Titanium deposited from $TiCl_4$ on amorphous silica and silicalite-1 as catalyst in aromatic hydroxylation reactions

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Titanium deposited from $TiCl_4$ on crystalline or amorphous SiO_2 catalyses the hydroxylation of phenol with aqueous H_2O_2. The amorphous silica-supported titanium shows a high rate of hydrogen peroxide conversion, however with a low selectivity towards aromatic hydroxylation products. A silicalite-supported titanium catalyst exhibits an efficiency towards hydroxylation products, based on hydrogen peroxide conversion, that is equal to that of titanium-silicalite-1 (TS-1), however with a lower activity.

Keywords: Phenol hydroxylation; hydrogen peroxide; titanium-silicalite-1; titanium-on-silicalite; titanium-on-silica; titanium tetrachloride

1. Introduction

Titanium-containing silicalite-1 (usually denoted as TS-1) has been reported to be a good catalyst for various selective oxidation reactions, using the clean reactant aqueous H_2O_2 as the oxidising agent [1–5]. Examples of such oxidation reactions are the direct hydroxylation of aromatic compounds [1], the epoxidation of olefins [1], the oxidation of alcohols to aldehydes and ketones [1], and the ammoximation of cyclohexanone to cyclohexanone oxime [2]. Recently, also the direct oxidation of saturated hydrocarbons was reported, using TS-1 as a catalyst and aqueous H_2O_2 as the oxidising agent [3–5].

In the TS-1 employed, titanium is presumed to be present as T-atoms, i.e. isomorphously substituting part of the silicon atoms, or at least associated to the zeolite framework [1,6,7]. The precise structure and mode of action of the titanium sites are still a matter of debate [7,8].

Systems containing titanium on amorphous silica are known to catalyse epoxidation reactions using organic hydroperoxides as the oxidising agent [9]. In a commercial process, viz. the epoxidation of propene with phenyl ethyl hydroperoxide, a titanium-on-amorphous silica serves as the catalyst. High selectivity and hydroperoxide efficiency have been reported. It seemed worthwhile to establish whether this type of catalyst is also able to catalyse aromatic hydroxylation reactions using aqueous hydrogen peroxide as the oxidant. Moreover the question arises whether crystalline silica might induce special oxidation properties in supported titanium species.

The present study compares such silica "surface-connected" Ti with the "built-in" Ti-SiO_2 system TS-1, using the hydroxylation of phenol as a test reaction.

Special focus is on titanium deposited on the external surface of crystalline silicalite-1, which system will be denoted as Ti/S-1.

2. Experimental

GAS-PHASE SYNTHESIS

Samples of Ti/Si-1^g were obtained by treating calcined silicalite-1 crystals, synthesised according to the method described by Sand and Ghamami [10], with $TiCl_4$ in the gas-phase as described below. The observed presence of defects in highly siliceous ZSM-5 (silicalite-1) [11] is expected to be enhanced in the silicalite-1 obtained through this synthesis method, due to the fast crystallisation procedure. In these defect sites we hoped–in the first instance–to insert titanium [12]. Thus, the silicalite-1 was subjected to the following treatment: First, the sample was calcined in air at 550°C for at least 8 hours to remove the organic template. Then the sample was heated by 1°C/min to 450°C in a flow of dry nitrogen. After pretreating the sample for at least 6 hours at 450°C under nitrogen, the stream of nitrogen was saturated at room temperature with $TiCl_4$. The sample was then treated with the flow of $TiCl_4/N_2$ for two hours at 450°C. Prior to cooling, the sample was flushed for two hours with dry nitrogen at 450°C to remove excessive $TiCl_4$. The system was kept free from air and moisture until it had cooled down to room temperature. Two different batches of silicalite-1, with different crystal sizes, were treated according to this method. The catalyst obtained from silicalite-1 with an average crystal length (c-axis) of 100 μm will be denoted as Ti/S-1^g A, that with average crystal length of 15 μm as Ti/S-1^gB.

