

## 4 TITANIUM

Nick Serpone[1a], Mary A. Jamieson[1b] and E. Pelizzetti[1c].

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### INTRODUCTION

The extent of coordination chemistry of titanium appears attenuated during 1985. By contrast, the interesting chemistry occurring in systems containing  $TiO_2$  and related oxides continues unabated. The present review covers those papers cited in Chemical Abstracts Volume 101, No. 23 through Volume 104, No. 4. The major focus is again on titanium oxides. Several review articles have appeared that may be of interest to the readers of this work.

Nabivanets and coworkers[2] have reviewed such properties of titanium(III)

in solutions as complex stability constants, electrical potentials, and molar absorptivities, and have further discussed these in terms of their relevance to the determination or separation of titanium. Thermal studies reported in 1983 on titanyl and zirconyl oxalate complexes have been reviewed[3], as have nmr x-ray diffraction analyses on Ti-V hydrides[4]. Reviews on (i) the physical, thermal and crystallographic character of the series  $Ti_nO_{2n-1}$ ,  $Ti_nO$ ,  $Ti_nO_{n-1}$ ,  $Ti_{n-1}O_n$  and  $Ti_{2nH}O_n$  [5], (ii) the mechanism of oxidative ammonolysis of toluene on a vanadium-titanium oxide catalyst[6], and (iii) the selective thin-film treatments (e.g., TiN) for photothermal conversion of solar energy[7] have also appeared.

#### 4.1 HYDRIDES

The semi-empirical SCF-MO-LCAO method has been used by Ivanovskii and coworkers[8] to study the electronic structure and chemical bonding in nonstoichiometric titanium (and zirconium) hydrides. The results are compared with the band structure calculations and experimental x-ray emission and photoelectron spectra. The authors also considered the influence of the concentration of hydrogen vacancies and the tetragonal distortions of the crystal lattice on the electronic energy spectrum[8].

Nuclear magnetic resonance (nmr) studies and magnetic susceptibility measurements have been reported for  $Ti_{(1-x)}V_xH_2$  ( $0.04 \leq x \leq 0.65$ )[9] and  $TiCoH_x$ [10]. Entropy and enthalpy measurements on the electrochemical reaction of  $TiMn_{1.5}$  hydride electrode in aqueous alkaline solution have been reported by Yayama et al.[11]. The study reveals no heat change upon hydrogenation of the electrode which occurs during the electrochemical reaction. Hydrogen evolution at potentials below -1.075V vs. Ag/AgCl under open-circuit conditions was rationalized in terms of a "local cell" model[12].

## 4.2 NITRIDES

The Korringa-Kohn-Rostoker(KKK)-Green function and KKK-CPA methods have been utilized to calculate the electron densities and densities of electronic states for  $\text{TiN}_x$  ( $x = 0.75, 1$ ). The calculated results agree well with existing experimental evidence for vacancy-induced changes in the electronic structure of  $\text{TiN}$ [13]. Titanium nitrides of various compositions react with hydrogen at 573-1073K for up to 100 hrs. X-ray diffraction analyses on the products show no crystal structural changes for N:Ti ratios of less than 0.3, though solid solutions of ternary compounds are formed which contain large quantities of hydrogen. Further, a body-centered tetragonal type specimen with N:Ti  $\approx 0.4$  transforms into a hcp-type ternary compound upon hydrogenation; the hydrogen content was twice as much as nitrogen. Upon hydrogenation, specimens of N:Ti  $> 0.5$  yielded ternary compounds of fcc structure, wherein the amount of hydrogen absorbed was significantly less than that in ternary compounds with hcp structure[14].

## 4.3 PHOSPHATES

X-ray diffraction and EPR spectroscopy have been employed to determine the position of Cu in the lattice of  $\text{Cu}_x\text{Nb}_{1-x}\text{Ti}_{1+x}(\text{PO}_4)_3$  ( $0 \leq x \leq 1$ ) and  $\text{Cu}_{1+x}\text{Cr}_x\text{Ti}_{2-x}(\text{PO}_4)_3$  ( $0 \leq x < 1$ ), both of which have a Nasicon-type structure [15].  $\text{CuTi}_2(\text{PO}_4)_3$  has been prepared, oxidized to  $\text{CuTi}_4(\text{PO}_4)_6$ , and characterized by x-ray crystallography [15].

High-resolution IR transmission measurements at 10-300K on  $\text{KTiOPO}_4$  crystals have elucidated the hydroxide ion bands[16]. Additionally,  $\text{KTiOPO}_4$  exhibits an extremely short wavelength titanate emission at 390nm, which is quenched at  $\approx 100\text{K}$ . The luminescence has been discussed[17] in terms of a self-trapped exciton that gains mobility at higher temperatures.

## 4.4 SULFIDES

The preparation of titanium disulfides of different stoichiometries,  $\text{Ti}_{(1+x)}\text{S}_2$  ( $0 \leq x \leq 0.1$ ), has been reported; the lattice parameters have been determined. The results are discussed in terms of the addition of excess Ti to the octahedral interstices in the van der Waals gap[18]. Chemical vapor deposition from gaseous  $\text{TiCl}_4$  and  $\text{H}_2\text{S}$  yields different nonstoichiometric compositions of  $\text{Ti}_{(1+x)}\text{S}_2$ . The excess of Ti(x) in  $\text{Ti}_{(1+x)}\text{S}_2$  decreases to 0.01 as the ratio  $\text{H}_2\text{S}/\text{TiCl}_4$  increases to 20. The apparent chemical diffusion coefficient of Li in  $\text{Ti}_{1.01}\text{S}_2$  is  $4.0 \times 10^{-13} \text{ m}^2 \text{ s}^{-1}$ [19].

Bernard *et al.*[20] have prepared the layered titanium dichalogenides  $(\text{NH}_3)_y\text{TiS}_2$  ( $0.4 \leq y \leq 0.6$ ) and characterized them by x-ray diffraction, vapor pressure measurements, thermogravimetric analysis, and SQUID magnetometry. The compounds rapidly lose  $\text{NH}_3$  at ambient temperature to form a stage II structure. The ionic formulation  $(\text{NH}_4)_y(\text{NH}_3)_{y''}\text{TiS}_2$  best describes these compounds, wherein the more strongly bound  $\text{NH}_3$  is best described as  $\text{NH}_4^+$ . It appears that redox reactions play an important role in  $\text{NH}_3$  intercalation into  $\text{TiS}_2$ , and likely into other  $\text{TiX}_2$  hosts[20].

Structural studies on hydrated lithium intercalates of  $\text{TiS}_2$  and  $\text{TiSe}_2$ [21],  $\text{c-TiS}_2$ [22], and  $\text{Tl}_2\text{TiS}_4$ [23] have appeared. Two hydrates were observed in Li-intercalated  $\text{TiX}_2$  ( $\text{X} = \text{S}, \text{Se}$ ): one contains a monolayer and the other a bilayer of water molecules between the  $\text{TiS}_2$  layers. Structures were determined for  $\text{Li}(\text{H}_2\text{O})\text{TiX}_2$ ,  $\text{Li}(\text{H}_2\text{O})_2\text{TiX}_2$ ,  $\text{Li}_{0.4}(\text{H}_2\text{O})\text{TiX}_2$ , and  $\text{Li}_{0.4}(\text{H}_2\text{O})_2\text{TiX}_2$ [21]. Figure (1) shows results obtained for studies on  $\text{c-TiS}_2$ [22], while Figure (2) illustrates the crystal structure of  $\text{Tl}_2\text{TiS}_4$ . The structure of  $\text{Tl}_2\text{TiS}_4$  has been described by Klepp[23] as a mixed packing of Tl atoms and S atoms, composed of puckered  $\text{TiS}_2$  layers, in which the Ti atoms occupy the octahedral interstices.

The stability of the intercalated phases in  $\text{Ag}_x\text{MS}_2$  ( $\text{M} = \text{Ti}, \text{Nb}, \text{and Ta}$ ) has been elucidated by x-ray diffraction and emf measurements[24]. Extensive

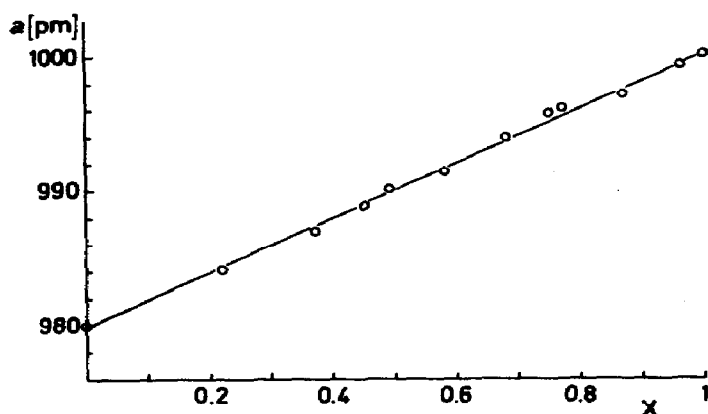


Figure 1. Variation of the cubic lattice parameter 'a' with the copper level 'x' in  $\text{Cu}_x\text{Ti}_2\text{S}_4$  phases prepared by anodic oxidation of the thiospinel  $\text{CuTi}_2\text{S}_4$  in copper(I) electrolytes at 300K, from reference 22.

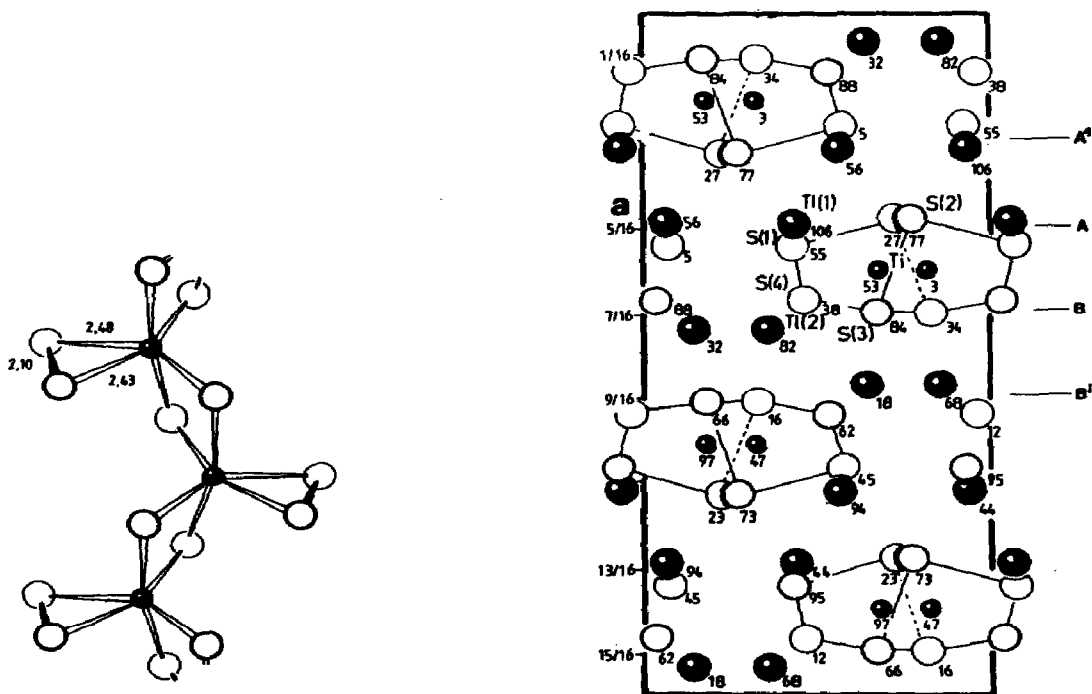


Figure 2. The (a) molecular and (b) crystallographic projection on the [001] plane of  $\text{Tl}_2\text{TiS}_4$ , from reference 23.

X-band ESR measurements on  $M_xTiS_2$  ( $M = V, Cr, Mn, Fe, Co, Ni; 0 \leq x \leq 1$ ) at 300 - 77K have shown variations in the intra- and inter-layer spacings upon intercalation of guest atoms. While  $Fe_xTiS_2$  and  $Ni_xTiS_2$  show no ESR signals and magnetic interactions are ineffective in  $V_xTiS_2$ , dipolar interactions appear dominant in  $Cr_xTiS_2$  and  $Mn_xTiS_2$  [25].

#### 4.5 HALIDES

Choudhury and coworkers[26 - 30] report extensive studies on phase transitions in manganese and zinc fluorotitanate compounds. Raman spectra of  $MnTiF_6 \cdot 6H_2O$ ,  $MnTiF_6 \cdot 6D_2O$ ,  $ZnTiF_6 \cdot 6H_2O$  and  $ZnTiF_6 \cdot 6D_2O$  single crystals were studied under different polarizations in the temperature range 77 - 300K. The observed bands are assigned to the various vibrational modes[26 - 28]. A Raman study of  $MnTiF_6 \cdot 6D_2O$  reveals a structural phase transition between 200 and 228K, and asymmetry in the shape of the spectrum at  $220 - 360cm^{-1}$ . The asymmetry arises from coupling between the  $\nu_{as}(Mn-O)$  and  $\delta(TiF_6)$  modes present in this region[27]. Additionally, it seems that for the frequency shift, the quartic interactions, quadratic in the soft mode coordinates, are important; for the linewidth, the pure vibrational dephasing (elastic scattering) process is important[29]. Infrared spectra of  $ZnTiF_6 \cdot 6H_2O$  and  $MnTiF_6 \cdot 6H_2O$  were obtained in the temperature range 166 - 300K [30]. Two vibrational modes (at 435 and  $485cm^{-1}$ ) appear below 185K in the spectrum of  $ZnTiF_6 \cdot 6H_2O$ ; whereas above  $T_o = 203K$ , only one vibrational mode is present. The spectrum of  $MnTiF_6 \cdot 6H_2O$  shows two vibrational modes (at 440 and  $485cm^{-1}$ ) below 169K, and one vibrational mode above  $T_o = 254K$  [30]. The temperature dependence (77 - 400K) study of the nmr linewidths of  $^1H$  and  $^{19}F$  in  $NiTiF_6 \cdot 6H_2O$  shows separate abrupt changes in the  $^1H$  width (122 - 126K) and the  $^{19}F$  width (131 - 134K). The data confirm the existence of two transitions in the known structural transformation region. An anomaly near 205K suggests the possibility of a third transition. Cheung and Lichti[31] have discussed this temperature dependence in terms of

reorientations of the octahedral complex ions.

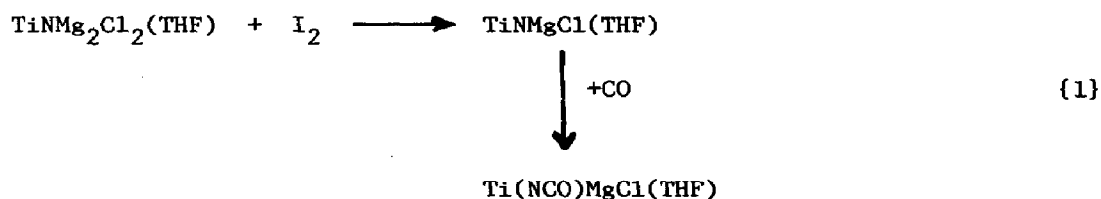
Reaction of  $\text{TiO}_2$  in 40% HF with an excess of 30%  $\text{H}_2\text{O}_2$  and KOH, followed by the addition of aqueous HF to adjust the solution pH, results in the formation of  $\text{K}[\text{Ti}(\text{O}_2)\text{F}_3] \cdot \text{H}_2\text{O}$ , with the peroxide bonded to the Ti(IV) center in a triangular bidentate manner ( $\text{C}_{2v}$ ). The product was characterized by infrared and laser Raman spectroscopies[32].  $\text{K}_2\text{TiOF}_4$  has been prepared via three methods[33]: (a) solid state reaction between  $\text{K}_2\text{TiF}_6$ ,  $\text{TiO}_2$  and KF; (b) pyrohydrolysis of  $\text{K}_2\text{TiF}_6$  at 723 and 823K; and (c) thermal decomposition of  $\text{K}_2\text{Ti}(\text{O}_2)\text{F}_4 \cdot \text{H}_2\text{O}$ . In all three methods, the reaction products are mixtures of several compounds, including the kryolith-phase  $\text{K}_{2+x}\text{TiO}_x\text{F}_{6-x}$  and  $\text{TiO}_2$ . At 403K,  $\text{K}_2\text{Ti}(\text{O}_2)\text{F}_4 \cdot \text{H}_2\text{O}$  forms  $\text{K}_2\text{Ti}(\text{O}_2)\text{F}_4$  via loss of  $\text{H}_2\text{O}$ , and at 503K the peroxo group decomposes to yield  $\text{K}_2\text{TiOF}_4$  as the main product.  $\text{K}_2\text{TiOF}_4$  crystallizes tetragonally; an analysis of its infrared spectrum suggests infinite  $-\text{Ti}-\text{O}-\text{Ti}-\text{O}-$  chains[33].

The infrared spectrum of  $\text{TiF}_4$ , consisting of a single band at  $772\text{cm}^{-1}$ , was recorded on the products of the reaction between  $\text{TiCl}_4$  and NaF at 900 - 1200K. The band at  $772\text{cm}^{-1}$  is due to the  $\nu_3$  stretching vibration[34]. The Raman spectrum of the trigonal  $[(\text{NH}_4)_2\text{TiF}_6]$  complex in the temperature range 10 - 298K confirms the presence of four modes, as predicted by group theory. Tentative assignments are reported by Jenkins[35].

