Surface Chemistry of Titania (Anatase) and Titania-supported Catalysts

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1 Introduction

Titania is the principal white pigment in the world and has wide applications in various branches of industry such as the production of plastics, enamels, artificial fibres, electronic materials and rubber.[1] In the field of catalysis the interest in TiO_2 is mainly due to its application as catalyst or support. In many catalytic reactions titania demonstrates neither a high activity nor a high selectivity,[2] but in some cases it is among the most efficient of catalysts. For instance, TiO_2 is a classical photocatalyst for water decomposition and for other photocatalytic processes.[3—5] It shows very good properties in the Claus process ($SO_2 + 2H_2S \rightarrow 3S + 2H_2O$).[6] Sulfate-modified titania is one of the few superacids that are at present the only known heterogeneous catalysts for Friedel–Crafts acylations, and it is active in a number of other organic synthetic reactions.[7] However, titania is mainly used as a support. This is of course due, to some extent, to its good mechanical properties, its inertness and its low price. In contrast to silica, which is one of the most widely used supports, and whose normal role is to ensure that the supported phase has a large surface area, titania interacts in many cases with the supported active phase. This behaviour determines the unique catalytic properties of the latter. Thus, vanadia–titania catalysts are the best ones for a number of selective oxidation reactions. In particular, they have found industrial application in the oxidation of *o*-xylene[8] and in the $DeNO_x$ process[6] ($NO_x + NH_3 \rightarrow N_2 + H_2O$). Other titania-supported oxides such as Fe_2O_3, MoO_3, WO_3, MnO_2 and CuO also exhibit a high activity and selectivity in the latter reaction.[6]

Noble metals are of special interest. Very often their activity with respect to CO hydrogenation strongly increases when they are supported on titania.[9] This is associated with the so-called strong metal–support interaction (SMSI) which will be considered below. Despite the fact that such catalysts have not yet found industrial applications, they have been the subject of numerous investigations, and the effective use of titania as a promoter is a result of these studies.[10] TiO_2 is also used as an additive for improving the properties of some supports such as alumina. The use of titania in the field of catalysts is schematically presented in Figure 1.

The properties of the titania surface are decisive for its catalytic application. On the one hand, the catalytic activity and selectivity of TiO_2 itself depend directly on the kind and concentration of the different active sites, and, on the other, the surface affects the formation of definite structures of the active phase of titania-supported catalysts. Other important characteristics of TiO_2, such as its adsorption ability and its pigmentation, also depend on the surface properties.

The breaking of the crystal lattice at the surface leads to the appearance of ions with a lower coordination number than that in the bulk. They are named coordinatively unsaturated surface (c.u.s) ions and have a tendency for additional coordination. The c.u.s. cations (in this case Ti^{n+}) possess an uncompensated positive charge and coordinate molecules with a free electron pair, *i.e.* they are Lewis acids, while the c.u.s. oxygen anions are Lewis bases and adsorb acidic molecules. Even after evacuation at high temperatures, at which most admixtures are desorbed, residual hydroxy groups exist on the oxide surfaces. They may have an acidic or basic character. The surface properties also depend on the deviations from stoichiometry *e.g.* the existence of various forms of excess oxygen possessing different oxidation activities and, *vice versa*, formation of a reduced oxide which is responsible for the reduction properties of the samples. Various admixtures may also affect the adsorption sites.

The adsorption sites are usually not directly observable (*e.g* the c.u.s. ions) or the data on them are scarce (surface OH groups). For that reason, their interaction with so-called *probe molecules* is investigated. The properties of the adsorption sites are determined by the characteristics (stability and spectral features) of adsorbed probe molecules.[11]

Titania is usually encountered as three different modifications: anatase, rutile and brookite.[12] The latter modification has no practical importance owing to its low stability. Anatase is thermodynamically stable up to 800 °C and an anatase–rutile transition occurs above this temperature. The rutile obtained, however, does not change into anatase after cooling owing to the high activation energy of the back transition. Both anatase and rutile crystallize in a tetragonal lattice. The coordination number of titanium is 6, and that of oxygen, 3. The two modifications differ in number of common edges of the TiO_6 octahedra: 4 for anatase and 2 for rutile. It is anatase that is more widely used for catalytic purposes. That is why we shall concentrate on this crystallographic modification.

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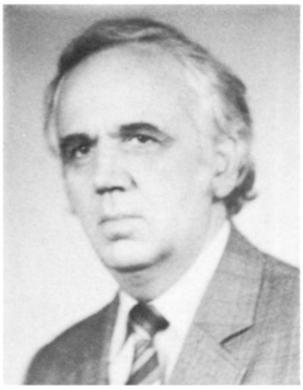

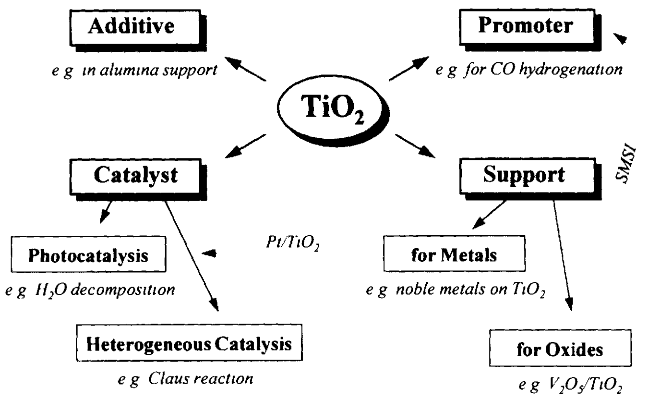

Figure 1 Application of TiO_2 in the field of catalysis.

2 Preparation of Titania

Different methods for synthesis of titanium dioxide result in products with different structures (anatase or rutile), crystallinity and contaminants. As a consequence, the surface properties of TiO_2 strongly depend on the preparation technique. There are two main methods for obtaining titania for industrial purposes.[1,5] The first is the so-called 'sulfate method'. The titanium source (usually ilmenite, $FeTiO_3$) is dissolved in sulfuric acid, the resulting solution is purified to remove iron, and then hydrolysed. The precipitate, titania in hydrous form, is calcined in order to eliminate water. The product obtained has the structure of anatase since the sulfate ions stabilize this modification. TiO_2 prepared *via* the 'sulfate route' always contains sulfate ions which affect its surface acidity (see Section 4.1.).

