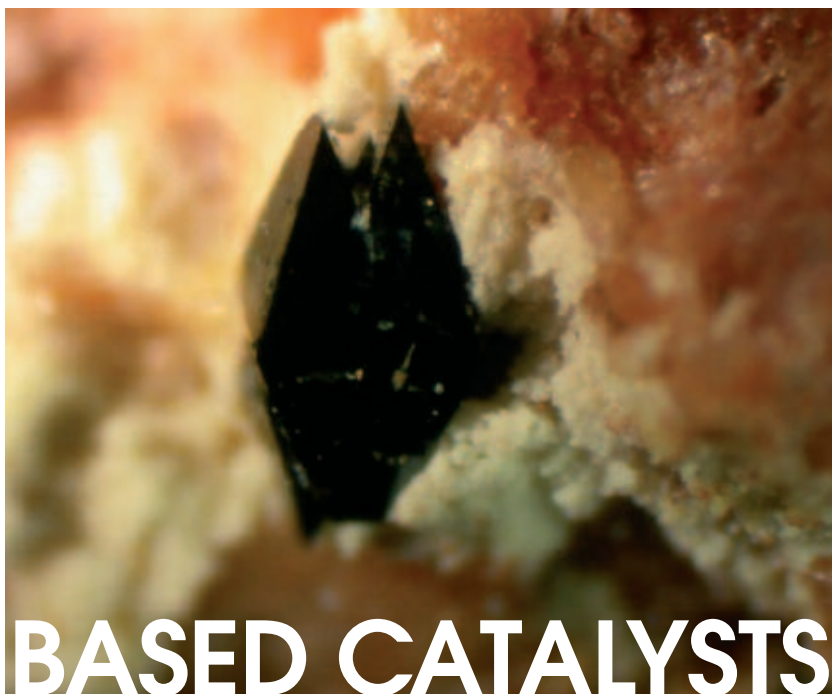*Mariangela Cozzolino, Riccardo Tesser, Martino Di Serio*
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TiO$_2$/SiO$_2$ BASED CATALYSTS

The aim of this contribution is to provide a picture of the state of the art
about the silica-supported titania (TiO$_2$/SiO$_2$) catalysts to clarify the structure-property relationships.

Titania-silica, including both mixed and supported oxides, represents a class of materials that have attracted much attention in recent years. These solids have extensively been used as efficient catalysts and supports in a wide variety of reactions, such as: selective oxidations [1] and epoxidations of olefins with alkyl hydro-peroxide [2], isomerization [3], dehydration [4], esterification and transesterification reactions [5-7]. In the last decades, a large volume of literature has been generated on titanium-substituted zeolites in the framework, including TS-1 [8], Ti-β [9], Ti-incorporated ordered mesoporous silica [10, 11] and amorphous xerogels. Despite good activity with alkyl hydroperoxides in epoxidation reactions [1, 2], the catalytic performances of most the solids mentioned above with hydrogen peroxide appeared far from that of TS-1, whose catalytic performance resulted superior to titania-silica mixed catalysts but limited sterically to relatively small reactants.

Devoted to prof. Elio Santacesaria in honour of his 65th birthday and of his constant contribution to innovative new processes development in industrial chemistry.

To overcome this drawback, new catalytic systems, based on zeolitic or amorphous materials (Ti-MCM-41 [12], Ti-MCM-48 [13], Ti-HMS [14] and Ti-MSU [15]), were developed. However, their catalytic activity was quite small as compared to that shown by TS-1 and Ti-β-zeolites. So, alternative approaches were developed for the covalent attachment of Ti species onto the mesoporous silica surface.

In the last years, the utility and applications of supported metal oxides on silica substrates have attracted growing interest towards the production of highly dispersed catalysts [16-19].

An interesting example is given by supported titania on silica catalysts (TiO$_2$/SiO$_2$), which have been considered as advanced support materials as substitutes for pure TiO$_2$. The higher mechanical strength, thermal stability and specific surface area of the supported titania oxides, respect to TiO$_2$, have attracted much attention and driven the interest towards the use of these materials not only as catalytic supports, but also as catalysts through the generation of new catalytic active sites [2-7]. In general, the applications of titania/silica materials as catalysts and supports fall into three categories based on their unique physico-chemical properties [20]: (i)

photocatalysis that is associated with the support effect and the quantum-size of the particles; (ii) acid and/or oxidation catalysis that are related to the generation of new acid sites due to the interaction of SiO_2 with TiO_2; and (iii) excellent catalytic support materials that possess enhanced thermal and mechanical stability due to SiO_2 while preserving the catalytic performance of TiO_2. A recent review, proposed by X. Gao and I.E. Wachs [20], focused on the investigation and development of amorphous titania-silica mixed oxides as catalysts, attributing special emphasis on the structural characterization and establishment of the relationships between the structural characteristics and the reactivity properties. A comparison with the structural properties of the supported titania/silica oxides has also been reported.