A review by Galitskii et al.[36] discusses the preparation of high-purity  $\text{TiCl}_4$  by chlorination of synthetic titanates. The formation and structures of  $\text{RbTiCl}_3$  and  $\text{CsTiCl}_3$  in  $\text{RbCl}-\text{Ti}-\text{TiCl}_3$  and  $\text{CsCl}-\text{Ti}-\text{TiCl}_3$  systems has been reported[37]; they are isotopic with the structure of  $\text{CsNiCl}_3$ , with space group  $\text{P}6_3/\text{mmc}$ . The preparation, characterization and solution properties of  $\text{MgCl}_2 \cdot \text{TiCl}_4 \cdot 4\text{L}$  ( $\text{L} = \text{EtOAc}$ , THF,  $\text{HCO}_2\text{Et}$ ),  $\text{MgCl}_2 \cdot \text{TiCl}_4 \cdot 2\text{EtOAc} \cdot 2\text{L}$  ( $\text{L} = \text{HCO}_2\text{Et}$ ,  $\text{BzOEt}$ ),  $\text{MgCl}_2 \cdot \text{TiCl}_4 \cdot 2\text{EtOAc}$  and  $(\text{MgCl}_2)_3 \cdot \text{TiCl}_4 \cdot (\text{SnCl}_4)_2 \cdot 12\text{EtOAc}$  have been investigated[38]. The  $\text{TiCl}_6^{4-}$  and  $\text{TiCl}_6^{3-}$  species were identified by electronic spectra from solutions of  $\text{TiCl}_2$  and  $\text{TiCl}_3$  in  $\text{NaCl}-\text{KCl}$  melts. By contrast,  $\text{TiCl}_2$  and  $\text{TiCl}_3$  in  $\text{KCl}-\text{NaCl}-\text{NaF}$  melts form  $\text{TiCl}_3\text{F}_3^{3-}$  and  $\text{TiCl}_2\text{F}_4^{3-}$  [39].

The energy terms and partial charge densities of core-excited states have been estimated for  $MCl_4$  ( $M = Ti, Si, C$ ) by SCF- $X_\alpha$  scattered-wave calculations and a muffin-tin approximation. The results are in good agreement with data obtained from x-ray absorption and electron energy-loss spectra. The absorption edge of  $TiCl_4$  is dominated by antibonding  $d(e)$  and  $d(t_2)$  orbitals [40]. Following a vibrational analysis on  $trans-[TiCl_2(H_2O)_4]^+$ , molecular constants, force constants, compliance constants and centrifugal distortion constants were evaluated using the kinetic constants method[41].

High-precision calorimetry has been employed to determine the heats of reaction leading to the formation of complexes from reaction of  $TiCl_4$  with ethyl acetate, acetone or methylethylketone in benzene solutions. The reactions involve three stages, with formation of 1:1 and 1:2 complexes together with dissociation of the acceptor complex formed first with the initial solution[42].  $TiCl_4 \cdot 2CH_3CN$  is obtained via interaction of the components, followed by crystallization from acetonitrile. X-ray diffraction studies show monoclinic crystals, space group  $P2_1/c$ , with "a" 5.982(8), "b" 13.50(2) and "c" 13.15(2) $\text{\AA}$ , and the two N atoms cis to each other[43,44]. Magnesium reduces  $TiCl_4(THF)_2$  in THF under nitrogen to  $TiNMg_2Cl_2(THF)$ ; this species reacts further with CO to yield  $TiCONMg_2Cl_2(THF)$ . The amide character of N in  $TiNMg_2Cl_2(THF)$  is suggested by the reaction between  $TiCONMg_2Cl_2(THF)$  and MeI to give  $Me_2NCOME$  in 73% yield. The following reactions were also studied[45].



The kinetics and mechanism of the chemisorption and reaction of  $TiCl_4$  with copper films were studied gravimetrically by Dobruskin and coworkers[46]. The reaction is catalysed by oxygen. In an effort to improve the efficiency of



magnesium consumption in the manufacture of titanium sponge, the mechanism of reduction of titanium chlorides by magnesium was investigated in a salt melt (34.6%  $\text{TiCl}_2$ , 19.1%  $\text{TiCl}_3$ , 21.1%  $\text{NaCl}$ , 25.2%  $\text{KCl}$ )[47].

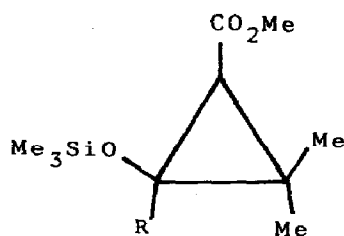
The hydrolysis of titanium(IV) in chloride media has been studied by determining the  $[\text{Ti(IV)}]/[\text{Ti(III)}]$  ratios in solutions of  $\text{TiCl}_4$  equilibrated with hydrogen gas at 298K in 3M (Na)Cl; the  $\text{Ti(OH)}_2^{2+}$  species predominates in the concentration ranges  $0.5 \leq [\text{H}^+] \leq 2\text{M}$  and  $1.5 \times 10^{-3} \leq [\text{Ti(IV)}] \leq 0.05\text{M}$ . Reduction potentials were evaluated from equilibrium data, and as a function of  $[\text{H}^+]$  [48]. The nature of Ti(III) in absolute ethanol in the presence of HCl has been established from electronic and ESR spectra. The ESR signals were assigned to the species  $[\text{TiCl}_{6-n}(\text{EtOH})_n]^{3-n}$  ( $n = 1, 2, 3, 4$ ); the complexes with  $n = 2, 4$  have *cis* structures. Only  $\text{TiCl}_3(\text{EtOH})_3$  obtained in the absence of HCl[49].

$\text{TiCl}_4$  reacts with 2-pyridylphenylacetonitrile (L) and 1,2-dicyano-1,2-di(phenyl)-1,2-(2-pyridyl)ethane (L') in 1,2-dichloroethane or ether to yield  $\text{TiCl}_4\text{L}$  and  $(\text{TiCl}_4)_2\text{L}'$ , respectively[50]. Chelation, metal uptake and distribution ratio of  $\text{OC}[\text{N}(\text{CH}_2\text{O}_2\text{CC}_6\text{H}_4\text{OH}-\sigma)_2]_2$  with  $\text{TiCl}_4$  are reported by Siddiqi and coworkers[51]. The resulting complexes were characterized by elemental analyses, infrared spectroscopy and molar conductance. The preparation of  $\text{TiL}_2$  ( $\text{H}_2\text{L}$  = rubeanic acid) from  $\text{TiCl}_4$  and  $\text{H}_2\text{L}$  has been reported, along with proposals for monomeric and polymeric structures of  $\text{TiL}_2$ [52].

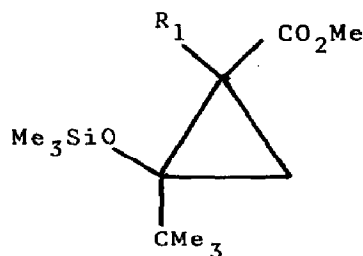
Catalyst complexes have been prepared from  $\text{TiCl}_4$ . Polystyrene cross-linked with 5-7% divinylbenzene and combined with  $\text{TiCl}_4$  in  $\text{CS}_2$  forms a stable complex containing 4.5% Cl capable of catalysing the conversion of aromatic aldehydes, carboxylic acids, ketones and some alcohols into the corresponding acetals, esters, ketals and ethers, respectively. The complex is also effective for the Friedel-Crafts alkylation reaction[53]. Reaction of  $\text{TiCl}_4$  with EtOH, ProH (or other alcohols) or lithium alcoholate in an organic solvent in the presence of a  $\text{NH}_4\text{NO}_3$ ,  $\text{NH}_4\text{I}$ , or  $\text{NH}_4\text{CNS}$  solution in liquid  $\text{NH}_3$  or in the presence of an organic amide affords alkyl ortho-titanates. These complexes can catalyse polyester synthesis and epoxy resin curing[54]. Aromatic ketones react

smoothly in basic media in the presence of  $\text{TiCl}_3$  to give reductively coupled products according to the increase of reducing power of the  $\text{Ti(III)}$  ion with increasing pH. Thus, benzil, benzoin and methoxybenzoin are reduced to the corresponding alcohols[55]. The reduction of the acyclic diketone  $\text{MeCOCMe}_2\text{C(OMe)}$  by different hydrides in several solvents yields the  $(\pm)$ - and meso-diol; the  $(\pm)$ -diol predominates in most cases. By contrast, the meso-diol is favored in the presence of  $\text{TiCl}_4$ . A cyclic model is suggested to account for the induction phenomena observed[56]. Alkenyl sulfides can be reduced to the corresponding alkyl sulfides with  $\text{Et}_3\text{SiH}$  in the presence of  $\text{TiCl}_4$ . The reduction apparently proceeds via (phenylthio)alkyltitanium intermediates[57].

The treatment of the cyclopropanecarboxylate derivatives (1) and (2) with  $\text{PhSeCl}$  in  $\text{CH}_2\text{Cl}_2$  in the presence of  $\text{TiCl}_4$  yields  $\text{RCOCMe}_2\text{CH(SePh)CO}_2\text{Me}$  ( $\text{R} = \text{H}, \text{Me}$ ), and  $\text{Me}_3\text{CCOCR' (SePh)CO}_2\text{Me}$  ( $\text{R}' = \text{H}, \text{Me}$ ), respectively. Similarly, the



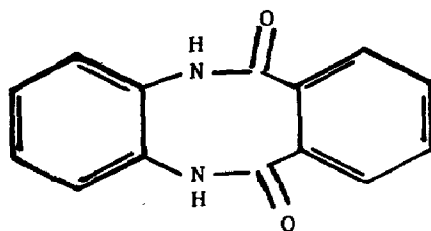
(1)



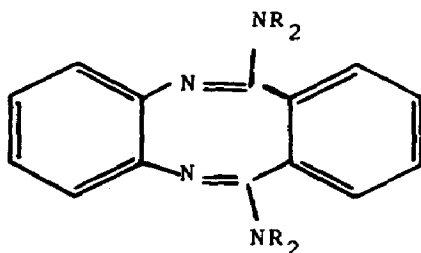
(2)

synthesis of  $\text{Me}_3\text{COCH}_2\text{CH(CO}_2\text{Me)SC}_6\text{H}_4\text{-NO}_2\text{-m}$  is given.  $\text{TiCl}_4$  promotes the ring cleaving reaction[58]. Titanium tetrachloride induces the functionalization of the dibenzodiazocinedione (3). Upon reaction of (3) with 1-methylpiperazine,  $\text{TiCl}_4$ , and  $\text{PhOMe}$ , the dibenzodiazocine (4) ( $\text{NR}_2 = 4\text{-methyl-1-piperazinyl}$ ;  $\text{R}_1 = \text{H}$ ) obtains[59].

Bikushev[60] has investigated the activity of catalytic systems composed of an alkylaluminum halide,  $\text{TiCl}_3$ , and a phosphonate in the stereospecific polymerization of propylene. Chemical and kinetic methods were employed to



(3)



(4)

demonstrate the disproportionation of the alkylaluminum halides in the presence of a phosphonate and formation of new catalytic complexes. Spectroscopic analyses (XPS, ir, nmr) and solvent extraction methods have confirmed that  $\text{TiCl}_4 \cdot 2\text{Et}_2\text{O}$  reacts with the  $3\text{TiCl}_3 \cdot \text{AlCl}_3$  catalyst in the solid state (reaction 2). The surface structure of the catalyst is described by a three-layer model [61]. EPR spectroscopy was used to study the reactions in the catalytic system



$\text{TiCl}_4$ -- $\text{PhCOMe}$ -- $\text{Al}(\text{Bu}^i)_3$  as a function of their relative concentration effects. Six types of bi- and tri-nuclear paramagnetic  $\text{Ti}^{3+}$  centers are formed in the system; those containing  $\text{PhCOMe}$  are stable compared to  $\text{Ti}^{3+}$  complexes which have no electron-donor ligands[62]. The kinetics of the surface photochemistry in adsorbed mixtures of  $\text{TiCl}_4$  and  $\text{Al}_2(\text{CH}_3)_6$  have been studied by UV-laser-induced photodeposition. In addition to the individual adsorbed-phase photoreactions of  $\text{TiCl}_4$  and  $\text{Al}_2(\text{CH}_3)_6$ , a new photoreaction channel was observed in the presence of

both. The new channel is ascribed to a two-component photoreaction in the adsorbed mixture, as deduced from pressure dependency studies of the reaction rate. The data could be qualitatively understood in terms of a Langmuir-Hinshelwood mechanism in conjunction with competitive adsorption of  $\text{TiCl}_4$  and  $\text{Al}_2(\text{CH}_3)_6$  [63].

The selective methylation of homo-propargyl alcohols to give alkenols, after hydrolysis, is catalysed by  $\text{TiCl}_4$ -- $\text{AlMe}_3$  in  $\text{CH}_2\text{Cl}_2$ . The alkenols  $\text{HOCHRCH}_2\text{CH}=\text{CR}'\text{Me}$  ( $\text{R} = \text{H, Me, Et}$ ;  $\text{R}' = \text{H, Me, Et, Pr, Me}_2\text{CH, Bu, pentyl, Ph}$ ) have been obtained [64]. The oligomerization of propene in the presence of  $\text{Co}_2\text{O}_3$ -- $\text{TiCl}_4$ -- $\text{Et}_2\text{AlCl}$  gives predominantly 4-methylpentenes. Similar oligomerization in the presence of  $\text{NiO}$ -- $\text{TiCl}_4$ -- $\text{Et}_2\text{AlCl}$  yields mainly 2-methylpentenes and dimethylbutenes [65].

A kinetic study on propylene polymerization in the presence of the catalyst system composed of  $\text{MgCl}_2$ --supported  $\text{TiCl}_4$  with  $\text{Et}_3\text{Al}$  and ethyl benzoate ( $\text{EtOBz}$ ) was undertaken by Kashiwa and Yoshitake [66] to elucidate the role of  $\text{EtOBz}$ , known to increase stereospecificity of the product. It seems that  $\text{EtOBz}$  modifies the isotactic specific centers so as to increase the  $k_p(\text{isotactic})$  value. As a result, the productivity and molecular weight of the isotactic polymer are increased [66]. Spitz and coworkers [67, 68] have carefully examined the precatalyst system  $\text{MgCl}_2$ -- $\text{TiCl}_4$ --aromatic ester for propene polymerization. There was found to be (a) a continuous decrease in the polymerization rate during polymerization, characterized by a deactivation index not dependent on the precatalyst but on the cocatalyst; (b) isotacticity control by the  $[\text{Al}]/[\text{aromatic ester}]$  ratio in the cocatalytic solution; and (c) fast and reversible control of kinetics and tacticity by the  $[\text{Al}]/[\text{aromatic ester}]$  ratio. Infrared studies suggest that the role of the electron donor is to (i) control the fixation of  $\text{TiCl}_4$  on  $\text{MgCl}_2$  in the precatalyst; and (ii) regulate the isospecificity of the active site by contact with the alkylaluminum-aromatic ester complex; and (iii) slows polymerization in the cocatalytic solution [67]. The pressure dependence of propene polymerization

under these conditions reveals an immediate onset of polymerization after  $C_3H_6$  introduction at approx. 333K [68]. Kashiwa and coworkers[69, 70] investigated the copolymerization of ethylene with propylene in the presence of a  $MgCl_2$ -- $TiCl_4$ -- $Et_3Al$ -- $EtOBz$  catalyst system, as well as a catalyst system composed of  $MgCl_2$ -- $TiCl_4$ -- $AlEt_2Cl$ --2-ethoxyethanol/n-decane. Both catalyst systems exhibit very high activity relative to the conventional  $TiCl_3$ -- $AlEt_2Cl$  system. However, the two catalyst systems do differ with respect to the microstructure of the copolymer product. Specifically, the  $MgCl_2$ -- $TiCl_4$ -- $AlEt_2Cl$ --2-ethoxyethanol/n-decane system brings about more random distribution of the monomeric units and also decreases regiospecificity with regard to the arrangement of the propylene unit[69]. The copolymerization of ethylene with  $\alpha$ -olefins (propylene, butene-1,4-methyl-1-pentene) catalysed by  $MgCl_2$ --supported  $TiCl_4$  combined with  $Et_3Al$  at temperatures  $\leq 443K$  is homogeneous. Of the three types of co-monomers, propylene exhibits the highest reactivity, most frequently causes the termination of a polymer growing via chain transfer reaction, and produces copolymers having the broadest molecular weight distribution[70].

X-ray diffraction and thermal analysis were employed to examine the polymorphism of  $TiI_4$ . A cubic phase transition occurs at 387K to a triclinic crystal. A second triclinic modification takes place on treating the first one in vacuo[71]. Reaction between  $TiI_4$  and  $CsI$  affords  $Cs_2TiI_6$ ; thermal stabilities are reported[72].

#### 4.6 OXIDES, $TiO_x$ and $TiO_2$

The stability and interaction of crystallographic shear planes in  $TiO_{2-x}$  (rutile) have been examined by theoretical methods[73]. The model predicts that the nonstoichiometry can largely be accommodated by crystallographic shear planes which interact to form arrays. The model also reproduces the various structural features found for this material.

The interaction of  $SO_2$ ,  $CO$ ,  $H_2O$  and  $O_2$  with the nearly perfect ( $10\bar{1}2$ )

surface of corundum  $\text{Ti}_2\text{O}_3$  has been investigated[74].  $\text{SO}_2$  adsorbs dissociatively onto  $\text{Ti}_2\text{O}_3$ , and catalyses the complete oxidation of the surface to  $\text{TiO}_2$  and  $\text{TiS}_2$ . The reaction is accompanied by large-scale surface disorder and by an increase in the work function. The chemisorption mechanism of CO is tentatively identified as dissociative adsorption at defect sites.

Hydrated oxides of titanium and antimony were prepared by simultaneous precipitation of  $\text{TiCl}_4$ ,  $\text{SbCl}_5$  or  $\text{SbCl}_3$  by  $\text{NH}_4\text{OH}$  at pH 7 and 343K. The specific surface area of the oxide hydrates decreases as the  $\text{Sb}^{3+}$  or  $\text{Sb}^{5+}$  oxide hydrate concentration increases. On aging, the specific surface area passes through a maximum at 7-10 mol%  $\text{Sb}_2\text{O}_x$ , then decreases to a minimum at 50-70 mol%  $\text{Sb}_2\text{O}_5$ , and then increases. The results are explained in terms of phase composition changes[75].

In the Russian literature there are two articles of interest: (1) a thermodynamic study of the high-temperature reduction of titanium, zirconium, molybdenum and tungsten oxides in nitrogen[76], and (2) a study of the effects of titanium and calcium oxides on the activity of an ammonia synthesis catalyst on an iron-aluminum borate support[77].