The other widespread technique for manufacturing titania is the vapour-phase oxidation of $TiCl_4$:

$$TiCl_4 + O_2 \rightarrow TiO_2 + 2Cl_2 \qquad (1)$$

The products are characterized by a narrow particle size distribution, the average diameter being 20 nm. The main contaminant is Cl, and, sometimes, Si and Al. The surface of this type of titania is deeply dehydroxylated. However, the phase purity is not high. For instance, the typical commercial fumed TiO_2 (anatase) made by Degussa contains 25% of rutile.

On a laboratory scale, titania is usually prepared from $TiCl_4$ or titanium alcoholates.[13] $TiCl_4$ is hydrolysed by water at 5—10 °C and after that ammonia is added to obtain hydrous titania. The product formed is pure anatase, whereas rutile is produced when the reaction is held above 80 °C. The degree of surface hydroxylation may be controlled by the temperature of the subsequent calcination. The samples prepared in this way usually contain chloride ions but their concentration may be minimized by washing of the final (calcined) product. To obtain chlorine-free titania one usually hydrolyses titanium alcoholates [the preferred compounds are $Ti(OC_3H_7)_4$ and $Ti(OC_4H_9)_4$ since the lighter alcoholates react very violently]. The products are of high purity, the carbon contaminants being eliminated by calcination of the products.

Titanium dioxide is also produced by oxidation of metallic titanium by oxygen or water as well as by hydrolysis of titanium compound in the gas phase.

As already noted, heating of anatase at 800 °C results in the formation of rutile. Some contaminants and additives decrease the transition temperature, which is often a reason for deactivation of anatase-supported catalysts.

3 Surface Chemistry of Anatase

The name of *anatase* originates from the Greek $\alpha\nu\alpha\tau\alpha\sigma\iota\varsigma$ (upward tension, upwards direction) and is due to the long form of its crystals. The cleavage planes mainly exposed on the anatase surface are 100 and 011≡101 (≡ means isostructural). However, the faces 100≡010, 110, 111, 112 and 113 are also observed, although to a smaller extent.[12] The same faces are characteristic of the crystallites of disperse samples but the high concentration of crystal edges, steps and corners should also be taken into account.

The best way of studying the titania surface is to investigate the properties of the separate faces using single crystals and look for an anology with disperse samples. Since appropriate anatase single crystals are not available,[1] information on the surface chemistry of anatase has to be based on studies of disperse samples. Most results have been obtained by IR spectroscopy. Along with the properties reported in the literature which are common, many differences have also been observed. The latter are due to: (*i*) sample morphology (mainly quantitative differences) and (*ii*) the strong influence of impurities (which results in a qualitative change in the properties).

3.1 Surface Hydroxy Groups

Hydrated titania obtained by hydrolysis of titanium salts has the crystal structure of anatase or rutile.[14] It is assumed that its surface is completely hydroxylated. Drying even at room temperature leads to irreversible dehydroxylation. The degree of dehydroxylation is a function of the heating temperature and titania slowly loses its water when calcined up to 600 °C. Samples prepared by 'dry' methods (*e.g.* fumed anatase) are characterized by a strongly dehydroxylated surface. However, even after evacuation at 700 °C, the so-called residual hydroxy groups are present on the anatase surface.[15—20] They are observed in the 3800—3600 cm^{-1} region of IR spectra. Their surface localization has been proved by isotopic exchange with heavy water[12] and by interaction with coadsorbed molecules.[17,18,20] At least 12 kinds of OH groups have been reported by different authors. It has been established that some of them are due to impurities, *e.g.* the band at 3740 cm^{-1} appears as a result of the presence of silicon.[17,20] Most authors report the existence of two kinds of residual hydroxy groups on anatase, which produce IR absorption bands at 3715 and 3675 cm^{-1}.[14—16] These two bands are readily observable after evacuation at about 300—400 °C. An increase in the evacuation temperature (combined with the use of modern evacuation techniques) results in a complex spectrum[18,19] containing a set of low-intensity bands in the 3800—3600 cm^{-1} region. The problem of the precise interpretation of the different hydroxy groups of anatase has not been solved. The more complex spectrum of highly dehydroxylated samples is probably due to different spectral behaviours of hydroxy groups which are identical from a crystallographic viewpoint but different with respect to their more distant surroundings (*e.g.* neighbouring sites which may or may not be occupied by OH groups).

Water adsorption on strongly dehydroxylated anatase takes place in two ways: part of the water molecules are dissociated forming hydroxy groups again, while the major part of the water is adsorbed molecularly[19] [in the IR spectra this is demonstrated by the $\delta(H_2O)$ band at 1600 cm^{-1}]. Repetition of the hydroxylation and dehydroxylation cycles leads to a decreasing concentration of the sites for dissociative adsorption, probably owing to surface reconstruction.[15] There are many differences between the results obtained for the concentration of residual surface hydroxy groups on anatase. The methods which exclude OH groups from adsorbed water show that the concentration of residual hydroxyls is about 0.5 OH nm^{-2}.[21] Thus, irrespective of the fact that this concentration depends on the morphology of the samples and their pretreatment, it may be stated that only a small part of the anatase surface is covered by hydroxy groups.

3.2 Surface Acidity

In order to estimate surface acidity, adsorption of weak (CO, benzene) and strong (ammonia, pyridine) bases is usually studied.[11] A typical probe molecule for fine determination of Lewis acidity is CO. Carbon monoxide is coordinated by a σ-bond to metal cations which have no d electrons, *e.g.* Ti^{4+}. The stronger the bond, the higher the IR stretching frequency of adsorbed CO. Testing oxidized anatase (containing no Ti^{3+} ions) with CO reveals the existence of two kinds of c.u.s. Ti^{4+} ions differing in electrophility.[15—19] The stronger sites (ν_{CO} at 2208 cm^{-1}) are usually denoted by α,