However, despite the large number of papers devoted to the amorphous mixed TiO_2-SiO_2 oxides, only few attention has been paid to investigate the molecular structure of the supported Ti-sites onto silica and its influence on their catalytic behaviour.

In the present paper, recent results about the preparation, characterization and catalytic studies of silica-supported titania (TiO_2/SiO_2) catalysts prepared by using Ti-alkoxides as precursors have been reviewed on the basis of combined results of different preparation/characterization techniques and research-investigations. In this way, we shall try to provide a picture of the state of the art about the supported TiO_2/SiO_2 catalysts to clarify the structure-property relationships. Special emphasis will be attributed to the importance of the influence of the variables involved in the preparation routes on both the surface molecular dispersion and reactivity properties of the supported titanium sites onto silica surface.

Most of the experimental aspects shown in this paper have been for a long time an intense field of research of Prof. Santacesaria's research group.

Preparation of supported titania/silica materials

It is well known that the silica surface is quite inert with respect to the other oxide supports and, consequently, it is quite difficult to reach monolayer dispersion of titanium oxide species on silica, because many factors seem to determine the dispersion capacity of the silica surface. The structure of the surface of silica is characterized by either siloxane groups with the oxygen on the surface ($\equiv$Si-O-Si$\equiv$) or one of three types of hydroxyls: isolated hydroxyls, ($\equiv$SiOH), H-bonded hydroxyls ($\equiv$SiO-H···OH-Si$\equiv$) and geminal hydroxyls (=Si(OH)$_2$) whose relative concentration depends on the calcination temperature as well as on the ambient humidity and storage time [21].
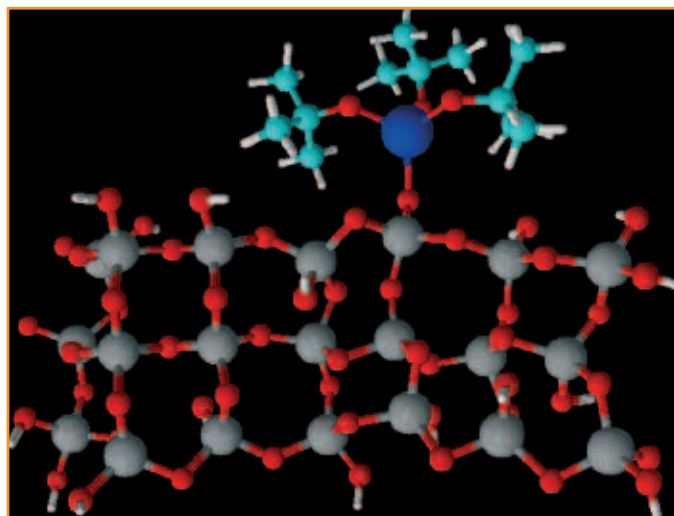

Fig. 1 - Reaction of a Ti-alkoxide molecule with one hydroxyl of silica (grey: silicon; red: oxygen; white: hydrogen; sky-blu: carbon; blu: titanium)

The preparation of highly dispersed metal oxides on silica by impregnation, liquid-phase grafting or chemical vapour deposition methods often involve a highly reactive precursor, such as $TiCl_4$, (Cp_2)$TiCl_2$), or Ti-alkoxides, to react with the surface hydroxyls on silica [22-24]. The titration of the surface hydroxyls with Ti-precursors can be either monofunctional (one Ti-alkoxide molecule titrating one OH group, see Fig. 1) or bifunctional (one Ti-alkoxide molecule titrating two OH groups, see Fig. 2) depending on the pre-treatment temperature, the reaction temperature, and the size and reactivity of the precursor [20].
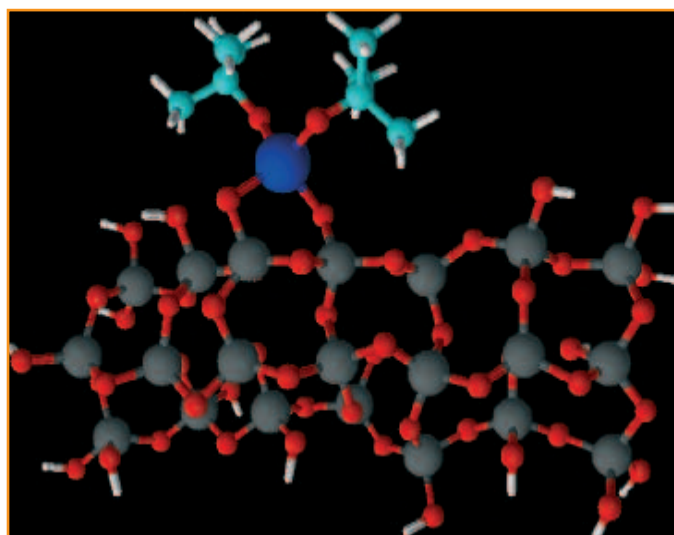