A sample of an amorphous silica (silica for chromatography, type C-560, BET surface area 450 m^2/g, Chemische Fabrik Uetikon) was also treated with $TiCl_4$ in the way described above. This sample will be denoted as Ti/$SiO_2{}^g$.

LIQUID-PHASE SYNTHESIS

Ti was also deposited on amorphous silica and silicalite-1 by treatment with a diluted solution of $TiCl_4$ in n-heptane, according to a method described in a patent [9]. Thus, amorphous silica or silicalite-1 was refluxed in n-heptane until all the water present had been removed azeotropically. Then the $TiCl_4$ was added as a solution in n-heptane, and the mixture was refluxed until no more HCl-gas evolved. Subsequently water was added and again the mixture was refluxed until no more HCl-gas evolved. The n-heptane was either evaporated or decanted, and the resulting catalyst was washed with water, dried in air at 120°C and calcined in air at 500°C. The samples thus obtained will be denoted Ti/SiO_2^{lq} and $Ti/S\text{-}1^{lq}$ for $TiCl_4$ treated SiO_2 and silicalite-1, respectively. Sample Ti/SiO_2^{lq} was prepared with an amount of $TiCl_4$ calculated to react with 15% of the available surface OH-groups. The samples $Ti/S\text{-}1^{lq}1$ and $Ti/S\text{-}1^{lq}2$ differ only in the amount of $TiCl_4$ that was added to the silicalite-1, which was 2.0 and 0.2 ml of $TiCl_4$, respectively, per g silicalite-1 in 400 ml n-heptane.

CHARACTERISATION

Powder X-ray diffraction data were collected on a Philips PW 1840 diffractometer, using the Cu-Kα line.

Infrared spectra were recorded on a Bruker IFS 66 FT-IR spectrometer, using samples pressed into KBr wafers.

SEM photographs were taken of samples covered with a thin layer of gold or platinum by sputtering. The microscope used was a JEOL JSM-35 scanning microscope.

EDAX analyses were performed on the samples as prepared for SEM, using an EDAX International Inc. 9100 system.

Wet chemical analysis, ICP-AES (inductively coupled plasma-atomic emission spectroscopy) was used to determine the molar ratio of Si/Ti in the samples, and was performed on samples dissolved in aqueous HF/H_2SO_4, using a Perkin-Elmer Plasma 40 apparatus.

PHENOL HYDROXYLATION

The catalytic performance of the samples was investigated in direct aromatic hydroxylation as follows: 10 g of phenol, 32 g of methanol (as a solvent) and 0.5 g of catalyst were heated to reflux (80°C) before 5.0 ml of 30% aqueous H_2O_2 was added dropwise over a period of 10 min. Product analysis was performed using HPLC analysis, H_2O_2 conversion was monitored using standard iodometric titration.

3. Results and discussion

GAS-PHASE TITANATED SYSTEMS

Upon SEM examination of the Ti/S-1^g samples, obtained from silicalite-1 treated with gaseous $TiCl_4$, small particles could be observed on the external surface of the silicalite crystals, which were not present prior to the treatment with $TiCl_4$. As can be seen from the SEM-micrographs (fig. 1), these particles seem to be crystalline. Similar particles were observed on the surface of the amorphous silica after high temperature $TiCl_4$ treatment. Table 1 lists the crystal c.q. particle sizes of the silicalite and amorphous silica samples used and the size of the observed particles.

Upon studying the samples with FT-IR spectroscopy, no changes in the spectrum could be detected upon $TiCl_4$ treatment of the silicalite in the region 4000–400 cm^{-1}, i.e. the band at ~ 960 cm^{-1}, believed to be indicative of isomorphously substituted titanium in silicalite-1, is not present.

X-ray diffraction did not show any difference between the treated and non-treated samples, either.

EDAX analysis showed that the titanium present in the Ti/S-1^g is mainly concentrated in the particles on the external surface, and that these particles do not contain chlorine or silicon. Unfortunately, oxygen cannot be detected by EDAX analysis, but it is most likely that these particles consist of some oxidic titanium phase.

