

New TiF₄/SiO₂ Catalysts for Liquid-phase Epoxidations with Aqueous H₂O₂

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Ti-supported amorphous silica catalysts are prepared using a simple and original route with TiF₄ and are very active in epoxidation reactions with aqueous hydrogen peroxide solutions.

There has been an increasing interest over the last years in the synthesis of heterogeneous catalysts for oxidation reactions in the liquid phase.¹ These catalysts usually contain transition metal cations, *e.g.* Ti⁴⁺, V⁴⁺ or Cr³⁺,²⁻⁷ that can be incorporated *via* direct synthesis at framework positions in zeolites or aluminophosphates. One of the most beautiful examples is TS-1, the titanium substituted silicalite-1, a zeolite with remarkable properties in the oxidation of small organic molecules with dilute hydrogen peroxide at low temperature.⁸

However, the synthesis of transition metal substituted zeolites is not always easy as it requires the absence of alkali cations and very low Si:Al ratios. Moreover, catalytic reactions are limited to small substrates capable of entering the zeolite channels, *i.e.* with a kinetic diameter smaller than 5.5–7 Å. Therefore, catalysts where transition metal cations are on the outer surface of various supports may provide advantage with respect to zeolites, particularly for the oxidation of large and bulky substrates. The Ti/SiO₂ system is known to catalyse the epoxidation of alkenes with alkyl hydroperoxides.⁹ However, it was reported that this type of catalyst was not very active with aqueous H₂O₂ solutions because of (i) the hydrophilic character of the silica support and (ii) the decomposition of H₂O₂ over small TiO₂ particles formed during the synthesis. Several methods have been used to prepare these materials, the most common being the reaction of surface silanol groups with TiCl₄.¹⁰ Recently, it has been reported that Ti–Si mixed oxides could also catalyse the epoxidation of alkenes with alkylperoxides.¹¹

We report here a novel and very simple route to prepare Ti/SiO₂ solids with highly dispersed surface-connected Ti atoms which are active catalysts in epoxidation reactions with aqueous H₂O₂ as oxidant.

Catalysts are prepared in the following manner:¹² TiF₄ (1.94 g) was dispersed in 2-methoxydiethyl ether (diglyme) (500 ml). The solution is heated to 60 °C under stirring for *ca.* 1 h. Then, silica (50 g) (precipitated silica FK 310) (Degussa) was directly added to the clear solution and stirring is maintained at 60 °C for *ca.* 2 h. Occasionally, similar preparations could be performed with water or acetone as solvent, or using various supports like the non-porous fumed silica A 200

(Degussa). The solid is then filtered and dried in vacuum at 120 °C.

Samples are calcined in air at 500 °C for 4 h. Treatments with alkaline solutions are performed by dispersing the catalyst (1 g) in water (20 ml), followed by dropwise addition of a solution of NaOH or NH₄OH (1 mol dm⁻³) to raise the pH to *ca.* 8. The solid is then filtered, washed several times (distilled water) and dried at 120 °C in vacuum for 12 h.

The total amount of Ti and F originally introduced in the synthesis in the form of TiF₄ are in the solid phase, as shown by chemical analysis (Table 1). Calcination of the samples in air at 550 °C does not change the chemical composition of the samples, *i.e.* Ti and F are still present in calcinated materials. Table 1 shows that when catalysts are synthesized in acetone or water, the amount of Ti on the solid is relatively low compared with that obtained in diglyme. Similarly, the use of A 200 as

Table 1^a

Sample	Ti (mass%)		F (mass%)	
	Preparation	Solid	Preparation	Solid
1	0.5	0.35	0.8	0.7
1c	0.5	0.5	0.8	0.8
2	1.5	1.35	2.4	2.3
2c	1.5	1.5	2.4	2.4
2d	1.5	1.32	2.4	0.1
3	3.0	2.65	4.8	4.2
3c	3.0	2.9	4.8	4.8
4 ^b	1.5	0.96	2.4	1.21
5 ^c	1.5	0.8	2.4	0.92

^a When not mentioned, samples were prepared with silica FK 310 in diglyme, samples 1, 2, 3, 4 and 5 were dried in vacuum at 120 °C, samples 1c, 2c and 3c calcined at 500 °C. Sample 2d was obtained from defluorination of sample 2c with NH₄OH. ^b Sample 4 was prepared in diglyme with A 200 as silica. ^c Sample 5 was prepared with FK 310 in H₂O.