Harada and coworkers[78] prepared  $\text{TiO}_2$  from aqueous  $\text{TiCl}_4$  by three different methods: (a) neutralization with a 14%  $\text{NH}_4\text{OH}$  solution; (b) hydrolysis in water at >353K; and (c) hydrolysis in a 0.5N  $\text{HCl}$  solution. X-ray diffraction and thermal analyses of the resulting  $\text{TiO}_2$  reveal that the degree of crystallization and photocatalytic activity increase in the order (a) < (b) < (c).  $\text{TiO}_2$  has also been prepared from  $\text{TiCl}_4$  or  $\text{Ti}(\text{Pr}^i\text{O})_4$ , and its nature investigated by thermal analysis, x-ray diffraction, measurements of specific area and catalytic activity for CO oxidation. The polymorphic form of the  $\text{TiO}_2$  prepared from  $\text{TiCl}_4$  changes from anatase to rutile at 923-1173K; this temperature is significantly higher than that for the same compound from  $\text{Ti}(\text{Pr}^i\text{O})_4$ . The catalytic activity of the  $\text{TiO}_2$  prepared from  $\text{TiCl}_4$  is greater than 3-fold as high as that of the  $\text{TiO}_2$  from  $\text{Ti}(\text{Pr}^i\text{O})_4$  in the CO oxidation reaction[79]. Moreover,  $\text{TiO}_2$  catalysts prepared[80] from  $\text{Ti}(\text{Pr}^i\text{O})_4$  can be

modified in terms of surface and internal electronic structure by the preparative method employed. The hydrolysis of  $\text{Ti}(\text{Pr}^i\text{O})_4$  followed by calcination at temperatures  $\leq 1273\text{K}$  yields  $\text{TiO}_2$ . Upon an increase in the calcination temperature up to  $823\text{K}$ , there is an increase in anatase content and crystallite size. At  $823\text{--}873\text{K}$ , a mixture of anatase and rutile obtains; while at higher temperatures, only rutile is obtained[81]. The photocatalytic activity of these  $\text{TiO}_2$  powders was examined in aqueous isopropanol, aqueous  $\text{Ag}_2\text{SO}_4$ , and aqueous  $\text{Ag}_2\text{SO}_4$  containing isopropanol. Abrahams *et al.*[82] report that an increased photocatalytic activity is obtained in the decomposition of  $\text{H}_2\text{O}$ , acetic acid and propan-2-ol when the x-ray amorphous  $\text{TiO}_2$  is heated at  $623\text{K}$  for 1-4 hrs.

$\text{TiO}_2$  incorporated into Nafion or clay films was prepared via treatment of the  $\text{TiO}_2$  with  $\text{Ti}(\text{III})$  followed by oxidation. ESR spectroscopy has characterized the state and chemical reactivity of the titanium species in Nafion. Both systems exhibit photocatalytic activity in the reduction of methylviologen with oxidation of triethanolamine[83].

Electronic absorption spectroscopy of 4-dimethylaminoazobenzene adsorbed onto  $\text{TiO}_2$ (anatase) has been used to identify OH groups remaining on the surface after thermovacuum pretreatment. The observed behavior was explained in terms of the change in  $\text{Ti}^{3+}$  surface concentration with temperature[84]. Busca *et al.* [85] have examined the interaction of methanol with pure and KOH-doped  $\text{TiO}_2$ (anatase) using TPD, FT-ir and catalytic studies. The results indicated a number of hydrogen-bonded and chemisorbed species on the  $\text{TiO}_2$  surface. KOH poisons the Lewis and Brønsted acid sites of  $\text{TiO}_2$ . Further, the methoxy groups on  $\text{TiO}_2$  are formed by several mechanisms, including: (a) methanol dissociation on acid-base pairs, (b) reaction of methanol with surface OH groups, and (c) possibly decomposition of chemisorbed species[85].

The influence of temperature and chlorine contamination on the surface area and morphology of  $\text{TiO}_2$ (anatase) was examined in connection with typical catalyst preparation and reactions conditions. Adsorption, wide-angle x-ray diffraction

and SEM techniques show that chlorinated samples have lower surface areas and exhibit lower resistance to sintering than does blank  $\text{TiO}_2$ [86]. High-resolution electron microscopy was used to determine the fine structure of extended defects occurring within samples of mechanically deformed and reduced  $\text{TiO}_2$ (rutile),  $\approx\text{TiO}_{1.9966}$  [87]. The stoichiometry dependence of the dissolution temperature and the phase limits of nonstoichiometric  $\text{TiO}_{2-x}$  ( $x = 1.9966, 1.9979, 1.9986$ ) were established by in situ transmission electron microscopy (TEM). The defect structure formed during dissolution and the reprecipitation of extended defects upon cooling have also been studied[88]. Crackel and Struve[89] have verified dye-to-surface nonradiative excitation transfer as an important decay mode for  $S_1$  state cresyl violet separated from a  $\text{TiO}_2$  surface by 80 - 509Å.

ESR spectra of  $\text{TiO}_2$  containing copper(II) impurity ions subsequent to mechanical activation reveals that Cu(II) is stabilized in octahedral and square pyramidal sites of the  $\text{TiO}_2$  lattice. Mechanical activation of anatase gives the rutile phase[90]. Samples of the ternary  $\text{CuO--TiO}_2\text{--Sb}_2\text{O}_5$  system were investigated by ESR, x-ray phase and structural analyses. A solid solution with rutile structure is formed for 0.07/0.93/0.0012-0.13  $\text{Sb}_2\text{O}_5/\text{TiO}_2/\text{CuO}$ , in which Sb is pentavalent and the isolated Cu ions and their associates are located at nodal sites in the rutile lattice[91].

Graetzel and Rotzinger[92] have examined the influence of crystal lattice structures of  $\text{TiO}_2$  and  $\text{SrTiO}_3$  on the conduction band energy. EHMO calculations on model complexes show that the energy levels of the LUMO's involving predominantly the  $3d\pi$  orbitals  $xy, xz$  and  $yz$ , and of titanium, are sensitive to the lattice structure. A Raman spectroscopic study of  $\text{TiO}_2$  coatings shows that upon laser annealing, the amorphous coatings are transformed into microcrystals of anatase structure at lower laser intensities, and a mixture of anatase and rutile structures at higher intensities[93]. The experimental determination of the total light distribution in an aqueous solution of  $\text{TiO}_2$  for an almost non-absorbing wavelength reveals that the extinction coefficient exhibits a



non-linear dependence on the concentration at high solute concentrations[94].

Thermogravimetry has established the nature of the intrinsic and extrinsic defects in  $\text{TiO}_2$  and  $\text{NbO}_2$ , as determined for  $\text{Nb}_y\text{Ti}_{1-y}\text{O}_{2\pm x}$  solid solutions[95]. Pure  $\text{TiO}_2$  is an oxygen-deficient oxide, while  $\text{NbO}_2$  is a metal-deficient oxide. The main defects in  $\text{TiO}_2$  are oxygen vacancies, doubly ionized  $\text{V}_\text{O}^{\bullet\bullet}$  or singly ionized  $\text{V}_\text{O}^\bullet$ , and interstitial  $\text{Ti}_i^3$ . The nature of intrinsic defects in  $\text{TiO}_2$  are Schottky defects. The surface acidity of four different anatase preparations was studied by FT-ir spectroscopy of adsorbed benzene, ammonia, pyridine, carbon monoxide and carbon dioxide. The surface chemistry depends on the preparation method. Pure anatase does not exhibit Brønsted acidity; however,  $\text{SiO}_2$  or sulfate impurities in the  $\text{TiO}_2$  cause a significant enhancement of Brønsted acidity[96]. Babuji and Radhakrishna[97] observed that the UV-visible transmittance of  $\text{TiO}_2$  thin films on a glass substrate decreases on increasing the film thickness from 65 to 160nm. The spectra suggest the existence of an absorption edge in the UV region.

Temperature-programmed desorption (TPD) of  $\text{CO}$ ,  $\text{H}_2$ ,  $\text{CO}_2$  and  $\text{H}_2\text{O}$  has probed the adsorptive properties of  $\text{TiO}_2$  surfaces with different oxidation states[98]. The oxidation state, varying from  $\text{Ti}^{4+}$  to  $\text{Ti}^{2+}$ , can be altered via vacuum annealing of an oxidized Ti foil at 573 - 1073K. Carbon monoxide is weakly adsorbed in a carbonyl fashion on coordinatively unsaturated cation sites, while  $\text{CO}_2$  adsorbs in a linear molecular fashion at exposed cation sites or as monodentate carbonates at surface oxygen anions. Titania surfaces are inert to  $\text{H}_2$  adsorption and dissociation. Water adsorbed both molecularly and dissociatively, with molecular hydrogen evolution becoming more extensive on surfaces which were initially more reduced. The results of this investigation have been discussed in terms of the role of  $\text{TiO}_2$  oxidation state in  $\text{CO}$  hydrogenation over  $\text{TiO}_2$ -supported metal catalysts[98]. An infrared study of  $^{12}\text{C}^{16}\text{O}$  and  $^{13}\text{C}^{16}\text{O}$  adsorbed at 77K on  $\text{ZnO}$ ,  $\text{TiO}_2$ ,  $\text{BeO}$ ,  $\text{Al}_2\text{O}_3$  and  $\text{SiO}_2$  provides details on two kinds of interactions between the adsorbed molecules[99]. One interaction is chemical in nature, involving the weakening of the electron-donating ability of the metal ion after occupation of the adjacent sites with

adsorbed molecules. The second type of interaction is dipole coupling.

Studies of changes in hydrated  $\text{TiO}_2$  during heat treatment have been reported. During thermal treatment at 293 - 673K and 773 - 973K of  $\text{TiO}_2 \cdot 0.53\text{H}_2\text{O} \cdot 0.05\text{SO}_3$ , dehydration and desulfatization, respectively, occur. These processes are accompanied by the generation of active centers on the  $\text{TiO}_2$  crystal surface, resulting in a change in the light absorption coefficient[100]. The same authors[101] report on the changes in the proton structure of hydrated  $\text{TiO}_2$  during thermal treatment. Hydrated titania, prepared by thermal hydrolysis of  $\text{H}_2\text{SO}_4$  solutions of titanium(IV) sulfate compounds, was investigated with respect to structure and state of protons during aging in air and heat treatment[102].

Thin-film  $\text{TiO}_2$  prepared by sputtering methods under certain specified conditions exhibits single-crystal rutile behavior. Quantum efficiencies are comparable for all samples, and linear Mott-Schottky plots obtained with little frequency dispersion for suitable doping densities[103]. Anodization of unalloyed titanium (T40) in different electrolytes ( $\text{H}_2\text{SO}_4$  and  $\text{Na}_2\text{SiO}_3$ ) was performed to determine the amount of foreign ions incorporated into the oxide layers during the film growth. The resulting anodic oxide films were characterized by nuclear microanalysis, electron spectroscopy and glow discharge spectroscopy[104].

$\text{TiO}_2$  photoanodes have also been prepared by the plasma spray technique on titanium, graphite and  $\text{Al}_2\text{O}_3$  substrates. Electrochemical and photo-electrochemical characteristics of these systems are reported for oxygen-saturated solutions of sodium hydroxide at pH 13 [105]. The electrode performance is insensitive to the plasma power and  $\text{TiO}_2$  powder granulation; it is dependent on the purity of the spraying material, to the substrate and to the nature of the heat treatment. Zarks et al. [106] report characteristic changes in the process of formation of a crystalline phase of hydrated  $\text{TiO}_2$ , specifically the dielectric characteristics, electrical conductivity and features of the paramagnetic centers. These processes are caused by a growth

of a crystalline phase, by the anatase-to-rutile transition, by the complex chemical composition of the sample, and by the inclusion in the composition of solid particles[106].

Roy and coworkers[107, 108] have utilized a modification of the photocurrent onset potential method to obtain a flat-band potential,  $V_{fb}$ , value for  $TiO_2$  in 0.1M NaOH. A more reliable  $V_{fb}$  value is obtained by illuminating the semiconductor with high-frequency chopped light during the potential scan, with a rate significantly slower than the chopping frequency of the light source. The potential increase of vacuum-treated  $TiO_2$ (anatase) dispersed in 1M  $HClO_4$  with or without formic acid has been measured under illumination using an  $In_2O_3$  probe[108]. The following observations were made: (a) The  $TiO_2$  particles have an electron potential 240 meV higher than that of the Fermi level of n- $TiO_2$  crystal under illumination in the absence of formic acid; (b) Upon the addition of formic acid, the potential increases by 173meV, a value high enough to reduce water in the presence of a suitable catalyst. A photoelectrochemical method is reported by Jarrett[110] to measure the density of states at a  $TiO_2$ /electrolyte surface. Additionally, the Schottky barrier height for several redox couples was obtained for the surface containing this measured density. Photocurrent and photovoltage transients at n- $TiO_2$ /electrolyte junctions have been measured using nanosecond-laser pulse excitation. Two different types of build-up were observed, both independent of excitation intensity and external resistance[111].

Electrochemical and photoelectrochemical methods have characterized colloidal  $TiO_2$  particles at the optical rotating disk electrode (ORDE)[112]. The electron-transfer reactions between the particles and the electrode are irreversible, while the kinetics of the system obey both the Tafel and Levich relations. Other parameters determined included (a) quantum efficiencies for the photogeneration of majority carriers, (b) the number of electrons in the conduction band, and (c) their quantum efficiency and lifetime[112]. Coulostatic pulse relaxation experiments have been performed on some colloid

chemical aspects of the oxidized titanium/electrolyte interface. An analysis of the experimental results, calculations and known models has led Smit[113] to a modified colloid chemical site dissociation site binding model, having low values for the Helmholtz layer capacitance and at least two parallel impedance branches on the electrolyte side. A  $\text{TiO}_2$  membrane cell was devised by Yonezawa et al.[114] to study the photoelectrochemical processes at a  $\text{TiO}_2$ /aqueous solution interface. Photocurrent measurements would seem to suggest that the electrons and holes generated in  $\text{TiO}_2$  with band-gap irradiation produce reduction at the dark side and oxidation at the illuminated side of the  $\text{TiO}_2$  membrane, respectively.

The behavior of thin metal layers of gold present on n- $\text{TiO}_2$  electrodes cannot be explained by the conventional potential barrier model for metal-semiconductor contacts[115]. However, it seems that the discontinuous structure of the metal layer is responsible for the anomalous photovoltaic effect. Doping thin-film polycrystalline n- $\text{TiO}_2$  photoanodes with such elements as Al, Y, Cr, Fe, Zn, Cd, La, Nd, Ce, La-Cr and Y-Cr has been reported[116]. Simultaneous doping with Y-Cr or La-Cr not only enhances the quantum efficiency of the photoanode, but also extends its spectral response to visible light. The latter effect is attributed to the formation of a d band[116]. The photoelectrochemical behavior of a ruthenium-doped  $\text{TiO}_2$  crystalline electrode ( $\text{Ti}_{0.97}\text{Ru}_{0.03}\text{O}_2$ ) reveals (a) sensitization to visible light, and (b) reduction of the overpotential for oxygen evolution, both in the dark and under illumination[117]. The  $\text{Ru}^{4+} \rightarrow \text{Ti}^{4+}$  electronic transition is responsible for the subbandgap photoresponse. Furthermore, the semiconductor surface becomes positively charged under positive polarization of the electrode, and the Fermi level is pinned, facilitating charge transfer from the filled levels of water molecules to the semiconductor conduction band, therein leading to oxygen evolution.

Viehbeck and DeBarry[118] have studied the electrochemistry of Prussian blue films on spark anodized n- $\text{TiO}_2$  electrodes, and report evidence for four

redox states for Prussian blue. Moreover, they discuss the photoelectronchromic behavior of this system[118]. Photoelectrolysis in an electrolyte containing water soluble aromatic compounds affords the formation of hydrophobic organic layers on the  $\text{TiO}_2$  surface. The reaction yields a hydrophilic and hydrophobic pattern on the electrode surface. The phenol/ $\text{TiO}_2$  system has been studied in detail[119].

Antonucci and coworkers[120] have shown the mechanism of oxygen evolution on  $\text{TiO}_2$  photoanodes by relating structural properties and electrochemical properties to the performance of photoelectrochemical cells of five specimens of lowest and highest photoelectrochemical efficiency. The mechanism of the discharge-ionization of hydrogen on a  $\text{TiO}_2$ (rutile) surface, as well as solid solutions based on it, have been discussed[121]. A simplified method of fixing a titanium oxide redox system onto the surface of a titanium cathode, as well as details on the reduction of nitrobenzene on these cathodes have been reported by Beck and Gabriel[122].

Nonmetallized  $\text{TiO}_2$  powder incorporated into a thin, porous layer above a metallized substrate photosensitizes the decompositions of water and acetic acid in an aqueous gas-phase environment. Quantum efficiency values suggest that this structure has a catalytic activity comparable to dispersions of partially metallized powders[123]. Serwicka[124] has examined the interaction of water vapor with polycrystalline  $\text{TiO}_2$ (anatase) by ESR techniques at room temperature and 77K. The results suggest a photocatalytic decomposition of the water vapor at the  $\text{TiO}_2$  surface.

In order to convert solar energy via decomposition of water, the formulation of a corrosion-resistant semiconductor anode material sensitive to the visible spectral range is a prerequisite. As such, a system has been examined that consists of a heterostructure of a relatively narrow-band semiconductor (GaAs) and a protective coating based on a corrosion-resistant wide-band semiconductor ( $\text{TiO}_2$ )[125]. Another suggested route is to chemically process an oxide ( $\text{TiO}_2$ ,  $\text{ZrO}_2$ ,  $\text{HfO}_2$ ,  $\text{SrTiO}_3$ ,  $\text{Sr}_2\text{TiO}_4$ ,  $\text{SrZrO}_3$ ,  $\text{Sr}_3\text{Zr}_2\text{O}_7$ ,  $\text{KTi}_6\text{O}_{13}$ ,

BaTiO<sub>3</sub>) by cycling in CS<sub>2</sub> and oxygen, followed by combination with platinum or nickel. Visible light illumination of TiO<sub>2</sub>(anatase) generates hydrogen from a 1:1 H<sub>2</sub>O/Pr<sup>i</sup>OH system[126]. Inoue and coworkers[127] have observed enhanced photocatalytic activity on depositing a thin TiO<sub>2</sub> film on ferroelectric substrates having a polarization vector. The ferroelectrics were (a) a LiNbO<sub>3</sub> single crystal with a polarization vector perpendicular to the surface; (b) a LiTaO<sub>3</sub> single crystal with the polarization vector parallel to the surface; and (c) α-Al<sub>2</sub>O<sub>3</sub> single crystal for comparative purposes. From the TiO<sub>2</sub>-thickness dependence upon hydrogen evolution from water decomposition, it was shown that the ferroelectric polarization field works to enhance the photocatalytic activity of the combined semiconducting TiO<sub>2</sub> films, particularly for the perpendicular polarization[127].