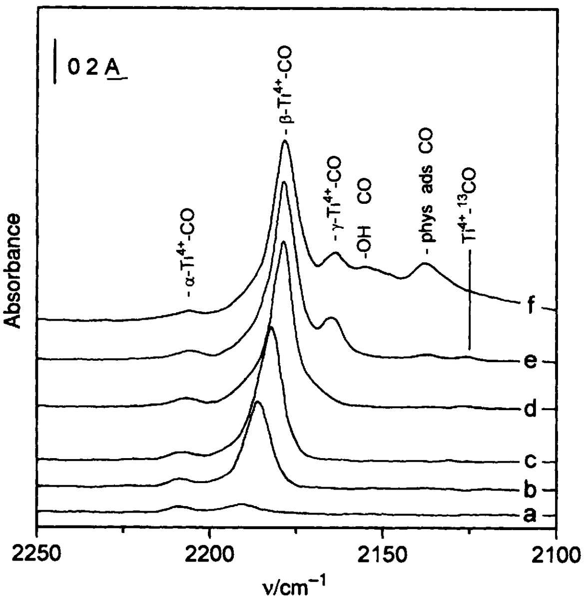

Figure 2 FTIR spectra of CO adsorbed on anatase at 100 K (a–e) Increasing amounts of CO and (f) an equilibrium pressure of 2 Torr CO (K Hadjiivanov and J C Lavalley, unpublished results)

while β is used for the weaker ones (ν_{CO} at 2190 cm^{-1}) The increase in the equilibrium pressure results in saturation of the α sites with CO at about 2 Torr, whereas the β sites are not fully occupied even at pressures above 100 Torr Both adsorption forms are weak and are easily destroyed by evacuation As a rule, the concentration of α sites is lower and some samples with a regular crystal shape may even have no α sites[18]

When CO is weakly adsorbed, the number of monitored sites could be increased by lowering the temperature of adsorption Carbon monoxide adsorption on anatase at *ca* 100 K (see Figure 2) also leads to detection of both (α and β) types of sites and C$-$O stretching modes are observed at 2206 and 2175 cm^{-1}[22] The band at 2175 cm^{-1} is very intense, which implies that in addition to the sites detected at room temperature (β'), some sites which are inert at room temperature (β'') are involved in the adsorption An additional band at 2165 cm^{-1} is also observable and corresponds to CO adsorbed on c u s Ti^{4+} sites possessing a very low electrophility (γ sites)

The increase in CO coverage (at both ambient and low temperatures) leads to a shift in maxima of the ν(CO) bands to lower frequencies owing to two overlapping effects static and dynamic shifts The static shift is produced by interaction of the admolecules through the support, while the dynamic interaction is usually of a dipole–dipole type and occurs through-space[22] The dynamic interaction is observed when the admolecules are parallel, are localized in the same neighbourhood and on the same plane, and vibrate with the same intrinsic frequency The latter condition allows elimination (and calculation) of the dynamic shift by the use of ^{13}CO–^{12}CO isotopic mixtures A dynamic shift is observed with the bands at 2175 and 2165 cm^{-1},[22] *i e* the β and the γ sites are situated on definite anatase faces, whereas with the carbonyls formed on the α sites (2208 cm^{-1} band) at least one of the requirements for dynamic shift is not satisfied

The question about the detection of Ti^{3+} ions using CO adsorption is still open It has been reported that Ti^{3+}–CO carbonyls on partially reduced anatase give absorption bands at 2115 cm^{-1}[17] According to other studies,[18] Ti^{3+} ions cannot be observed by testing with CO because they are oxidized by the latter Indeed, Ti^{3+} ions on anatase possess a very strong reduction ability and are oxidized even by water to Ti^{4+}[10]

Studies on the adsorption of strong bases lead to simultaneous and selective detection of both Lewis and Brønsted acidities When ammonia is coordinated to c u s cations, usually the δ_s(NH$_3$) band at about 1200 cm^{-1} is analysed[11] This band is sensitive to the strength of the bond formed the stronger the bond, the higher the frequency Ammonia protonation, *i e* formation of NH$_4^+$, shifts the symmetric N$-$H deformation modes of 1680 cm^{-1} However, the band typical of ammonium ions is δ_{as}(NH$_4^+$) at about 1450 cm^{-1} Ammonia adsorption on anatase leads to the appearance of two bands in the 1500—1000 cm^{-1} region about 1220 (weak) and at 1180 (strong) cm^{-1}[15,17,18,20] The latter band is shifted to 1145 cm^{-1} at maximum coverage These results have been considered for a long time as evidence for the presence of two kinds (namely α and β) of titanium cations differing in electrophility[15,17] This is in agreement with both the qualitative detection of α and β titanium cations by CO adsorption and the lower concentration of the α sites However, some experimental results contradict this opinion (*i*) the amount of adsorbed ammonia significantly exceeds the amount of CO adsorbed at room temperature,[18] and (*ii*) using another strong base, pyridine, it is possible to detect one type of Lewis acid sites only[17] Recently it has been established that the band at 1220 cm^{-1} is produced by dissociated ammonia since a new type of OH groups (3658 cm^{-1}) appear at the same time[18] The original OH groups of anatase do not protonate ammonia, but those at 3658 cm^{-1} display a weak Brønsted acidity and form NH$_4^+$ groups at equilibrium ammonia presssures Thus, the band at 1180 cm^{-1} characterizes ammonia coordinated to Lewis acid sites and this mode is not sensitive enough to distinguish between α and β sites The data obtained by adsorption and coadsorption of NH$_3$ and CO show the existence of several types of c u s titanium ions (Table 1) It is seen that in order to perform an efficient surface analysis of titania supported catalysts (*i e* to establish the location of the active phase and the eventual existence of a bare titania surface), combined testing by CO and NH$_3$ should be employed

Ammonia and pyridine adsorption show that the original OH groups of anatase exhibit no Brønsted acidity However, titania hydroxy groups protonate trimethylamine which is a stronger base[15] The acidity of hydroxy groups is determined more precisely and quantitatively by the hydrogen bond method Weak bases (*e g* benzene) form a hydrogen bond with the protons of the hydroxy groups during adsorption The higher the mobility (acidity) of this proton, the stronger the bond formed and the more pronounced the weakening of the O$-$H bond, respectively This causes a shift of the OH stretching modes to lower frequencies Benzene adsorption on anatase[20] leads to an average shift of the OH stretching modes by about -120 cm^{-1}, which corresponds to a weak acidity of the surface hydroxy groups It is interesting that preadsorption of ammonia on Lewis acid sites decreases the absolute value of this shift, and it then amounts to -60 cm^{-1}, *i e* NH$_3$ transmits electrons through the substrate and causes a twofold decrease of anatase surface hydroxyl acidity

At present, no sufficiently good probe molecule for determination of surface basicity is known Most often CO$_2$ is used for this purpose Adsorption of CO$_2$ on anatase proceeds (*i*) on Lewis acid

Table 1 Characteristic IR frequencies of probe molecules (CO, NH$_3$) adsorbed on different sites of the anatase surface