Fig. 2 - Reaction of a Ti- alkoxide molecule with two hydroxyls of silica (grey: silicon; red: oxygen; white: hydrogen; sky-blu: carbon; blu: titanium)

Two types of Ti species, highly dispersed surface TiO_x species and TiO_2 crystallites, may be present on the silica surface, depending on chemical composition, namely TiO_2 loading, and preparation conditions [18, 22, 25-27].

First attempts to prepare TiO_2/SiO_2 oxides were carried out by using the "incipient wetness impregnation" of a silica substrate from a solution of Ti-precursors. According to this procedure, the support is contacted with a solution of appropriate concentration, corresponding in quantity to the total known pore volume of the support, or slightly less. Unlike the "wet impregnation", this method allows a more precise control of the concentration of the active titanium oxide on the support, even if it suffers from the tendency of many metal-based species to agglomerate on the surface of the support during dehydration.

Castillo *et al.* [18] studied the deposition of titanium over silica (GRACE S432, BET surface area of 320 m2/g) by using three methods: (a) precipitation with $TiCl_4$ and ammonium hydroxide in aqueous solution, (b) grafting with Ti (IV) isopropoxide in isopropyl alcohol, and (c) grafting with a solution of $TiCl_4$ in *n*-hexane. They found that the method of preparation influences deeply the morphology and dispersion of the coated oxide. They found that, unlike the impregnation which permits to deposit TiO_2 at the external parts of the silica particles, the grafting method provides the best external superficial dispersion of titania, preventing the formation of crystallites. Anchored titania should form a monolayer on silica and a crystalline phase of rutile or anatase can be observed only for a 15-20% by weight of TiO_2 loading charge, depending on the silica surface [18].

More recently, Gao *et al.* [22] proposed a two-steps impregnation procedure of 2-propanol solution of titanium isopropoxide to prepare highly dispersed TiO_2/SiO_2 samples with loadings higher than 8% by weight of TiO_2. The silica support used was Cabosil EH-5 (S_{BET}=332 m2/g). According to this procedure, the maximum surface coverage of $Ti(O-Pr^i)_4$ precursor was found to be ~4 Ti atoms/nm2. In this way, it is possible to charge onto silica surface high amounts of TiO_2 (~15%wt), preventing the surface agglomeration of the supported Ti-species.

Santacesaria *et al.* [28, 29] obtained in a one grafting step the maximum of TiO_2 grafted, 8% wt and 17% wt, on two different silica of surface area 282 m2/g (Davison Grace S432) and 450 m2/g (Aldrich) respectively, showing the strong importance of silica surface area and the number of hydroxyl on support in the grafting reaction.

Moreover, also the solvent plays an important role as it may contribute to determine the surface structure of the catalytic compo-

nent. From scrutiny of the literature, it is evident that no systematic studies have been made on the influence of the solvent employed in the preparation of titanium-supported silica catalysts in the chemical environment of titanium.

Capel-Sanchez *et al.* [30] have recently addressed the attention to the role played by the solvent in the chemical environment of titanium, trying to understand the relationships with its performance in the epoxidation of primary alkenes with hydrogen peroxide. The samples were prepared by dispersing titanium isopropoxide (0.75 g) in an organic solvent (cyclohexanol, 1-phenylethanol, 1-hexanol, 2-(2-ethoxyethoxy)ethanol, diglyme, and acetophenone) and then mixing the solution with the silica substrate. These solvents were selected in order to obtain quite different affinities between the Ti-isopropoxide precursor and the solvent, and therefore to determine hydrolysis rates of this precursor with the hydroxyl groups of the silica. One large difference observed was the amount of titanium incorporated to the silica substrate. The highest Ti loading (see Fig. 3) was achieved using acetophenone and diglyme solvents, but lower with alcohols. The alcohol groups of the solvent can react with grafted species lowering their concentration on the surface because grafting reaction is an equilibrium reaction.

