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# INFLUENCE OF CHLORINE ON THE SURFACE AREA AND MORPHOLOGY OF $TiO_2$

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## ABSTRACT

Changes in BET surface area and morphology of $TiO_2$ (anatase) were studied as a function of temperature and level of chlorine contamination. The objective was to study the behavior of $TiO_2$ supports under typical catalyst preparation and reaction conditions, using adsorption, wide angle X-ray diffraction and scanning electron microscopy. Chlorinated samples had lower surface areas compared to blank $TiO_2$ and showed a significant loss of resistance to sintering. Chlorine also retarded the phase transformation of anatase to rutile.

## INTRODUCTION

Catalyst preparation by impregnation techniques often results in incorporation of chlorine onto the support. Chlorine comes mainly from the precursor metal salt solutions used to impregnate the support. Another source for chlorine contamination is HCl that is added in order to adjust the pH of the precursor metal salt solutions. Furthermore, the addition of HCl is of importance to achieve appropriate control over the surface concentration of acidic sites on the support and to facilitate metal deposition. Part of the chlorine is subsequently lost depending on the drying and reduction conditions during catalyst preparation. The residual chlorine content influences the acidity of the support and has an important bearing on the catalytic properties as shown for naphtha reforming $Pt/Al_2O_3$ catalysts [1-3]. For some support materials, chlorine also influences the BET surface area and pore structure. This has been observed previously for MgO [4] which is known to exhibit support effects on Ru, Au and bimetallic Ru-Au catalysts [5-7]. MgO undergoes bulk hydration to $Mg(OH)_2$ during the impregnation step in aqueous phase. Subsequent heating to 673°K restores the oxide, resulting in the formation of small pores and an increase in surface area from 15 to 350 $m^2/gm$. This surface area increase was found to be strongly dependent on the amount of chlorine remaining on the support. Chlorine contaminations up to 1 wt% resulted in steep reductions in MgO surface area. On samples containing more than 1 wt% chlorine, the surface area remained low ($\sim$ 25 $m^2/g$) irrespective of the thermal treatment. Chlorine seemed to cause an

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earlier release of water and a decrease in the dehydration temperature of $Mg(OH)_2$ [4].

The influence of chlorine, even though not fully understood, is of importance for catalyst preparation, in particular when both acidic support sites as well as high metal dispersions are desired. The latter goal might be difficult to achieve in cases where the support surface area is sensitive to chlorine content.

The objective of this study was to examine the role of chlorine on the surface area of $TiO_2$. $TiO_2$ is an interesting catalyst support material because of SMSI effects reported for Group VIII noble metals, resulting in high metal dispersions that are stable at high temperatures [8,9]. Previous work showed that on $TiO_2$ supports even a metal with low Tamman temperature, such as gold, can be maintained in high dispersion up to a temperature of 700°C [10]. However, these results were obtained on a catalyst that was virtually free of chlorine. The behavior of $TiO_2$ catalyst supports as a function of chlorine contamination is not well understood, and the results of this study are important for the design and preparation of highly dispersed $TiO_2$ supported catalysts.

## EXPERIMENTAL

The Glidden $TiO_2$ used for this study was prepared by hydrolysis of titanium isopropylate, followed by washing and drying at 105°C under vacuum. Aliquots of the support were impregnated with four different hydrochloric acid solutions (1.44, 2.4, 2.88 and 3.36 moles/l), followed by drying in air in a dessicator for 48 hrs. In our previous work on MgO, it was found that it did not matter whether the chlorine was derived from aqueous HCl or a chlorine containing metal precursor salt solution of comparable pH (1.7 - 2.0) [4]. Thus, this investigation was restricted to samples treated in aqueous HCl only. Chlorine remaining on the support after completion of impregnation and drying was determined by neutron activation analysis. Aliquots of $TiO_2$ samples having different chlorine contents were subjected to the following thermal treatment routine:

Each sample was placed into a Pyrex glass reactor loop and gradually heated in a stream of flowing $N_2$ gas to the treatment temperature. The temperature was kept constant for 2 hrs followed by a slow cooling to room temperature. The samples so obtained were then used for further experimentation.