Salvador[128,129] and Decker[128] have examined the generation of hydrogen peroxide during water photoelectrolysis at n-TiO<sub>2</sub> using a rotating ring-disk electrode (RRDE). Mechanisms describing oxygen evolution via the photogeneration of H<sub>2</sub>O<sub>2</sub>, which are consistent with the observed results at the RRDE, were postulated[128]. A kinetic model based on the photogeneration of surface species, intermediates of the oxygen evolution reaction, has allowed a quantitative explanation for the main transient features observed as a function of semiconductor band bending and photon flux. Two parallel mechanisms are believed to be involved in this model: i) a time-dependent cathodic back reaction of photogenerated surface intermediates with conduction band electrons, opposite to the anodic photocurrent; and ii) a band-bending modulation due to the accumulation of positive charge at the semiconductor surface produced by hole trapping at active OH<sup>-</sup> surface groups[129]. Rives-Arnaud[130] has published a polemic in response to a paper by Muraki et al.[131] on the photocatalytic oxidation of water to hydrogen peroxide by irradiation of aqueous TiO<sub>2</sub> suspensions.

The rotating ring-disk technique has been employed to study the competition between the oxidation of H<sub>2</sub>O and that of Br<sup>-</sup> at an illuminated TiO<sub>2</sub>(rutile)

anode. The study was performed as a function of the  $\text{Br}^-$  concentration at the surface, the light intensity, the electrode potential, and the surface pretreatment. A mechanism is proposed[132].

Kalyanasundaram and Graetzel[133] have studied the efficiency and long-term stability of colloidal and high surface-area powdered  $\text{TiO}_2$  as mediators in the light-induced cleavage of water to hydrogen and oxygen, and the cleavage of  $\text{H}_2\text{S}$  to hydrogen and sulfur. Specifically, they investigated the charge transfer phenomena occurring at the  $\text{TiO}_2$ /solution interface, new methods of dispersing highly active catalysts on the  $\text{TiO}_2$  surface, and overall light-to-chemical energy conversion efficiencies in the water cleavage reaction. The quantum yields of hydrogen production have been optimized as a function of pH, component concentration and nature of photocatalyst in the  $\text{Ru}(\text{bpy})_3^{2+}$  (bpy = 2,2'-bipyridine)/methylviologen/EDTA/catalyst system[134]. Of the various heterogeneous catalysts studied, Pt was the most efficient of the supported (on  $\text{TiO}_2$ ) metals. Optically and polarographically measured initial photo-reduction rates of methylviologen on polycrystalline  $\text{TiO}_2$  electrodes at open circuit have been shown[135] to compare well with the reduction rates calculated from the currents at the intersection of the photocurrent- and inverted dark current=voltage curves. The roles of light intensity, pH and platinization on the reduction rates of various relays have been discussed. The same authors [136] have observed that the consumption of holes produced upon 350-420nm irradiation of the  $\text{TiO}_2$  sols or suspensions in polyvinyl alcohol/methylviologen system shows a significant dependence on the the bulk solution pH. An optimal quantity of  $\text{OH}^-$  ions was deemed necessary in order to allow for the specific adsorption of the polyvinyl alcohol onto the  $\text{TiO}_2$  surface and favor its hole scavenging action.

In the presence of an adsorbed reactant (polyvinyl alcohol or  $\text{SCN}^-$ ) for positive holes produced in colloidal  $\text{TiO}_2$  particles upon illumination, an excess of long-lived electrons remains on the particles and finally reacts with a substrate in the bulk solution. On the other hand, in the presence of an electron scavenger such as methylviologen or a deposited metal such as Pt, an

excess of long-lived holes remains which finally reacts with an oxidizable compound. These processes were observed in the reduction of water to yield hydrogen, the reduction of  $C(NO_2)_4$  and halothane, and the oxidation of  $Br^-$  and various organic compounds[137].

The photocatalytic oxidation of ethane over  $TiO_2$  has been studied[138] at room temperature as a function of reactant partial pressure, UV light intensity, the amount of catalyst, and the residence time. On the basis of the experimental critical mass of the catalyst, an expression permitting the calculation of the critical mass of the  $TiO_2$  catalyst for any type of photocatalytic reactor was derived[138]. Stepanenko and coworkers[139] have reported on the heterogeneous and homogeneous photooxidation of  $C_{2-5}$  hydrocarbons and 1-hexene in the gas and liquid phases using titanium-containing catalysts. The  $TiO_2$ -sensitized photooxidation of several benzenes has been examined in order to establish the origin of the ring hydroxylating species[140]. In agreement with other studies, the major pathway for the formation of the hydroxyl group of phenols is pH-dependent. At low pH, the oxygen atom originates mostly from solvent water; whereas at higher pH, the hydroxyl group of phenols comes essentially from molecular oxygen.

The oxidation of CO with oxygen is catalysed by CoTPP (TPP = tetraphenylporphyrin) on  $TiO_2$  at 194K. This catalyst exhibits unique features in terms of oxygen adsorption, the poisoning of adsorbed oxygen, and the insolubility of the complex in benzene[141]. Cyclohexene has been employed as an organic probe for the mechanism in the  $TiO_2$ -photocatalysed oxidation of bromide in acetonitrile[142]. The results suggest a mechanism in which the photoexcited semiconductor effects a one-electron oxidation of adsorbed bromide, yielding surface-bound bromine atoms. These could potentially abstract hydrogen from cyclohexene to initiate autooxidation, or could migrate along the semiconductor surface, producing  $Br_2$ , which migrates into solution where it is rapidly trapped in conventional electrophilic addition[143]. Rose and Nanjundiah[144] have measured the rate of photooxidation of  $CN^-$  by  $TiO_2$



(anatase) as a function of  $\text{TiO}_2$  particle size and platinization, and solution pH. The reaction rate constants increase with increasing  $\text{TiO}_2$  particle surface area, with platinizing, and on lowering the pH from 14 to 11. Doped  $\text{TiO}_2$ (anatase) (with various elements) can photolyse the production of  $\text{H}_2\text{SO}_4$  from sulfur in water into which oxygen was bubbled[145].

A pulse reactor and a continuous dilution flow reactor have been used to determine the activity of binary oxide catalysts in the dehydrogenation of ethylbenzene and ethylcyclohexane. The catalysts were composed of  $\text{TiO}_2$  and other first period transition metal oxides. A mechanism is proposed, based on the correlation between the activity and the surface acid-base property[146].  $\text{TiO}_2$  has been incorporated into the catalyst system for the oxidative dehydrogenation of butane to maleic anhydride[147]. Ohtani *et al.* [148] find that extra-fine crystallites of brookite  $\text{TiO}_2$  exhibits marked photocatalytic activity for the dehydrogenation of propan-2-ol in aqueous solution and silver metal deposition in  $\text{Ag}_2\text{SO}_4$  solution.

Thiazine and oxazine dyes have been photoelectrochemically reduced in colloidal  $\text{TiO}_2$  suspensions with bandgap excitation[149];  $^{57}\text{Fe}$  Moessbauer spectroscopy was employed to monitor the kinetics of the photoreduction of  $\text{Fe}^{3+}$  to  $\text{Fe}^{2+}$  via illuminated  $\text{TiO}_2$  particles suspended in an  $\text{FeCl}_3$  electrolyte [150]. For the latter study, a kinetic model was proposed, based on competition between the forward reduction of  $\text{Fe}^{3+}$  and the back oxidation of  $\text{Fe}^{2+}$  and controlled by semiconductor band/redox couple energetics. UV irradiation of  $\text{TiO}_2$  anchored onto porous Vycor glass at 77K in the presence of  $\text{N}_2\text{O}$  or oxygen leads to the formation of an unstable nitrogen-containing radical ( $\text{N}_2\text{O}^-$  or  $\text{N}_2\text{O}_2^-$ ) and the  $\text{O}_2^-$  anion radical, respectively[151]. The addition of oxygen onto the catalyst at 77K in the presence of the nitrogen-containing radical leads to the disappearance of the latter species and to the formation of  $\text{O}_2^-$ , which is suggestive that the electron transfer occurs easily between species adsorbed on the anchored  $\text{TiO}_2$ . The reactions were studied using ESR spectroscopy and isotopically labeled compounds.

Visible light hydrogen generation from water was observed from solutions containing a  $\text{TiO}_2$  sol charged with a redox catalyst and containing 8-quinolinol metal complexes  $\text{M}(\text{QO})_n$  ( $\text{M} = \text{Pt}^{2+}, \text{Pb}^{2+}, \text{Bi}^{3+}, \text{Ir}^{3+}$ ;  $n = 2, 3$ ) as sensitizers [152]. The reaction mechanism apparently involves electron transfer from the triplet excited state of the sensitizer into the conduction band of  $\text{TiO}_2$ . The most suitable sensitizers for water decomposition were  $\text{Ir}(\text{QO})_3$  and  $\text{Pt}(\text{QO})_2$ . Bahnemann and coworkers [153] have established that the electrons and positive holes formed in  $\text{TiO}_2$  suspensions upon exposure to UV light could be characterized by optical absorption. By direct detection of these surface states, a kinetic study of heterogeneous electron transfer reactions at the  $\text{TiO}_2$ /solution interface was performed. Also, by examination of the separation of the  $\text{e}^-/\text{h}^+$  pair, it was possible to establish the chemical and physical principles of such reactions [153].

Several studies of the catalytic hydrogenation of CO and  $\text{CO}_2$  and methanation of  $\text{CO}_2$  as a function of the type of catalyst have been cited. Dao and Pruchnik [154, 155] have examined these reactions on catalysts prepared by the decomposition of palladium, nickel, cobalt and iron acetylacetonate (acac) complexes impregnated on  $\gamma\text{-Al}_2\text{O}_3$  and  $\gamma\text{-Al}_2\text{O}_3$ . The additional presence of  $\text{TiO}_2$  or  $\text{MoO}_3$  in the  $\text{Al}_2\text{O}_3$  enhances the activity of the palladium catalysts [154]. They also looked at the hydrogenation and methanation reactions over catalysts containing 0.7 wt% Rh, obtained by impregnation of  $\text{Rh}(\text{acac})_3$  on  $\gamma\text{-Al}_2\text{O}_3$ ,  $\text{TiO}_2/\gamma\text{-Al}_2\text{O}_3$ ,  $\text{MoO}_3/\gamma\text{-Al}_2\text{O}_3$  and  $\text{TiO}_2\text{-MoO}_3/\gamma\text{-Al}_2\text{O}_3$  [155]. The catalytic activity of Rh in the hydrogenation of CO and  $\text{CO}_2$  was studied as a function of the electrical properties of the  $\text{TiO}_2$  support [156]. This was accomplished by doping the  $\text{TiO}_2$  with lower- and higher-valency cations. Doping with lower-valency ions ( $\text{Mg}^{2+}$ ,  $\text{Al}^{3+}$ ) hardly influences the electrical conductivity of  $\text{TiO}_2$  or the specific activity of the Rh. An increase in the electrical conductivity of  $\text{TiO}_2$  of 1-2 orders of magnitude was achieved by incorporating  $\text{W}^{6+}$  ions into the  $\text{TiO}_2$ . This favorable effect has been attributed [156] to the enhanced electron transfer from  $\text{TiO}_2$  to Rh, which promotes the dissociation of

CO. Infrared spectroscopy and temperature-programmed techniques were utilized by He et al. [157] to examine and compare the interaction of CO/CO<sub>2</sub>/H<sub>2</sub> with ZnO, TiO<sub>2</sub> and ZrO<sub>2</sub>. The reactive characteristics of the oxides suggest that CO hydrogenation occurs via a formate-methoxide mechanism. It appears that TiO<sub>2</sub> does not hydrogenate CO or CO<sub>2</sub> into methanol[157].

The photolytic decomposition of phenol in oxygenated aqueous suspensions of lightly-reduced TiO<sub>2</sub>(anatase) was investigated at the optimum pH 3.5 [158, 159]. The reaction followed first-order kinetics up to high conversions, for which the apparent rate constant depends on the initial phenol concentration, and an activation energy of 10 kJ/mol. The products at the initial stage of reaction were identified as hydroquinone, pyrocatechol, 1,2,4-benzenetriol, pyrogallol, and 2-hydroxy-1,4-benzoquinone. These intermediates undergo further photocatalytic oxidation, via acids and/or aldehydes, to CO<sub>2</sub> and H<sub>2</sub>O. A reaction scheme involving OH radicals as real reactive species has been prepared[158]. Their formation occurs via holes and via H<sub>2</sub>O<sub>2</sub> from oxygen.

Infrared spectroscopy and pulse reactor techniques were employed to monitor the isomerization of propylene oxide over TiO<sub>2</sub>. A mechanism was inferred that involved an adsorbed substrate bound to the titanium atom through the oxygen atom[160].

Hydrated TiO<sub>2</sub> catalyses the esterification of phthalic anhydride by primary alcohols (Linevol 79) via formation of a homogeneous organotitanate catalyst species[161]. Proton nmr, infrared and Raman spectroscopies, as well as x-ray phase analysis and thermogravimetry were used to characterize the products of the reaction between TiO<sub>2</sub>·nH<sub>2</sub>O and NaOH. The products contain three types of nonequivalent OH groups, bridging, terminal and hydrogen-bonded to water[162]. Dvernyakova et al. [163] have determined the composition of the thermolysis products of TiO<sub>2</sub>·nH<sub>2</sub>O, CaCO<sub>3</sub>·nH<sub>2</sub>O and their 1:1 mixtures during heating at 423 - 1423K. Also investigated were the kinetics of the reaction of TiO<sub>2</sub>·nH<sub>2</sub>O with CaCO<sub>3</sub>, the dependence of the CaTiO<sub>3</sub> yield on the degree of dispersion of TiO<sub>2</sub>·nH<sub>2</sub>O, and the effect of the degree of dispersion of

$\text{TiO}_2 \cdot n\text{H}_2\text{O}$  on the crystal formation of  $\text{CaTiO}_3$ [163].

In the presence of  $\text{TiO}_2$ ,  $\text{CO}_2$  and  $\text{SO}_3$  are produced via the photoinduced oxidation of cis-2-butene and  $\text{SO}_2$ , respectively[164]. A flow-type reactor was used to study the photocatalytic effects of  $\text{TiO}_2$  on the photochemical reaction of trans-2-butene and trans-2-butene/ $\text{NO}_2$ /air systems. Trans-2-butene was rapidly oxidized to  $\text{CO}_2$  by oxygen in the presence of  $\text{TiO}_2$  under irradiation. Addition of  $\text{NO}_2$  to the reaction system reduced the  $\text{CO}_2$  yield, which indicates that  $\text{NO}_2$  depresses the photocatalytic activity of  $\text{TiO}_2$ [165]. UV illumination of pre-oxidized or pre-reduced  $\text{TiO}_2$  powder, which has been exposed to  $\text{N}^{18}\text{O}$  in the dark at 295K, results in photoadsorption, photoexchange, and photodecomposition form  $\text{N}_2\text{O}$  and  $\text{N}_2$ . The addition of 2-butanol to  $\text{N}^{18}\text{O}$  suppresses the isotopic exchange[166].

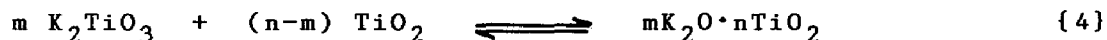
Malinowski and coworkers[167] have published a preliminary note on a study of reactions of organic substrates (methanol, acetone, acetic acid, ethylacetate, butyl acetate) on low-valent titanium heterogenized on  $\text{SiO}_2$  or  $\text{TiO}_2$  support materials. They also compared these reactions with those in the in the presence of a homogeneous system. Comparative studies on the kinetics and mechanism of the chlorination of  $\text{TiO}_2$ (anatase) and  $\text{V}_2\text{O}_5$  with  $\text{CCl}_4$  were performed[168]. Approximate first-order kinetics were observed and an apparent activation energy of  $118 \pm 7$  kJ/mol calculated for the chlorination of  $\text{TiO}_2$ . A dissociative adsorption of  $\text{CCl}_4$  apparently precedes the reaction, and the transformation of  $\text{CCl}_4$  to  $\text{CO}_2$  was assumed to occur via the formation of an adsorbed  $\text{COCl}_2$  intermediate[168].

Itaya et al. [169] have discussed the electron transfer reactions in the open-spaced crystal of Prussian blue (PB) by photooxidation at n- $\text{TiO}_2$ . The reduction of PB occurs at the  $\text{TiO}_2$  electrode, though the corresponding oxidation is not possible in the dark.

#### 4.7 OXIDES, $\text{MTiO}_x$

The molar enthalpies of reaction at 970K for the sodium and potassium

titanates in reactions 3 and 4 were determined by high-temperature



solution calorimetry; for which  $(m, n) = (1, 1), (4, 5), (1, 2), (1, 3)$  and  $(1, 6)$  in reaction 3, and  $(m, n) = (1, 1), (2, 3), (1, 2), (1, 4)$  and  $(1, 6)$  for reaction 4 [170]. The x-ray crystal structure of  $\text{Na}_4\text{Ti}_5\text{O}_{12}$  reveals the compound to be monoclinic, space group  $C2/m$ , with corrugated layers of  $\text{Ti}_5\text{O}_{12}$  held together by sodium ions[171].

Balasubramanian[172] reported a new preparatory method for  $\text{SrTiO}_3$ ; it involves the calcining (873K or 973K; 12 hrs) of crystals obtained by mixing solutions of EDTA complexes of strontium and titanium. The resulting  $\text{SrTiO}_3$  product was characterized by crystal structure analysis, ESR spectroscopy and electrical conductivity measurements.

