

# Oxidation of aniline over titania pillared montmorillonite clays

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## Abstract

Titania pillared clays (Ti-PILC) have been synthesized employing conventional stirring (method I) and ultrasonic agitation (method II) techniques followed by hydrothermal treatment. The characterization results revealed the formation of Ti-PILC with significant reduction of time when ultrasonic method was used. Subsequent hydrothermal treatment on the samples has resulted in the increase in the crystallinity and the transformation of anatase  $\text{TiO}_2$  to rutile  $\text{TiO}_2$ . The rutile phase is more prominent in the samples prepared by stirring method. UV–Vis studies on the samples exhibit blue shift in the absorption band due to the quantum size effect. This indicates that a major part of  $\text{TiO}_2$  in the pillared clay could be well below 10 nm in size, which is supported by XRD and the average pore size. The pillared clay catalysts have proved to be promising in aniline oxidation with  $\text{H}_2\text{O}_2$ , selectively forming azoxybenzene under the working conditions. The aniline conversion and the product distribution largely depended on the catalyst concentration,  $\text{H}_2\text{O}_2$  to aniline mole ratio, the nature of the solvent and the oxidant. Higher conversion of aniline and greater selectivity for azoxybenzene was obtained with methanol as the solvent.

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## 1. Introduction

The oxidation of aniline is an important reaction for the synthesis of its oxygenated derivatives such as hydroxylamine, nitroso, nitro, azo and azoxy compounds. Among these, the preparations of nitroso and azoxy compounds have assumed special importance as synthetically useful intermediates. Aromatic nitroso compounds are used in the vulcanization of rubber, stabilization of halogenated materials and as antioxidants in lubricating oil (Zengel, 1983), whereas azoxybenzenes are employed as dyes, reducing agents, chemical stabilizers and polymerization inhibitors. Some derivatives of azoxybenzenes are used as

liquid crystals in electronic display and therapeutic medicines (Sakuae et al., 1993). Consequently, a variety of oxidation methods (both in homogenous and heterogenous media) using stoichiometric and catalytic routes have been reported. For example, arylamines can be oxidized with stoichiometric oxidants such as peracetic acid (White and Emmons, 1962)  $\text{MnO}_2$  (Wheeler and Gonzalez, 1964),  $\text{Pb}(\text{OAc})_4$  (Baumgarten et al., 1965) and  $\text{Hg}(\text{OAc})_2$  (Wenkert and Wickberg, 1962). Oxidation of aniline in homogenous medium is reported over transition metal complexes of titanium, vanadium (Sheldon and Dakka, 1994), iron (Huang et al., 2001) and molybdenum complexes (Tollari et al., 1993). In the heterogenous medium, various types of molecular sieves (Selvam and Ramaswamy, 1996; Waghmode et al., 2001) and mesoporous silica containing nanometric dispersed titanium oxide (Tuel and Hubert-Pfalzgraf, 2003) have been

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reported to effectively catalyze the oxidation of aniline to azoxybenzene.

Pillared interlayered clays (in short, PILCs) are a class of molecular sieve-like materials with a large pore size, high surface area, microporous structure, acidic properties and good thermal stability (Gil et al., 2000). These solids show interesting properties toward adsorption and catalysis. Depending upon the nature of the pillars, pillared clays are used in different types of reactions. For example, alumina pillared clay is used as hydrotreating catalysts (Albertazzi et al., 2005), iron pillared clay in ethylbenzene dehydrogenation (Huerta et al., 2003) titania pillared clay in the photocatalytic degradation of organic substances in water (Ooka et al., 2003) and in oxidation reactions (Del Castillo et al., 1996). Novel methods like ultrasound (Pérez-Zurita et al., 2005) and microwave irradiation (Singh et al., 2004) for the synthesis of pillared clays have also been reported in literature reducing the intercalation time.

This paper investigates the effect of synthesis conditions on the properties of titania pillared montmorillonite clay (Ti-PILC) employing ultrasonic and conventional techniques and presents the catalytic activity of the samples for the oxidation of aniline with aqueous H<sub>2</sub>O<sub>2</sub>. The influence of the concentration of oxidant and catalyst, nature of oxidant and solvents on the oxidation of aniline is being reported.

## 2. Experimental

### 2.1. Synthesis of titania pillared clay (Ti-PILC)

The chemical components used in this study are Na–montmorillonite, referred to as Na–MMT, (Kunipia-F, Kunimine Industrial Company), with the structural formula of (Na<sub>0.35</sub>K<sub>0.01</sub>Ca<sub>0.02</sub>)(Si<sub>3.89</sub>Al<sub>0.11</sub>)(Al<sub>1.60</sub>Fe<sub>0.08</sub>Mg<sub>0.32</sub>)O<sub>10</sub>(OH)<sub>2</sub> nH<sub>2</sub>O and the cation exchange capacity of 1.2 meq/g and titanium tetraisopropoxide (Aldrich, 97%). The pillared clay samples were prepared by conventional method followed by hydrothermal treatment (HT) (method I) according to the procedure earlier reported by Ooka et al. (1999). Titanium tetraisopropoxide was added to 1 M HCl solution under vigorous stirring at 333 K. The HCl/alkoxide molar ratio was maintained at unity. The resulting slurry was peptized at 333 K to give a clear TiO<sub>2</sub> sol. An aqueous slurry of the raw clay (1 wt.%) was added to this sol under vigorous stirring condition. The resulting suspension was stirred for 3 h at 323 K. The product obtained was then centrifuged and washed with distilled water several times in order to remove the excess TiO<sub>2</sub> sol. This sample was divided into two parts. The first part was dried at 373 K for 4 h and subsequently calcined at 773 K for 3 h and designated as S. The second part was dispersed in water (2 wt.% slurry) and hydrothermally treated in an autoclave at 423 K (150 °C) for 1 h. The hydrothermally treated product was centrifuged, washed and dried in air at 373 K for 4 h and calcined at 773 K for 3 h.

This sample was labeled as SHT-150-1. Similar samples were prepared wherein the temperature was kept constant and the duration was varied for 2, 6, 12 and 24 h (Table 1). Similarly two more samples were prepared at a HT temperature of 473 K and 523 K for 2 h. In method II, the synthesis procedure is similar to method I except that ultrasonication (US) was employed in place of stirring (Katdare et al., 1999) to the sol containing Na–MMT and titanium tetraisopropoxide (Aldrich, 97%). Ultrasonication was done for 20 min at ambient temperature (Shesin, Japan, operating frequency 38 kHz) followed by hydrothermal treatment (USHT). The Ti-PILC pillared clay samples thus prepared are listed in Table 1.