BET surface areas were determined by the single point method using a Quantachrome Monosorb surface area analyzer. A mixture of 30% $N_2$ in He gas was used, with $N_2$ as adsorbent at a temperature of -195.8°C. WAXS experiments were performed after each thermal treatment in a Philips X-ray powder diffractometer. $CuK_\alpha$ radiation was used with a crystal monochromator. Electron microscopy studies were carried out using a JEOL JEM-100CX microscope. The ASID-4D scanning device was employed to generate secondary electron images at magnifications up to 100,000 using 100 kV electrons. Infrared spectra were recorded using a Digilab FTS-20 Fourier Transform Infrared Spectrometer.

RESULTS AND DISCUSSION

The BET surface area, the morphology and phase transformation of titania as a function of temperature and chlorine content are reported and discussed in this section. These results are evaluated in terms of possible formation of surface compounds, or bulk reaction with HCl under simulated catalyst preparation conditions.

The BET results on blank $TiO_2$ showed a high surface area of 118 $m^2/g$ at 110°C, which increased slightly on heating to 300°C followed by a sharp decrease at 600°C to less than 8 $m^2/g$. $TiO_2$ samples containing chlorine showed a lower surface area than blank $TiO_2$ upon similar thermal treatment. Increasing the chlorine content resulted in systematic reduction of surface area (Fig. 1). The slight difference in surface area between blank $TiO_2$ and the sample that had been soaked in $H_2O$ might be due to compaction of $TiO_2$ particles that have undergone surface hydroxylation in the presence of water. Similar interparticle aggregation and compaction has been explained on the basis of surface tension effects during drying of $SiO_2$ [11].

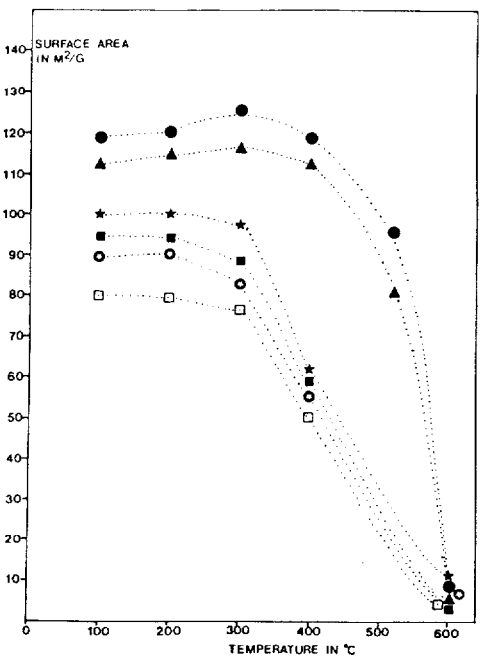



FIGURE 1 BET surface area as a function of thermal pretreatment and chlorine content of the fresh samples (before thermal treatment). Points obtained at 600°C are spread out on the graph for clarity. Treatment at indicated temperature for 2 hrs. ● Blank $TiO_2$; ▲ $TiO_2$ soaked in distilled water; ★ $TiO_2$ soaked in aq. HCl (2.06 wt% chlorine); ■ $TiO_2$ soaked in aq. HCl (2.40 wt% chlorine); ✪ $TiO_2$ soaked in aq. HCl (2.55 wt% chlorine); □ $TiO_2$ soaked in aq. soaked in aq. HCl (3.30 wt% chlorine).

WAXS patterns of blank $TiO_2$ after various thermal treatments are shown in Figure 2. At 110°C, the blank $TiO_2$ was X-ray amorphous. Only after heating to 300°C did peaks characteristic of anatase appear. These peaks became sharper after treatment at 600°C indicating an increased degree of crystallinity (Fig. 2).