A photoelectrochemical system composed of  $\text{SrTiO}_3$  single-crystal electrodes as electron acceptors and two adsorbed cyanine dyes (2,2'-diethylthiacarbocyanine and 2,2'-diethyloxadicarbocyanine) in their excited states (electron donors) was examined in terms of the energetic threshold for dye-sensitized photocurrent at the electrode[173]. The heats of adsorption (6 - 10 kcal/mol) show the dye molecules are weakly adsorbed by the electrode, while fluorescence spectra of the dyes revealed the influence of pH on the photophysics of the dyes. The oxidation potentials of the dyes were evaluated by cyclic voltammetry; the  $\text{SrTiO}_3$  electrodes show a pH dependent flatband potential. The photocurrent is also pH-dependent[173]. The photoelectrochemical properties of  $\text{Nb}_2\text{O}_5$ ,  $\text{Sb}_2\text{O}_3$  and  $\text{V}_2\text{O}_5$  doped

on  $\text{SrTiO}_3$  ceramic electrodes were reported by Yoon and Kim[174]. Irradiation of an electrochemical cell consisting of a semiconductor ( $\text{TiO}_2$ ,  $\text{SrTiO}_3$ ) anode, a metal cathode, and an aqueous electrolyte solution with ionizing radiation stimulated the electrochemical decomposition of water. The ionizing radiation was in the form of accelerated electrons with energy 4 MeV, x-rays of 70 keV,  $\gamma$ -rays, and neutrons from a nuclear reactor[175].

The preparation of  $\text{BaTiO}_3$  via thermal decomposition of  $\text{BaTiO}(\text{C}_2\text{O}_4)_2 \cdot 4\text{H}_2\text{O}$  has been simultaneously examined by emanation thermal analysis, thermogravimetry, DTA and evolved-gas analysis [176]. Nabivanets and Omel'chenko[177] have looked at the optimum conditions (pH and component concentrations) for the production of  $\text{BaTiO}_3$  via coprecipitation by examining the solubility in the  $\text{BaCO}_3$  --  $\text{Ti}(\text{OH})_4$  --  $\text{NaHCO}_3$  --  $\text{H}_2\text{O}$  system. The photoelectrochemical behavior of donor-doped  $\text{BaTiO}_3$  ceramic anodes has been compared with that of hydrogen-reduced  $\text{BaTiO}_3$  and hydrogen-reduced  $\text{SrTiO}_3$  [178]. Donor-doped  $\text{BaTiO}_3$  has a response to visible light without mechanical polishing and seems unaffected by chemical etched. Hydrogen-reduced  $\text{BaTiO}_3$  also has photoresponse in the visible; however, it is modulated upon mechanical polishing.

The catalytic decomposition of  $\text{N}_2\text{O}$  was studied as a function of 'x' over  $\text{Sn}_{1-x}\text{V}_x\text{O}_2$  and  $\text{Ti}_{1-x}\text{V}_x\text{O}_2$  ( $0 \leq x \leq 0.2$ ) solid solution. The catalytic activity decreases as a function of the V content up to  $x = 0.03$ , then increases as x increases. The surface activity correlates with varying the charge transfer effects in the catalyst as x increases. The variations of activity appear to be related to the developing electronic state of a V sublattice[179]. Thermal decomposition of  $\text{Ti}_{1-x}\text{Cr}_x\text{O}_{2-x}(\text{OH})_x$ , with the In OOH-type structure, results in the formation of the mixed rutile-type oxides  $\text{Ti}_{n-2}\text{Cr}_2\text{O}_{2n-1}$ [180].

Single phases of  $\text{Fe}_{1-a}\text{Ti}_a\text{O}_y$  (phase I, rhombohedral,  $y = 1.5$ ,  $a = 0.5, 0.42, 0.35, 0.25$ ; phase P, orthorhombic,  $y = 1.67$ ,  $a = 0.67, 0.6, 0.5, 0.33$ ; phase S, spinel,  $y = 1.33$ ,  $a = 0.27, 0.2$ ) have been prepared by solid-state reactions of  $\text{Fe}_2\text{O}_3$ ,  $\text{TiO}_2$ (rutile) and iron carbonyl at 1323 - 1573K[181]. The electronic structures of  $\text{TiO}_6^{8-}$ ,  $\text{TiO}_6^{9-}$  and  $\text{TiO}_6\text{Fe}_4$  clusters, which simulate  $\text{TiO}_2$ ,  $\text{Ti}_2\text{O}_3$  and  $\text{FeTiO}_3$ (ilmenite) crystals, respectively, were determined by the SCF- $X_\alpha$  scattered-wave method. The dependence of the electronic structure spin density distribution on the number of unpaired electrons in the Fe atoms has been reported for the  $\text{TiO}_6\text{Fe}_4$  cluster. The spin densities of the Ti and Fe atoms were shown [182] to interact via O atoms (i.e., indirect exchange interaction).

Zunic and coworkers[183] have determined the x-ray crystal structure of a modification of  $\text{ThTi}_2\text{O}_6$ , obtained from the melt at 1373K. The crystal is monoclinic, with near-hexagonal close-packing of the O atoms, and Th and Ti atoms occupy octahedral sites. The coordination about Ti is a distorted octahedron; about Th, it is a distorted square antiprism. The Ti coordination polyhedra form layers parallel to the (100) face and are connected by zigzag chains of the Th coordination polyhedra which run in the [001] direction[183].

#### 4.8 OXIDES, $\text{M}/\text{TiO}_2$

In the dynamic  $\text{V}_2\text{O}_5/\text{TiO}_2$ (anatase) system, the state of vanadium depends on the loading of  $\text{V}_2\text{O}_5$  and the calcination temperature. Vanadium is present as a surface species coordinated to the  $\text{TiO}_2$ (anatase) surface at low contents of  $\text{V}_2\text{O}_5$  on  $\text{TiO}_2$ . At intermediate  $\text{V}_2\text{O}_5$  contents on  $\text{TiO}_2$ , V is also present as  $\text{V}_2\text{O}_5$  crystallites. At high calcination temperatures, the ratio of

surface vanadium and  $V_2O_5$  crystallites is affected, with consequential formation of a  $V_xTi_{1-x}O_2$  solid solution[184]. Busca et al. [185] have characterized the surface of a low-content vanadium catalyst, prepared by grafting a high-surface-area  $TiO_2$  support. The methodologies employed include diffusion reflectance, ESR and Fourier-transform infrared spectroscopies. The grafting reaction of vanadium takes place on all surface OH groups of  $TiO_2$ , leaving  $Ti^{4+}$  exposed. The vanadium sites are isolated on the surface and have labile oxidative and coordinative states[185]. It has been shown[186] that oxygen adsorption isotherms at 273 - 723K and 0.05 - 2 torr obey the Langmuir model for the adsorption of molecular oxygen on the  $V_2O_5/TiO_2$  systems. The two maxima observed at 523 and 673K in the 0.55 torr adsorption isobars have been ascribed to  $O^{2-}$  chemisorption and to its diffusion to the microcrystal interior, respectively. Raman spectroscopy and XPS were utilized to characterize the small  $V_2O_5$  crystallites supported on  $TiO_2$ (anatase) in situ under oxidizing and reducing conditions at elevated temperatures. At such temperatures, the  $V_2O_5$  crystallites are readily reduced by hydrogen to  $V_2O_3$ , and reoxidized to  $V_2O_5$  crystallites in flowing air[187]. Emf measurements have also been carried out to determine the formation thermodynamic (partial) functions of  $V_2O_5$  solid solutions with  $TiO_2$  at several temperature intervals[188].

Rusiecka[189] has characterized the active phase of the  $V_2O_5/TiO_2$  catalysts by ESR spectroscopy. Various amounts of  $V_2O_5$  ( $\leq 20$  mol%) were deposited on  $TiO_2$ (anatase, rutile), and ESR spectra of the samples recorded initially, after catalytic oxidation of o-xylene, and after reoxidation in air. The amount of reduction taking place on the catalyst during reaction was determined by the strength of the  $V^{4+}$  signal[189]. The observed



low selectivity for phthalic anhydride during o-xylene oxidation was explained[190] by the formation of needle-shaped crystallites of  $V_6O_{13}$  at low vanadium concentrations on  $V_2O_5/TiO_2$  (anatase) coated catalysts. ESCA, x-ray diffraction, SEM, and infrared and ESR spectroscopies were used to characterize vanadium oxide/titanium oxide catalysts in relation to activity and selectivity for oxidation and ammoxidation of alkylpyridines[191].

Electron microscopy and electron diffraction studies of  $V_2O_3$ -doped  $TiO_2$  reveal the presence of two different types of planar defects[192]. At dopant concentrations <3%, isolated (101) and (132) faults appear, while at  $V_2O_3$  concentrations >5%, an ordering of the defects is observed. At  $[V_2O_3]$  up to 13%, a new family ( $M_nO_{2n-1}$ ,  $M = V+Ti$ ) of ordered phases forms[192].

Several groups[193 - 197] have studied oxidation reactions catalysed by  $V_2O_5/TiO_2$ . German and coworkers[193] investigated these catalysts calcined at 973 - 1273K in the ammoxidation of  $\beta$ -picoline and 5-ethyl-2-methylpyridine. The optimal calcination temperature was found to be 1073K. The kinetic study of low-temperature oxidation of toluene and its derivatives over  $V_2O_5$  and  $V_2O_5/TiO_2$  in a differential flow reactor reveals that complete oxidation follows the mechanism of conjugate reoxidation of the catalyst surface[194]. Rate constants for the ammoxidation of  $MeC_6H_4R$  ( $R = H, 3-Me, 3-CN, 3-NO_2, 3-Cl, 2-OH, 2-NH_2, 2-Br$ ), pseudocumene, mesitylene,  $MeC_6H_4R'$  [ $R' = 3,5-(CMe_3)_2, 2,6-Cl_2$ ], 5-tert-butyl-m-xylene, durene and 2,3,5,6-tetrachloro-4-tert-butyltoluene were established at 653K. It appears that (a) o-cresol is the most reactive, (b) 2,3,5,6-tetrachloro-4-tert-butyltoluene is the least reactive, (c) reactivity decreases in the presence of benzene, and (d) the reactivity increases with basicity in the order toluene, pseudocumene, and mesitylene[195].

Skrzypek *et al.* [196] suggested that in the catalytic air oxidation of *o*-xylene over  $V_2O_5/TiO_2$ , the limiting step can be described by the Langmuir-Hinshelwood kinetic model, wherein a surface reaction between *o*-xylene and oxygen occurs, chemisorbed on separate active sites. In another study, the interaction of  $V_2O_5$  with  $TiO_2$  (anatase) in the *o*-xylene oxidation reaction has been examined [197].

Measurable catalytic activity in the gas-phase water decomposition reaction under illumination with bandgap light has been observed in the presence of a Ta-doped  $TiO_2$  catalyst, previously prereduced and coated with NaOH [198]. Rate enhancement occurs upon addition of  $RuO_2$ .

[ $Ti/Cr_2O_3 + TiO_2$ ] composite electrodes, prepared by a ceramic method, have been used in the heterogeneous anodic oxidation of aliphatic alcohols and ethers in 1M  $H_2SO_4$  [199]. A new catalyst for the oxidation of butene to maleic anhydride has been reported. The highest selectivity is observed for the catalyst composed of U--Mo--O supported on  $TiO_2$ , with  $U/Mo = 1/10$  and  $Mo/Ti = 1/8$ . X-ray diffraction, and infrared and UV-visible spectroscopies revealed the existence of  $UO_2MoO_4$ ,  $MoO_3$  and  $TiO_2$  phases [200]. Liu and coworkers [201] studied catalyst structure and reaction selectivity for the photooxidation of methanol catalysed by supported  $MoO_3/TiO_2$ . Although the photo-efficiency of the  $MoO_3/TiO_2$  catalyst is about one-fifth that of pure  $TiO_2$ , the enhanced selectivity in suppressing secondary oxidation reactions is significant.

Sun and Ding [202] have prepared a catalyst containing 3%  $Fe_2O_3$  supported on  $TiO_2$  by impregnating  $TiO_2$  with a solution of  $Fe(NO_3)_3$ , and subsequently drying it at 373K and calcining at 823K for 5 hr. The catalyst was then characterized at various

steps in the water-gas shift reaction. Other supports ( $\text{MgO}$ ,  $\gamma\text{-Al}_2\text{O}_3$ ) were also employed and comparisons made[202]. Moessbauer spectroscopy has been used to study the interaction of the coordinatively unsaturated sites of  $\text{TiO}_2$  supporting Fe or Fe-Ir. It would appear that the coordinatively unsaturated sites of  $\text{TiO}_2$  serve as a template for  $\text{Fe}^{2+}$  as well as for the Fe-Ir cluster[203].

X-ray, Moessbauer and ESR methods were used to elucidate the structure of  $\text{TiO}_2\text{-Fe}_2\text{O}_3$  polycrystalline solids containing 0 - 10% Fe. The catalysts were prepared by coprecipitation and by impregnation, and treated in air at 773 - 1273K. The method of preparation is discussed in relation to photocatalysis in the photoreduction of dinitrogen to ammonia[204]. The nature of the surface species present on 10% Fe/ $\text{TiO}_2$  in the low-temperature reduced state (558K) has been investigated[205] after short reaction times in 10%  $\text{CO/H}_2$  at 558K and 1 atm pressure. The results show that the surface is covered with approx. 46  $\mu\text{mol/g}$  of CH and large quantities of surface carbidic carbon during reaction. The first growth stages of ultrathin films of iron and platinum deposited on the (001) face of  $\text{TiO}_2$  have been characterized[206] by Auger electron spectroscopy (AES), secondary electron emission and work function changes. Thorp and Eggleston [207] have monitored the changes in the amplitude of the  $\text{Fe}^{3+}$  feature in the ESR spectra of a series of pigment-like Fe-doped  $\text{TiO}_2$  powders during and subsequent to optical irradiation. Doping levels were in the range 30 - 670 ppm Fe. In contrast to what has been reported for Fe-doped single-crystal  $\text{TiO}_2$ , the  $\text{Fe}^{3+}$  concentration in these powders is affected only by light of wavelength  $>700\text{nm}$ . The results are discussed in terms of the deep impurity level system proposed in 1979 by Mizushima and coworkers [207].

The morphology and microstructure of thin films (15 - 20nm) of composition  $x\text{RuO}_2-(1-x)\text{TiO}_2$  have been determined by electron diffraction and electron microscopy. These films represent the microheterogeneous system formed of finely dispersed rutile-type phases of  $\text{TiO}_2$  and  $\text{RuO}_2$ [208]. The electrocatalytic redox mechanism of the ruthenium oxide/titanium oxide system in relation to its use in chlorine manufacture via electrolysis was investigated by x-ray excited photoelectron spectroscopy (XPS) [209]. The growth of the pyrolytic  $\text{RuO}_2/\text{TiO}_2$  interface was observed step-by-step after 1, 3, 5, 10 and 25 coatings. Kishi [210] has reviewed the laboratory-scale preparation, characterization and electrochemistry of  $\text{RuO}_2/\text{TiO}_2$  type dimensionally stable anodes.  $\text{TiO}_2$  containing a few percent ruthenium was investigated by ESR and x-ray diffraction. Prolonged treatment in hydrogen at <623K or the addition of Nb(V) to the rutile structure gives paramagnetic Ru(III) in solid solution. On increasing the temperature of the hydrogen treatment, reduction to Ru(II) in solid solution occurs, followed by reduction to Ru(0) as a segregated phase[211]. Bartelt[212] has discussed the properties and advantages of  $\text{RuO}_2/\text{TiO}_2$  anodes, as well as improvements of the anodes by insertion of an intermediate layer of electrically well conducting oxides, active layer modification, or changes in the anode electrochemical parameters. In fact, the degradation mechanism of electrodeposited  $\beta\text{-PbO}_2$  on a  $\text{RuO}_2/\text{TiO}_2$ -loaded titanium substrate has been studied[213]. An XPS study of the  $\text{RuO}_2/\text{TiO}_2$  surface electron configuration has been reported, as well as the effects of surface oxidation and reduction processes[214]. Blazey and coworkers[215] have shown, by paramagnetic resonance studies, the presence of both  $\text{Ru}^{5+}(4\text{d}^3)$  and  $\text{Ru}^{3+}(4\text{d}^5)$  in oxygen octahedral coordination of  $\text{TiO}_2$  single

crystals doped with ruthenium.

A radiochemical study reports on the dissolution selectivity of the components of  $\text{RuO}_2/\text{TiO}_2$  anodes in chloride solution carried out as a function of pH at an anodic current density of  $0.2 \text{ A/cm}^2$  and 363K. The selectivity is explained in terms of the presence of the components in the coating composition, not only in the combined oxide form, but also as individual phases[216]. The same authors[217] also investigated this selectivity as a function of the phase composition of the coating and the corrosion resistance of the coating as a function of its composition.  $\text{RuO}_2/\text{TiO}_2$  anodes can be prepared by applying solutions of ruthenium chloride hydroxide and  $\text{TiCl}_4$ , drying at 423K, and decomposing at 723K. The anodes were analysed by PIXE spectroscopy with a germanium detector, and the relative loss of ruthenium during thermal decomposition was determined to be  $\approx 21\%$ [218].

The corrosion resistance of  $\text{RuO}_2/\text{TiO}_2$  anodes has been determined during electrolysis of seawater[219] and chlorate electrolysis[220]. The effect of low chloride content and the changing temperature of seawater in the electrolysis process on anode corrosion resistance has been investigated[219]. The chlorate electrolysis, a neutron activation method was used to determine the effect of the composition of the  $\text{NaCl}$ -- $\text{NaClO}_3$  electrolyte[220].

Various groups have examined the oxygen evolution from chloride solutions at  $\text{RuO}_2/\text{TiO}_2$  anodes. Quam and Yin[221] have examined the effect of pH on the kinetics of oxygen evolution. Two methods have been described[222] for determining the rate of oxygen evolution: one is based on the use of the effect of equivalent acidification of a solution as a result of oxygen evolution; the other is based on compensation of the equilibrium value during contact of the anode with a chlorinated sol. Bune

et al.[223] have described a method which allows the determination of the effect of anode composition and solution composition on the kinetics of the secondary reaction of oxygen evolution under chlorine electrolysis conditions. Both Bune[224] and Kokoulina [225] and their coworkers have investigated the influence of anions on the kinetics of the oxygen evolution reaction. Specifically, polarization curves were obtained in acid and alkaline perchlorate, sulfate, and phosphate solutions and in acid chloride solutions. In the presence of the more strongly adsorbed anions, some increase in oxygen overvoltage was observed [225]. Polarization measurements as well as gas chromatographic analyses of the composition of gaseous products of the electrolysis were utilized to determine the effect of foreign anions (sulfate, phosphate, perchlorate) on the reaction kinetics[224].

