

## Synthesis, Characterization and Catalytic properties of silicon containing Anatase (TiO<sub>2</sub>)

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**Abstract:** A novel silicon containing Anatase is synthesized and characterized using different techniques such as XRD, SEM, C & N analysis, TG/DTA, FT-IR, ESR, UV-Vis, XPS, <sup>29</sup>Si MASNMR and benzene hydroxylation reaction. The results show that the silicon is incorporated in to the Anatase framework and synthesized samples are well crystalline.

Key words: Titanium, Silicon, XRD, SEM, TG/DTA, FT-IR, MAS NMR, benzene hydroxylation.

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### 1. Introduction

Titania powders are used as supports for the preparation of catalysts for the reduction of nitrogen oxides [1]. Since the process involves redox reactions, the electronic structure and the interactions of the adsorbed species with the substrate, are expected to play an important role. Doping of the TiO<sub>2</sub> solid with altrivalent ions but with similar size to Ti<sup>IV</sup>, may improve greatly the catalytic activity of the catalysts prepared [2-6]. Moreover, since extensive work has been carried out concerning the photo catalytic activity of TiO<sub>2</sub>/water interface is of great interest for the regulation of the surface potential and hence the aggregation and/or adsorption of charged species. On the basis of ion size considerations, ions such as Li<sup>+</sup>, Mg<sup>2+</sup>, W<sup>6+</sup> and Nb<sup>5+</sup> may be introduced into the titania lattice. The introduction into the lattice of powdered titania of these ions is effected by heating mixtures of titania powders with small volumes of concentrated dopant solutions (dry or wet impregnation). The calcinations process results not only in the loss of specific surface area due to sintering but also in solid phase transformations. Titanium oxide exists

in three polymorphic phases: rutile (tetragonal, density = 4.250 Mg m<sup>-3</sup>), anatase (tetragonal, 3.890 Mg m<sup>-3</sup>) and brookite (orthorhombic, 4.120 Mg m<sup>-3</sup>). The lower density solid phases are less stable and undergo transformation into rutile in the solid state. The transformation is accelerated by heat treatment and occurs at temperatures between 450 and 1200°C [7], while it depends on the nature, the structure and the preparation conditions of the precursor phase. Anatase doped with various metal ions has also been reported at low temperatures either by hydrolysis of titanium(IV) tetrachloride or/and titanium tetraisopropoxide in the presence of dopant ions [8,9] or by adsorption from solution and co-precipitation [10]. The problem with the preparation methods reported in the literature is the lack of control of the conditions during the formation of the new anatase nuclei and their further crystal growth. It is important to note that the kinetics of the formation of precipitates is very important both for the reproducibility of the preparations and for their final physicochemical characteristics [11].

While pure anatase is prepared by hydrolysis of  $TiCl_4$  in solution and in the gas phase [12] or by sol-gel methods [13-17], there are very limited reports on the quantification of the preparation conditions and their relative importance with respect to the physicochemical characteristics of the preparations.

In the present work we have studied the formation of anatase in ethylene glycol solutions of titanium ions as a function of the solution composition both in the absence and in the presence of  $Si^{4+}$  dopant ions. The oxide preparations (with and without the dopant ions) were characterized by XRD, SEM, TG/DTA, FT-IR, ESR, UV-Vis, XPS and  $^{29}Si$  MAS NMR techniques. The latter measurements aimed at investigating the effect of the preparation methods and of the presence of metal ions in the crystallizing medium on the phase stability of the precipitated titania.

## 2. Experimental

### 2.1 Chemicals and catalyst preparation

To solution of Ethylene glycol (54.74 g, 99.8%, s.d.fine, India), an appropriate amount of Hexamethylenimine (8.74 g, 99%, Aldrich, USA) was added. To the resultant liquid mixture, a solution of the required quantity of Tetraethylorthosilicate (7.34 g, 98%, Aldrich, USA) was added drop wise under vigorous stirring. 6.54 g of Titaniumtetrabutoxide (98%, Aldrich, USA) was added slowly to the above solution. The clear liquid thus obtained was stirred for 8 h in order to complete the hydrolysis of TEOS and  $Ti(OBu)_4$ . The chemical composition of the initial gel was :

$TiO_2$ : 1.835  $SiO_2$ : 4.638 HEM: 46.80 EG

The crystallization was carried out at 473K, typically for 15d under static conditions. The solid obtained was filtered, washed with distilled water, and dried at 373K for 5h in static air.