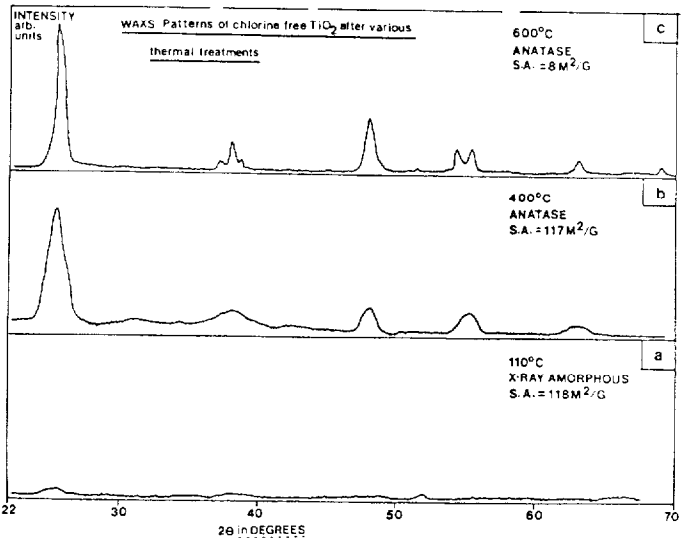



FIGURE 2 Wide angle X-ray scattering patterns of chlorine free $TiO_2$ obtained after thermal treatments at indicated temperature for 2 hrs. Corresponding surface areas are also indicated.

While the $TiO_2$ treated in distilled water was X-ray amorphous after drying at 110°C for 2 hrs, WAXS peaks characteristic for anatase were visible in the chlorinated samples after similar thermal treatment at 110°C for 2 hrs (Fig. 3). WAXS failed to detect any bulk compound formation such as $Ti(OH)_2Cl_2$, a compound that can form with aqueous HCl at low temperatures [12]. This points to an increased crystallinity of $TiO_2$ in the presence of chlorine. A similar effect was observed by Dolmatov et al. [13]. $TiO_2$ precipitated from aqueous $Ti^{4+}$ salt solutions was X-ray amorphous, while $TiO_2$ precipitated from $H_2SO_4$ solutions was already in the form of anatase with lower surface area.

In an aqueous medium, $H_2O$ dipoles are likely to be attracted by $Ti^{4+}$ ions due to the 63% ionic character of the Ti-O bond according to Pauling's electronegativity values [14]. Based on energetic considerations, formation of hydroxyl groups is favored on the $TiO_2$ surface. Presence of hydroxyl groups on $TiO_2$ surfaces has been convincingly proved by infrared spectroscopy [16-20]. IR bands in the 3700 $cm^{-1}$ region are generally assigned to OH stretching vibrations on the anatase surface. The band at 1605-1615 $cm^{-1}$ is due to the OH bending vibration of residual adsorbed

water. After adsorbing HCl on $TiO_2$, Primet et al. [20] observed a new, sharp band at 3540 $cm^{-1}$. On our own samples which were exposed to aqueous HCl during preparation, there was no difference in the IR spectrum of blank vs. HCl treated $TiO_2$. We suspect that the band at 3540 $cm^{-1}$ was due to adsorption of molecular HCl from the gas phase, while the aqueous medium used in our case would certainly lead to complete dissociation of HCl and thus adsorption of chloride ions. In view of the ionic bonding of $OH^-$ groups on $TiO_2$ surfaces [15], one would expect ionic exchange with the chloride ions.