An analysis of the mechanism of chlorine reaction at  $\text{RuO}_2/\text{TiO}_2$  anodes has appeared in the Russian literature[226]. The hydrogenation of CO catalysed at  $\approx 500\text{K}$  by (a) 17%  $\text{Ru}/\text{TiO}_2$ , (b) 2.6%  $\text{Ru}/\text{SiO}_2$ , (c) 1.5  $\text{Ru}/13\text{x-zeolite}$  and (d) 5%  $\text{Ru}/\text{MgO}$  yields methane and 1-alkenes as primary products. Specific activity of the catalysts varies in the order (a)  $\gg$  (c)  $>$  (b)  $>$  (d); whereas selectivity for methane formation varies as (b)  $>$  (c)  $>$  (a)  $>$  (d). The single most important factor in determining the total product distribution is the availability of adsorbed hydrogen, which varies in the order (b)  $>$  (c)  $>$  (a)  $>$  (d)[227].

Titanium dioxide-supported cobalt catalysts, prepared by alkoxide and impregnation methods, have been examined by EXAFS in order to identify the local structures which contribute to the superior properties of catalysts prepared by the alkoxide method [228].

Sun and coworkers[229] have reviewed work on strong metal-

support interaction (SMSI) using rhodium or platinum deposited on  $\text{TiO}_2$  thin films. Results from thermal desorption spectroscopic, AES and static SIMS experiments are discussed. A method has been reported[230] for the preparation of new catalysts containing  $\text{ORhC}_3\text{H}_5$  ( $\text{C}_3\text{H}_5$  = allyl),  $\text{ORhH}$  and  $[\text{Rh}]_n$  moieties. They were prepared via reaction of  $\text{Rh}(\text{C}_3\text{H}_5)_3$  with surface OH groups of  $\text{TiO}_2$ , followed by chemical treatments with hydrogen. The catalysts reportedly show higher activities for  $\text{C}_2\text{H}_6$  hydrogenolysis and  $\text{C}_2\text{H}_4$  hydrogenation than a conventional impregnation rhodium catalyst[230].

Shapiro et al.[231, 232] have explored the nature of the strong interaction between metal(Rh) and support ( $\text{TiO}_2$ ) using x-ray photoelectron and secondary-ion mass spectra. The results are indicative of a local interaction between Rh and reduced Ti cations as a consequence of high-temperature reduction of  $\text{Rh/TiO}_2$  [231]. Surface-sensitive electron spectroscopies, CO chemisorption measurements, and Auger sputter profiling were employed to study the SMSI in  $\text{Rh/TiO}_2$  model catalysts. Further, the oxidation dynamics of reduced  $\text{TiO}_2$  surfaces as a function of annealing temperature were examined. The high temperature reduction of  $\text{Rh/TiO}_2(110)$  catalysts to an SMSI state is reportedly accompanied by the formation of a suboxide of Ti on the Rh particles, thereby blocking CO chemisorption sites[233]. Samples of  $\text{Rh/TiO}_2$  and  $\text{Rh/SrTiO}_3$  catalysts, subjected to thermal treatments under hydrogen and in vacuo, have been examined by nmr, ESR and quantitative adsorption techniques to ascertain the dependence of SMSI effects on hydrogen strongly adsorbed at high temperatures [234]. The loss of  $\text{H}_2$  chemisorption capacity upon high-temperature reduction occurs only in  $\text{Rh/TiO}_2$ , and is accompanied by extensive incorporation of hydrogen in the support in the form of

hydride-type species.

An nmr study of hydrogen adsorption on  $\text{Cl}_3\text{Rh}/\text{TiO}_2$  catalysts reveals the presence of two types of adsorbed hydrogen on the metal and the modification of the metal-hydrogen interaction with the extent of the adsorption[235]. The hydrogen reduction of  $\text{Rh}/\text{TiO}_2\text{-V}_2\text{O}_5$  and  $\text{Rh}/\text{V}_2\text{O}_5$  catalysts at  $\geq 298\text{K}$  was investigated by Miller and coworkers[236]. The results are consistent with the formation of  $\text{H}^+$  species during metal reduction and spillover hydrogen atoms during support reduction.

The support interaction between rhodium and  $\text{TiO}_2$  supports has been investigated by several groups for the catalysed carbon monoxide hydrogenation reaction. Catalysts composed of 1-2 wt% Rh supported on  $\text{TiO}_2$  were employed for hydrogenation of CO to  $\text{C}_{1-6}$  hydrocarbons, methanol and ethanol. At 0.13-1.20% C conversion, Richards and Newman[237] find no specific selectivity to any single product, though temperature-programmed reduction was interpreted in terms of the presence of both bulk Rh (weak support interaction) and dispersed Rh (strong support interaction) species. Catalytic activity is significantly influenced by reduction conditions, to give maximum activity per weight for reduction at 673K for 2 hr[238]. Tamaru and coworkers[239, 240] have examined highly loaded (25 and 60 wt%)  $\text{Rh}/\text{TiO}_2$  for CO hydrogenation, as well as the effects produced on varying the pretreatment conditions, the supports and the metal precursors [241]. For the 25 wt%  $\text{Rh}/\text{TiO}_2$  catalyst subjected to reduction at 573 and 723K, the  $\text{Rh}/\text{TiO}_2$  ratio lies in the strong metal-support interaction range (SMSI) after reduction. The catalytic activity is significantly lower in the SMSI state than after reduction at low temperatures[239]. Moreover, the studies support the view that SMSI is due to migration of  $\text{TiO}_x$  ( $1 < x < 2$ ) on the metal



surface[240]. Chuang and coworkers[242-244] have reported on the effects of alkali metal addition on the hydrogenation of CO over Rh/TiO<sub>2</sub>. The rate of CO conversion, as well as the hydrogenation activity of the catalysts, decreases in the order: unprotonated > Li > K > Cs [242, 244]. The ability of the alkali species to promote the selectivity for oxygenated compounds apparently increases in the order: unprotonated < Li < K ≈ Cs [243]. The activities and selectivities of Rh/TiO<sub>2</sub> and alkali-promoted Rh/TiO<sub>2</sub> appear to be correlated with their catalytic abilities for hydrogenation, CO dissociation and CO insertion.

The rate of hydrogenation of several unsaturated compounds mediated by Rh-Ru/TiO<sub>2</sub> catalysts decreases in the order: 1-hexene > cyclohexene > *o*-nitrophenoxide > MeC≡CCH(OH)Me > Me<sub>2</sub>CO [245].

Rh/TiO<sub>2</sub> is known to be a very active catalyst for the methanation of carbon monoxide with water. The presence of platinum further enhances the catalytic activity[246]. In a study of this reaction over Rh/ZrO<sub>2</sub>, Rh/Al<sub>2</sub>O<sub>3</sub>, Rh/TiO<sub>2</sub>, Rh/SiO<sub>2</sub>, and Rh/MgO catalysts, high activity was achieved for Rh/ZrO<sub>2</sub> and Rh/TiO<sub>2</sub> at 573K. Also, the CO dissociation ability of the catalyst appears to be an important factor in obtaining high activity[247]. Methane formation appears to occur through the water-gas shift reaction, followed by hydrogenation of carbonaceous species formed via CO (or CO<sub>2</sub>) dissociation.

Infrared spectroscopy was instrumental in the examination of carbon monoxide and oxygen over supported rhodium films. The reactivity was investigated for various CO/Rh/M (M = Al<sub>2</sub>O<sub>3</sub>, SiO<sub>2</sub>, TiO<sub>2</sub>) ratios[248].

Yamaguti and Sato[249] examined the simultaneous production of hydrogen and oxygen upon photolysis of water vapor on NaOH-coated Rh/TiO<sub>2</sub> and Pd/TiO<sub>2</sub> catalysts. The rate of water

photolysis seems strongly dependent on the amount of NaOH loaded on the catalyst, and on the water vapor pressure. The maximized photolysis rate on the Rh/TiO<sub>2</sub> catalyst obtains for 15 wt% NaOH coating and 2 toor of water pressure. The relationships between photolysis rate and light intensity, wavelength and thernal back-reaction rate were also explored[249].

Catalysts of nickel supported on TiO<sub>2</sub>, BeO, MgO, ZnO, Al<sub>2</sub>O<sub>3</sub>, Cr<sub>2</sub>O<sub>3</sub>, SiO<sub>2</sub>, ZrO<sub>2</sub>, ThO<sub>2</sub> and UO<sub>2</sub> have been prepared by coprecipitation with different precipitants and by impregnation of the basic nickel carbonate with a salt of the support[250]. The least efficient support for nickel dispersion is TiO<sub>2</sub>, while the most efficient supports appear to be SiO<sub>2</sub> and Al<sub>2</sub>O<sub>3</sub>. The following observations were also made: i) each support increases the specific catalytic activity value of nickel with respect to unsupported nickel; ii) the specific catalytic activity increases up to a limiting value as the support content increases; iii) the most efficient supports in the hydrogen-water deuterium exchange reaction are TiO<sub>2</sub> and Zr<sub>2</sub>O<sub>2</sub>; and iv) the influence of the support on the specific catalytic activity is due to the participation of the support surface in the activation of the water molecule[250]. Controlled-atmosphere electron microscopy and gravimetric measurements were performed to determine the effects of depositing powdered TiO<sub>2</sub> on nickel surfaces with respect to the formation of filamentous carbon from acetylene and ethane[251]. Filamentous carbon formation is suppressed initially on those portions of the nickel surface containing TiO<sub>2</sub> when samples are directly heated in a hydrocarbon environment to 1000K. However, effective passivation of the nickel surface is achieved at all temperatures via pretreatment of the TiO<sub>2</sub>/Ni samples in hydrogen at approx. 770K. The results obtained indicate that reduced TiO<sub>2</sub> species

migrate over metal surfaces under reducing conditions and collect into  $\text{TiO}_2$  particles under oxidizing conditions. Thus, the idea that reduced  $\text{TiO}_2$  species on metal surfaces may be the origin of SMSI for titania-supported metal particles is confirmed[251]. Malinkowski *et al.*[250] have examined supported titanium and Ni-Ti catalysts and non-supported Ni-Ti catalysts in the Fischer-Tropsch reaction at 523-573K. The supports included  $\text{TiO}_2$ ,  $\text{SiO}_2$ ,  $\text{Al}_2\text{O}_3$  and HZSM-5 zeolite. The presence of titanium increases the yield of higher hydrocarbons in the reaction[252].

The Russian literature cites an electron microscopic study of  $\text{TiO}_2/\text{Pd}$  and  $\text{ZnO}/\text{Pd}$  thin film systems modeling the surface layer of a catalyst[253].

The kinetics and mechanism of platinum deposition by photoelectrolysis in illuminated suspensions of  $\text{TiO}_2$  have been established. It has been proposed[254] that the  $\text{TiO}_2$  particles are subject to strong internal electric fields which lead to efficient hole-electron-pair separation, yet these particles contain a large number of traps that cause recombination. Sato [255] has prepared  $\text{Pt}/\text{TiO}_2$ (anatase) catalysts by the photoelectrochemical deposition of Pt from a  $\text{H}_2\text{PtCl}_6$  solution, and characterized their properties for CO and  $\text{H}_2$  adsorption by infrared spectroscopy and volumetric analyses. Apparently, i) dispersion of Pt depends on the commercial source of  $\text{TiO}_2$ , ii) good Pt dispersion is achieved by photodeposition of Pt followed by photoreduction employing a sacrificial reducing agent, and iii) Pt dispersion is lowered by photoelectroplating the Pt in the presence of the reducing agent. Also, photoimpregnation of  $\text{H}_2\text{PtCl}_6$  followed by calcination in air and reduction in hydrogen yields well-dispersed  $\text{Pt}/\text{TiO}_2$ [255]. Moessbauer spectroscopic methods were utilized to elucidate the sorption of platinum(II)

chloro complexes from  $K_2[PtCl_4]$  solutions on  $TiO_2 \cdot nH_2O$  modified by tin(II) compounds[256]. The complex sorption mechanism is thought to involve ion exchange, and complexing and oxidation-reduction reactions.

Titanium dioxide gels containing platinum and ruthenium have been prepared by calcining hydrogels made by the hydrolysis of a mixture composed of titanium(IV) oxide hydrosol,  $H_2PtCl_6$ ,  $RuCl_3 \cdot xH_2O$ , and various alkali hydroxides[257]. In the presence of such gels, evolution of hydrogen occurs upon radiation (500W high-pressure mercury lamp) of a methanol-water mixture. The rate of hydrogen evolution depends on the amount and type of alkali hydroxide used in the gel preparation. X-ray diffraction studies show that the fractions of microcrystalline anatase- and rutile-type modifications formed in the  $TiO_2$  gels varies with the alkali hydroxides employed[257].

Recent examinations of SMSI in  $Pt/TiO_2$  catalysis attribute the inhibition of chemisorption and catalysis to the presence of a reduced titanium oxide,  $TiO_x$ , on the surface of Pt crystallites. Spencer's[258] equilibrium calculations show that titanium, dissolved in platinum in vacuo, is unlikely to segregate to the crystallite surface, though any traces of  $H_2O$  (present under normal reducing conditions) would be sufficient to give adsorbed oxygen on surface titanium atoms thereby greatly enhancing surface segregation. The calculated rates of diffusion, either Ti in Pt metal or adsorbed species on the Pt surface, are too slow at low temperatures for significant SMSI to occur, even though adsorbed  $TiO_x$  is stable under both high- and low-temperature reducing conditions[259]. The failure of  $Pt/TiO_2$  catalysts to show SMSI effects after low-temperature reduction has been attributed[260] to kinetic, rather than equilibrium, limitations. Two possible

ways of forming the  $\text{TiO}_x$  layer are proposed with (i) being more important: (i) formation of  $\text{TiO}_x$  at the Pt/ $\text{TiO}_2$  interface, followed by transport across the Pt surface; (ii) reduction of  $\text{TiO}_2$  to yield a Pt/Ti alloy, followed by diffusion, surface segregation and oxidation[260].

Small-angle x-ray scattering measurements have been carried out on  $\text{TiO}_2$  supports and Pt/ $\text{TiO}_2$  catalysts that were reduced at low and high temperatures[261].

Chemisorption of  $\text{H}_2$ , CO and  $\text{O}_2$  on 2 wt% Pt/ $\text{TiO}_2$  was examined to establish a satisfactory method for measuring the Pt dispersion on  $\text{TiO}_2$ [262]. High-temperature reduction of Pt/ $\text{TiO}_2$  results in a sharp decrease in  $\text{H}_2$  and CO chemisorption capacities and catalytic activity. Oxidation-reduction treatments restore the usual catalyst properties. The magnitude of  $\text{H}_2$  uptake suppression (and thus in SMSI formation) increases at higher  $\text{TiO}_2$ /Group VIII metal ratios, as does higher reduction temperature and extended reduction times at a given elevated temperature[263].

Differential scanning calorimetry has been used to determine isothermal, integral heats of adsorption of  $\text{H}_2$  and CO on Pt/M ( $\text{M} = \text{TiO}_2$ ,  $\text{SiO}_2$ ,  $\eta\text{-Al}_2\text{O}_3$ , and  $\text{SiO}_2\text{-Al}_2\text{O}_3$ ). A comparison of the results for the various supports suggests that the adsorption capacity for CO and  $\text{H}_2$  can be decreased by an alteration in the chemical nature of surface Pt atoms, as well as by the physically blocking the Pt surface by migrating  $\text{TiO}_x$  species[264]. Vannice and coworkers[265] have reported on Auger electron spectroscopic (AES) and electron-stimulated desorption (ESD) experiments on titanium dioxide single-crystal and powder surfaces in the presence and absence of platinum.

Evidence of the structural interaction between Pt and  $\text{TiO}_2$  can be obtained from TEM studies on the morphology of the Pt/ $\text{TiO}_2$

surface. On heating the Pt/TiO<sub>2</sub> catalyst at 873 - 973K in a hydrogen atmosphere, the highly dispersed Pt is transformed into polygonal particles, possessing an epitaxial multiplane structure. The appearance of  $\eta$ -TiO<sub>2</sub> defect in the vicinity of the Pt and TiO<sub>2</sub> contacting point is likely the direct cause of epitaxial growth of Pt microparticles. Chen et al.[266] suggested the presence of a metal-semiconductor interaction for the Pt/TiO<sub>2</sub> system as an explanation for the observed morphology.

The electrochemical behavior of platinized TiO<sub>2</sub> electrodes has been examined in order to understand the role of the Pt layer on the TiO<sub>2</sub> electrode in photoelectrochemical and photocatalytic reactions. Platinization of single-crystal electrodes causes an increase in the rate of hydrogen evolution reactions, but does not affect the kinetics of oxygen evolution. However, both hydrogen and oxygen evolution reactions are accelerated upon platinization of polycrystalline TiO<sub>2</sub> electrodes[267]. The results show that the electronic equilibrium between Pt and the TiO<sub>2</sub> single crystal is established only when TiO<sub>2</sub> is biased relatively negative such that bands bend down towards the surface (or up only a small amount), but equilibrium between Pt and polycrystalline TiO<sub>2</sub> is always attained. So, for single-crystal TiO<sub>2</sub>, it should be difficult to transfer electrons to Pt when TiO<sub>2</sub> is anodically polarized due to a relatively thick tunnelling barrier. By contrast, polycrystalline TiO<sub>2</sub> contains many impurity levels, grain boundaries, etc., such that electrons can be transferred from TiO<sub>2</sub> bulk to Pt via these levels. A drastic decrease in photocurrent at a TiO<sub>2</sub> electrode modified with Pt has been observed, in contrast to a 70% increase in photocurrent for a TiO<sub>2</sub> electrode modified with photodeposited gold[268]. The photocurrent inhibition is the result of the inability of

photodeposited or electrodeposited platinum to reach a saturation level on  $\text{TiO}_2$ , but rather continue to form deposits at the electrode surface.