### 2.2 Characterization

X-ray diffraction patterns were recorded on a Rigaku (D/MAX III VC) instrument in the  $2\theta$  region of 15-100°. Scanning electron microscope pictures were taken using a JEOL JSM 5200 microscope. Chemical analysis was carried out by XRF using a Rigaku 3070 X-ray Spectrometer. TG/DTA analysis was carried out using TG/DTA32 SII Seiko instruments in nitrogen atmosphere from room temperature to 1000°C. The framework IR spectra were recorded in the diffuse reflectance mode using 300 : 1 ratio sample in KBr (Nicolet 60SXB). Electron spin resonance spectra of the as-synthesized titanium silicates in room temperature and liquid nitrogen temperature were obtained using a Bruker 200D spectrometer. The UV-Vis. diffuse reflectance spectra were recorded using a Pye Unicem (SP-8-100) UV-Vis. spectrometer in the 200-900nm region. XPS measured at 10<sup>-8</sup>mm using Vg Scientific, ESCA-II MK3 instrument. All spectra corrected at carbon C1s. MASNMR spectra were recorded in the solid state with a Bruker DRX 500 spectrometer operating at a field of 11.7 Tesla.  $^{29}Si$  NMR spectra were recorded at 99.3 MHz, 2 $\mu$ s (45°) pulse width and repetition time of 2s. Tetramethylsilane was used as standard.

### 2.3 Catalytic experiments

The liquid phase benzene hydroxylation reactions were conducted in a glass batch reactor. In a typical reaction, 0.1 mol of the substrate, and x mmol of  $H_2O_2$  (35 wt% aq., x = 30, 50, 67 and 100) were reacted over the

catalyst in the presence of acetonitrile under vigorous stirring (ca 800 rpm). H<sub>2</sub>O<sub>2</sub> was slowly injected drop-wise using a syringe pump (Sega, USA) during 30 min. The products were collected at various intervals of reaction times and were analyzed by high resolution capillary gas chromatography (HP 5880, using Flame Ionization Detector). The H<sub>2</sub>O<sub>2</sub> selectivity is defined as the moles of H<sub>2</sub>O<sub>2</sub> consumed in the formation of oxygenated benzene products and the phenol selectivity is defined as the moles of phenol obtained among the total moles of oxygenated benzene products formed in the reaction.

### 3. Results and discussion

#### 3.1 Characterization of the Catalysts

X-ray diffraction pattern of silicon containing Anatase TiO<sub>2</sub> is presented in Figure 1. From XRD spectra, it was found that the sample is Anatase type and crystalline with no crystalline phase impurity. This pattern is found to be stable upto

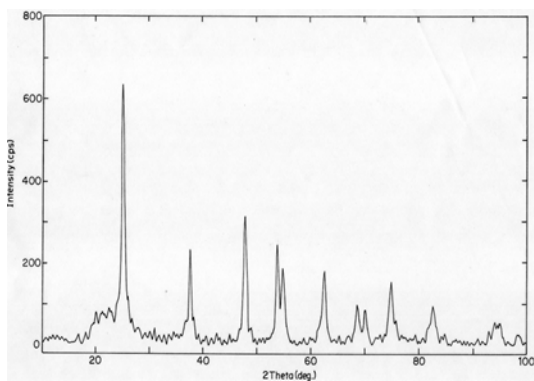


Fig. 1. X-ray diffraction pattern of silicon containing Anatase.

1000°C. The XRD pattern of dopant free anatase is similar. Elemental analysis of calcined (heating at the rate of 1.5°C/min to 550°C and kept at the same temperature for 8h and then

cooled) titanasilicate sample consist of Si/Ti = 3. The excess silicon present in the sample is as amorphous silica.

Figure 2 shows Scanning electron micrographs of the Anatase type sample having honeycomb structure with 6µm particle size. SEM also revealed that the sample is free from amorphous or other phase impurity materials. The BET surface area of the sample shows 140 m<sup>2</sup>/g with micropore volume 0.04 cm<sup>3</sup>/g. The Thermogravimetry/ Differential thermal analysis (TG/DTA) curves of the template containing Anatase type sample is presented in Figure 3. In the low temperature region up to 138°C, there is an endothermic weight loss of 3.50% is mainly due to the loss of

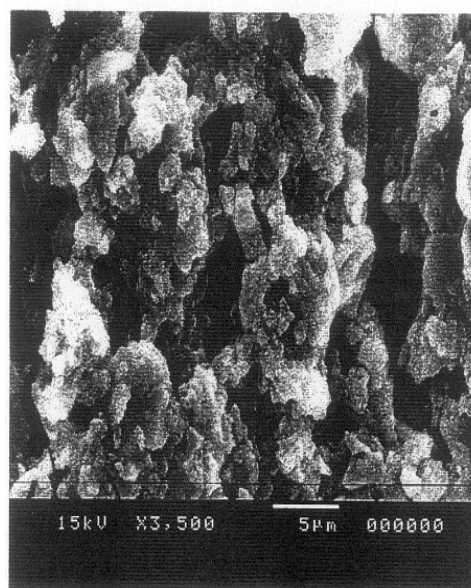


Fig.2.Scanning electron micrograph of silicon containing anatase.