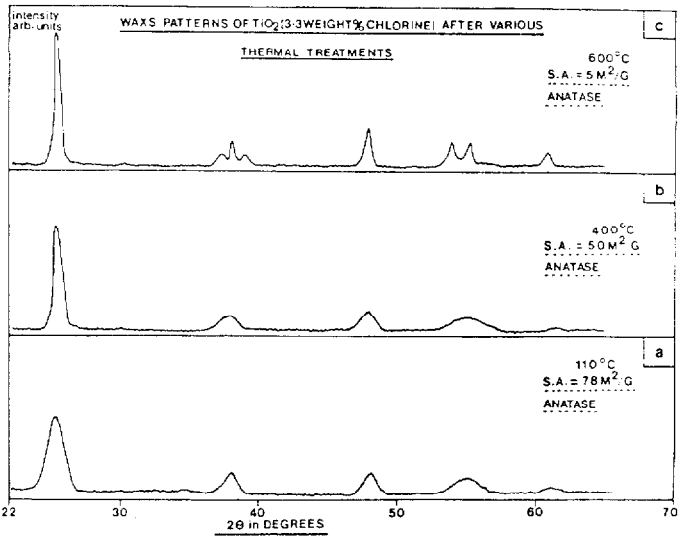



FIGURE 3 Wide angle X-ray scattering patterns of $TiO_2$ treated in aqueous HCl with a final content of 3.3 wt% chlorine as determined by neutron activation. Thermal treatments were carried out at indicated temperature for 2 hrs. Corresponding surface areas are also indicated.

If we assume that the chlorine detected by neutron activation analysis on the fresh samples before any thermal treatment was present in the form of surface $Cl^-$ groups, surface densities of approximately $3 \times 10^{14}$ to $7 \times 10^{14}$ $Cl^-/cm^2$ are obtained, in agreement with previous work carried out under similar treatment conditions [20,21]. The surface $Cl^-$ seems to be weakly bound and can be removed by heating. After heating to 400°C or higher a significant decrease in chlorine content to less than 0.17 wt% was observed in all four chlorinated samples.

These results suggest that surface chlorination rather than bulk chloride formation took place under our experimental conditions. Bulk reactions between HCl and $TiO_2$ such as:

$$TiO_2 + 4HCl \underset{}{\overset{K_1}{\rightleftharpoons}} Ti\,Cl_2 + 2\,H_2O + Cl_2 \qquad (1)$$

are thermodynamically unfavorable at room temperature. For example, the equilibrium constant $K_1$ has a value of $10^{-54}$ at 24°C [22].

If one attempts to dissolve $TiO_2$ (Illmenite ore) it is necessary to use concentrated hydrochloric acid (11.3 to 11.6 mole/l) to obtain a reasonable dissolution rate [23]. In fact, formation of a $TiO_2$ layer on Ti metal is known to prevent metal attack by HCl acid solutions [24-26]. To verify the absence of bulk dissolution, a sample of $TiO_2$ was slurried in an excess of 3.6M HCl for 48 hrs at room temperature. The supernatant liquid was then analyzed by atomic absorption spectroscopy. No evidence of dissolution of $TiO_2$ was found. Thus any significant bulk dissolution of titania under typical catalyst preparation conditions can be ruled out.