	Characteristic frequencies (ν/cm^{-1})		
Sites	CO adsorbed at 293 K	CO adsorbed at 100 K	NH$_3$ adsorbed at 293 K
α	$\theta_0^a \rightarrow 2208$ $\theta_{max}^b \rightarrow 2206$	$\theta_0 \rightarrow 2208$ $\theta_{max} \rightarrow 2206$	
β'	$\theta_0 \rightarrow 2192$ $\theta_{max} \rightarrow 2185$	$\theta_0 \rightarrow 2192$	$\theta_0 \rightarrow 1180$
β''	—	$\theta_{max} \rightarrow 2175$	$\theta_{max} \rightarrow 1145$
γ	—	$\theta_0 \rightarrow 2165$ $\theta_{max} \rightarrow 2164$	
Sites for dissociative adsorption	?	?	1220
OH groups	—	2155	—

[a] The value at zero coverage calculated by interpolation [b] The value at saturation

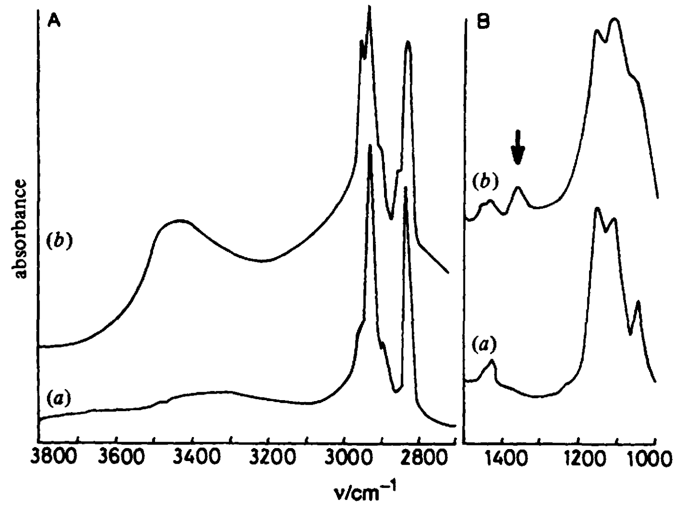

Figure 3 FTIR spectra of methanol adsorbed on (a) rutile and (b) anatase, evacuated at room temperature (reproduced with permission from ref. 23).

sites where linearly bonded CO_2 is formed,[17] and (*ii*) on basic sites, *i.e.* O^{2-} ions and OH groups. Carbonates are formed with the participation of the oxygen anions, while the hydroxy groups form hydrogencarbonates.[15,16] These compounds are decomposed during evacuation at room temperature, which indicates a weak surface basicity of anatase.

One can compare ammonia and water adsorption. In general it is nondissociative in both cases. However, these molecules dissociate on particular centres whose concentration is low. This is evidence for the presence of a certain proportion of strong acid–basic pairs on the anatase surface. The centres of dissociative adsorption are more precisely monitored by alcohols. On most oxides alcohol adsorption proceeds with breaking of the O–H bond. Dissociation of different alcohols also takes place on rutile, while on the majority of the anatase sites these compounds are adsorbed coordinatively.[23] The IR spectra of methanol adsorbed on both titania modifications are shown in Figure 3. The existence of coordinatively bound methanol on anatase is shown by the δ(COH) band at 1365 cm^{-1} (arrowed), whereas this band was not observed with methanol adsorbed on rutile since the O–H bond is broken during the dissociation.

This essential difference in surface chemistry of the two TiO_2 modifications is probably decisive for their different adsorption and catalytic properties. Thus, both anatase and rutile are n type semiconductors with almost the same bandgap. In this respect they meet the requirements for photocatalytic decomposition of water.[3,5] However, the anatase photoactivity is considerably higher. Obviously, the local structure of the catalytic site is also important. It is established that the photocatalytic decomposition of water (as well as the interaction of water with alkanes) on titania involves mainly molecularly adsorbed H_2O.[3] Thus, the lack of sites for dissociative adsorption on anatase seems to be an important reason for its photocatalytic properties.

3.3 Models of the Anatase Surface

Different models of the anatase surface have been proposed on the basis of its adsorption properties. Primet *et al.*[15] have considered the 001 face, supposing it to be the main face exposed on the surface. These authors are of the opinion that both types of surface hydroxy groups are localized on c.u.s. titanium cations, the band at 3715 cm^{-1} being characteristic of isolated hydroxy groups, and that at 3675 cm^{-1} of OH groups situated on neighbouring titanium cations. Dehydroxylation leads to surface reconstruction, which explains the nondissociative water adsorption. The c.u.s. titanium cations thus obtained represent the β sites, whereas the dehydroxylated titanium cations from unreconstructed centres are α sites. This pioneer model of the anatase surface takes into account the existence of face 001 only. However, 001 cannot be the only plane exposed on the surface. Another model,[21] focused on the four-coordinated Ti^{4+} sites from the 111 plane alone, has the same disadvantage. Busca *et al.*[17] have proposed a model considering the structure of most faces characteristic of the anatase crystallites (011, 010, 001 and 110). According to this model, the four-coordinated titanium cations from face 110 are the strong α sites, the five-coordinated cations from the other faces represent the weaker, β sites, and the hydroxy groups are localized on crystal lattice defects. Although much more advanced, this model cannot explain the variety of acid sites either. Evidently, the difference in properties of the titanium cations cannot be due to differences in their coordination number alone. Hadjiivanov *et al.*[18] have proposed a model explaining the high heterogeneity of titanium cations in anatase, taking also into consideration the effect of the second coordination sphere. According to this model, titanium cations from isolated acidic–basic pairs (c.u.s. Ti^{4+}–O^{2-}) are more electrophilic than the titanium ions from acidic–basic rows (c.u.s. $\cdots$ –Ti^{4+}–O^{2-}–Ti^{4+}–O^{2-}– $\cdots$). In the latter case the electrophility decreases owing to the formation of stronger bonds with two and not with one c.u.s. oxygen ion. Figure 4 presents a scheme for the anatase surface. It is obvious that regardless of their situation, all titanium cations may be divided into the following groups:

I. Four-coordinated Ti^{4+} (faces 110, 111 and 113 as well as the edges of the 110 face). These ions are referred to α sites. Owing to the different directions of the oxygen vacancies, CO molecules adsorbed on α sites are not parallel, which is the reason why no dynamic shift is observed with the α carbonyls.

II. Five-coordinated Ti^{4+}, participating in acidic–basic pairs (on the most characteristic faces, such as 101≡011 and 100≡010). These ions correspond to the β sites. At room temperature only half of the sites are occupied owing to an induced heterogeneity of the surface.

