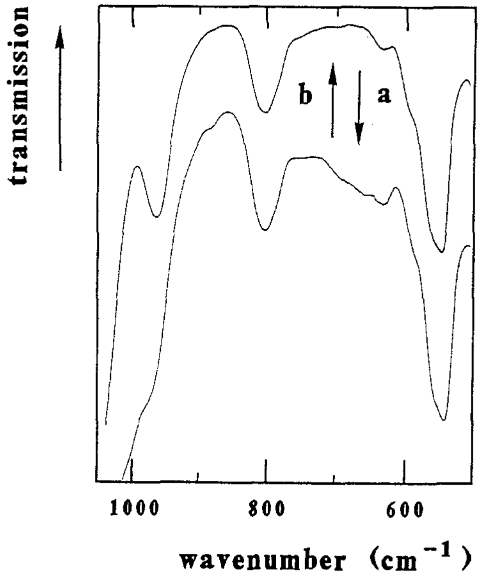


Fig. 2. IR spectra of sample 1, after H_2O_2 adsorption (a) and subsequent heating at 60 °C (b).

investigation of the four hydrothermally synthesized samples showed the presence of elongated columnar crystallites of orthorhombic symmetry. Small amounts of amorphous or poorly crystallized particles are present in samples 3 and 4, but could not be detected in samples 1 and 2. The average crystallite length and the titanium content of the four samples are given in table 3.

Fig. 1 shows the IR spectra of the different titanium silicalites in the region of 1050–500 cm^{-1}. In the spectrum of samples 1 and 2, a band is present at ±960 cm^{-1}, which has been ascribed in literature to titanyl (Ti = O) vibrations [2,3] or

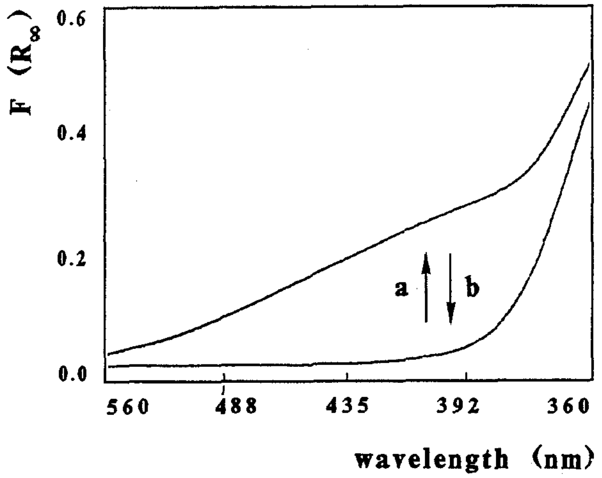


Fig. 3. Diffuse reflectance spectra of sample 1 after H_2O_2 adsorption (a) and subsequent heating at 60 °C (b).