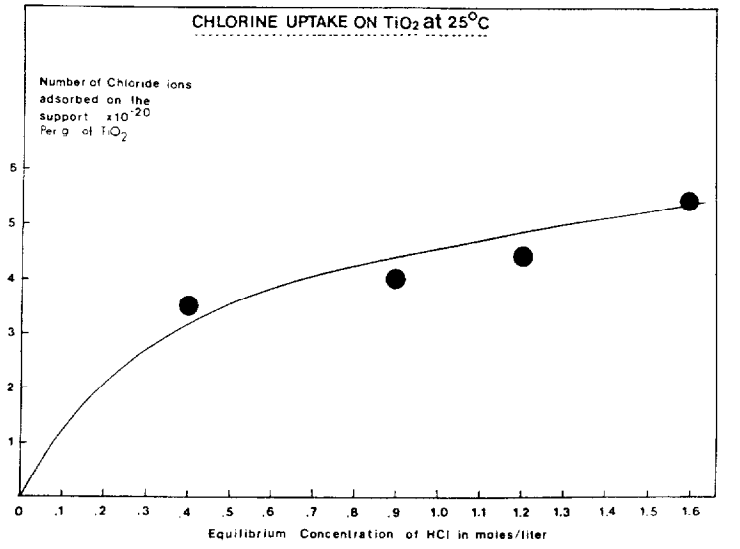
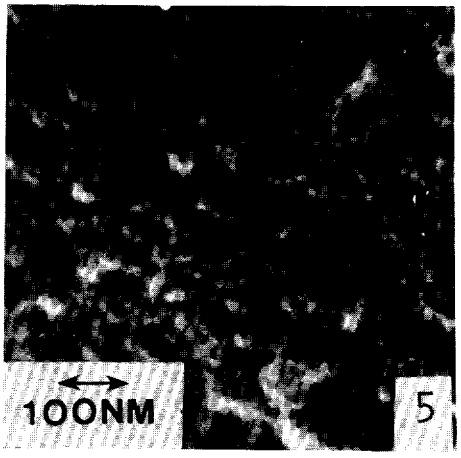
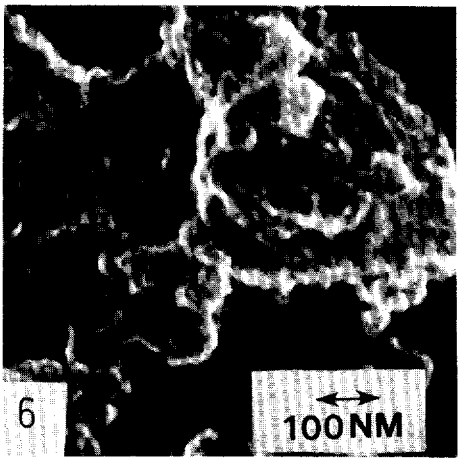



FIGURE 4 Equilibrium characteristics of chlorine uptake on $TiO_2$ in an aqueous medium. Plot indicates the number of chloride ions on the support as determined by neutron activation vs. equilibrium concentration of supernatant HCl.

At this point the question arises why the presence of surface chloride causes a decrease in BET surface area and an increase in crystallinity of anatase. It has been previously suggested that chloride impurities are responsible for a relatively easy loss of hydroxyl groups from anatase (Degussa P-25) [18]. A similar phenomenon has been reported for the $Mg(OH)_2$-MgO system where chlorine led to an earlier release of water from the bulk hydroxide and accelerated the nucleation of MgO and loss of porosity during the dehydration process [4]. In the case of $TiO_2$, there was no bulk hydroxide formation, but surface hydroxyl groups were present. These surface hydroxyl groups could easily be exchanged with chloride ions. The relative concentration of surface $Cl^-$ groups depends on the nature of ionic equilibrium in aqueous phase. This is illustrated in Fig. 4 which shows the surface chloride concentration on anatase as a function of the concentration of chloride ions in the supernatant aqueous phase under equilibrium conditions. It is plausible that increased $Cl^-$ uptake by the support could lead to a gradual replacement of surface $OH^-$ groups and consequently to partial dehydration of the sample. The loss of surface area due to chlorine is irreversible. Neither the removal of chlorine by outgassing at higher temperatures nor subsequent rehydration in aqueous medium can restore the high surface area. The surface area loss seems not to be due to bulk digestion of $TiO_2$, but rather due to morphological changes. To study the morphology, scanning electron microscopy was carried out on blank and chlorinated anatase samples at different stages of thermal treatment. Fig. 5 shows the morphology of blank $TiO_2$ without thermal treatment. The sample has a high degree of porosity. The corresponding chlorinated sample resembles closely the blank $TiO_2$ and has the same high degree of porosity (Fig. 6). After treatment at 400°C for 22 hrs, the blank $TiO_2$ does not show any significant change in porosity (Fig. 7) in agreement with the BET results. All the chlorinated samples irrespective of the chlorine content, show after treatment at 400°C a formation of platelike structures (Fig. 8a,b). Such platelike morphologies were observed only after treatment at 600°C in the case of chlorine free, blank $TiO_2$ (Fig. 9). At 600°C, on both the blank and the chlorinated sample a complete transformation to platelike morphologies is observed (Fig. 9 and 10) which is consistent with the low BET surface area results (Fig. 1). The micrographs shown are typical examples drawn from a large number of micrographs of different sample areas. Thus it can be concluded that chlorine favors the formation of platelike morphologies at lower temperatures and an earlier collapse of the pore structure. Once the platelike morphology has been reached, neither exposure to $H_2O$ nor to aqueous HCl has an effect on the BET surface area and morphology of both the blank and chlorine treated titania. Since outgassing at 400°C removed most of the chloride, any pore mouth blockage by surface chloride compounds can be ruled out.