III. Five-coordinated Ti^{4+}, participating in acidic–basic rows (faces 001 and 112 and edges 101 × 011). They are the γ sites.

IV. Ti^{3+} ions. Stoichiometric considerations show that the c.u.s. titanium cations situated on the edges of the 001 plane are of a Ti^{3+} type.[18] Since Ti^{3+} ions are not characteristic of oxidized anatase, they are assumed to be the places of localization of the residual hydroxy groups. Thus, the titanium cations are stabilized in the fourth valency.

The most appropriate centres for dissociative adsorption are situated on the 110 face, for two reasons: (*i*) the 110 face contains the most acidic four-coordinated Ti^{4+} ions; (*ii*) the cationic vacancies on this plane are bridged, *i.e.* two c.u.s. O^{2-} ions act together as a Lewis base. This point of view is in agreement with the low concentration of the centres for dissociative adsorption, but is not supported by direct experimental evidence.

It is important to establish the reason for the predominant molecular adsorption of alcohols and water on anatase and for their dissociative adsorption on rutile. The cleavage rutile planes contain five-coordinated Ti^{4+} and two-coordinated O^{2-} ions. Schemes of the 110 and 100 rutile faces are presented in Figure 5. It is seen that, in contrast with the case of anatase, the coordinative vacancies of the Ti^{4+} and O^{2-} ions are either not parallel or are situated in different layers. The same applies to the other faces of rutile. Thus, a two-centre adsorption of water (alcohol) molecules is possible on anatase, whereas on rutile dissociation is necessary to ensure binding of adsorbed molecules to two surface sites simultaneously.

The above model explains well the high heterogeneity of the anatase surface and the relative concentration of the different sites. It is also confirmed by the dependence of the concentration of the different sites on the sample morphology.[18] The main problems remaining are: (*i*) a detailed interpretation of the different OH groups; (*ii*) explanation of the heterogeneity of β sites (now it seems to us that this heterogeneity is induced, *i.e.* an adsorbed CO molecule changes the acidity of the cationic sites in the vicinity), and (*iii*) exact interpretation of the sites for dissociative adsorption. Elaboration of a precise model of the anatase surface explaining all properties is a question for the future.

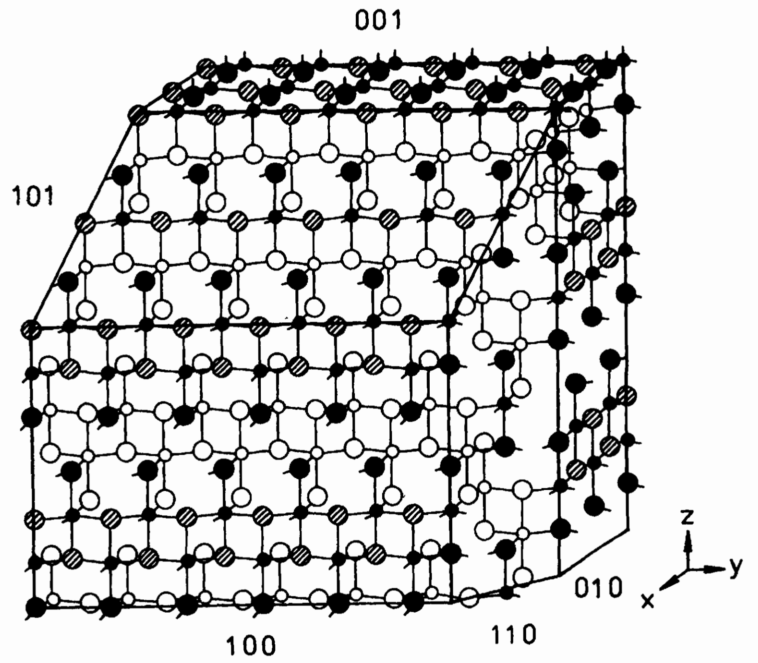

Figure 4 Scheme of an anatase crystal with different exposed faces. ●, c.u.s. Ti^{4+} ions; ○ saturated Ti^{4+} ions from the subsurface layers; ● c.u.s. O^{2-} ions; ⊘ saturated O^{2-} ions from the surface layers, ○ saturated O^{2-} ions from the subsurface layers.

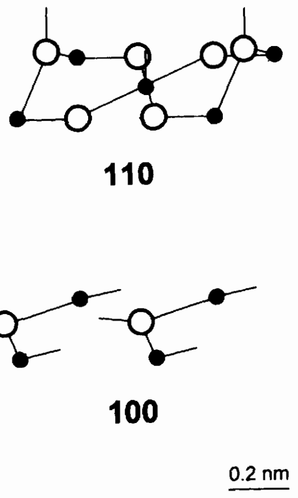

Figure 5 Schemes of the 'unit cells' of the 110 and 100 rutile planes. ● Ti^{4+} cations, ○ O^{2-} anions. The ions without vacancies (plane 110), although situated on the surface, are coordinatively saturated.

4 Surface Chemistry of Anion-modified Anatase

A new type of catalyst may be developed by synthesis of new substances with a new bulk structure or by modification of the surface of known substrates. Anatase is a typical example of the second possibility. It strongly adsorbs various anions and cations, which causes a pronounced change in its surface properties. We shall consider anatase modified by sulfates, phosphates and peroxides. In the two former cases the anions are adsorbed on Lewis acid sites and *via* ion exchange with surface hydroxy groups, while the OH groups alone participate in the formation of peroxide compounds.