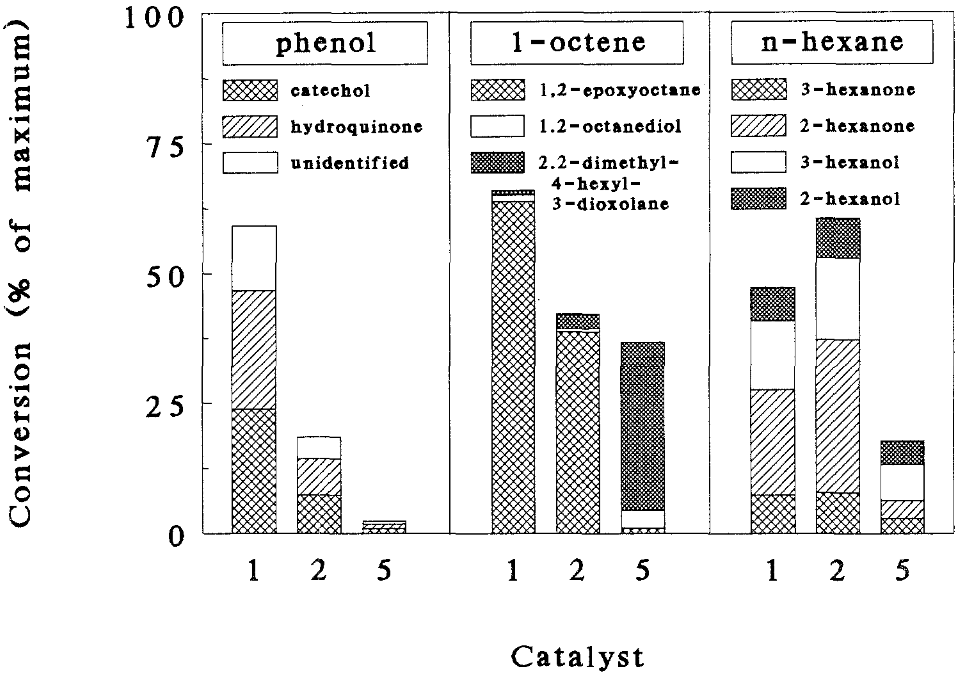
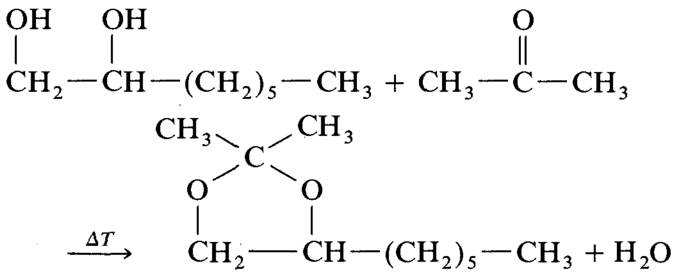


Fig. 4. Catalytic activity of samples 1, 2 and 5 in the oxidation of phenol, 1-octene and n-hexane by H_2O_2.

to vibrations of SiO_4 units bonded to a titanium atom [5]. This band is also present, though less intense, in sample 5, but is absent in the other 3 samples.

Adsorption of aqueous H_2O_2 and subsequent freeze drying causes a decrease of the 960 cm^{-1} band of samples 1 and 2 (fig. 2). Furthermore, a weak band is formed at ±880 cm^{-1}, which is in the range of O–O vibrations reported for titanium peroxo complexes [16,17]. In the visible spectrum the H_2O_2 treatment results in the formation of a band at 425 nm (fig. 3). The spectral changes are completely reversible: heating of the samples at 60 °C for a period of 2 hours restores the original IR and visible spectra.

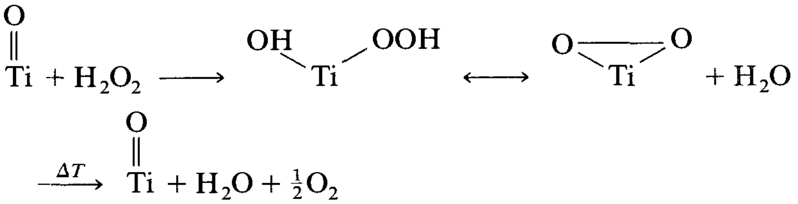
In the presence of samples 3, 4 and 6, formation of oxidation products was below detection limits in each of the catalytic test reactions, although H_2O_2 conversions were appreciable. The catalytic results for samples 1, 2 and 5 are shown in fig. 4. Sample 1 shows good activities and selectivities in the hydroxylation of phenol, the epoxidation of 1-octene and the oxyfunctionalization of n-hexane. Sample 2 is less active and less selective in the oxidation of phenol and 1-octene, although its activity and selectivity in n-hexane oxidation are high. Sample 3 at last is the least active of the three and has a very low selectivity in the epoxidation of 1-octene, giving mainly rise to the formation of 2,2-dimethyl-4-hexyl-3-dioxolane, probably via reaction of 1,2-octyleneglycol and acetone:



4. Discussion

The experiments described above suggest that the presence of an IR absorption band at 960 cm^{-1} is a necessary, though not sufficient condition, for titanium silicalites to be active and selective catalysts in the oxidation of hydrocarbons with diluted hydrogen peroxide. Indeed, titanium silicalites lacking this band (samples 3, 4 and 6), show no appreciable conversions in the oxidation of phenol, 1-octene and n-hexane. Samples 1 and 2, which are characterized by a relatively intense 960 cm^{-1} band, are more active in these three reactions than sample 5, which contains a less intense band.