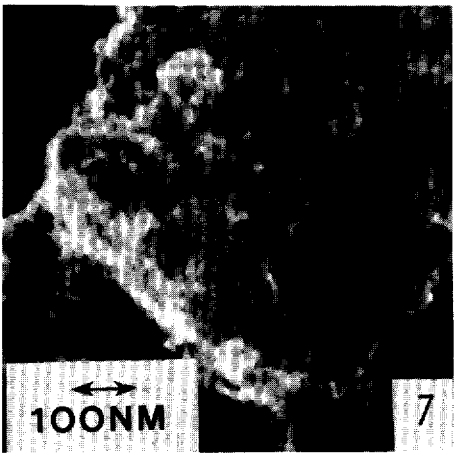




FIGURE 5 Scanning electron micrograph (SEM) of blank $TiO_2$ treated at 110°C for 2 hrs (microporous).

FIGURE 6 SEM of 3.3 wt% chlorine containing $TiO_2$ treated at 110°C for 2 hrs (microporous).

FIGURE 7 SEM of blank $TiO_2$ treated at 400°C for 2 hrs (porous).

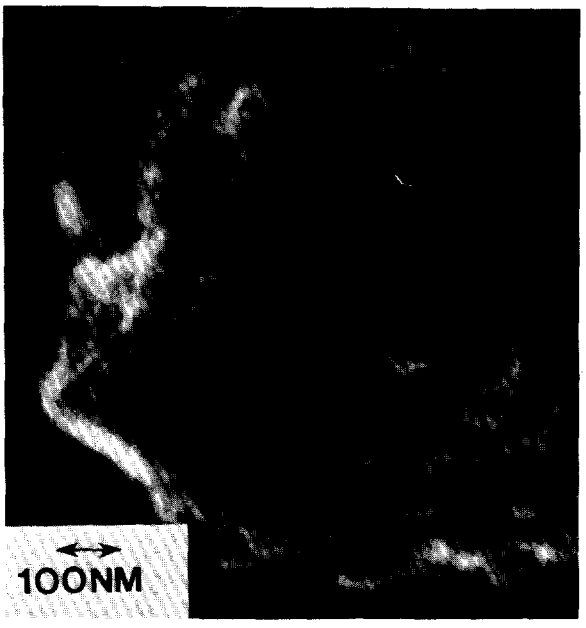



FIGURE 8a SEM of 3.3 wt% chlorine containing $TiO_2$ treated at 400°C for 2 hrs (formation of platelike morphology can be seen).