4.1 Sulfate-modified Anatase

Sulfur is often present in the commercial titanias, especially when they are prepared *via* the so-called 'sulfate method.'[14] It is also accumulated on titania-based catalysts during the Claus reaction. However, titania and zirconia modified by sulfuric acid or sulfates have been the subject of numerous investigations since 1983 when Hino and Arata[7] reported their superacidity and their unusual catalytic properties (see Introduction). Titania may be sulfated by treating with H_2SO_4, impregnation with $(NH_4)_2SO_4$ or adsorption of sulfur-containing compounds followed by oxidation. Part of the c.u.s. oxygen ions from the TiO_2 surface are replaced by sulfate ions on sulfated titania (**ST**).[24–25] These sulfates are stable up to *ca.* 600 °C and are characterized by a strong band (typical for them) at 1380 cm^{-1} which corresponds to S=O stretching modes. In principle **ST** dehydroxylation is more difficult than that of pure anatase.[19] In cases of strongly dehydroxylated **ST** samples the sulfate ions attract electron density from a neighbouring titanium cation *via* an inductive effect. As a result, the electrophility of the titanium ions increases. This enhanced Lewis acidity is detected by testing with CO; when adsorbed on sulfated α sites, CO produces an absorption band at 2215 cm^{-1}, while on sulfated β sites absorption is observed at 2200 cm^{-1}.[24] Busca *et al.*[17] have also reported formation of dicarbonyls. Ammonia adsorption on dehydroxylated samples shows mainly the presence of Lewis acidity.[24] However, weakly dehydroxylated **ST** exhibits Brønsted acidity (a strong IR band at 1445 cm^{-1} after ammonia adsorption resistant to evacuation) which is assumed to be due to monomeric SO_3H groups[24] or to polymeric sulfates.[25] At present it is not clear whether the enhanced Lewis or the generated Brønsted acidity are responsible for the unique catalystic properties of **ST**. The first supposition is supported by the absence of superacidity of sulfated silica (which, in principle, possesses no Lewis acidity). Nevertheless, the Lewis acidity of **ST** is not very high. The low temperature of the catalytic reactions indicates that most probably **ST** catalysts are bifunctional, *i.e.* both aprotonic and protonic acid sites participate in the catalytic process.[24]

4.2 Phosphate-modified Anatase

Phosphorus is often present as a pollutant in commercial titania samples. It is also used as a promoter in TiO_2-supported catalysts.[7] Phosphated anatase may be obtained by adsorption of phosphate ions from acidic solutions or by impregnation. By analogy with **ST** one may expect a change in surface chemistry of anatase after phosphatation. However, in contrast to sulfates, the phosphate anions block the Lewis acid sites of anatase.[26] Thus, in contrast with the pure oxide, phosphated anatase does not adsorb CO[26] and has a hydrophobic surface.[21] A hypothesis was proposed[26] according to which the role of phosphorus as a promoter in vanadia–titania catalysts consists in blocking of the free c.u.s. titanium cations which usually catalyse parasitic reactions (*e.g.* production of CO and CO_2 during *o*-xylene oxidation,[27] formation of N_2O in the $DeNO_x$ process,[28] *etc.*).

4.3 Peroxide-modified Anatase

Hydrogen peroxide also belongs to the class of anionic modifiers. As a rule, univalent anions are not sorbed strongly on anatase, but hydrogen peroxide interacts with the surface hydroxy groups according to the reaction:[29]

$$\text{Ti–OH} + H_2O_2 \rightarrow \text{Ti–OOH} + H_2O. \qquad (2)$$

These surface hydroperoxo groups begin to decompose at about 80 °C evolving oxygen. Hence, peroxide-modified anatase is not of interest for catalysis at high temperatures. Surface peroxide species are of importance in low-temperature catalytic and especially in photocatalytic reactions (in the latter case H_2O_2 is often a reaction intermediate). Peroxide-modified titania could find important applications in the synthesis of some molecularly deposited catalysts owing to its increased adsorption capacity relative to pure titania with respect to ions tending to form peroxides.[30]

5 Vanadia–Titania Catalysts

Among the titania-supported oxide catalysts, V_2O_5/TiO_2 (anatase) is the most important. It shows better catalytic properties in *o*-xylene oxidation than does vanadium oxide itself as well as vanadium oxide deposited on other oxides and, in particular, on rutile.[31] V_2O_5/TiO_2 catalysts are also the most commonly used for the $DeNO_x$ process. Vanadia–titania catalysts are usually prepared by impregnation, the most widely used vanadium source being vanadium oxalate. In recent years much attention has focused on the so called 'molecularly deposited' catalysts. They are prepared *via* ion-exchange or by grafting, *i.e.* by a reaction of vanadium compounds with the anatase surface hydroxy groups.

When vanadia is deposited on anatase, its surface acidity decreases. As a rule, its distribution on anatase is not uniform. Probe molecules (CO, NH_3) detect bare titanium ions even on catalysts containing a higher amount of V_2O_5 than that necessary for monolayer formation.[32] This disadvantage is avoided in the so-called molecularly deposited catalysts where the distribution is more homogeneous.

Many theories have been proposed to explain the unique effect of anatase as a support. Vejux and Courtine[33] have shown the crystallographic similarity between faces 001, 100 and 010 of anatase and face 010 of vanadium pentoxide. They are of the opinion that, during deposition, epitaxial growth of vanadium oxide crystals with exposure of the 010 face proceeds. This face contains V=O groups which are responsible for the good catalytic properties. In the case of active molecularly deposited catalysts, however, no separate V_2O_5 phase is formed and it may be assumed that the two-dimensional compounds possess a structure similar to that of face 010.

A series of investigations have shown that, depending on the vanadia coverage, various surface compounds are formed. Isolated monooxovanadyl groups and two-dimensional vanadium oxide clusters correspond to low coverages, whereas a separate V_2O_5 phase and polyvanadates are observed at higher coverages.[30] The nature of the surface vanadium–oxo species also depends on the calcination temperature,[27] as shown in Figure 6. At high temperatures, an anatase–rutile transition (favoured by vanadium additives) and dissolution of VO_2 in the isostructural rutile crystals with formation of a $V_xTi_{1-x}O_2$ (r) phase are among the reasons for catalyst deactivation.[8,27]

In all cases vanadia/anatase catalysts contain species with a double V=O bond. This bond is well monitored in the IR spectra by the 2ν(V=O) overtone at 2060—2054 cm^{-1}. Part of the surface vanadia species are also characterized by the presence of V–OH groups (bands in the 3680—3660 cm^{-1} region). These hydroxy groups cause the Brønsted acidity of the catalysts [a $\delta_{as}(NH^+_4)$ band at 1460 cm^{-1} after ammonia adsorption]. According to Bond *et al.*[34] it is the joint effect of the V=O and V–OH groups that determines the good catalytic properties of vanadia/anatase catalysts in selective oxidation reactions. The Lewis acidity of the V_2O_5/TiO_2 catalysts is weak: no V^{5+}–CO carbonyls are formed after CO adsorption. However, the stronger base ammonia is coordinated to V^{5+} sites [$\delta_s(NH_3)$ at 1240 cm^{-1}] causing rearrangement in the VO_x surface complexes and disappearance of the V=O bond.[30] It should be noted that all of the above considerations relate to oxidized catalysts which, however, are reduced and reoxidized during the reactions.