$\text{TiO}_2$  overlayers on polycrystalline platinum were characterized by XPS. Vacuum annealing of the  $\text{TiO}_2$  thin films has two significant effects: (a) most of the  $\text{Ti}^{4+}$  is reduced to  $\text{Ti}^{3+}$ ; and (b) an equilibrium coverage of the reduced species is attained for initial coverages of  $\text{TiO}_2 \geq 0.9$  monolayer. Depth profiles of annealed and non-annealed surfaces indicate that the reduced  $\text{TiO}_2$  species diffuses into the Pt[269]. Ko and Gorte[270] have examined the interactions between oxide support materials ( $\text{TiO}_2$ ,  $\text{Al}_2\text{O}_3$ ,  $\text{SiO}_2$ ,  $\text{Nb}_2\text{O}_5$ ) and clean platinum foil. For all of the oxides, temperature-programmed desorption shows no change in the adsorption behavior of  $\text{H}_2$  or  $\text{CO}$ . For  $\text{TiO}_2$ , AES results are indicative of the presence of segregated layers evenly covering Pt; complete suppression of  $\text{H}_2$  and  $\text{CO}$  adsorption occurs at an oxygen coverage of  $1 \times 10^{15} \text{ cm}^{-2}$ [270].

Ammonia is photocatalytically formed from an aqueous solution of azide ion using illuminated Pt/ $\text{TiO}_2$  semiconductor powder. Reaction products include  $\text{N}_2$ ,  $\text{NH}_3$  and small amounts of  $\text{N}_2\text{O}$  and  $\text{NO}_3^-$ [271]. Photolysis ( $\lambda_{\text{ex}} > 300\text{nm}$ ) of Pt/ $\text{TiO}_2$  suspended in an argon-purged acetonitrile solution of aliphatic or aromatic primary amines gave Schiff bases,  $\text{H}_2$  and  $\text{NH}_3$  at room temperature [272].

In the hydrogenation of acetone to isopropanol at 330K over 0.5% Pt/ $\text{TiO}_2$ , conversions of 75% with selectivities  $\geq 98\%$  are routinely achieved[273]. The results reveal that conversions decrease linearly with the reciprocal of the flow rate when the reaction is carried out in a continuous-flow microcatalytic reactor at a flow rate of 40 ml/min. Thus, reaction on the

catalyst surface was rate limiting. Kunimori and coworkers[274] observed a significant decrease in the catalytic activity for the  $\text{CO} + \text{H}_2$  reaction over  $\text{Pt}/\text{TiO}_2$  after high-temperature reduction at 773K. However, the catalytic activity almost recovered during the reaction, due to the reverse effect of oxygen atoms (or water molecules) formed. It has also been observed, by Damiani and Butt [275] that high-dispersion  $\text{Pt}/\text{TiO}_2$  catalysts in the normal state are slightly more susceptible to CO poisoning in the hydrogenolysis of methylcyclopropane than are comparable  $\text{Pt}/\text{SiO}_2$  or  $\text{Pt}/\text{Al}_2\text{O}_3$  catalysts.

Inasmuch as it is known that the surface properties of  $\text{Pt}/\text{TiO}_2$  are altered upon high-temperature hydrogen treatment, Lin et al.[276] have examined the influence of the change in surface properties of  $\text{Pt}/\text{TiO}_2$  on the electron transfer process across the solid-liquid interface, as studied by a dynamic potential sweep method for the liquid-phase photoreaction of carbon monoxide and water. Results show the following as a result of high-temperature hydrogen treatment: (i) a strong metal-semiconductor interaction between Pt and  $\text{TiO}_2$  occurs; (ii) electronic contact between Pt and  $\text{TiO}_2$  gradually changes from a Schottky to ohmic nature; (iii) the production of additional surface states; and (iv) a decreased energy barrier at the  $\text{Pt}/\text{TiO}_2$  interface. It was proposed that the change in the surface properties of  $\text{Pt}/\text{TiO}_2$  could bring about the direct charge transfer between CO and the  $\text{Pt}/\text{TiO}_2$  photoelectrode [276]. Kolchanova and Mikheeva[277] reported the reversible deactivation of sodium-promoted  $\text{Pt}/\text{TiO}_2$  catalysts for the oxidation of CO. The deactivation is reportedly due to increasing the strength of the Pt—CO bond, attributed to the variations in the chemical composition and structure of the CO-containing platinum compounds.



Pt/TiO<sub>2</sub> particles have been prepared from dispersions of clean colloidal Pt and TiO<sub>2</sub> particles. It was shown[278] that the binding of Pt to TiO<sub>2</sub> is primarily electrostatic in origin, and is only slowly reversed by charge reversal on the TiO<sub>2</sub> particles. Additionally, maximum coverage of Pt and TiO<sub>2</sub> is attained at pH 3 and corresponds to ≈20% of geometric close-packing due to lateral repulsions between bound Pt particles. The adsorption of EDTA suppresses the binding of the Pt to TiO<sub>2</sub>, and causes coagulation of Pt/TiO<sub>2</sub> particles. The Pt/TiO<sub>2</sub> catalyses the oxidation of the donors EDTA and oxalate when irradiated with light of energy greater than the bandgap of TiO<sub>2</sub>. Rates of hydrogen production obtained as a function of irradiation time, ionic strength of the solution, addition of polyvinyl alcohol, Pt concentration, and TiO<sub>2</sub> concentration have been determined[279]. Loy and Wolf[280] developed a flow-reaction system to study the steady-state kinetics of hydrogen evolution by photodissociation of water in the presence of Ru(bpy)<sub>3</sub><sup>2+</sup> (bpy = 2,2'-bipyridine), MV<sup>2+</sup> (methyl viologen), EDTA, and heterogeneous Pt/TiO<sub>2</sub> supported catalyst. Over a large range of reactant and catalyst concentrations, the reaction is zero-order, and does not exhibit Arrhenius-type behavior[280]. Water is reduced under UV illumination in a system consisting of Rh(bpy)<sub>3</sub><sup>3+</sup>/dextrose. The reaction is enhanced by TiO<sub>2</sub>-supported Pt[281]. A photocatalyst for decomposition of water has been prepared by photoplatinizing TiO<sub>2</sub>(anatase) powder and dispersing it into an aqueous polymer solution. The polymer was prepared via reaction of [Ru(bpy)<sub>2</sub>{4-(5-bromopentyl)-4'-methyl-2,2'-bipyridine}]Cl<sub>2</sub> with poly(4-vinylpyridine) in DMF, followed by treatment with hexadecyl bromide or N-(3-bromopropyl)-N'-hexadecyl-4,4'-bipyridinium dibromide. Hydrogen evolution during water photolysis is enhanced and the catalyst particles are

well protected against coagulation[282].

The photolytic dehydrogenation of isopropanol on Pt/TiO<sub>2</sub> catalysts has been studied in the gas and liquid phases[283]. In the gas phase, isopropanol undergoes photodehydrogenation at room temperature in acetone; and in the presence or absence of water vapor, produces an amount of hydrogen equal to the amount of acetone. In the liquid phase, as in the gas phase, the rate of photodehydrogenation increases in the presence of water. Apparently, isopropanol is not a sacrificial compound for reaction in the gas phase; though its role in the liquid phase is yet to be determined[283].

The characteristics of the cathodic deposition of Ag on TiO<sub>2</sub> electrodes under potentiostatic conditions have been established for two different types of electrodes. One TiO<sub>2</sub> electrode was heated at 723K, a high-defect type of electrode; while the other was heated at 1073K, a low-defect electrode[284]. Photoimaging layers of TiO<sub>2</sub> with Ag<sup>+</sup> adsorbed onto the film surface were spectrally sensitized with 1,1'-diethylquino-2,2'-cyanine iodide, chloride or tosylate, or 1,1'-sulfobutyl-2,2'-cyanine betaine. Supersensitization was achieved with 2-(p-dimethylaminostyryl)-benzthiazole[285].

Zinc oxide catalysts mixed with other metal oxides (TiO<sub>2</sub>, Al<sub>2</sub>O<sub>3</sub>) can be prepared by coprecipitation or impregnation techniques, and their activities studied for the decomposition of methanol to synthesis gas[286]. The maximum activity (total conversion of 46 mol%) was observed for a ZnO/TiO<sub>2</sub> catalyst coprecipitated from an aqueous ammonia solution. ZnO/TiO<sub>2</sub> catalysts, prepared via hydrolysis of chlorides, were characterized by x-ray photoelectron (XPS) and infrared spectroscopies, along with catalytic elimination reactions of

propanol and butanol[287, 288]. The XPS data suggests the presence of one phase in all the oxides ( $\text{ZnTiO}_3$ ), and another phase only in oxides with 64 and 95 mol%  $\text{ZnO}$ . Infrared-adsorbate spectra of pyridine were indicative of  $\text{Ti}^{4+}$  cations present on the surface of the  $\text{ZnTiO}_3$  phase and  $\text{Zn}^{2+}$  cations present on the surface of the other phase. Active sites for butene isomerization reactions were also examined[288].

The optical properties of ion-beam sputter deposited  $\text{SiO}_2$ - $\text{TiO}_2$  composite films have been examined with respect to the composition dependence of the optical parameters, the optical energy gap, and the absorption character[289]. Photoelectrochemical properties of  $p^+-n$  junction silicon electrodes coated with thin oxide films of titanium, tungsten or iron were examined in aqueous hydrogen iodide and iodine[290]. Effects of the nature of silicon-metal oxide junctions, the donor density in the oxide, the relations between the flatband potential of the oxide and the redox potential of the solution, on the efficiency for solar energy conversion were also discussed. Kulak and Poznyak[291] suggest a charge transfer mechanism to account for the dark conductivity and photoconductivity of  $n$ -Si with epitaxial  $\text{TiO}_2$  layers in 0.5N  $\text{K}_2\text{SO}_4$  solutions. The sol-gel process was employed to solve the problem of incorporating an organic dye in an inorganic oxide thin film. Thus, a variety of organic fluorescent dye molecules were embedded in  $\text{SiO}_2$  or in  $\text{SiO}_2$ - $\text{TiO}_2$  films[292]. Absorption and emission spectra were recorded; the data, along with the observed longer lifetimes and energy transfers between trapped dye molecules, and enhanced photostability, correlated with the effects of molecular matrix-isolation on these properties.

Seo and coworkers[293, 294] have studied the reduction of

SO<sub>2</sub> by CO over La<sub>2</sub>O<sub>3</sub>-impregnated TiO<sub>2</sub>, SiO<sub>2</sub> and Al<sub>2</sub>O<sub>3</sub>. TiO<sub>2</sub>-supported catalysts possess good catalytic activity, low COS selectivity, and high La<sub>2</sub>O<sub>3</sub> dispersion. Exposure to oxygen during the reaction reduces the catalytic efficiency, though activity is restored when oxygen input is prevented. It would appear that the oxygen lattice vacancy is the active site for the reaction[293].

The activity and selectivity of the commercial catalyst KVTs (vanadium and titanium oxides), and of the newly prepared catalyst K-3, have been examined in relation to the oxidative ammonolysis of 3-picoline[295]. A comparison of the two catalysts reveals the high activity and selectivity of the K-3 catalyst, affording a 90 - 93% yield of nicotinic acid amide and nitrile at total conversion of the starting material 3-picoline. Furthermore, the K-3 catalyst allows for 2-3 fold larger reactor productivity and decreases energy losses[295]. EPR spectroscopy was employed to characterize mechanically-activated TiO<sub>2</sub> and the high-SiO<sub>2</sub> zeolite ZSM-5. For both oxides, O<sup>-</sup> hole center associations were detected by a signal at  $\lambda = 8$  mm[296].

Photoluminescence studies of TiO<sub>2</sub> anchored onto porous Vycor glass were carried out relative to its photocatalytic activity. Quenching experiment results, interpreted in terms of the x-ray amorphous Ti—O moiety of the catalyst, suggest this moiety to be highly dispersed in the form of an individual complex on the surface. A charge-transfer excited complex explains the results[297].

#### 4.9 COMPLEXES

Pickering[298] has described the preparation and determination of visible and ir spectra, and magnetic moments, of

the  $d^1$  complex  $[\text{Ti}(\text{urea})_6]\text{I}_3$  specifically for use as a student experiment.

$\text{TiCl}_4$  reacts with  $(\text{NSCl})_3$  to give  $\text{TiCl}_4(\text{N}_2\text{S}_2)$  and  $(\text{S}_4\text{N}_5)_2[\text{Ti}_2\text{Cl}_{10}]$ , the latter of which is shown in Figure 3.

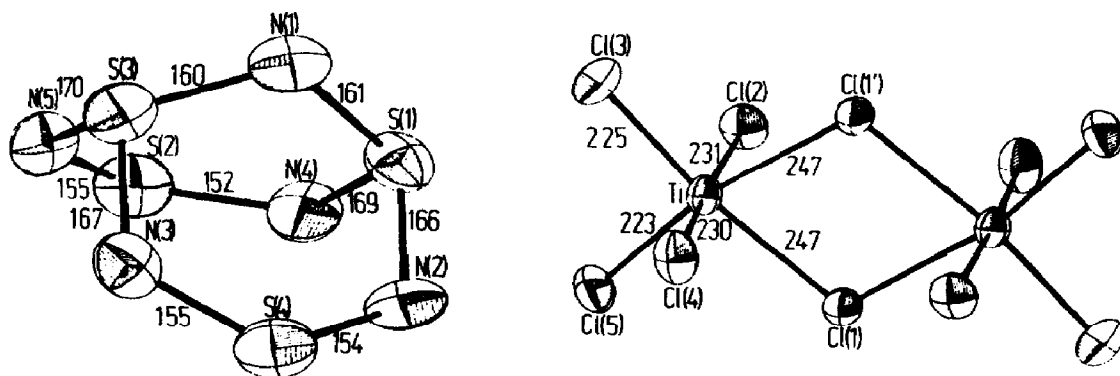


Figure 3. The crystal structure of  $(\text{S}_4\text{N}_5)_2[\text{Ti}_2\text{Cl}_{10}]$ , from reference 299.

According to infrared data, the  $\text{N}_2\text{S}_2$  ring in  $\text{TiCl}_4(\text{N}_2\text{S}_2)$  is bonded to Ti via the N atoms. The complex in Figure 3 is composed  $\text{S}_4\text{N}_5^+$  cations, which are nearly equivalent to those in  $[\text{S}_4\text{N}_5]\text{Cl}$ , and  $[\text{Ti}_2\text{Cl}_{10}]^{2-}$  anions; the latter are nearly identical to those in  $(\text{PCl}_4)_2[\text{Ti}_2\text{Cl}_{10}][299]$ . Electronic and ESR spectroscopic studies of titanium(III) thiocyanate complexes indicate that Ti(III) forms distorted tetrahedral and octahedral complexes with thiocyanate ions in ethanol; the two geometric species are in equilibrium. The tetrahedral complex is  $\text{Ti}(\text{OH})(\text{NCS})_3^-$ , wherein the thiocyanate is N-bonded to Ti[300].

Pazos and coworkers[301] have assigned a dimeric structure to  $[\text{TiX}_4\text{L}]$  and a monomeric structure to cis- $[\text{TiX}_4\text{L}_2]$  ( $\text{X} = \text{Cl}, \text{Br}$ ;  $\text{L} = \text{pyrazole}$ ). The preparatory procedure, infrared and Raman

spectra are reported. The preparation and crystal structure of  $[\text{TiL}(\text{THF})\text{Cl}]$  ( $\text{H}_2\text{L} = \text{N,N}'\text{-ethylenebis(salicylideneimine)}$ ) has been cited in the Chinese literature[302].  $\text{TiCl}_3 \cdot 3\text{THF}$  reacts with  $\text{Na}_2\text{L}$  in THF to afford the air-sensitive  $[\text{TiL}(\text{THF})\text{Cl}]$ ; the complex is orthorhombic, belongs to space group  $\text{Pbnm}$ , and possesses a pseudooctahedral geometry about Ti. Titanyl-acetylacetonate,  $[\text{TiO}(\text{acac})_2]$ , reacts with 1,4,7-triazacyclonone (L) in dry acetone, followed by treatment with aqueous KBr, to give  $[\text{Ti}_4\text{L}_4(\mu\text{-O})_6]\text{Br}_4 \cdot 4\text{H}_2\text{O}$ , as shown in Figure 4. The crystal structure

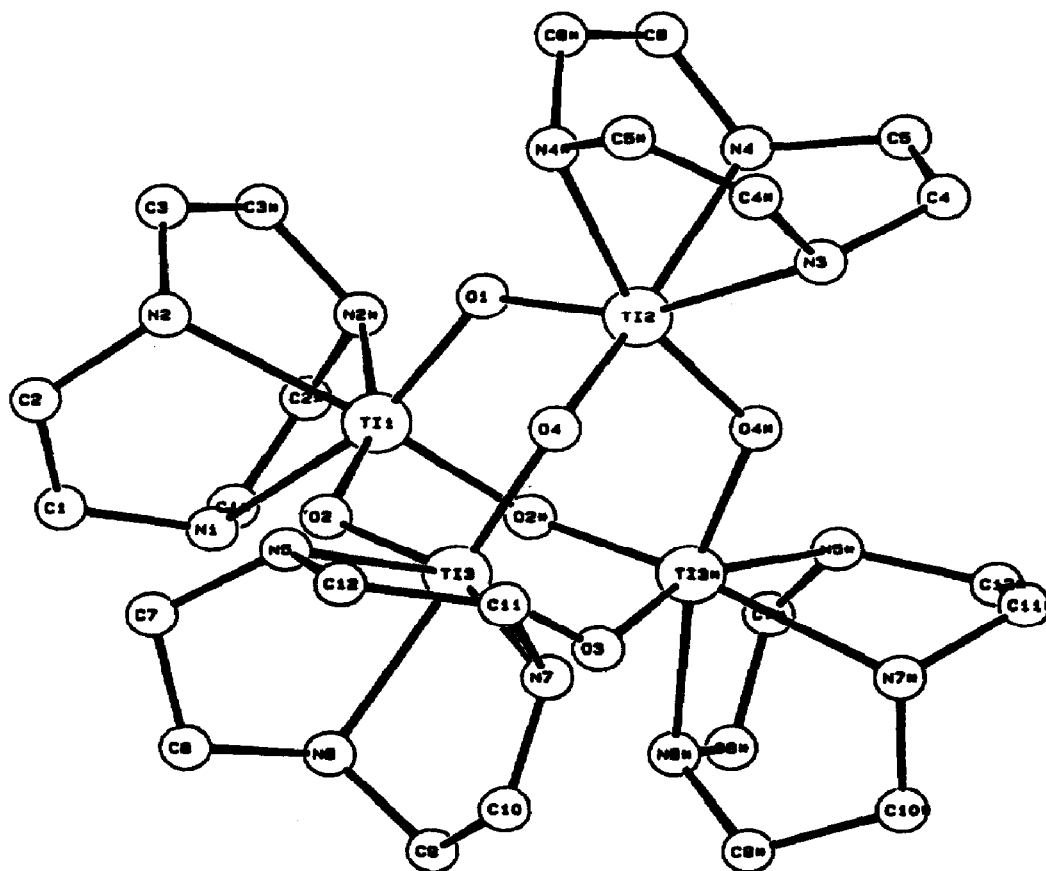
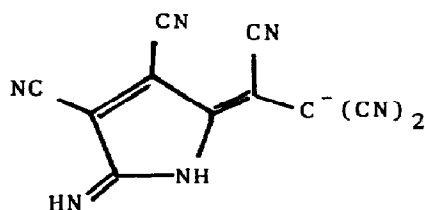


Figure 4. The structure of  $[\text{Ti}_4(\text{C}_6\text{H}_{15}\text{N}_3)_4(\mu\text{-O})_6]^{4+}$ , in which  $\text{N}(1)$ ,  $\text{Ti}(1)$ ,  $\text{O}(1)$ ,  $\text{Ti}(2)$ ,  $\text{N}(3)$  and  $\text{O}(3)$  lie on a mirror plane; from reference 303.

determination of this complex reveals the complex to be orthorhombic, space group  $Pnma$ , with each Ti atom in a distorted octahedral environment of three facially coordinated N atoms of the L ligand and three cis- $\mu$ -oxo groups[303]. Dessy et al.[304] have shown that the reduction of  $(NC)_2C=C(CN)_2$  with  $Ti(bpy)_3$  ( $bpy = 2,2'$ -bipyridine) at 193K in THF and  $MeNO_2$  under nitrogen gives the anion in structure (5). This anion can be converted to



(5)

the  $Ph_4As^+$  salt via treatment with  $AsPh_4Cl$  in water. The Russian literature [305] reports the complexing of titanium(IV) with some monoazo compounds based on pyrogallol.