### 2.2. Characterization of Ti-PILC

The qualitative identification of Ti-PILC samples was done by powder X-ray diffraction (PXRD) technique. The PXRD patterns of the Ti-PILC samples were recorded using Ni filtered Cu-K $\alpha$  radiation, ( $\lambda$ =1.5406 Å); graphite crystal monochromator and scintillation detector (Rigaku, Model D/MAX III VC, Japan;). The crystallite sizes of the Ti-PILC samples were calculated from FWHM of anatase (101) diffraction peak ( $2\theta$ =25.3°) using the Debye–Scherrer's equation (Klug and Alexander, 1974). The TiO<sub>2</sub> content in the samples was determined by elemental analysis using X-ray fluorescence technique on a Rigaku 3070 X-ray wavelength dispersive spectrometer.

The nitrogen adsorption–desorption isotherms of the calcined samples were determined by N<sub>2</sub> adsorption at 77 K (Coulter 100 CX Omnisorp). The monolayer volumes were taken at  $p/p_0$ =0.02

Table 1  
Physicochemical characterization data of TiO<sub>2</sub> pillared montmorillonite

Sample	Hydrothermal crystallization conditions	TiO <sub>2</sub> content <sup>a</sup> (wt.%)	Crystallinity of TiO <sub>2</sub> (%) <sup>b</sup>	Crystallite size of TiO <sub>2</sub> <sup>c</sup> (nm)
Na–clay	–	–	–	–
SHT-150-1	150 °C, 1 h	56	48	4.2
SHT-150-2	150 °C, 2 h	58	61	4.3
SHT-150-6	150 °C, 6 h	53	64	4.5
SHT-150-12	150 °C, 12 h	65	62	4.7
SHT-150-24	150 °C, 24 h	62	68	4.2
SHT-200-2	200 °C, 2 h	58	63	4.7
SHT-250-2	250 °C, 2 h	57	60	5.2
USHT-150-2	150 °C, 2 h	21	66	3.9
USHT-200-2	200 °C, 2 h	30	67	4.7
USHT-250-2	250 °C, 2 h	30	67	5.4
S	None	55	37	4.5
US	None	11	56	3.7

<sup>a</sup> Determined by elemental analysis using X-ray fluorescence method.

<sup>b</sup> % Anatase Crystallinity  

$$= \frac{\text{Area under the 101 reflection of the test sample}}{\text{Area under the 101 reflection of the reference sample}} \times 1000$$

<sup>c</sup> Calculated from (1 0 1) diffraction peak of anatase using Scherrer's equation.

where all the micropores are filled up. The microporous area was obtained from the  $t$ -plot of  $N_2$  adsorption data at higher partial pressures. BJH method was used to calculate the pore-size distribution.

The UV–Vis diffuse reflectance spectra of the solid samples were recorded in the region 200 to 600 nm using a spectrophotometer (Shimadzu UV2101 model) with  $BaSO_4$  as the reference material.

### 2.3. Catalytic activity

The Ti-PILC samples have been tested for the oxidation of aniline in a batch reactor at room temperature (300 K). In a typical reaction, the catalyst (200 mg) was dispersed in a solvent (10 ml) containing the substrate (3 mmol) and stirred. The oxidizing agent ( $H_2O_2$ , 30 wt.% in water), corresponding to substrate to oxidant mole ratio 1, was added in one lot. Aliquots were periodically collected (every 1 h.), centrifuged to remove the solid particles and analyzed by gas chromatographic technique using a capillary column, HP-5, 5% phenyl methyl siloxane ( $30\text{ m} \times 320\ \mu\text{m} \times 0.25\ \mu\text{m}$ ) and FID.

## 3. Results and discussion

### 3.1. Structural and textural properties

Fig. 1 shows the XRD patterns in the small angle region of Na–MMT and representative samples prepared by both the methods without and with hydrothermal treatment. Na–MMT showed the (001) diffraction peak at  $2\theta = 7^\circ$  (Fig. 1a). The ordered pillaring of layered materials will result in the shifting of the (001) to lower  $2\theta$  region (Sterte, 1986). However, all the pillared clay samples, both hydrothermally untreated and treated did not show the (001) peak. The absence of (001) peak in the lower region is due to the lack of a sufficiently ordered and oriented silicate layer structure. The poor long range ordering may be due to the damage to the clay layers caused by acid leaching. However, the observed small angle scattering indicates that the mesopores are included in the pillared clays, irrespective of the method of preparation.

In Fig. 1, the samples did not exhibit higher order basal reflection. Similar results on Ti-PILC were discussed in the literature (Ooka et al., 1999), which was characterized as a mixture of pillared structure and partially delaminated structure (Pinnavaia et al., 1984) from its TEM observation and good agreement of crystallite size with the average pore diameter. A similar agreement of the crystallite size determined by XRD and the average pore diameter in our samples suggests the formation of mixed structure in the pillared samples prepared.

Fig. 2(A) shows the XRD patterns of the hydrothermally untreated samples prepared by the conventional stirring (S) and ultrasonication (US) method. The X-ray diffraction peaks at  $2\theta = 25.3^\circ$ ,  $49^\circ$  and  $55^\circ$  were present in both the samples, indicating the presence of anatase titania (JCPDS: 21-1272). The sample prepared by ultrasonication (in shorter duration) exhibited higher crystallinity than the sample prepared by stirring method.