The influence of the solvent on the amount of the supported titanium was also analysed by Santacesaria *et al.* in several papers [7, 28-30]. They investigated the preparation of TiO_2/SiO_2 catalysts by contacting titanium tetra-isopropoxide with different solvents, such as: isopropanol, dioxane and toluene, followed by the *grafting* of the Ti-precursor molecules onto SiO_2 surface. They found that the amount of the titanium supported onto silica surface decreases
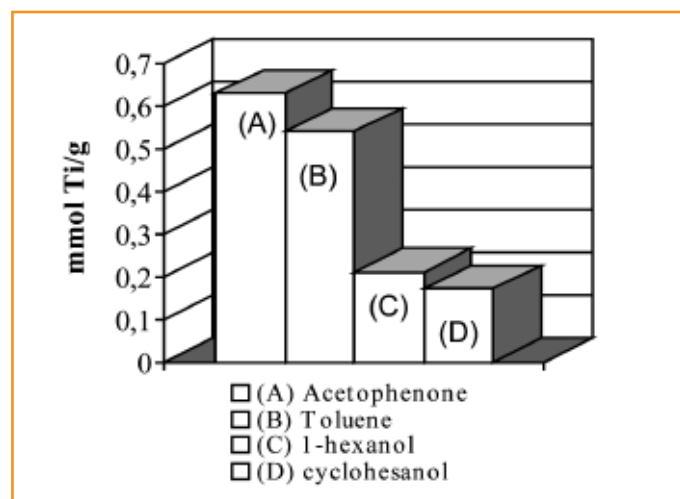

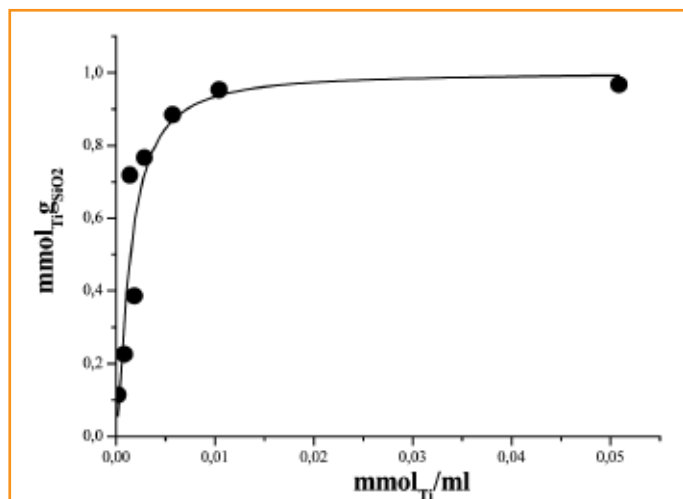Fig. 3 - Influence of the solvent on the amount of titanium supported onto silica surface from [31]

Fig. 4 - Adsorption isotherm of titanium tetra-isopropoxide grafted onto SiO$_2$ (data from ref. [29])

with the hydrophilic character of the solvent, while an almost quantitative *grafting* yield is obtained by dispersing the titanium precursor in toluene.

In particular, Santacesaria *et al.* [29] studied the grafting adsorption behaviour of titanium tetra-isopropoxide (Ti(O-Pr^i)$_4$) on the support (GRACE Davison, S432) by contacting solutions of increasing concentrations of the mentioned alkoxide, dissolved in dioxane, with a given amount of silica. This approach allowed to study the chemical adsorption until the surface saturation, by using the isotherm obtained, depicted in Fig. 4, as well as the surface monolayer coverage of the Ti(O-Pr^i)$_4$. As can be seen from Fig. 4, the obtained adsorption isotherm, can be interpreted as a Langmuir isotherm in line with the following relation:

$$K=(1/C^{eq})/(\Gamma^{\infty}/\Gamma^{\infty}-\Gamma^{eq}) \qquad (1)$$

By regression analysis experimental points can be well fitted by using the following values of the parameters: $K = 710.89$ [L/mol] e $\Gamma^{\infty}= 1.02$ mmolTi/gSiO$_2$. From the latter value, it is easy to deduce that the titanium alkoxide adsorbed monolayer corresponds to about 8.14% wt TiO$_2$. This value is in a close agreement with the findings of Gao *et al.* [22], giving 8.10% wt TiO$_2$ for the TiO$_2$ monolayer on silica. Moreover, as the hydroxyls density on the silica surface is 0.92 mmol$_{OH}$/g SiO$_2$ [29], by comparing this value with the mmol of titanium anchored on the surface, a stoichiometry of about 1 hydroxyl per Ti atom can be deduced. Another important observation is the strong affinity of titanium alkoxide with the silica surface, showed by the steep rise in the initial part of the adsorption isotherm. The present results [29] suggest

that the reactivity of the surface hydroxyl groups and the specific surface area of the silica determine the maximum surface coverage of an organometallic precursor for a one-step grafting. In the current preparation, the maximum surface coverage of the Ti(O-Pr^i)$_4$ precursor in a one-step grafting was found to be ~2.2 Ti atoms/nm^2, which is similar to the maximum trimethylsilyl (TMS) surface coverage of 2.2-2.7 groups/nm^2 [22]. However, after calcination step some of Si-OH groups become reexposed and can further react with more Ti(O-Pr^i)$_4$ precursor molecules. Thus, a higher loading of TiO$_2$ (20-26% wt TiO$_2$), which correspond to ~4-6 Ti atoms/nm^2, is reached by employing three grafting steps [28, 29]. Thus, it appears well evident that the dispersion capacity is closely related to the surface properties of the silica support, mainly to the concentration of the hydroxyl groups and the specific surface area of the starting support, and the preparation conditions (e.g., the pretreatment temperature, the grafting reaction/impregnation time, the reactivity and molecular size of the precursor).