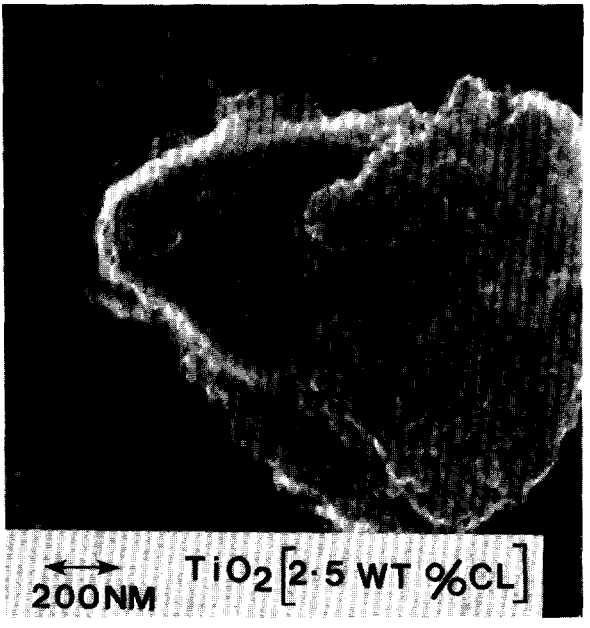



FIGURE 8b SEM of 2.55 wt% chlorine containing $TiO_2$ treated at 400°C for 2 hrs (formation of platelike morphology as seen in Fig. 8a).

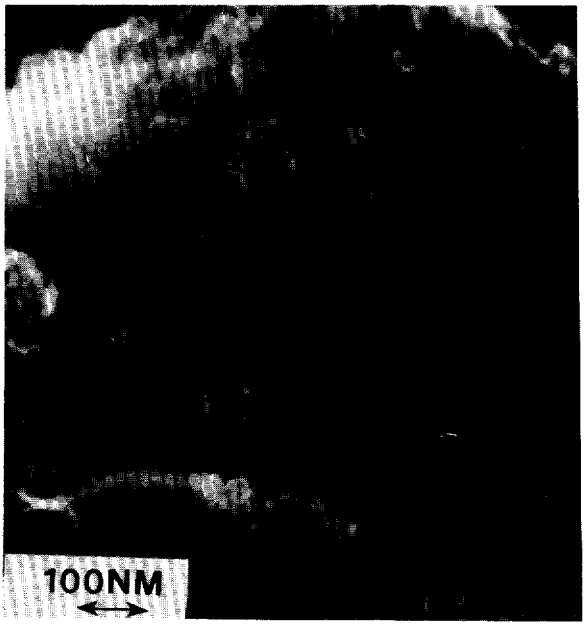



FIGURE 9 SEM of blank $TiO_2$ treated at 600°C for 2 hrs (platelike morphology).

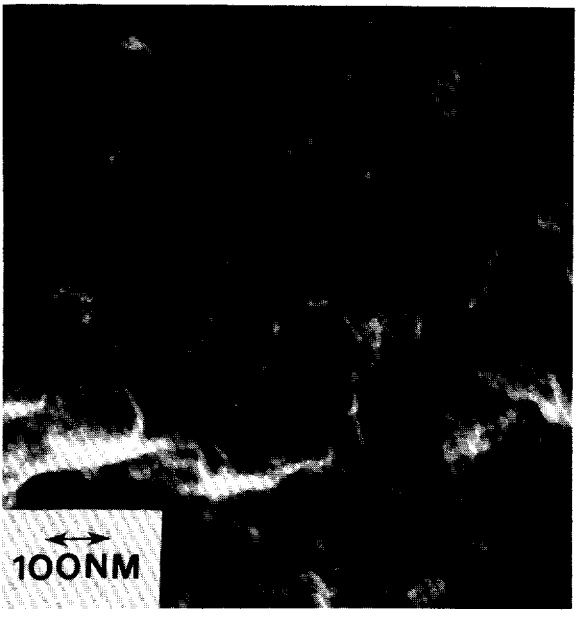



FIGURE 10 SEM of 3.3 wt% chlorine containing $TiO_2$ treated at 600°C for 2 hrs (platelike morphology).