To study the effect of duration of hydrothermal treatment on the crystallinity of the samples and phase change of anatase titania to rutile, the Ti-PILC samples prepared by method I were treated at 423 K for 1, 2, 6, 12 and 24 h. The crystallinity increased from 37% for untreated sample (S) to 68% for the sample SHT-150-24. As discussed earlier, the X-ray diffraction peaks due to anatase were present in all the samples. This peak became more intense with the duration of the hydrothermal treatment due to better crystallization of anatase phase (Fig. 2B). An additional peak at  $2\theta = 27.32^\circ$  attributed to rutile phase was observed in the sample SHT-150-1. The intensity of this peak increased with longer duration of hydrothermal treatment and became prominent in the samples SHT-150-12 and SHT-150-24 (Fig. 2B). It indicates that with longer duration of hydrothermal treatment, part of anatase phase is transformed to the more stable rutile phase due to the growth of anatase particles. This is in line with the thermodynamic stability of the three phases of titania viz; anatase < brookite < rutile. These results show that even

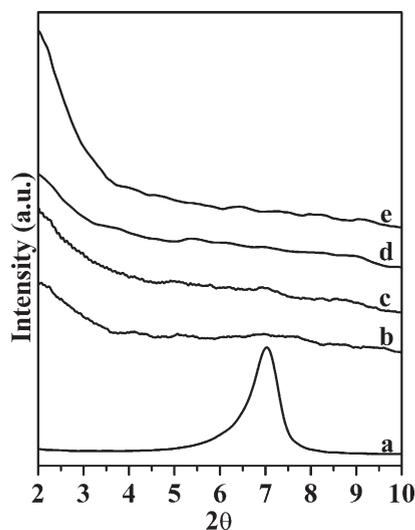


Fig. 1. XRD patterns in the small angle region of the raw clay and the Ti-PILC samples prepared by conventional stirring method (S) and ultrasonic method (US) followed by hydrothermal treatment (HT) for 2 h. a) Na–MMT (Na–montmorillonite), b) S (hydrothermally untreated), c) SHT-250-2 (hydrothermally treated), d) US (hydrothermally untreated), and e) USHT-250-2 (hydrothermally treated).

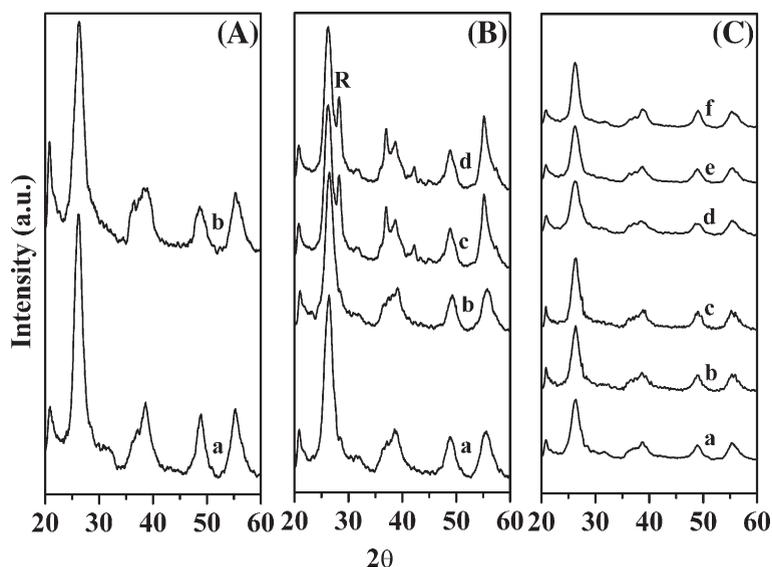


Fig. 2. (A) XRD patterns in the wide angle range of hydrothermally untreated Ti-PILC samples. a) S (conventional stirring method) and b) US (Ultrasonic method). (B) XRD patterns in the wide angle range of the Ti-PILC samples prepared by conventional stirring method (S) followed by hydrothermal treatment (HT) for various duration at 423 K. a) SHT-150-1, b) SHT-150-6, c) SHT-150-12 and d) SHT-150-24 \*R — Rutile. (C) XRD patterns in the wide angle range of the Ti-PILC samples prepared by conventional stirring method (S) and ultrasonic method (US) followed by hydrothermal treatment (HT) at different temperatures for 2 h. a) SHT-150-2, b) SHT-200-2, c) SHT-250-2, d) USHT-150-2 d) USHT-200-2 and e) USHT-250-2.

though the sample SHT-150-24 exhibited maximum crystallinity it also exhibited a higher content of rutile phase. The sample SHT-150-2 showed optimum crystallinity and a lower content of rutile phase. Hence, for further studies all the samples were hydrothermally treated for 2 h. The effect of hydrothermal treatment temperature on the Ti-PILC samples was studied by subjecting the samples prepared by method I to hydrothermal treatment at 473 and 523 K. The increase in the hydrothermal temperature did not have much effect on the crystallinity of the samples (60–63% for SHT and 66–67% for USHT samples) (Table 1). For comparison purposes the other set of samples synthesized by employing ultrasonication i.e., method II were hydrothermally treated at 423, 473 and 523 K for 2 h.

Fig. 2C shows the wide-angle X-ray diffraction patterns of the samples prepared by both conventional (S) and ultrasonication (US) methods, followed by hydrothermal treatment (HT) at different temperatures for 2 h. The peaks due to anatase titania are more intense in the X-ray patterns of the solids prepared by conventional method compared to the solids prepared by ultrasonication method. Usually the anatase phase is produced from the Ti species that are not incorporated as pillars during the hydrothermal treatment (Yamanaka et al., 1992;) but remain outside the clay structure (Brown, 1980), which is enhanced by the longer intercalation periods used in the conventional method. The samples prepared by

ultrasonication method have lower  $\text{TiO}_2$  content as compared to samples prepared by method I (Table 1). This is further supported by the lower intensity of the (001) peak of anatase titania in XRD patterns of the samples prepared by method II.

On the other hand, no distinct peak due to rutile phase was observed in US and USHT samples. However, tailing of the anatase peak in these samples indicates the presence of rutile phase in lower concentration as compared to the samples prepared by method I. Also use of ultrasonication in the preparation of Ti-PILC gives material with higher crystallinity (56%) in shorter duration (20 min.) as compared to conventionally prepared sample (37% in 3 h).

The crystallite size of the anatase titania in the pillared clay samples was calculated by the broadening of the X-ray diffraction (101) at  $2\theta = 25.3^\circ$  using the Debye–Scherrer's equation. The crystallite size of all the samples is listed in Table 1. As it can be seen the crystallite size of  $\text{TiO}_2$  did not vary much (4–5 nm) in both sets of samples. From this it can be concluded that the crystallite size of anatase is similar in all the samples regardless of the method of preparation.