Surface structures of TiO$_2$/SiO$_2$ catalysts

In the last years, the number of research articles devoted to the characterization of supported metal oxides has been growth in literature, mainly due to the combined use of in-situ Raman, UV-vis-NIR DRS and XANES spectroscopies, which resulted very informative to understand the surface structure of molecularly dispersed supported TiO$_2$/SiO$_2$ oxides under various conditions.

The structure of the Ti cations in supported TiO$_2$/SiO$_2$ oxides has extensively been investigated by means of X-ray diffraction analysis [7, 18, 30, 32]. In most of cases, it was revealed that the titanium phase was not observed by XRD below 8% wt of TiO$_2$ (~2 Ti atoms/nm^2) for TiO$_2$/SiO$_2$ prepared by impregnation and below 15% by weight of TiO$_2$ (~4 Ti atoms/nm^2) for the grafted ones. Weak XRD peaks of anatase were detected at higher loadings. However, the absence of lines from the crystalline phase in XRD patterns related to the samples at low Ti loading does not necessary rule out the presence of small particles on the surface of the investigated samples. In general, XRD analyses reported in literature confirmed, from a qualitative point of view, the higher titanium dispersion that can be obtained by using the alkoxide *grafting* method than the impregnation. At this purpose, several studies have been reported by several authors [7, 18, 28-30].

In a recent work, Cozzolino *et al.* [30] showed that the charging on SiO$_2$ of increasing quantities of TiO$_2$, by repeating more times the grafting operation of titanium alkoxide onto high-surface silica, do not give place to the formation of TiO$_2$ crystalline phase (Fig. 5).

The possibility to prepare dispersed TiO_2/SiO_2 multilayers by titanium alkoxide grafting on the silica substrate was also investigated by TEM micrographs, which showed the absence of well-defined crystalline TiO_2-phase on the surface of the support [30].

The formation of Ti-O-Si bridging bonds as consequence of the deposition of Ti species on the SiO_2 surface has thoroughly been investigated by using combined in-situ Raman, UV-vis-NIR DRS and XANES spectroscopies. It was found that the surface structure of TiO_x species on silica is a strong function of environmental conditions as well as the TiO_2 loading [20, 22].

In the dehydrated state, for a low loading of TiO_2 (1% wt), the sur-
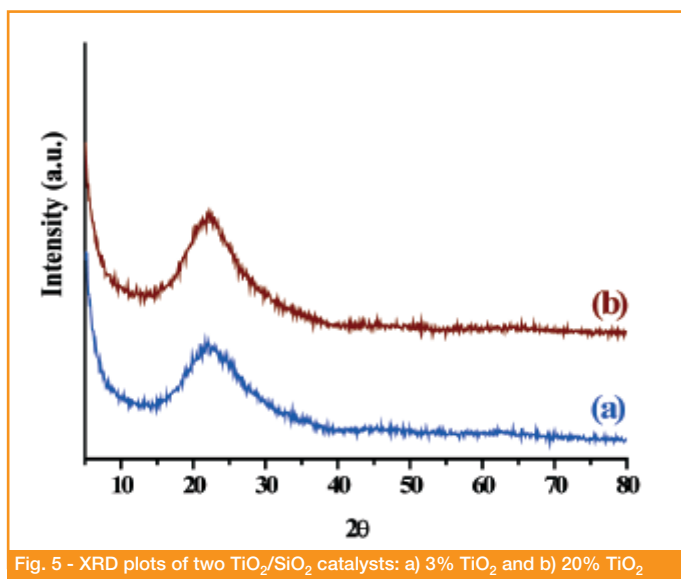

Fig. 5 - XRD plots of two TiO_2/SiO_2 catalysts: a) 3% TiO_2 and b) 20% TiO_2

face Ti atoms are predominantly located at isolated TiO_4 sites (the LMCT band ~47,600 cm^{-1}); while at a medium loading of 5%wt TiO_2, the silica surface may possess a higher amount of TiO_4 dimer or one-dimensional polymerized TiO_4 species; for higher Ti loadings (~4 Ti atoms/nm^2), two-dimensional, polymerized TiO_5 units are predominantly present on the silica surface [20, 22]. Upon hydration, some of the Ti-O-Si bridging bonds on these molecularly dispersed TiO_2/SiO_2 samples are hydrolyzed by H_2O molecules, which results in an increase in the average coordination number of the Ti cations by about 1, as indicated by XANES. Hydration also decreases the edge energies of the LMTC transitions of the higher loading samples of 5% and 17% TiO_2/SiO_2, suggesting an increase in the total number of Ti-O-Ti bonds [20, 22].