After sonification treatment of the Ti-containing samples, the particles were still present on the surface of the silicalite, indicating that they are chemically anchored.

In conclusion, these results show that the titanium is not incorporated into the zeolite framework under the conditions applied, but is present on the external surface of the silicalite. In fact it is doubted whether $TiCl_4$ can enter the pores of the MFI framework at the temperature applied in this study [13]. Work is in progress to study whether titanium is present on the outer surface of aluminium-containing ZSM-5 after treatment with $TiCl_4$ in the gas phase.

Upon examination of the Ti/$SiO_2{}^g$ sample by using IR-spectroscopy and XRD, no changes could be detected after the $TiCl_4$ treatment. SEM-micrographs (see fig. 2) show particles to be present that are similar to those observed on the $TiCl_4$-treated silicalite.

LIQUID PHASE TITANATED SAMPLES

Neither SEM, XRD nor FTIR analysis showed any changes in the samples before and after treatment with $TiCl_4$ in n-heptane. With EDAX analysis, no titanium could be detected on the external surface of the Ti/$SiO_2{}^{lq}$ nor of the Ti/S-1^{lq} samples. This might indicate that the titanium is distributed homoge-

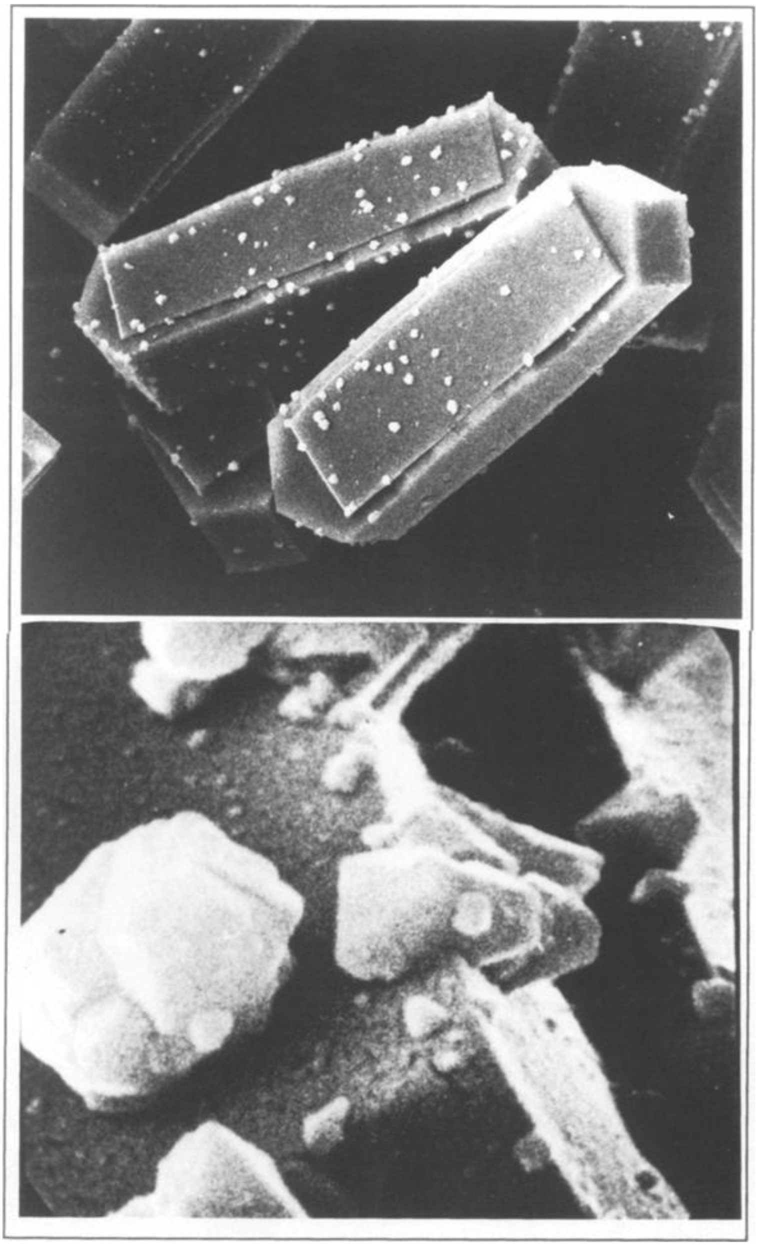

Fig. 1. SEM micrographs of Ti/S-1^{g}A. Top: enlargement 450 times; bottom: detail, enlargement 1800 times.