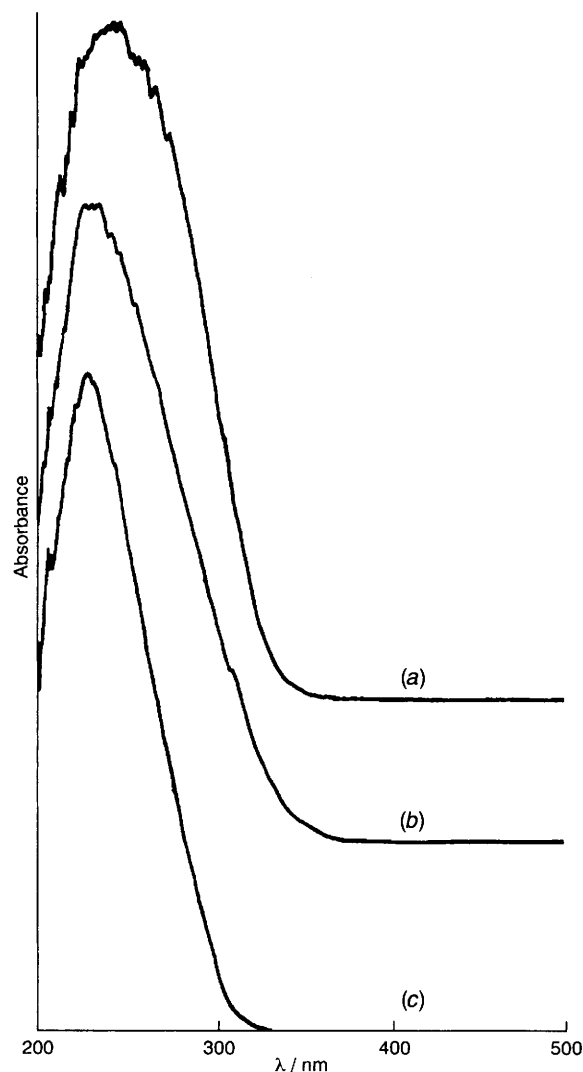


Fig. 1 Diffuse reflectance UV–VIS spectra of sample 2 as-synthesized (a), calcined (b) and defluorinated (c). Spectra were recorded on a Perkin-Elmer Lambda 9 spectrometer.

Table 2^a

Catalyst	Substrate	T/°C	C _{H₂O₂} (%) ^b	S _{H₂O₂} (%) ^c	T.T.Ep(%)	T.T.Diol(%)
2c	Cyclohexene	80	96	100	75	21
2c ^d	Cyclohexene	80	97	100	77	20
2d	Cyclohexene	80	94	100	87	7
2c	Oct-1-ene	95	85	66	56	0
2d	Oct-1-ene	100	90	59	53	0
Ti-Beta ^e	Oct-1-ene	110	90	22	13	7

^a Data were obtained after 3 h of reaction with 2 g catalyst, 0.5 mol alkene, 40 g diglyme, 25 mmol H₂O₂. ^b Conversion of hydrogen peroxide. ^c The selectivity vs. H₂O₂ is given by T.T.(Ep + Diol)/C_{H₂O₂}. ^d The catalyst was recovered by centrifugation and reused. ^e Ti-Beta was obtained following the recipe given in ref. 13.

silica support decreases the Ti content in the materials. For these samples, the fraction of fluorine retained on the silica surface was also lower than that obtained with FK 310 in diglyme. Diffuse Reflectance UV–VIS spectroscopy shows that calcined samples are free from TiO₂, even for relatively high surface Ti concentrations (Fig. 1). This clearly demonstrates the simplicity and the advantages of the present synthesis route with respect to more conventional ones using TiCl₄. The absorption edge is centred around 250 nm and the band width is characteristic of highly dispersed Ti atoms, probably in both tetrahedral and octahedral coordinations similar to those observed in Ti–Si mixed oxides or Ti/SiO₂ catalysts obtained by standard methods. Calcination of the samples in air slightly decreased the line width and shifted the absorption edge to about 240 nm (Fig. 1). The ¹⁹F solid-state NMR spectra of calcined samples show that most of the F⁻ anions are in a chemical environment comparable to that of fluorinated silica, obtained by treating FK 310 with an aqueous dilute solution of hydrofluoric acid. A band characteristic of Si–F entities was also observed in the IR spectra of calcined solids. This strongly suggests that TiF₄ loses some of its F⁻ anions by reaction with silanol groups on the silica surface to form Si–O–Ti moieties. HF that is locally formed probably reacts with the silica surface to give Si–F bonds, as evidenced by ¹⁹F NMR and IR spectroscopy. This assumption was also confirmed by a significant decrease of the signal due to Si–OH groups in ²⁹Si MAS NMR spectra.

Washing the calcined samples with alkaline solutions (NaOH or NH₄OH, pH = 8) resulted in the complete removal of fluorine, without modification of the Ti content (Table 1). Moreover, the treatment did not alter the dispersion of surface Ti atoms, as evidenced in UV–VIS spectra. As in the case of a thermal treatment, defluorination of the samples resulted in a decrease of the absorption width with a significant shift of the edge towards high energies (Fig. 1). Spectroscopic characterization of defluorinated samples shows the disappearance of both the IR band ascribed to Si–F bonds and the ¹⁹F NMR signal.

These solids have been used as catalysts in the epoxidation of cyclohexene and oct-1-ene with aqueous hydrogen peroxide. Results are summarized in Table 2. The catalyst (sample 2) is very active in the epoxidation of cyclohexene under both the calcined and defluorinated forms, which suggests that fluorine ions are not directly involved in the catalytic process. Nevertheless, the selectivity in epoxide slightly increases when fluorine was removed by treatment with alkaline solutions. Chemical analysis of the mixture at the end of the reaction gives

less than 1 ppm Ti in the liquid phase, indicating that all Ti remained on the solid surface under the working conditions. The catalyst can be recovered by centrifugation and re-used without any chemical or thermal treatment.

Concerning the epoxidation of oct-1-ene, the performances of the catalyst are similar before and after defluorination in ammonia. In both cases, the H₂O₂ conversion is high (> 85%) and the selectivity in epoxide very good as compared to that obtained over Ti-containing large pore zeolites like Ti-Beta (Table 2). A very interesting observation is the absence of diol derivatives, generally obtained by ring opening of the epoxide in the presence of protons. Other products of the reaction are aldehydes and ketones, formed by suroxidation of the epoxide.

We have thus prepared, using a very simple route, Ti-supported amorphous silica catalysts, very active in epoxidation reactions with H₂O₂. These catalysts behave like Ti-substituted large pore zeolites, with the advantage that they do not possess acid sites, which considerably increases the selectivity in epoxide.

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