Pronounced structural changes upon hydration were also provided by Raman analyses [22]. A Raman band appears at 940-960

cm^{-1}, which is most likely due to the Ti perturbed Si-OH. This is due to the adsorption of water that breaks the Ti-O-Si bridging bonds, resulting in the formation of Ti-OH hydroxyls as well as the Ti perturbed Si-OH.

Experimental evidences about the formation of the Ti-O-Si bridging bonds as consequence of the interaction between TiO_2 and SiO_2 come also from XPS surface analyse [7]. The blue shift of both O 1s and Ti $2p_{3/2}$ BE values of the TiO_2/SiO_2 catalysts with respect to pure TiO_2 could be associated with the formation of Ti-O-Si bonds, which results in an increase in the effective positive charge on Ti and a decrease in the effective negative charge on O since the Si atoms are more electronegative less polarisable than the Ti atoms [20, 22].

The higher positive charge on titanium is also indicative of the presence of Lewis acid sites [28].

The dispersion of TiO_2 on SiO_2 can be evaluated by the variation of the intensity ratios as a function of loading. The variation of the intensity ratios, I(Ti)/I(Si), as a function of the atomic composition nTi/nSi is presented in Fig. 6 for two silica (Davison Grace S432 S_{BET}=282 m^2/g [29]; Aldrich, S_{BET}=450 m^2/g [28]). In the same figure the calculated values obtained by the model proposed by Kerkhof and Moulijn [33] for a monolayer film are also reported.

The agreement between experimental and calculated values are indicative of a homogeneous distribution of the grafted species with monoatomic thickness. The lower values observed for all the other samples indicated an aggregation of titanium species onto the surface. As can be seen, on silica with lower surface area the monoatomic dispersion is achieved for a titanium loading lower than silica with higher surface area.

IR spectroscopy also provides interesting information about the formation of Ti-O-Si bonds in a simple way. The IR band observed at 910-960 cm^{-1} is widely accepted as the characteristic vibration due to the formation of Ti-O-Si bonds [34-42], whose position depends on the chemical composition of the sample as well as the instrument calibration. The intensity of this IR band, compared to that due to Si-O-Si at ca. 1,210 cm^{-1}, has been used as reference to evaluate the surface titanium dispersion [20, 22, 30].

In a recent work, Cozzolino *et al.* [30] have provided a semi-quantitative estimation of the surface dispersion of the supported titanium by using IR spectroscopy, for a series of TiO_2/SiO_2 catalysts, prepared by grafting increasing quantities of titanium alkoxide, dissolved in dioxane, on SiO_2 ((Davison Grace S432 S_{BET}=282 m^2/g). This was made by reporting the $A_{(Si-O-Ti)}/A_{(Si-O-Si)}$ ratio is reported as function of molar ratio n_{Ti}/n_{Si}. No linear increase of the ratio of

areas with the molar ratio n_{Ti}/n_{Si} was observed (see Fig. 7). This indicated that the surface dispersion slightly decreases by increasing the titanium loading, as consequence of calcination treatment that gives place to a moderate aggregation of the grafted species. The unitary dispersion has been obtained for a Titanium loading less than 0.02 n_{Ti}/n_{Si}, this value is in agreement with the data obtained with XPS (see Fig. 6).

A confirmation of the significant modification of the silica surface by the supported titanium oxide surface species was also obtained by Raman spectroscopy. A detailed investigation of the influence of Ti content on the final surface properties of the TiO_2/SiO_2 catalysts has been given by Cozzolino et al. [7]. With respect to the typical Raman signals of the silica support reported at ~410, 487, 607, 802 and ~976 cm^{-1}, they also detected two new Raman bands at ~915 and 1,111 cm^{-1}. These bands were assigned to silica vibrations perturbed by the presence of Ti, which are indicative of the formation of Ti-O-Si bridging bonds [38, 43]. The latter value (1,111 cm^{-1}) is very close to the one (1,115 cm^{-1}) detected in Ti-silicalites. These results suggested that the average coordination of Ti cations on the silica surface in the case of TiO_2/SiO_2 samples prepared by Grafting is comparable with that detected in the Ti silicalite framework. Moreover, no Raman bands due to TiO_2 crystallites (anatase) were observed in any case.