neously on the external surface of the samples, probably through reaction with surface hydroxyl groups. At the mild temperature applied (100°C) $TiCl_4$ will not enter the zeolite pores [13]. As can be seen from fig. 3, the external surface of

Table 1
Crystal and particle size of the materials prepared by gas phase $TiCl_4$ treatment

Sample	"SiO_2" particle size (μm)	"TiO" particle size (μm)
Ti/S-1^gA	100	2
Ti/S-1^gB	15	0.2
Ti/SiO_2^g	750	3

silicalite-1 is far from smooth. External surface areas of similar silicalite-1 samples, determined by the t-plot de Boer method, amount to 25–30 m^2/g [14].

AROMATIC HYDROXYLATION

The results obtained in the catalytic hydroxylation of phenol are shown in fig. 4 and 5, which show the conversion of hydrogen peroxide versus time for the various catalysts obtained, and in table 2, which shows the efficiency of the catalysts based on hydrogen peroxide conversion. For comparison, the catalytic

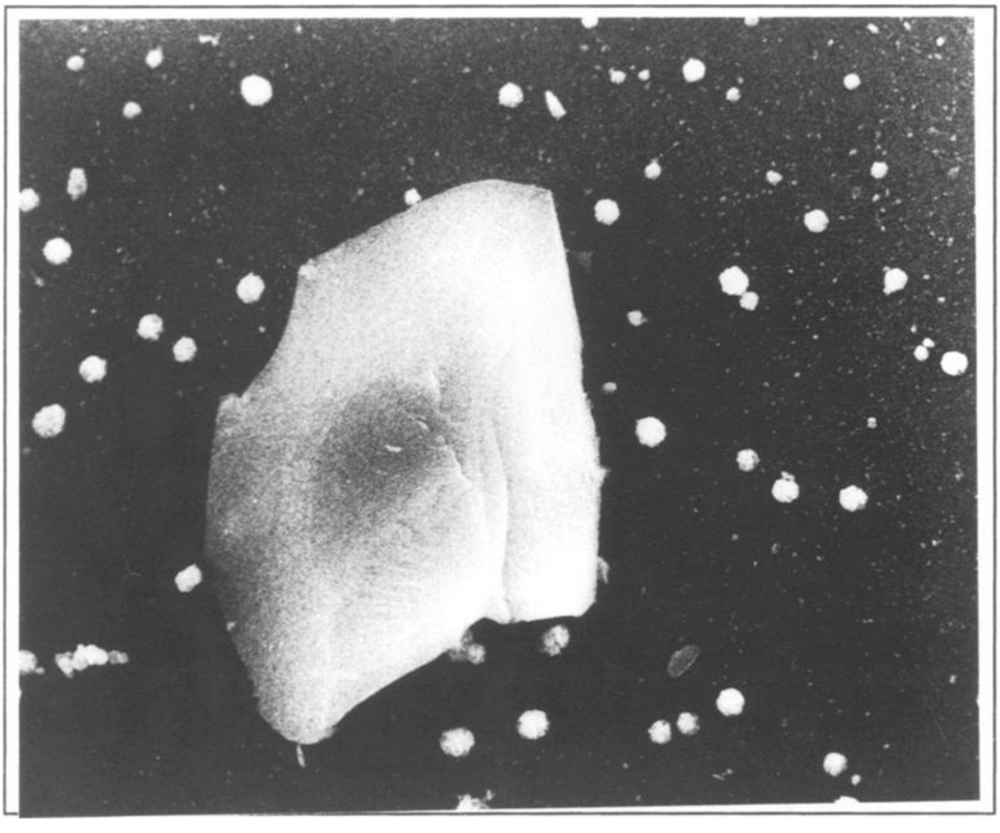

Fig. 2. SEM micrograph of Ti/SiO_2^g, enlargement 860 times.