It appears that the partial replacement of surface hydroxyl groups by chloride ions facilitates the recrystallization of anatase at lower temperatures. After 2 hrs at 700°C in air, the blank $TiO_2$ underwent a complete phase transformation from anatase to rutile. The chlorine treated samples showed under identical conditions X-ray peaks characteristic for both anatase as well as rutile (Fig. 11a,b). This indicates that chlorine exerts a retarding effect on the phase transformation of $TiO_2$.

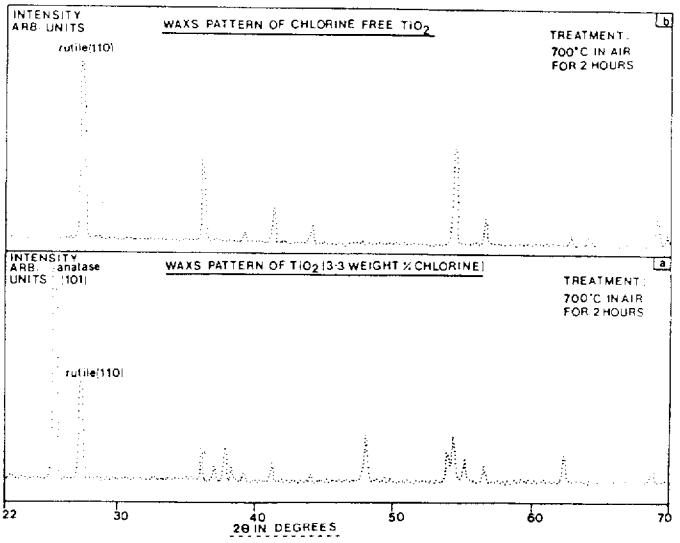



FIGURE 11 Influence of chlorine on kinetics of phase transformation from anatase to rutile observed by wide angle X-ray scattering experiments. a) $TiO_2$ with 3.3 wt% chlorine after treatment at 700°C for 2 hrs. Presence of both anatase and rutile phases. Relative intensities show that anatase is predominant. b) Chlorine free $TiO_2$: transformation from anatase to rutile.

The nature and concentration of impurities is known to control the defect structure of $TiO_2$ which in turn governs the kinetics of the phase transformation. Interstitial ions inhibit the transformation whereas substitutional ions can inhibit or accelerate the phase transofrmation to rutile [27]. Rao et al. reported that 5 at % $Cl^-$ inhibited the anatase/rutile phase transformation at 708°C [28]. Our experimental observations are in agreement.

## CONCLUSIONS

The role of chlorine impurities on surface area and crystallinity of the anatase phase of $TiO_2$ was investigated as a function of pretreatment temperature. The concentrations of chlorine were similar to those encountered under typical catalyst

preparation conditions. Chlorine had a detrimental effect on the BET surface area and favored the formation of platelike morphologies with sharply reduced porosity at a temperature as low as 400°C. At this temperature, chlorine free $TiO_2$ maintained high surface area due to microporosity. While chlorine accelerated the crystallization process of anatase, it retarded the phase transformation to rutile. These effects were not due to bulk dissolution of $TiO_2$ by the aqueous HCl used in our sample treatment. Apparently, a surface chloride formation via an exchange with surface $OH^-$ groups is the possible mechanism of chlorine uptake. The surface chloride is weakly bound and can be removed by heating to 400°C or higher. Although temperature is the dominant variable influencing surface area and morphology, chlorine has a clear-cut accelerating effect on the recrystallization of anatase resulting in an enhancement of crystallite growth and lower surface area. Such massive changes in morphology of $TiO_2$ manifested by the formation of platelike support patches and the associated high mobility of ions might contribute to the postulated transport of titania species onto metal particles which is invoked by one school of thought to explain the SMSI effect. If one attempts to prepare high-surface-area $TiO_2$ supported catalysts with adequate thermal stability for typical catalytic reaction conditions (up to 500°C), care has to be taken to minimize the chlorine content of the catalysts.

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