adsorbed water. In the temperature region of 138 to 546.1°C, there is one stage of exothermic weight loss (33.64%) due to the oxidative decomposition of the organic template occluded in the sample. Based on the total loss due to template removal and

the carbon and nitrogen analysis are C = 21.31% and N = 3.21% respectively. Number of template molecules in 100g of the sample is 0.296 (calculated from carbon content) and 0.229 (calculated from nitrogen content). The excess template due to carbon may be due to the presence of ethylene glycol molecule in framework. As per the XRD pattern it consists of small pore, but contain more template molecule. This may due to the presence of template molecule in the mesophase of the sample. The actual position of the template and ethylene glycol are not clear.

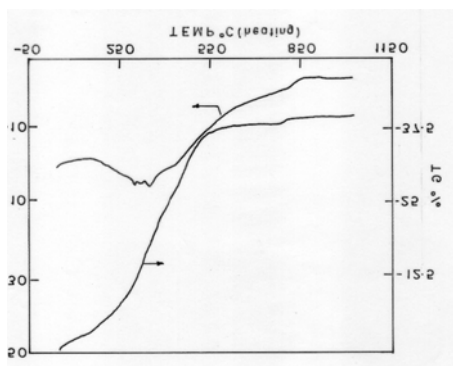
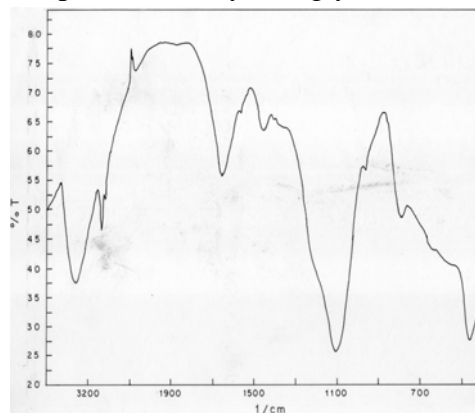


Fig.3 TG(a)/DTA(b) curves of silicon containing anatase.

The Fourier Transform Infrared (FT-IR) spectrum of the as-synthesized Anatase type sample in the framework region is shown in Figure 4. The different modes of tetrahedral linkages give bands at 1200 (wsh), 1105.1(vs), 964.3(w) 778.8(m), 600(wsh), 461(s)  $\text{cm}^{-1}$ . The bands can be assigned to asymmetric stretching, symmetric stretching, bending and pore opening vibrations of T-O-T linkages as described in earlier literature [18]. The peak at 964.3  $\text{cm}^{-1}$  is due to the Si-O-Ti bond [19] present in the Anatase type samples.

The Electron spin resonance (ESR) spectra of the sample in room temperature (298K) and at liquid nitrogen temperature (77K) are shown in Figure 5. The peaks are due to the presence of  $\text{Ti}^{3+}$  ions in the sample. The  $\text{Ti}^{4+}$  present in the synthesis gel was reduced into  $\text{Ti}^{3+}$  on reaction with template and ethylene glycol. The g



and g<sub>⊥</sub> at room temperature are 1.931

Fig. 4. FT-IR spectra of silicon containing anatase in the framework region.

and 1.962 and at liquid nitrogen temperature they are 1.906 and 1.970. This is similar to the earlier reports [20]. Diffuse reflectance spectra of Anatase is shown in Figure 6. Tetrahedral framework, Ti species have recently been shown to exist in TS-1 as opened  $(\text{SiO})_3\text{TiOH}$  and closed  $(\text{SiO}_4)_4\text{Ti}$  species with absorption bands at 220 and 270 nm respectively [21]. The DRS UV-Vis (ultra violet) spectra of the sample show an absorption maximum at 280 nm and a shoulder at 450 nm, suggesting the presence of isolated tetrahedral and octahedral Ti species in the lattice, respectively.

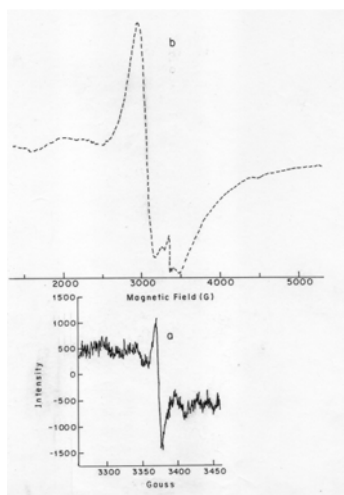


Fig. 5. ESR spectrum of silicon containing Anatase at a) room temperature (298K) and b) 77K.