Catalytic performances of TiO_2/SiO_2 oxides

It is well known that the catalytic performances of titanium oxide appear to be completely modified by the interaction with the silica
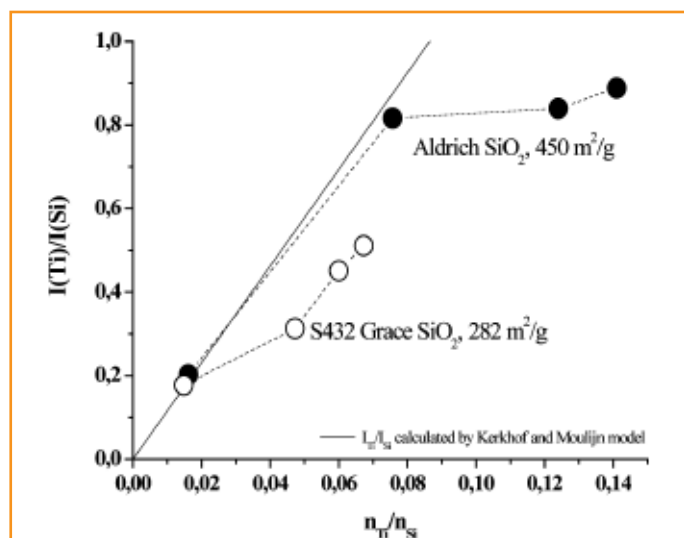

Fig. 7 - $A_{(Si-O-Ti)}/A_{(Si-O-Si)}$ as function of molar composition (n_{Ti}/n_{Si}) (data from ref [30])

Fig. 6 - XPS intensity ratios vs. n_{Ti}/n_{Si} ratio (data from ref. [28, 29])

support, which is associated to the changes in the molecular structure and coordination environment. With respect to pure TiO_2, the surface of the molecularly dispersed TiO_2/SiO_2 oxides is mainly characterized by the presence of redox sites as well as a low amount of acidic sites.

The peculiar catalytic performance of the highly dispersed TiO_2/SiO_2 catalysts in comparison with TiO_2 crystallites was early demonstrated by Sheldon for liquid-phase olefins epoxidation reactions with hydrogen peroxide and alkyl hydroperoxide [44, 45]. The pure TiO_2 phase is not active for the epoxidation reaction, while the highly dispersed TiO_2/SiO_2 catalysts exhibit high reactivity and high selectivity to epoxide [45]. Sheldon suggested that the active sites are the isolated monomeric titanyl $(SiO)_2Ti=O$ bonds on the silica surface. However, no experimental evidence has been found for this type of species. A recent work of Thomas and co-workers [46] investigated the catalytic performances of TiO_2/SiO_2, prepared by grafting Ti (IV) on the internal surface of MCM-41 by reaction of $((Cp_2)TiCl_2)$ and subsequent calcination. These materials showed a higher activity in epoxidation of olefins in the presence of tert-butyl-hydroperoxide (TBHP) than hydrothermally synthesized Ti-MCM-41 materials [47]. XANES/XAFS studies demonstrated that all Ti atoms are isolated and located on the wall of MCM-41 mesopores. This characterization study suggested that the surface active Ti centers on TiO_2/SiO_2 supported oxides for epoxidation reactions might also be isolated TiO_4 units instead of $(SiO)_2Ti=O$ species.

The catalytic properties of highly dispersed TiO_2/SiO_2 supported oxides in the epoxidation reaction of cyclooctene with cumene

hydroperoxide have recently been investigated by Cozzolino *et al.* [31]. The authors found the catalytic activity of epoxidation reaction of cyclooctene on the highly dispersed TiO_2/SiO_2 supported oxides a strong function of TiO_2 loading. In particular, they observed an increase of both activity and selectivity by increasing TiO_2 loading until to reach the surface monolayer coating (~8% wt TiO_2), and then a decreasing by depositing on the silica surface a greater amount of TiO_2. This catalytic behaviour was attributed to the structural characteristics of the surface-supported Ti species. As suggested by DR-UV analyses [30], at low Ti coverage, the surface of TiO_2/SiO_2 supported oxides is mainly characterized by isolated titanium sites in tetrahedrical coordination, which correspond to the active species in olefins epoxidation reactions. By further increasing the TiO_2 loading by repeating more times the grafting operation of titanium alkoxide on the surface of silica, an increase of the polymerization degree of Ti species occurs, giving place to a large amount of polymerized Ti-sites on SiO_2, which showed much lower activity in olefins epoxidation reaction. This study revealed that two requirements are fundamental to obtain good catalytic performances, such as: high dispersion of the catalytically active component within the matrix (site isolation) and high supported metal-species stability in order to prevent leaching phenomena [2, 46, 48].