The spectral changes induced by H_2O_2 chemisorption on samples 1 and 2 strongly suggest that hydrogen peroxide activation occurs by formation of titanium peroxo compounds. Evidence for the formation of such species is found by the disappearance of the 960 cm^{-1} titanium IR band and the creation of bands at 880 cm^{-1} in the IR and at 425 nm in the visible spectrum, which are typical for titanium peroxo compounds. Reverse spectral changes are observed under thermal decomposition of the peroxo complexes. These features are reminiscent of those reported for an amorphous solid titanium hydroxyperoxo compound, prepared by reaction of $TiCl_4$ with an acidified H_2O_2 solution [18]. This material has a band at ±420 nm in the visible spectrum and IR bands at 1040 and 860 cm^{-1}, which are ascribed to titanium peroxo species. When it is evacuated at 400 °C, the three bands completely disappear, and simultaneously an IR band at ±950 cm^{-1} is formed, which was ascribed to titanyl species on the TiO_2 surface. The striking correspondence with the spectral characteristics of H_2O_2 treated titanium silicalites offers strong support for the assignment of the 960 cm^{-1} IR band in titanium silicalites to titanyl vibrations rather than to vibration modes of SiO_4 with titanium neighbours. The activation of H_2O_2 on titanium silicalite can therefore be schematically represented as follows:



Under catalytic reaction conditions, decomposition of H_2O_2 to O_2 is competitive with the use of H_2O_2 as partial oxidant. On samples 1 and 2 this competition is in favour of the catalytic oxidation, on sample 5 decomposition of H_2O_2 becomes more important, and on samples 3, 4 and 6 only decomposition is observed. Activation of H_2O_2 for selective oxidation is believed to occur only on titanyl species, whereas H_2O_2 decomposition is also catalyzed by other titanium compounds.

In the three catalytic test reactions, samples 1, 2 and 5 show basically the same type of oxidizing activity, but the relative importance of the side reactions differs. In phenol oxidation, condensation of phenolic compounds results in the formation of tarry byproducts, which can eventually block the pores of the catalyst. Sample 1 is the only catalyst on which these side reactions are reduced and which therefore allows selective hydroxylation of phenol. In 1-octene oxidation, ring opening in 1,2-epoxyoctane by water or acetone, gives rise to the formation of 1,2-octanediol and 2,2-dimethyl-4-hexyl-3-dioxolane. In the presence of sample 3, 1,2-epoxyoctane is almost completely converted to the acetal, whereas high selectivities for 1,2-epoxyoctane are obtained on sample 2 and especially on sample 1. For hexane oxidation no side reactions are observed, and all three catalysts show comparable selectivities. It is believed that the high amount of side reactions on sample 3 arises from the residual acidity of the sample, which is due to incomplete dealumination. Indeed, condensation, hydrolysis and solvolysis are typical acid catalyzed reactions. The lower selectivity of sample 2 compared to sample 1 in 1-octene and particularly in phenol oxidation, is also ascribed to the presence of traces of acidity. This acidity is related to impurity levels of tri valent ions (Al and Fe), which were introduced during the hydrothermal synthesis as could be confirmed by chemical analysis.

5. Conclusions

The presence of an IR band at ± 960 cm^{-1}, ascribed to titanyl groups, was found to be a critical, though not necessarily sufficient condition for the activity of titanium silicalites in oxygenations of aromatics, olefins and alkanes by aqueous H_2O_2. Activation of H_2O_2 occurs on the titanyl group by formation of titanium peroxo complexes. The presence of acidity, even at impurity levels, should be avoided in titanium silicalites in order to obtain high selectivities in the oxygenation reactions. Purity of the catalyst is particularly critical in the hydroxylation of aromatics, and to a lesser extent in the epoxidation of olefins. Alkane oxidation finally is the least demanding reaction since no acid catalyzed side reactions are observed.

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