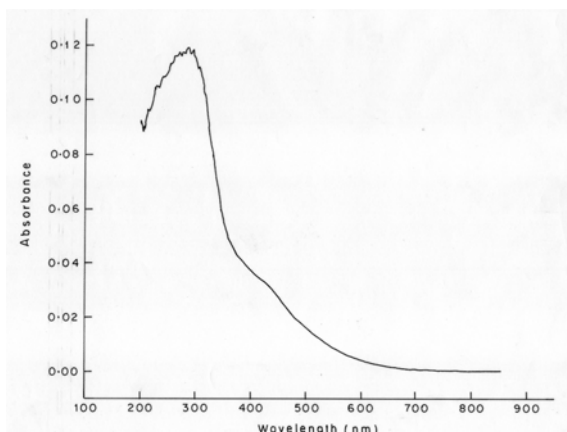


Fig. 6. UV-Vis spectrum of silicon containing Anatase in the as-synthesized form.

The X-ray photoelectron spectroscopy (XPS) data obtained for the various elements of the sample in as-synthesized form are as follows. The binding energies of Carbon = 289, Titanium = 462 and 468, Silicon = 106.75 and Oxygen = 636.25 eV. The analysis of XPS intensity ratios indicate a surface enrichment of titanium (Figure 7). The surface concentration of Ti (Si/Ti = 2.6) is either equal or slightly higher than the

bulk values reported for the titanium silicate sample reported in this paper. It is interesting to note that the  $Ti_{2p_{3/2}}$  binding energy is higher than the 457.8-458.0 eV value accepted for octahedral  $Ti^{4+}$ . It is believed that the increase in binding energy (462.2 and 468 eV) is associated with the tetrahedral coordination of titanium [22].

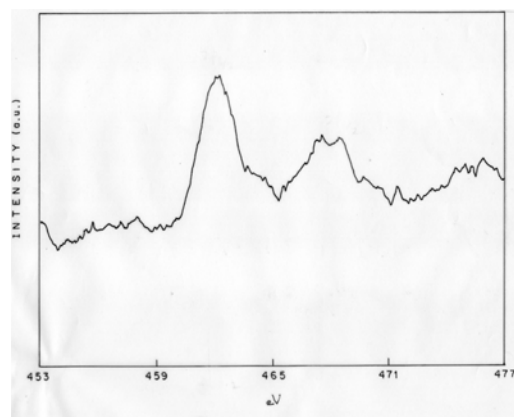


Fig.7. XPS spectrum of silicon containing Anatase for titanium.

Figure 8, the Anatase type phase,  $^{29}Si$  solid-state Nuclear Magnetic Resonance (NMR) spectrum with magic angle spinning (MAS) recorded on a Bruker 500DX spectrometer. It shows four lines with chemical shifts -96.81, -100.12, -105.15 and -111.77 ppm referenced to tetramethylsilane. By comparing the chemical shifts with other titanosilicate minerals such as zorite and Lorenzenite, the three resonance's at -96.81, -100.12 and -105.15 can be assigned [23] to  $Si(Si:3Ti)$ ,  $Si(2Si:2Ti)$  and  $Si(3Si:Ti)$  and the resonance at -111.77 ppm can be assigned to  $Si(4Si:0Ti)$ .

### 3.2 Hydroxylation of benzene

The effect of the substrate to  $H_2O_2$  molar ratio in the hydroxylation of benzene over TS-1 (Titanium silicalite - 1) and Anatase type/ $H_2O_2$  systems are

presented in Table 1. With increasing benzene/H<sub>2</sub>O<sub>2</sub> molar ratio, both the H<sub>2</sub>O<sub>2</sub> selectivity utilization towards the formation of phenol, and its further oxidation products (like p-benzoquinone, catechol and hydroquinone) and phenol selectivity among products were also increased as expected. However, the benzene conversion and H<sub>2</sub>O<sub>2</sub> selectivity towards oxygenated benzenes are considerably higher (two to three times) in anatase type sample than could be achieved in the presence of TS-1. The corresponding increase in reaction rate (T.O.F) is about 3 times (Table 1). The benzene conversion, H<sub>2</sub>O<sub>2</sub> selectivity,