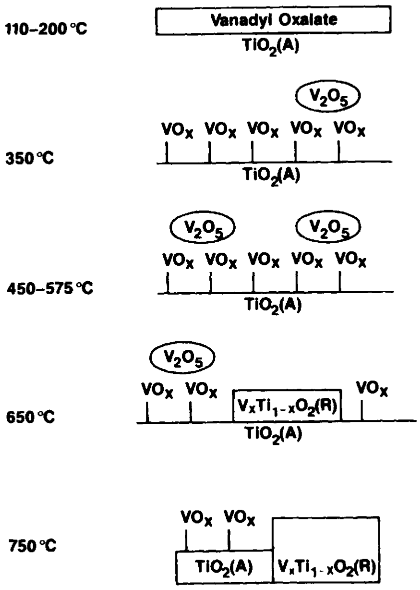

Figure 6 Model of evolution of V_2O_5/TiO_2 with calcination temperature (reproduced with permission from ref. 27*b*).

Many researchers have pointed out the lack of activity of titania in the oxidation of *o*-xylene, but Wachs *et al.*[27] have demonstrated that anatase leads to the full oxidation of some of the reaction intermediates. Thus, the bare titania surface of vanadia/anatase catalysts lessens their selectivity. This point of view could also be extended to other reactions and catalysts. For instance, during the $DeNO_x$ process, NH_4NO_3-like species are formed on the anatase surface.[28] These species decompose to the undesired reaction product, N_2O. Hence, one of the reasons for N_2O formation over titania-supported oxide catalysts could be the incomplete covering of the titania by the active phase. These examples show that the design of the TiO_2-supported oxide catalysts is of great importance for their catalytic performance.

6 Titania-supported Metal Catalysts

One of the main reasons for the numerous studies of titania-supported metal catalysts is the so-called strong metal–support interaction (SMSI). However, even in the absence of a SMSI effect these catalysts are of interest. Thus, platinized titania exhibits a much higher activity in a series of photocatalytic reactions than pure anatase.[5] Combined $Pt-RuO_2/TiO_2$ catalysts are the most promising ones for photocatalytic water cleavage.

6.1 Preparation of Titania-supported Metal Catalysts

In most cases metal salts are precursors for preparation of supported metals. After deposition, the metal ions are reduced. Both the pre-reduction treatment and the reduction conditions are found to affect the structure of the metal formed and especially the average particle size. In a number of catalytic reactions (the so-called structure-sensitive reactions) the catalytic properties strongly depend on the metal particle size.[35] In addition, the catalytic performance of bimetallic catalysts is affected by the homogeneity of distribution

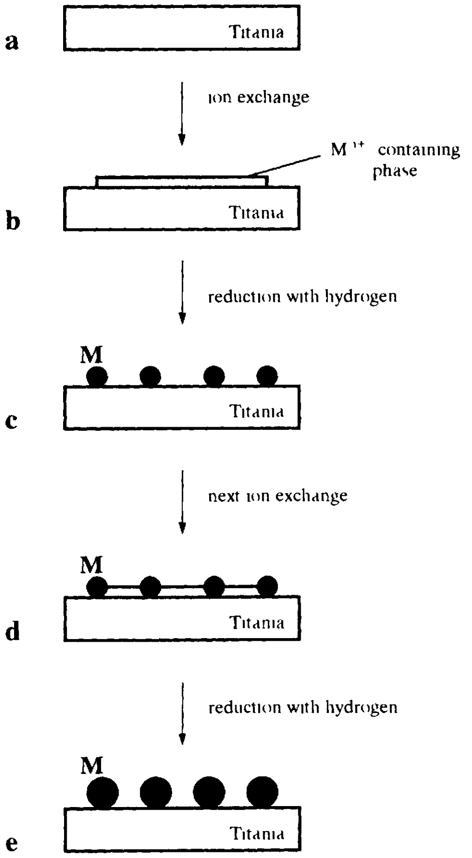

Figure 7 Principal scheme of the multi ion-exchange process

of the two metals in the separate particles That is why the design of supported metal and bimetal catalysts is crucial

The techniques used most often for preparation of supported metals are impregnation and ion exchange [35] Here we shall discuss two methods of deposition of noble metals which are specific for titania TiO_2 is an effective photocatalyst for deposition of noble metals from solutions of their salts [5] This process is used for the synthesis of mono- and bi-metallic catalysts supported on titanium dioxide [36] The amounts of deposited metals are controlled by the concentration of their ions in the solutions The main restriction to the method is that it can be applied to photosensitive systems only

Recently Hadjiivanov *et al* [37a] proposed the multiple ion-exchange method, the model system used being Pt–TiO_2 Platinum-containing ions are adsorbed initially on anatase CO adsorption reveals the occupation of Ti^{4+} Lewis acid sites during the process Testing with CO again after the reduction of Pt^{n+} shows that part of the initially occupied adsorption sites are liberated This phenomenon allows subsequent ion exchange, *etc* (see Figure 7) The increase in platinum content is smaller than 100% owing to physical blocking of part of the exchange sites by metal particles The catalysts obtained by repeated ion exchange are characterized by a high dispersion and a narrow metal particle size distribution It has been established that the process may also be applied to the system Ag–TiO_2 [37b] At present the question about whether other supports may be used is still open

6.2 A Strong Metal–Support Interaction (SMSI)

The consideration of the surface and catalytic properties of titania-supported noble metals is associated with SMSI, which is one of the most interesting and most studied effects in catalysis The term SMSI was introduced by Tauster *et al* [38] to denote the effect responsible for the drastic decrease in CO and H_2 chemisorption on titania-supported metals after increasing the reduction temperature from 200 to 500 °C The following peculiarities of SMSI have to be noted (*i*) the effect occurs only when the hydrogen adsorption on the supported metals is dissociative, (*ii*) it is not due to change in the metal particle sizes Catalytic systems have been denoted as LTR (low temperature of reduction) and HTR (high temperature of reduction) depending on whether this temperature is below or above 300 °C The present enormous interest in SMSI could not have arisen from the low chemisorption capacity of the HTR catalysts only However, they have also demonstrated some unusual catalytic properties The TOF (turnover frequency, *i e* the activity per surface metal atom) of LTR and HTR catalysts towards structure-insensitive reactions is almost the same, but structure-sensitive reactions proceed at a much lower rate on HTR catalysts, *i e* in the presence of SMSI