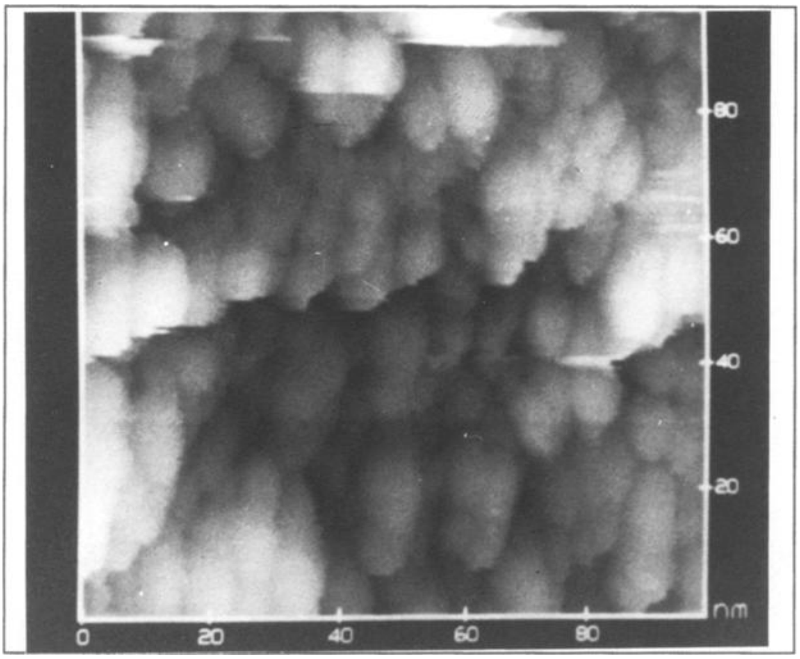

Fig. 3. STM image of the external surface of silicalite-1.

performance of a sample of TS-1 obtained through direct synthesis according to Padovan et al. [15] was also tested.

As can be seen from figs. 4 and 5 and from table 2, all the samples obtained through gas phase $TiCl_4$ treatment as well as the liquid phase $TiCl_4$ treated samples show activity towards aromatic hydroxylation. It must be noted that the

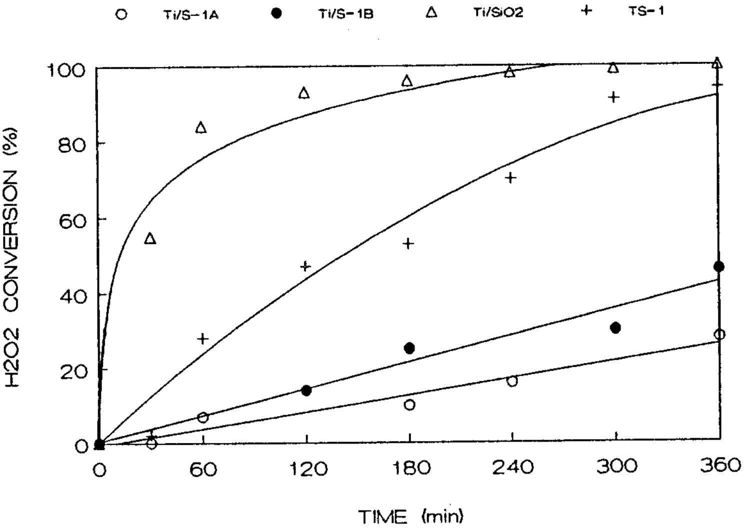

Fig. 4. H_2O_2 conversion in phenol hydroxylation using the catalysts prepared with gaseous $TiCl_4$.