#### 4. Conclusions

A novel Silicon containing Anatase is discovered and it is characterized by XRD, SEM, TG/DTA, C & N analysis, FT-IR, ESR, UV-Vis, XPS, MASNMR and catalytic properties. XRD pattern shows that the sample is similar to the reported one. SEM shows its uniform morphology. TG/DTA shows the

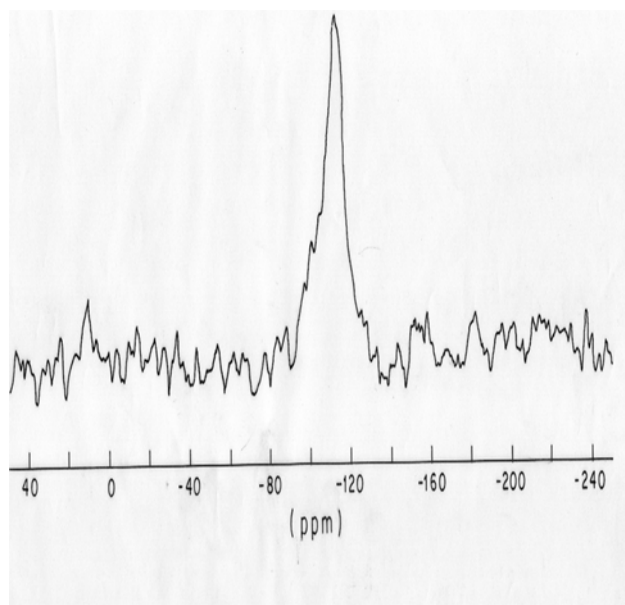


Fig. 8. <sup>29</sup>Si MAS NMR spectrum of silicon containing anatase.

rate of reaction (TOF), and phenol selectivity increase by increasing benzene to H<sub>2</sub>O<sub>2</sub> molar ratio. A small amount of secondary oxidation products (10 to 20%) like p-benzoquinone, catechol, and hydroquinone formed due to further hydroxylation of primarily formed phenol, were also obtained.

presence of two stages of weight loss (37.14 %). Similar results are obtained on carbon and nitrogen analysis. FT-IR shows the presence of Si-O-Ti bond. ESR shows the presence of Ti<sup>3+</sup> ions. Presence of Tetrahedral and octahedral

Table 1: Effect of Benzene to H<sub>2</sub>O<sub>2</sub> Molar Ratios on the Oxidation of Benzene over TS-1 and silicon containing Anatase.<sup>a</sup>

Benz/H <sub>2</sub> O <sub>2</sub> molar ratio	Catalyst	Conv (%)	H <sub>2</sub> O <sub>2</sub> sel (%) <sup>b</sup>	TOF(h <sup>-1</sup> ) <sup>c</sup>	Product selectivity (%) <sup>d</sup>			
					PH	PBQ	CA	HQ
1.0	TS-1	11.6	13.7	2.9	82.0	10.4	4.6	3.0
	Anatase	35.2	27.1	9.0	85.6	9.2	2.0	3.2
1.5	TS-1 type	9.8	16.6	2.4	86.9	9.0	2.5	1.6
	Anatase type	30.5	33.0	7.5	89.5	7.3	1.4	1.8
2.0	TS-1	8.7	19.2	2.1	90.1	6.0	2.3	1.6
	Anatase type	26.8	40.1	6.5	90.4	6.0	1.5	3.1
3.0	TS-1	6.4	20.6	1.5	92.8	4.9	1.4	0.9
	Anatase type	20.4	42.3	4.6	95.0	2.9	3.1	1.0

<sup>a</sup> - Catalyst (15 wt% with respect to substrate, H<sub>2</sub>O<sub>2</sub> was slowly fed into the reaction mixture for a period of 30min. Temperature 333K and Reaction time 8h.

<sup>b</sup> - Calculated considering the utilization of one mole H<sub>2</sub>O<sub>2</sub> in the formation of phenol + two moles for the formation of catechol, hydroquinone and p-benzoquinone, and mole % H<sub>2</sub>O<sub>2</sub> selectivity is based on the mole of H<sub>2</sub>O<sub>2</sub> used.

<sup>c</sup> - Turn over frequency = moles of H<sub>2</sub>O<sub>2</sub> converted for producing phenol + secondary products (catechol, hydroquinone and p-benzoquinone per mole of Ti per h.

<sup>d</sup> - PH = phenol, PBQ = p-benzoquinone, CA = catechol and HQ = hydroquinone.

titanium were observed by UV-Vis and XPS analysis. Multiple Silicon environments are observed by <sup>29</sup>Si MASNMR. Silicon containing Anatase found to be a better catalyst compared to TS-1 in benzene hydroxylation reactions.

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