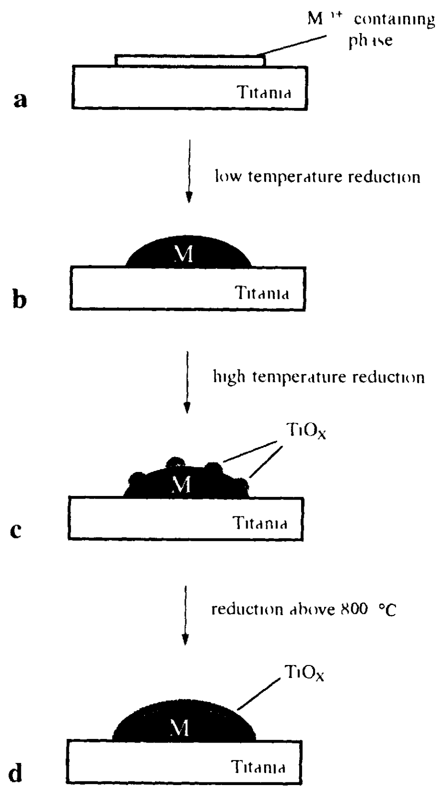

Figure 8 Titania supported metal catalysts reduced at different temperatures (a) Before reduction, (b) a metal particle on titania formed after low temperature reduction, (c) partial coverage of the metal particle with TiO_x moieties after high temperature reduction, and (d) full encapsulation of the metal particle into the support after reduction at a very high temperature (see text)

Many hypotheses have been proposed to explain SMSI Initially electronic effects were considered to be the cause, but now the following explanation is accepted [9,10] titania from HTR catalysts is partly reduced and a suboxide phase migrates onto the metal particle (see Figure 8) Thus, the part of the metal surface partially covered by TiO_x is blocked As a result, the chemisorption capacity of the metal strongly decreases and structure-sensitive reactions, which need a larger ensemble of metal atoms, are suppressed The existence of admixtures, *e g* Na^+, facilitates the migration of TiO_x moieties and SMSI occurs at lower temperatures of reduction [39] At a higher reduction temperature partial or complete encapsulation of the metal particles in titania may occur Other effects that are reported to occur on reduction above 800 °C are the formation of intermetallic compounds and alloys

The large interest in SMSI is strengthened by one more phenomenon With some metals such as platinum supported on titania the TOF of hydrogenation of CO as well as of compounds containing a carbonyl group increases by up to two orders of magnitude after HTR It is supposed that the suboxide phase, being a strong reducer, favours the dissociation of CO, extracting oxygen, while the metal serves as catalyst for the hydrogenation of the carbon obtained However, there is some evidence that, although associated with

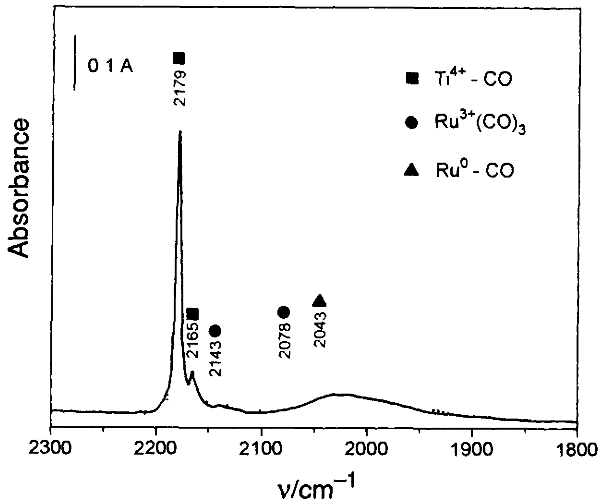

Figure 9 FTIR spectra of CO (1 Torr) adsorbed on a LTR Ru/TiO_2 catalyst at 100 K (solid line) and after heating to 373 K in a CO atmosphere, followed by cooling again to 100 K (dotted line) (K Hadjiivanov and J C Lavalley, unpublished results)

SMSI, the increase in the CO hydrogenation rate is not directly provoked by SMSI because (*i*) it has been established that water (which is produced in the CO + H_2 reaction) oxidizes the suboxide and SMSI disappears, (*ii*) in some cases even LTR Me/TiO_2 catalysts have a higher TOF than does the corresponding metal deposited, say, on silica

It is evident that the suboxide phase is not unchangeable during CO hydrogenation On the contrary, reduced titanium ions can probably be oxidized directly not only by water but also by CO [18] It seems that in this case HTR is needed to ensure the initial formation of the suboxide phase on the metal particles During the reaction the titanium cations formed are altervalent, *i e* they are reduced by hydrogen but oxidized by water and CO, thus facilitating CO dissociation This mechanism also explains the varying effect of HTR on different metals For instance, CO is difficult to dissociate on Pt and that is why Pt/TiO_2 catalysts strongly enhance their TOF after HTR The IR spectrum of CO adsorbed on a LTR Ru/TiO_2 catalyst is shown in Figure 9 At 100 K all of the ruthenium is in the Ru^0 state, but heating in a CO atmosphere up to 373 K is accompanied by formation of Ru^{n+}, *i e* the activation of CO in this case is not hindered This explains the small effect of the reduction temperature and the type of support on the TOF of supported ruthenium during hydrogenation of the CO bond [39]

7 Conclusions

7.1 Heterogeneity

The anatase surface is highly heterogeneous Three kinds of Lewis acid sites (differently coordinated Ti^{4+} ions) and at least two kinds of hydroxy groups are present on the surface This high heterogeneity is due to the exposure of different planes on the real crystallites

7.2 Local Arrangement

The local arrangement of the anionic and cationic vacancies on the anatase surface determines the lack of centres for dissociative adsorption of water and alcohols This particular anatase property is relevant to (*i*) the low hydroxyl coverage of anatase, and (*ii*) its (photo)catalytic behaviour

7.3 Anions

Adsorbed anions strongly affect the surface properties of anatase Surface sulfates increase the Lewis acidity, whereas phosphates block the Lewis acid sites Both anions induce a Brønsted acidity

7.4 Design

The design of titania-supported oxide catalysts is very important since a bare titania surface often leads to parasitic reactions and decreases the selectivity of the catalysts

7.5 SMSI

Titania-supported metals reduced above 300 °C are characterized by a strong metal-support interaction (SMSI) This effect strongly decreases the chemisorption capacity of the supported metals and is due to their coverage by Ti-suboxide moieties

7.6 Turnover Frequency

The TOF of some metals in CO hydrogenation is enhanced when supported on titania This effect is also due to covering of the metal particles with a Ti-containing phase but the catalysts are not in the SMSI state during the reaction

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