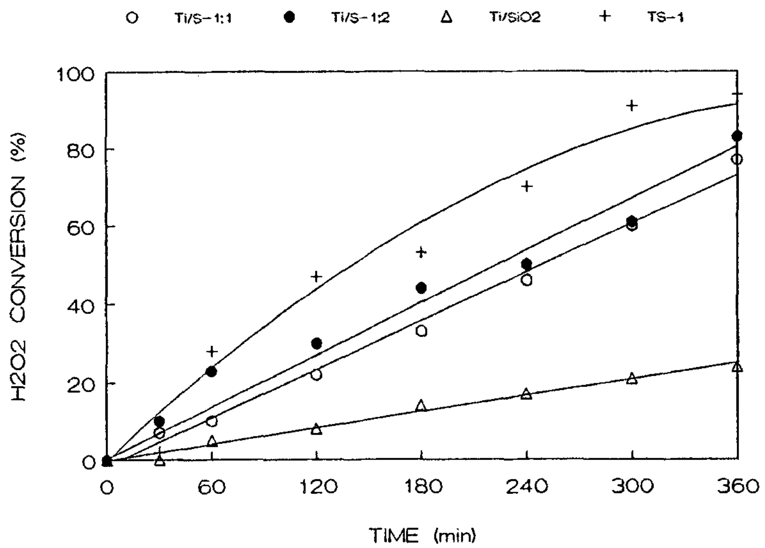

Fig. 5. H_2O_2 conversion in phenol hydroxylation using the catalysts prepared with $TiCl_4$ in n-heptane.

silicalite based catalysts show a much higher actitivity for aromatic hydroxylation with hydrogen peroxide than do the amorphous silica based systems. Surprisingly, the main product found in the hydroxylation of phenol with hydrogen peroxide over the titanated samples is hydroquinone (1,4-dihydroxybenzene), whereas only small amounts of catechol (1,2-dihydroxybenzene) were detected. In the literature on o/p ratio of around 1 is reported for this reaction catalysed

Table 2
Catalytic hydroxylation of phenol [a] over Ti-silicalite and Ti-silica

Sample	Si/Ti [b]	Efficiency [c]	H_2O_2 conversion [d]
SiO_2	–	0	2
S-1	–	0	3
TiO_2	–	–	0
Ti/SiO_2^{g}	16	5	100
Ti/S-1^{g}A	660	84	28
Ti/S-1^{g}B	200	48	46
TS-1	80	83	94
Ti/SiO_2^{lq}	130	20	24
Ti/S-1^{lq}1	120	57	77
Ti/S-1^{lq}2	150	50	83

[a] See experimental for conditions and formulation.
[b] Molar ratio as determined by ICP-AES.
[c] % dihydroxybenzenes formed/% H_2O_2 converted.
[d] % H_2O_2 converted after 6 hours of reaction.

by TS-1 [1,8]. Our results may indicate an enhanced regioselectivity that is not observed for TS-1, or a relatively fast consecutive reaction of the o-isomer.

As shown in fig. 4, the catalytic activity of the Ti/S-1^g samples is lower than that of TS-1. However, from table 2 it can be seen that the efficiency based on the amount of hydrogen peroxide consumed is the same for the samples of Ti/S-1^gA (84%) and TS-1 (83%). The efficiency of the other silicalite based samples is around 50%, whereas the efficiency of the amorphous silica based systems is very low: 20% for the liquid phase synthesised sample, and only 5% for the gas phase synthesised sample.

Given the limited exposure of Ti in the small particles on the external surface of the gas-phase treated samples, and the high activities and efficiencies obtained in the catalytic experiments, some Ti sites probably exhibit very high catalytic activities. It may be possible that Ti sites on the interface of the particles and the SiO_2 surface contribute significantly to the catalytic activity. Alternatively, small amounts of titanium present on the silicalite surface in between these particles could be responsible for the catalytic activity.

4. Conclusion

Titanium deposited on the outer surface of silicalite-1 leads to systems that are active in the hydroxylation of phenol with aqueous hydrogen peroxide. A sample obtained through gas phase deposition of $TiCl_4$ on large crystals of silicalite-1 is just as efficient as the TS-1 in the hydroxylation of phenol with hydrogen peroxide, although its activity is lower.

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