Fig. 3(A) and (B) shows the adsorption–desorption isotherms of nitrogen on the Na–MMT, and the samples prepared by the method I and method II (hydrothermally untreated and treated at different temperatures for 2 h). The isotherms of all the samples are identical and seem

to be nearly type IV characteristic of solids that include both micropores and mesopores [BDDT classification] (Brunauer et al., 1940). BET surface area and the total pore volume of the samples varied from 64 to 137 m<sup>2</sup> g<sup>-1</sup> and 0.21 to 0.24 cm<sup>3</sup> g<sup>-1</sup> (method I) and 67 to 152 m<sup>2</sup> g<sup>-1</sup> and 0.22 to 0.29 cm<sup>3</sup> g<sup>-1</sup> (method II). The TiO<sub>2</sub> content of the samples varied from 55 to 65 wt.% (method I) and 11 to 30 wt.% (method II). The large difference between the TiO<sub>2</sub> content of the samples prepared by the two methods is due to the differences in the duration of the synthesis period in these two methods. As mentioned earlier, the prepared pillared clays were considered to be a mixture of pillared structures and partially delaminated structures. Thus, TiO<sub>2</sub> possibly existed in the interlayer regions as well as on the external surface of the pillared clay.

The *t*-plot method was used to analyze the pillaring state of the samples. The results are shown in Fig. 4 and Table 2. Fig. 4 shows the *t*-plots of Na–MMT along with the samples synthesized by the two methods. The volume of nitrogen adsorbed on the pillared samples is very much larger than that on Na–MMT, which supports the development of the porous structure upon pillaring of TiO<sub>2</sub> in the montmorillonite clay. Na–MMT did not show any clear bending on its *t*-plot, which is characteristic of solids possessing only micropores. The *t*-plots of all the pillared samples show a bending point. This type of *t*-plot is characteristic of porous solids possessing both micro- and mesopores. The micropore parameters obtained by the analysis of *t*-plot are shown

in Table 2. The parameters indicate that all the samples developed microporosity. This large microporosity is not accountable only with the delaminated structure, which indicates that a considerable amount of TiO<sub>2</sub> exists as pillars in the interlayer region of the samples. This is also supported by the good agreement between the TiO<sub>2</sub> crystallite size and average pore diameter (Tables 1 and 2).

### 3.2. Spectral analysis of the samples

#### 3.2.1. Diffuse reflectance UV–Vis spectra

The reflectance spectra obtained by differentiating the ordinate of the diffused reflectance UV–Vis spectra of the standard sample Degussa (P-25) along with the samples prepared by method I and method II (hydrothermally untreated and treated at different temperatures for 2 h) are shown in Fig. 5. At longer wavelengths, the shape of the absorption peak of P-25 shows a tailing effect. This effect is due to the overlap of the absorption of rutile, a minor phase in P-25 (20%), on absorption of anatase (80%). The tailing of the absorption peak of anatase is more in the samples prepared by method I and becomes prominent with the increase in the hydrothermal treatment temperature. In the case of the samples prepared by method II, the tailing effect is less and the sharp absorption edges are indicative of a lower concentration of rutile phase (as supported by XRD). A clear blue shift in the absorption edge maxima is seen in the pillared clay samples as compared to P-25, which has

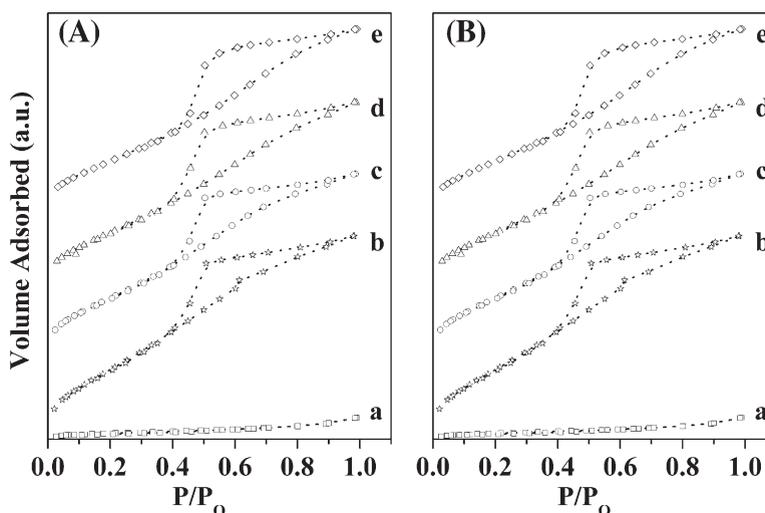


Fig. 3. A) N<sub>2</sub> adsorption isotherms at 77 K of the raw clay and the Ti-PILC samples prepared by conventional stirring method (S) followed by hydrothermal treatment (HT) at different temperature for 2 h. a) Na–MMT, b) S (hydrothermally untreated), c) SHT-150-2, d) SHT-200-2 and e) SHT-250-2. B) N<sub>2</sub> adsorption isotherms at 77 K of the raw clay and the Ti-PILC samples prepared by ultrasonic method (US) followed by hydrothermal treatment (HT) at different temperature for 2 h. a) Na–MMT, b) US (hydrothermally untreated), c) USHT-150-2, d) USHT-200-2 and e) USHT-250-2.

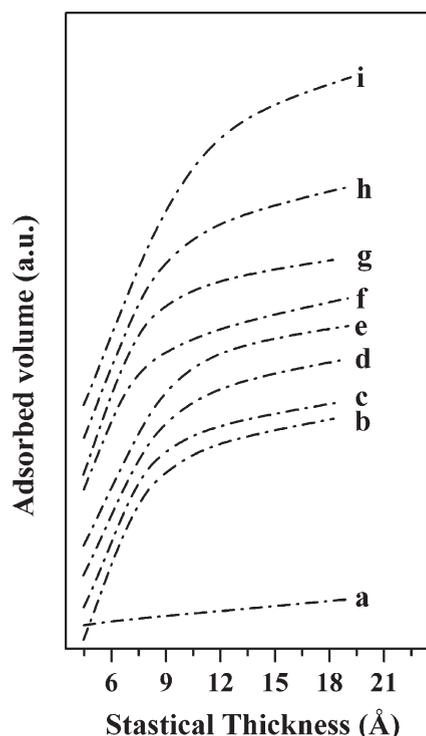


Fig. 4.  $t$ -plots of the raw clay and the Ti-PILC samples prepared by conventional stirring methods (S) and ultrasonication (US) followed by hydrothermal treatment (HT) at different temperature for 2 h. a) Na–MMT, b) S (hydrothermally untreated), c) SHT-150-2, d) SHT-200-2, e) SHT-250-2, f) US (hydrothermally untreated), g) USHT-150-2, h) USHT-200-2 and i) USHT-250-2.

well grown anatase crystallites in size ( $\sim 20$  nm) due to the quantum size effect. This blue shift is an indication of the quantum size effect (Brus, 1983; Anpo et al., 1985,

1987), which is observable in particles whose size is below 10 nm.