Recent developments in the chemistry of titanium (and vanadium) porphyrins, with special emphasis on oxygen adducts, low valent metalloporphyrins, and related systems with sulfur and selenium, have been reviewed by Guillard and Lecomte[306]. The known crystal structures and reduction of the EXAFS spectra of  $[Ti(O_2)=TPP]$  and  $[Ti(=O)=TPP]$  (TPP = mesotetraphenylporphyrinato) have been used to ascertain the reliability of a method devised to probe the reality of the peroxide structure of two peroxoiron(III) porphyrinates using EXAFS spectroscopy[307].

2,3-pyridinedicarboxamide reacts in quinoline, with and without  $C_6H_3Cl_3$  or pyridine, in the presence of  $TiCl_4$  to give  $[TiLCl_2]$  ( $H_2L$  = tetra-2,3-pyridineporphyrazine).  $[TiL(OH)_2]$  forms upon hydrolysis. The complexes were characterized by infrared and electronic spectra[308].

The crystal structures of  $(AsPh_4)_2MCl_5X \cdot 2CH_2Cl_2$  ( $M = Ti, U, Re, W$ ;  $X = O, NO, Cl$ ) show the complexes crystallize in three different structure types with essentially equal packing densities. In  $(AsPh_4)_2TiCl_6 \cdot CH_2Cl_2$ , the two  $(AsPh_4)^+$  ions are paired around an inversion center such that the three phenyl groups of one ion face three phenyl groups of the other ion in a staggered arrangement; the fourth phenyl group points away from the inversion center. The  $(AsPh_4)_2^+$  groupings are aligned to give parallel rows in which contacts between the fourth phenyl groups exist[309].

Titanium(IV) isopropoxide reacts in benzene under nitrogen with salicylideneaniline (HL) to give  $[TiL_2(OPr^i)_2]$ [310], and with salicylidene-2-aminopyridine (HL') in different stoichiometric ratios to yield  $[TiL'_x(OPr^i)_{4-x}]$  ( $x = 1, 2$ ). The latter reaction product may further react with tert-butylalcohol to obtain  $[TiL'_x(Obu^t)_{4-x}]$ [311].

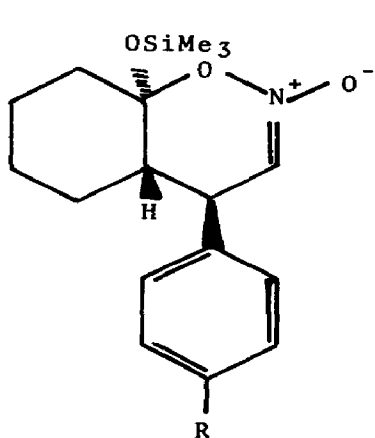
Sharpless and coworkers[312, 313] have demonstrated that  $Ti(OPr^i)_4$  mediates the ring-opening of 2,3-epoxy alcohols and amides with a wide variety of nucleophiles. For example, 3-propyloxiranemethanol reacts under mild conditions with fair to excellent C-3 regioselectivity employing cyanides, halides, thiophenol, selenophenol, thiocyanate, azide, amines, carboxylates, carboxylic acids, *p*-toluenesulfonate anion, and alcohols as nucleophiles[312].

The  $\beta$ -hydroxy esters  $R^1R^2C(OH)CH_2CO_2R$  can be prepared via reaction of ketene  $CH_2=C=O$ ,  $R^1COR^2$  ( $R^1 = Or, Me$ ;  $R^2 = H$ ;  $R^1 = R^2 =$

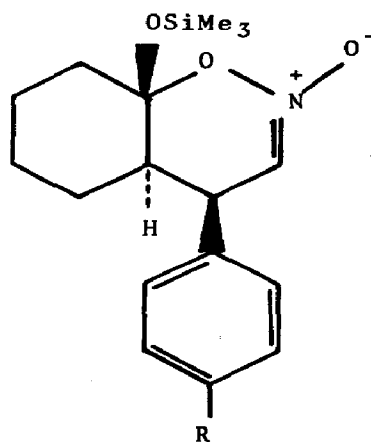


Me), and  $\text{Ti}(\text{OPr}^i)_4$ . Polyinsertion of ketene and aldehyde into the  $\text{Ti}-\text{O}$  bonds leads to the di-, tri- and tetra-esters. The presence of excess ketene gives rise to acetyl derivatives of the esters and 6-alkyl-3,4,5,6-tetrahydro-2,4-pyrandiones[314]. In the presence of  $\text{Ti}(\text{OPr}^i)_4$  acting as a catalyst,  $\text{RSR}'$  ( $\text{R}, \text{R}' = p\text{-MeC}_6\text{H}_4, \text{Me}; \text{Ph}, \text{Me}_3\text{C}; p\text{-ClC}_6\text{H}_4, \text{CH}_2\text{CH}_2\text{OH}; \text{PhCH}_2, \text{Me}$ ) undergoes asymmetric oxidation by tert-butyl hydroperoxide in the presence of (+)-dialkyltartrate to give the chiral sulfoxides  $\text{RSOR}'$  in good yield. An example,  $p\text{-MeC}_6\text{H}_4\text{SMe}$  is oxidized by  $\text{Me}_3\text{COOH}$  in  $\text{ClCH}_2\text{CH}_2\text{Cl}$  at 253K to give a 60% yield of (-)- $p\text{-MeC}_6\text{H}_4\text{SOMe}$  with an enantiomeric excess of 88.3%[315].

Reaction between 1-(trimethylsiloxy)cyclohexene and trans- $p\text{-RC}_6\text{H}_4\text{CH=CHNO}_2$  ( $\text{R} = \text{H}, \text{Me}, \text{MeO}, \text{cyano}$ ) in  $\text{CH}_2\text{Cl}_2$  containing a stoichiometric excess of  $\text{Ti}(\text{OPr}^i)_2\text{Cl}_2$  at 183K yields the isomeric bicyclic nitronates ( $\delta$ ) and ( $\lambda$ ) with relative preferential ul topicity as primary products[316]. This is

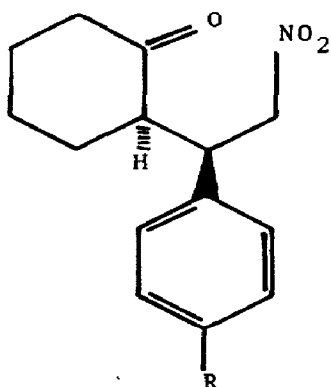


(δ)

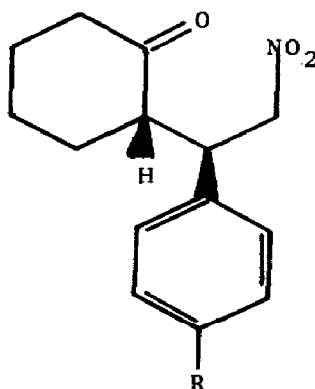


(λ)

opposite to that for the corresponding reactions of enolates or enamines. Upon separation of (8) and (9), followed by cleavage with KF-MeOH, 2:1 - 4:1 mixtures of the cyclohexanones (8) and (9) obtain, having like stereochemical topology. Compound (7) (where

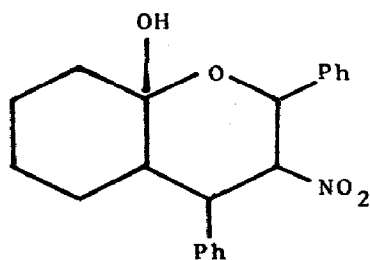


(8)

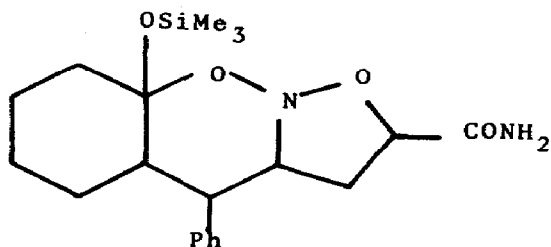


(9)

R = H) additionally yields perhydrobenzopyran (10) via a  $F^-$ -catalysed nitroaldol addition with PhCHO; the cycloadduct (11) is obtained from a [3 + 2]-dipolar cycloaddition to acrylamide. This



(10)



(11)

Michael addition reaction reveals an unlikely stereochemical topicity combination of trigonal centers induced by Lewis acids, which overrides the influence of the donor component configuration [316].

$\text{Ti}(\text{OBu})_4$  reacts with unsaturated alcohols to give  $[\text{Ti}(\text{OBu})_3(\text{OR})]$  ( $\text{R} = \text{CH}_2\text{CH}_2\text{OC}(\text{O})\text{C}(\text{CH}_3)=\text{CH}_2$ , furfuryl,  $\text{CH}_2\text{C}\equiv\text{CH}$ , 2,5-dimethyl-4-(vinylethynyl)-4-piperidyl,  $\text{C}(\text{CH}_3)_2\text{C}\equiv\text{CCH}=\text{CH}_2$ ). The products were characterized by infrared and  $^1\text{H}$  nmr spectroscopies [317]. The electronic structure of  $[\text{pol-Ti}(\text{OBu})_4 + \text{CH}_3\text{OH}]$  has been elucidated by DV- $X_\alpha$  cluster calculations. Substitution of a methoxyl ligand for a butoxyl ligand introduces a characteristic localized state close to the Fermi level; this state may play a crucial role in the photocatalytic decomposition of water [318]. The Russian literature [319] cites the use of  $\text{Ti}(\text{OBu})_4$  as a catalyst in the transesterification of methylacrylate by butyl alcohol. The reaction involves an exchange of alkoxy groups between methylacrylate and  $\text{Ti}(\text{OBu})_4$ , followed by  $\text{Ti}(\text{OBu})_4$  regeneration via alkoxy exchange with butyl alcohol. The activation energy for the reaction remains constant at 21.3 kcal/mol as methylacrylate concentration increases from 0 - 0.05M. At 0.05M methyl acrylate, the activation energy is 24.5 kcal/mol [319].

Foel [320] has described the synthesis of a monomeric 3-methyl-1-penten-3-oxy derivative of titanium,  $\text{Ti}[\text{OC}(\text{C}_2\text{H}_5)(\text{CH}_3)\text{CH}=\text{CH}_2]_4$ , taking place via an alcohol interchange reaction. The complex can also be prepared from the chloride. The complex was characterized by elemental analysis, molecular weight determination, and infrared and  $^1\text{H}$  nmr spectra [320].

Titanium tetrachloride reacts with  $o\text{-ClC}_6\text{H}_4\text{OH}$  in various molar ratios in benzene under different experimental conditions to

yield  $\text{Ti}(\text{OC}_6\text{H}_4\text{Cl})_x\text{Cl}_{4-x}$  ( $x = 1-4$ ) complexes. The compounds possess a dimeric structure with chlorophenoxy groups acting as bridges[321]. The synthesis and x-ray crystal structure of the sterically demanding phenoxide derivatives of titanium,  $\text{Ti}\{O-2,4,6\text{-tert-Bu}_3\text{C}_6\text{H}_2\}_2(\text{NMe}_2)_2$ , have been reported by Jones et al.[322]. The catalytic activity of the  $\text{PhOTiCl}_3\text{-AlEt}_2\text{Cl}$  system for the polymerization of ethylene has been studied; the EPR spectrum shows a signal characterizing the reduction of  $\text{Ti}^{4+}$  to  $\text{Ti}^{3+}$ . Both the activity and the EPR signal increase on increasing the Al/Ti molar ratio to 1.75. However, at a molar ratio  $> 1.75$ , the EPR signal remains constant while the activity of the complexes decreases. The optimum reaction parameters include an Al/Ti molar ratio of 1.5 - 1.85, a reaction temperature of 303 - 313K, reaction times of 15 minutes, and a Ti concentration in the complex of 0.15 - 0.20 molTi/liter[323].

The preparation, and physical and spectral characterization of the  $\beta$ -diketonate complexes  $\text{TiCl}_2\text{L}_2$  (HL = benzoylacetone, dibenzoylmethane, *p*-methoxybenzoylacetone, *p*-chlorobenzoylacetone) have been re-examined by Sun and Ren[324]. These air-stable, water insoluble complexes readily undergo hydrolysis in aqueous organic solvents with the formation of a  $\text{TiO}_2$  precipitate, and exhibit some antitumor properties. The mass spectrum of the dimer of titanyl acetylacetonate has been reported[325] and discussed in terms of the dissociation of odd and even neutral fragments. The intensity of ions arising from the dimer is relatively higher than that from ions due to the polymerization of other metal acetylacetonates in the vapor phase. The  $\beta$ -diketonate complex  $[\text{Ti}(\text{acac})_3]_2\text{TiCl}_6$  (acac = acetylacetonate) has been employed as an oxidation catalyst for cyclohexane in the liquid phase[326]. Poluboyarov and coworkers[327] have carried out ESR studies on the

titanium(3+) complexes formed in the catalytic system  $(\text{Ti}(\text{acac})_2\text{Cl}_2 + \text{Et}_2\text{AlCl})$  for homogeneous polymerization. Also investigated were the changes in coordination state of  $\text{Ti}^{3+}$  upon interaction with ethylene, carbon monoxide, and pyridine. Reaction of substituted o-benzoquinones with  $\text{TiF}_4$  (and  $\text{SnF}_4$ ) yields  $\text{TiF}_3\text{L}$  (and  $\text{SnF}_3\text{L}$ ) ( $\text{HL} = \text{o}$ -semiquinone). ESR results suggest a trigonal bipyramidal structure for  $\text{TiF}_3\text{L}$  in nonpolar solvents, and an octahedral structure in polar solvents for  $\text{TiF}_3\text{LS}$  ( $\text{S} = \text{organic solvent}$ )[328].

Ogino[329] has reviewed the unusually rapid substitution reaction rates of metal(III)-EDTA complexes, where  $\text{M(III)}$  is  $\text{Ti(III)}$ ,  $\text{Cr(III)}$ ,  $\text{Fe(III)}$ ,  $\text{Os(III)}$ , and  $\text{Ru(III)}$ . The rapid rates are probably the result of the mediation of transient seven-coordinate structures in solution. The kinetics of the reduction of  $[\text{Ru}_2(\text{OAc})_2(\text{C}_2\text{O}_4)_2(\text{H}_2\text{O})_2]^-$  by  $\text{Ti(HEDTA)}$  show several distinct stages[330]. The first stage is a substitution reaction giving rise to a multinuclear intermediate. The second stage involves a rate-limiting electron transfer reaction within the assembled multinuclear complex. Subsequent slower stages correspond to the breakup of the multinuclear  $\text{Ru(II)}_2\text{—Ti(IV)}$  complex formed by electron transfer[330].

Rodriguez and coworkers[331] have prepared and characterized (infrared and  $^1\text{H}$  nmr spectroscopies) the cis- $\text{TiCl}_4(\text{HL})_2$  complexes ( $\text{HL} = \text{RC}_6\text{C}_4\text{CH}=\text{NC}_6\text{H}_4\text{OH-}\underline{\text{o}}$ ;  $\text{R} = \text{H}$ , 2-Cl, 4-Cl, 2-OMe, 4-OMe, 4-Me, 4- $\text{NO}_2$ ). The ligands appear to be monodentate and bonded to Ti through the phenolic oxygen atom. Good yields of high-purity  $\text{TiO}(\text{HL})_2 \cdot 2\text{H}_2\text{O}$  ( $\text{H}_2\text{L} = \text{L-ascorbic acid}$ ) have been obtained[332].

Octahedral  $\text{TiX}_4\text{L}$  ( $\text{L} = \text{dithiooxamide}$ ;  $\text{X} = \text{Cl}$ ,  $\text{Br}$ ) complexes can be prepared via addition of  $\text{L}$  in  $\text{CH}_2\text{Cl}_2$  to  $\text{TiX}_4$  under dry and inert conditions. Electronic, infrared and UV spectra, and

conductivity data indicate coordination through the S atom of the C-S group[333]. The same authors[334] have prepared  $TiX_4 \cdot TEDTO$  ( $TEDTO$  = tetraethyldithiooxamide;  $X = Br, Cl$ ) by a similar reaction. Spectral characterization (electronic, infrared, UV) and conductivity data indicate coordination via the thiocarbonyl S atom, with the most likely structure being octahedral with the  $TEDTO$  ligand in the cis position[334]. The preparation and characterization of  $TiL_4$  ( $HL$  = 5-aminoindazolyl dithiocarbamic acid) was reported by Kureshy et al.[335]. The infrared spectral results were interpreted in terms of octahedral structures in which two of the dithiocarbamate moieties are bound symmetrically and two others are bound unsymmetrically to the metal ion.

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