This aspect was particularly emphasized by Capel-Sanchez *et al.* [31] which highlighted the importance of using cyclohexanol in the synthesis of Ti/SiO_2 solids in order to obtain highly effective epoxidation catalysts. The using of cyclohexanol favours selective hydrolysis of the titanium precursor mainly on the H-bridging hydroxyl groups of the silica, resulting in isolated titanium species. An in-dept discussion about the strong impact of the structural characteristics on catalytic properties of the molecularly dispersed TiO_2/SiO_2 in methanol oxidation, widely used as "probe-reaction" to evaluate the nature of Ti-sites, has been reported by Gao and co-workers [22]. With respect to pure TiO_2 crystallites, they found that the molecularly dispersed TiO_2/SiO_2 catalysts are much more active for methanol oxidation and are highly selective to the redox products.

The increased oxidizing potential of the Ti(IV) cations, due to the formation of Ti-O-Si bridging bonds, are in relation with the exper-imentally detected increased BE values of Ti $2p_{3/2}$ and O1s and the higher LMCT transitions of the Ti atoms in the molecularly dispersed TiO_2/SiO_2 catalysts described above [22].

In addition, it is important to point out that, with respect to pure TiO_2-phase which possesses only strong Lewis acidic sites, the highly dispersed TiO_2/SiO_2 catalysts show lower acidity in terms of both density and strength [7]. The acid sites present on the surface of TiO_2/SiO_2 solids may catalyze the transesterification of triglycerides to produce biodiesel [7, 49]. Also in this case, it was found that the catalytic activities increase until the monolayer surface coverage, then decrease [7].

A recent investigation of the surface acidity of TiO_2/SiO_2 supported oxides by means of FT-IR spectroscopy of adsorbed probe molecules, CO and NH_3, has been reported by Bonelli *et al.* [50]. This study strongly suggested that the interaction between titania and silica in silica-supported titania catalysts gives place to supported Ti^{4+} sites, characterized by a weaker Lewis acidity than on pure TiO_2. Two kinds of Lewis acid sites, differing in the electrophilic properties of the respective Ti^{4+} cations, were detected: a) isolated Ti^{4+} sites (2,177-2,173 cm^{-1}) mainly at low Ti loading and b) "associated" Ti^{4+} sites (2,194-2,183 cm^{-1}). It is possible to attribute the decrease of the yield-values, observed by grafting TiO_2 amounts higher than surface monolayer coverage (~8%wt TiO_2), to the disappearance of the isolated sites onto the surface of catalysts. This effect appeared more pronounced for the catalysts with high TiO_2 loading (~20% wt TiO_2), whose FTIR normalized spectra of adsorbed CO showed a larger concentration of "associated" sites with respect to the solids with smaller amount of supported titania. Moreover, FTIR measurements of NH_3 adsorbed evidenced for these catalysts an increase of Brønsted acid sites, assigned to the increase of Ti-OH groups with respect to the silica support, as consequence of grafting reaction of titanium isopropoxide.

According to these characterizations, lower activities in the transesterification reaction were found for the mentioned solids and lower activity and selectivity in epoxidation reaction [7].

Conclusions

The insights achieved in this work, on the basis of the most recent results reported in the literature, highlighted that several factors

Catalizzatori a base di TiO$_2$/SiO$_2$ RIASSUNTO

Il presente contributo riporta i recenti risultati riguardo la preparazione, caratterizzazione e le prestazioni catalitiche dei catalizzatori costituiti da biossido di titanio supportato su silice (TiO$_2$/SiO$_2$). Lo scopo principale è quello di dare una visione dello stato dell'arte riguardo i catalizzatori TiO$_2$/SiO$_2$ per chiarire le relazioni esistenti tra la struttura e le proprietà catalitiche.

may be critical in controlling the dispersion capacity of surface titanium oxide species on silica: the concentration of the hydroxyl groups and the specific surface area of the starting support, and the preparation conditions (e.g., the pretreatment temperature, the grafting reaction/impregnation time, the solvent used, the reactivity and molecular size of the precursor). It appears to be evident the higher are the hydroxyl concentration and the specific surface area of silica, the higher is the surface dispersion of the supported Ti-species. The combined results from all the characterization techniques investigated allow to suggest that the molecularly dispersed TiO_2/SiO_2 catalysts possess predominantly isolated TiO_4

species until to the monolayer surface coverage of the precursor molecules, which corresponds to ~2 Ti atoms/nm^2 by employing a one-step grafting procedure of $Ti(O-Pr^i)_4$ on SiO_2. The reactivity properties of the TiO_2/SiO_2 catalysts are a strong function of the structural characteristics as the reactivities of epoxidation/oxidation reactions have been related to the exposed isolated TiO_4 sites as well as the fraction of Ti-O-Si bonds.

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