Similar absorption edges among the pillared clay samples suggest that the crystallite size of  $\text{TiO}_2$  was similar to one another. This is in agreement with the crystallite sizes determined from XRD data (Table 1). Thus, from the UV absorption spectra it can be concluded that the major part of  $\text{TiO}_2$  in the pillared clay could be well below 10 nm in size.

### 3.3. Catalytic studies

It is known that the oxidation of aniline can be carried out with hydroperoxides in the presence of catalytic amount of certain metal compounds (Howe and Hiatt, 1970). Among the various materials that have been reported active in this reaction, TS-1 is the most explored (Gontier and Tuel, 1994; Selvam and Ramaswamy, 1995). MCM-41 modified with transition metals such as Cu, Cr, V, (Gomes et al., 2005) and ETS-10 (Waghmode et al., 2001) molecular sieves were also found to be active for the selective oxidation of aniline. However, these reactions were carried out at non-ambient conditions. To our knowledge,  $\text{TiO}_2$  pillared clays have not yet been reported for this reaction though they are extensively used for the photocatalytic decomposition of various pollutants (Ooka et al., 1999, 2003). Nevertheless, the aim of this study was to find out whether the pillared clay samples prepared could be active in the oxidation of aniline with hydroperoxides at ambient temperature.

In this paper we have investigated the effect of various parameters on the oxidation of aniline over  $\text{TiO}_2$  pillared clay.

Table 2  
Structural and textural data of the raw clay and the  $\text{TiO}_2$  pillared samples

Sample	Specific surface area <sup>a</sup> ( $\text{m}^2 \text{g}^{-1}$ )	Microporous surface area <sup>b</sup> ( $\text{m}^2 \text{g}^{-1}$ )		Total pore volume <sup>b</sup> ( $\text{cm}^3 \text{g}^{-1}$ )	Microporous volume <sup>b</sup> ( $\text{cm}^3 \text{g}^{-1}$ )	Average pore diameter <sup>b</sup> (nm)
		Internal	External			
Na–clay	13	3	10	0.02	0.002	0.09
SHT-150-1	233	135	98	0.24	0.09	4.2
SHT-150-2	215	123	92	0.22	0.08	4.2
SHT-150-6	191	98	93	0.21	0.07	4.4
SHT-50-12	172	64	108	0.22	0.05	5.1
SHT-150-24	191	76	115	0.24	0.06	4.9
SHT-200-2	197	101	96	0.22	0.07	4.5
SHT-250-2	191	92	99	0.21	0.06	4.6
USHT-150-2	249	152	97	0.24	0.10	3.9
USHT-200-2	208	100	108	0.24	0.07	4.7
USHT-250-2	213	67	146	0.29	0.06	5.5
S	237	137	100	0.24	0.09	4.1
US	223	145	78	0.22	0.09	3.9

<sup>a</sup> Calculated from nitrogen adsorption isotherm using the BET equation.

<sup>b</sup> Determined from nitrogen adsorption isotherm.

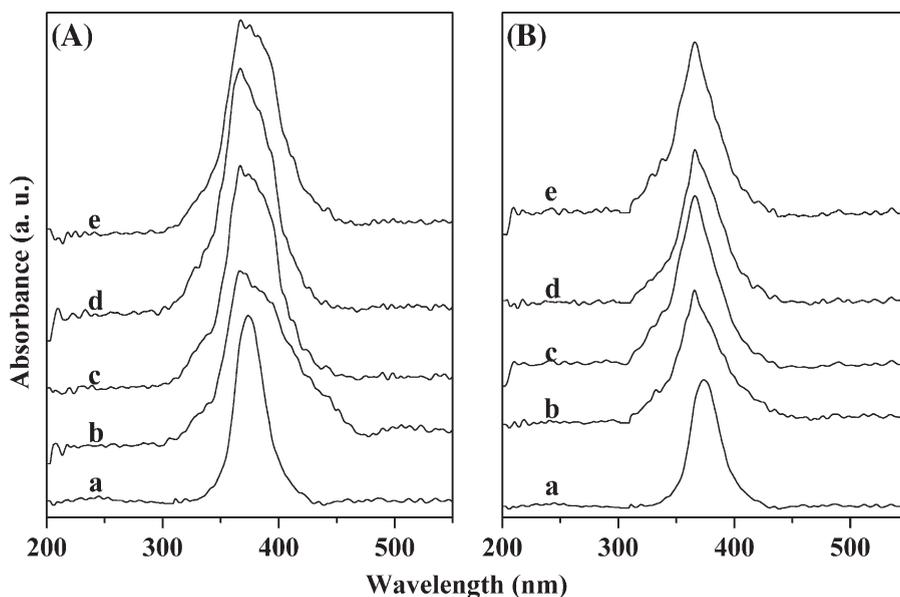


Fig. 5. (A) UV–Vis DRS spectra of pure anatase and the Ti-PILC samples prepared by conventional stirring method (S) followed by hydrothermal treatment (HT) at different temperature for 2 h. a) Degussa (P-25), b) S (hydrothermally untreated), c) SHT-150-2, d) SHT-200-2 and e) SHT-250-2. (B) UV–Vis DRS spectra of pure anatase and the Ti-PILC samples prepared by ultrasonic method (US) followed by hydrothermal treatment (HT) at different temperature for 2 h. a) Degussa (P-25), b) US (hydrothermally untreated), c) USHT-150-2, d) USHT-200-2 and e) USHT-250-2.

### 3.3.1. Effect of solvent

In liquid phase reactions, the performance of the catalyst greatly depends on the nature of the solvent used. The solvent affects both the conversion and the product selectivity. NSB was formed in high yield with peroxotungstophosphate (PCWP) catalyst in  $\text{CHCl}_3$  whereas it was inactive in methanol (MeOH). An intermediate behaviour was observed in *tert*-butanol (Sakuae et al., 1993). Gontier and Tuel (1994) reported that the rate of formation of AZOXY depended on the differences in the polarities and the solubility of the reaction products formed in different solvents.

The reaction was carried out using different solvents viz; methanol (MeOH), acetonitrile (MeCN) and acetone. Acetone was chosen since it has been reported that it can help prevent the poisoning of the catalytic sites during the reaction (Tuel et al., 1991). Water was not used, as the solubility of aniline in water is negligible at reaction temperature. The sample SHT-200-2 was used to study the effect of solvents on the oxidation of aniline. Table 3 shows the conversion and the product selectivity. Although azoxybenzene (AZOXY) is the major product in all the three solvents, the conversion decreases in the order methanol > acetonitrile > acetone, whereas the selectivity is in the order of methanol > acetone > acetonitrile. The observed differences may be due to the different polarities of the solvent and/or solubility of the different products of the

reaction. Similar studies have been reported in the literature by various authors (Gontier and Tuel, 1994; Waghmode et al., 2001) on the oxidation of aniline, wherein selective formation of azoxybenzene (98%) was reported at higher temperatures (343 K).

### 3.3.2. Effect of catalyst concentration

Table 4 presents the data on the conversion and selectivity of the oxidation of aniline over SHT-200-2, as a function of catalyst concentration. It is well known that the catalyst concentration can influence the activity and the selectivity of the products formed. The oxidation of aniline over SHT-200-2 was studied in the catalyst concentration range of 1–30 wt.%. An increase in the concentration of the catalyst (from 1 to 20 wt.% of the substrate) increased the conversion of aniline from 2 to 50 wt.%. At lower catalyst concentration (1 wt.%) NSB (80%) was the major product formed. With gradual increase in the catalyst concentration NSB disappeared rapidly whereas the selectivity to AZOXY increased (99%). The use of higher catalyst concentration increased the selectivity towards AZOXY at the beginning of the reaction. The conversion of aniline increases two fold in 8 h duration when the catalyst concentration is increased from 10 to 20 wt.%, although, the selectivity remained constant. A further increase in the catalyst concentration to 30 wt.% did not increase the conversion of aniline. This may be due to the decomposition of  $\text{H}_2\text{O}_2$  which becomes more prominent

Table 3  
Effect of the nature of the solvents on oxidation of aniline over S-HT-200-2<sup>a</sup>

Solvent	Conversion (wt.%)	Product selectivity (wt.%) <sup>b</sup>			
		NSB	NB	AZO	AZOXY
Methanol	50	–	–	1	99
Acetonitrile	46	5	–	2	93
Acetone	34	–	2	1	97

<sup>a</sup>Reaction conditions: solvent: 10 ml; aniline=3 mmol; aniline/H<sub>2</sub>O<sub>2</sub>: 1 (mole ratio); Time: 8 h; catalyst conc. 20 wt.%; Temp.: 300 K. <sup>b</sup>NSB — nitrosobenzene, NB — nitrobenzene, AZO — azobenzene, AZOXY — azoxybenzene.

with increase in catalyst concentration. However, a maximum conversion equivalent to that of 20 wt.% sample was obtained in 7 h thereby decreasing the reaction duration marginally (Table 4). Ti-PILC samples prepared in this study are active in this reaction is clear from the blank experimental results. In the absence of a catalyst, the reaction was found to be very slow (1% in 24 h) and only NSB was detected at the end of the reaction.

### 3.3.3. Effect of oxidant concentration

Catalytic oxidation in the liquid phase using H<sub>2</sub>O<sub>2</sub> is usually carried out with low H<sub>2</sub>O<sub>2</sub>/substrate ratios. This is done to maximize the peroxide selectivity and to decrease the formation of over-oxidized products. The results of the effect of H<sub>2</sub>O<sub>2</sub> concentration on the conversion and product distribution in the oxidation of aniline are presented in Table 5. Aniline conversion increases with increase in the molar ratio of H<sub>2</sub>O<sub>2</sub>/aniline and is maximum when H<sub>2</sub>O<sub>2</sub> to aniline ratio is increased to 3 mol%. However by doubling the mole ratio from 1 to 2 or further to 3 of H<sub>2</sub>O<sub>2</sub> to aniline

Table 4  
Effect of catalyst concentration on oxidation of aniline over S-HT-200-2<sup>a</sup>

Time (h)	Catalyst conc. (mg/g aniline)	Conversion (wt.%)	Product selectivity (wt.%) <sup>b</sup>			
			NSB	NB	AZO	AZOXY
8	1	2	80	–	–	20
8	2	5	45	–	–	55
8	5	17	14	–	3	83
8	10	28	–	1	1	98
8	20	50	–	–	1	99
7	30	51	–	–	1	99
24	0	1	100	–	–	–
8 <sup>c</sup>	20	23	77 <sup>d</sup>	–	23	–

<sup>a</sup> Reaction conditions: solvent: 10 ml; aniline=3 mmol; aniline/H<sub>2</sub>O<sub>2</sub>: 1 (mole ratio); solvent: methanol; Temp.: 300 K.

<sup>b</sup> NSB — nitrosobenzene, NB — nitrobenzene, AZO — azobenzene, AZOXY — azoxybenzene.

<sup>c</sup> Experiment with TBHP as the oxidant at the same mole ratio and under identical conditions.

<sup>d</sup> Non-selective products.

Table 5  
Effect of H<sub>2</sub>O<sub>2</sub> to aniline ratio on oxidation of aniline over S-HT-200-2<sup>a</sup>

H <sub>2</sub> O <sub>2</sub> /aniline (mole ratio)	Catalyst conc. (mg/g aniline)	Conversion (wt.%)	Product selectivity (wt.%) <sup>b</sup>			
			NSB	NB	AZO	AZOXY
1	20	50	–	–	1	99
2	20	54	–	–	1	99
3	20	56	–	–	1	99

<sup>a</sup>Reaction conditions: solvent: 10 ml; aniline=3 mmol; Time: 8 h; solvent: methanol; Temp.: 300 K. <sup>b</sup>NSB — nitrosobenzene, NB — nitrobenzene, AZO — azobenzene, AZOXY — azoxybenzene.

did not significantly alter the conversion of aniline, the increase is only from 50 to 56 wt.%. Nevertheless, the product selectivity remained unaffected.

### 3.3.4. Effect of nature of oxidant

In order to study the effect of the nature of oxidant on the conversion and product distribution in the oxidation of aniline, TBHP was used. The aniline conversion was found to be lower with TBHP on SHT-200-2 (Table 4). This is apparently due to the inaccessibility of TBHP molecule to the pores of the pillared clay. Our results indicate that the non-selective oxidation reactions become important with TBHP. Azobenzene was the minor product formed. Significantly, no azoxybenzene was detected at the end of the reaction duration.

### 3.3.5. Oxidation of aniline on pillared clays prepared by different methods

The results of the oxidation of aniline using the samples (hydrothermally untreated and hydrothermally treated for 2 h at different temperatures) prepared by method I and

Table 6  
Oxidation of aniline over titania pillared clays prepared by different methods

Catalyst	Conversion (wt.%)	Product selectivity (wt.%) <sup>b</sup>			
		NSB	NB	AZO	AZOXY
S	35	–	1	–	99
SHT-150-2	39	–	2	–	98
SHT-200-2	50	–	–	1	99
SHT-250-2	51	–	2	–	98
US	45	–	–	–	100
USHT-150-2	47	–	–	–	100
USHT-200-2	54	–	–	–	100
USHT-250-2	53	–	–	–	100

Reaction conditions: aniline=3 mmol; aniline/H<sub>2</sub>O<sub>2</sub>: 1 (mole ratio); catalyst wt.%; 20; solvent: methanol (10 ml); time: 8 h; Temp: 300 K. <sup>b</sup>NSB — nitrosobenzene, NB — nitrobenzene, AZO — azobenzene, AZOXY — azoxybenzene.

method II using aqueous  $\text{H}_2\text{O}_2$  as oxidant and methanol as solvent at 300 K in a batch reactor are presented in Table 6. The hydrothermally untreated ultrasonically prepared sample (US) gave higher conversion of aniline than that prepared by conventional stirring method (S). Upon hydrothermal treatment of the samples prepared by both the methods, the conversion of aniline increased significantly. The maximum conversion was obtained for the samples treated at 473 K for 2 h. Although the samples prepared by method II have lower  $\text{TiO}_2$  content, they show conversion similar to the samples prepared by method I. This proves that the reaction takes place in the interlayer region of the pillared clay and that the  $\text{TiO}_2$  that is present on the surface of the clay does not take part in the oxidation of aniline.

In all the samples tested for the oxidation of aniline azoxybenzene (AZOXY) was the only product formed. Phenylhydroxylamine was obtained within the first hour of the reaction and was not detected later. Traces of nitrobenzene (NB) and azobenzene (AZO) were also detected at the end of the reaction duration. Nitrosobenzene (NSB), which was formed at the beginning of the reaction, slowly disappeared as the reaction progressed and was not detected after 2 h. On the other hand, the amount of AZOXY increased continuously. This result suggests that most probably, the highly reactive NSB might have been converted into azoxybenzene either by the condensation of the primary intermediate phenylhydroxylamine with NSB (Becker and Sternson, 1980) or by the condensation of NSB with unreacted aniline which leads to the formation of azobenzene (Faessinger and Brown, 1951) which is then further oxidized to azoxybenzene (Newbold, 1962). It was reported that nitrosobenzene (NSB) was the major product formed over TS-1 catalyst at low temperature (273 K) using acetonitrile as solvent (Selvam and Ramaswamy, 1996).

#### 4. Conclusion

Successful pillaring of Na–montmorillonite with titania sol has been carried out by employing two different methods viz; conventional stirring and ultrasonic agitation techniques with and without hydrothermal treatment. The use of ultrasonic technique has resulted in the formation of the desired Ti-PILC material in shorter duration (20 min) at room temperature. The use of hydrothermal treatment has increased the crystallinity of the samples. The  $\text{TiO}_2$  was present in the pillared clay structure as anatase and rutile phase. The rutile phase content was more in the samples prepared by conventional stirring as compared to the samples prepared by ultrasonication technique. With the increase in the hydrothermal duration the concentration of the rutile phase

increased. This result is also supported by the UV–Vis diffuse reflectance spectroscopic data. The catalytic activity of Ti-PILC samples has been examined for the oxidation of aniline at room temperature. The results show that aniline could be oxidized selectively to azoxybenzene at ambient temperature. The conversion of aniline and the distribution of products depended on the experimental parameters used. In particular the nature of the solvent, oxidant concentration and catalyst concentration influence the reaction.

The Ti-PILC samples prepared in a shorter duration by using ultrasonic method at ambient temperature is as active in the oxidation of aniline at room temperature as the pillared clays prepared by the conventional method which involve longer duration of synthesis period at higher temperature.

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#### References

- Albertazzi, S., Baraldini, I., Busca, G., Finocchio, E., Lenarda, M., Storaro, L., Talon, A., Vaccari, A., 2005. Noble metal containing Al/Ce/Mg pillared montmorillonite clay as catalysts in the hydrotreating of LCO fractions. *Applied Clay Science* 29, 224–234.
- Anpo, M., Aikawa, N., Kubokawa, Y., Che, M., Louis, C., Giamello, E., 1985. Photoluminescence and photocatalytic activity of highly dispersed titanium oxide anchored onto porous Vycor glass. *Journal of Physical Chemistry* 89, 5017–5021.
- Anpo, M., Shima, T., Kodama, S., Kubokawa, Y., 1987. Photocatalytic hydrogenation of propyne with water on small-particle titania: size quantization effects and reaction intermediates. *Journal of Physical Chemistry* 91, 4305–4310.
- Baumgarten, H.E., Staklis, A., Miller, E.M., 1965. Reactions of amines. XIII. The oxidation of *N*-Acyl-*N*-arylhydroxylamines with lead tetraacetate. *Journal of Organic Chemistry* 30, 1203–1206.
- Becker, A.R., Sternson, L.A., 1980. General catalyzed condensation of nitrosobenzene and phenylhydroxylamine in aqueous solution. *Journal of Organic Chemistry* 45, 1708–1710.
- Brown, G., 1980. In: Brindley, G.W., Brown, G. (Eds.), *Crystal Structures of Clay Minerals and their X-ray Identification*. Associated Minerals, Miner. Soc., London, p. 361.
- Brunauer, S., Deming, L.S., Deming, W.E., Teller, E., 1940. On a theory of the van der Waals adsorption of gases. *Journal of American Chemical Society* 62, 1723–1732.
- Brus, L.E., 1983. A simple model for the ionization potential, electron affinity, and aqueous redox potentials of small semiconductor crystallites. *Journal of Chemical Physics* 79, 5566–5571.
- Del Castillo, H.L., Gill, A., Grange, P., 1996. Hydroxylation of phenol on titanium pillared montmorillonite. *Clays and Clay Minerals* 44, 706–709.

- Faessinger, R.W., Brown, E.V., 1951. The preparation of pyridine azo compounds. *Journal of American Chemical Society* 73, 4606–4608.
- Gil, A., Gandia, L.M., Vicente, M.A., 2000. Recent advances in the synthesis and catalytic applications of pillared clays. *Catalysis Reviews. Science and Engineering* 42, 145–212.
- Gomes, H.T., Selvam, P., Dapurkar, S.E., Figueiredo, J.L., Faria, J.L., 2005. Transition metal (Cu, Cr, and V) modified MCM-41 for the catalytic wet air oxidation of aniline. *Microporous and Mesoporous Materials* 86, 287–294.
- Gontier, S., Tuel, A., 1994. Oxidation of aniline over TS-1, the titanium substituted silicalite-1. *Applied Catalysis. A, General* 118, 173–186.
- Howe, G.R., Hiatt, R.R., 1970. Metal catalyzed hydroperoxide reactions. I. Subsequent effects in the oxidation of aniline. *Journal of Organic Chemistry* 35, 4007–4012.
- Huang, H., Sommerfeld, D., Dunn, B.C., Lloyd, C.R., Eyring, E.M., 2001. Ferrate(VI) oxidation of aniline. *Journal of the Chemical Society. Dalton Transactions* 8, 1301–1305.
- Huerta, L., Meyer, A., Choren, E., 2003. Synthesis, characterization and catalytic application for ethylbenzene dehydrogenation of an iron pillared clay. *Microporous and Mesoporous Materials* 57, 219–227.
- Katdare, S.P., Ramaswamy, V., Ramaswamy, A.V., 1999. Ultrasonication: a competitive method of intercalation for the preparation of alumina pillared montmorillonite catalyst. *Catalysis Today* 49, 313–320.
- Klug, H.P., Alexander, L.E., 1974. *X-ray Diffraction Procedure*, 2nd edition. Wiley, New York, p. 697.
- Newbold, B.T., 1962. Oxidations of substituted Azo- and hydrazobenzenes with peracetic acid. *Journal of Organic Chemistry* 27, 3919–3923.
- Ooka, C., Akita, S., Ohashi, Y., Horiuchi, T., Suzuki, K., Komai, S., Yoshida, H., Hattori, T., 1999. Crystallization of hydrothermally treated TiO<sub>2</sub> pillars in pillared montmorillonite for improvement of the photocatalytic activity. *Journal of Materials Chemistry* 9, 2943–2952.
- Ooka, C., Yoshida, H., Horio, M., Suzuki, K., Hattori, T., 2003. Adsorptive and photocatalytic performance of TiO<sub>2</sub> pillared montmorillonite in degradation of endocrine disruptors having different hydrophobicity. *Applied Catalysis. B, Environmental* 41, 313–321.
- Pinnavaia, T.J., Ming-Shin, T., Landau, S.D., Raythatha, R.H., 1984. On the pillaring and delamination of smectite clay catalysts with polyoxy cations of aluminium. *Journal of Molecular Catalysis* 27, 195–212.
- Pérez-Zurita, M.J., Pérez-Quintana, G.J., Hasblady, A.J., Maldonado, A., de Navarro, C.U., De Abrisqueta, A., Scott, C.E., 2005. Synthesis of Al-PILC assisted by ultrasound: reducing the intercalation time and the amount of synthesis water. *Clays and Clay Minerals* 53, 528–535.
- Sakuae, S., Tsubakino, T., Nishiyama, Y., Ishii, Y., 1993. Oxidation of aromatic amines with hydrogen peroxide catalyzed by cetylpyridinium heteropolyoxometalates. *Journal of Organic Chemistry* 58, 3633–3638.
- Selvam, T., Ramaswamy, A.V., 1995. Selective catalytic oxidation of aniline to azoxybenzene over titanium silicate molecular sieves. *Catalysis Letters* 31, 103–113.
- Selvam, T., Ramaswamy, A.V., 1996. A new catalytic method for the selective oxidation of aniline to nitrosobenzene over titanium silicate molecular sieves, TS-1, using H<sub>2</sub>O<sub>2</sub> as oxidant. *Chemical Communications* 10, 1215–1216.
- Sheldon, R.A., Dakka, J., 1994. Heterogeneous catalytic oxidations in the manufacture of fine chemicals. *Catalysis Today* 19, 215–245.
- Singh, V., Sapehiya, V., Kad, G.L., 2004. Ultrasound and microwave activated preparation of ZrO<sub>2</sub>-pillared clay composite: catalytic activity for selective, solventless acylation of 1, *n*-diols. *Journal of Molecular Catalysis. A, Chemical* 210, 119–124.
- Sterte, J., 1986. Synthesis and properties of titanium oxide cross-linked montmorillonite. *Clays and Clay Minerals* 34, 658–664.
- Tollari, S., Cuscela, M., Porta, F., 1993. Catalytic oxidation of primary aromatic amines to the corresponding nitroso compounds by H<sub>2</sub>O<sub>2</sub> and [Mo(O)(O<sub>2</sub>)<sub>2</sub>(H<sub>2</sub>O)(hmpa)] (hmpa = hexamethylphosphoric triamide). *Journal of Chemical Society Chemical Communication* 19, 1510–1511.
- Tuel, A., Moussa-Khouzami, S., Ben Taarit, Y., Naccache, C., 1991. Hydroxylation of phenol over TS-1: surface and solvent effects. *Journal of Molecular Catalysis* 68, 45–52.
- Tuel, A., Hubert-Pfalzgraf, L.G., 2003. Nanometric monodispersed titanium oxide particles on mesoporous silica: synthesis, characterization, and catalytic activity in oxidation reactions in the liquid phase. *Journal of Catalysis* 217, 343–353.
- Waghmode, S.B., Sabne, S.M., Sivasankar, S., 2001. Liquid phase oxidation of amines to azoxy compounds over ETS-10 molecular sieves. *Green Chemistry* 3, 285–288.
- Wenkert, E., Wickberg, B., 1962. General methods of synthesis of indole alkaloids. II. A flavopereirine synthesis. *Journal of American Chemical Society* 84, 4914–4919.
- White, R.W., Emmons, W.D., 1962. The chemistry of permaleic acid. *Tetrahedron* 17, 31–34.
- Wheeler, O.H., Gonzalez, D., 1964. Oxidation of primary aromatic amines with manganese dioxide. *Tetrahedron* 20, 189–193.
- Yamanaka, S., Inoue, Y., Hattori, M., Okumura, F., Yoshikawa, M., 1992. Preparation and properties of clays pillared with silica-titania sol particles. *Bulletin of Chemical Society of Japan* 65, 2494–2500.
- Zengel, Hans G., 1983. New industrially feasible process for the production of nitrosobenzene. *Chemie Ingenieur Technik* 55, 962–963.