Available online at www.sciencedirect.com

ELSEVIER

Catalysis Today 116 (2006) 99–110

CATALYSIS TODAY

www.elsevier.com/locate/cattod

Which sites are the active sites in TiO_2–SiO_2 mixed oxides?

Bruno Notari [a], Ronald J. Willey [a,*], Marta Panizza [b], Guido Busca [b]

[a] Department of Chemical Engineering, Northeastern University, Boston, MA 02115, USA
[b] Dipartimento di Ingegneria Chimica e di Processo, Universita' di Genova, P.le Kennedy, I-16129 Genova, Italy

Abstract

TiO_2–SiO_2 mixed oxides are very important industrial materials and catalysts. They have found several industrial applications and attracted great interest in academic and industrial research laboratories. While significant progress has been made in the understanding of their properties, the mechanism of their catalytic action is still debated. We summarize the past and recent literature on the subject. Tanabe (1974, 1981) has attributed the catalytic activity to the formation of Brønsted acidity, and his proposal has been supported by a number of reports even recently. On the other hand, our work has provided evidence that high purity TiO_2–SiO_2 mixed oxides DO NOT have Brønsted acidity. When used as catalysts for the isomerization of 1-butene, the reaction products consist of linear butenes only, with no skeletal isomerization nor other products typical of acid catalysis. Pure TiO_2 has high catalytic activity and gives the same reaction products. The discrepancy with previous results is very likely due in some instances to the presence of acid-inducing impurities in materials used in early works and in others to the fact that methods used to detect Brønsted acidity, reliable with certain solids, give erroneous results with others. A reexamination of these methods is strongly recommended. Finally many studies relied on the low temperature catalytic activity in 1-butene isomerization to linear butenes, overlooking the fact that only skeletal isomerization is the real proof of Brønsted acidity.

Keywords: Acidity; 1-Butene; Isomerization; Titanium dioxide; Silica

1. Introduction

Correlation of catalytic performances with some critical property of solid catalysts has long been a desired goal in heterogeneous catalysis. Once these properties are identified, attempts for improving the catalytic performances through their modification can proceed through a rational process rather than at random. This "catalysts by design" approach has been very successful in the past for the improvement of many catalysts.

This sequence of events took place after the discovery of the catalytic properties of TiO_2–SiO_2 mixed oxides in several reactions, isomerization of olefins [1], epoxidation of olefins with hydroperoxides [2] and the selective oxidation of a number of organic compounds by crystalline titanium silicalite-1 or TS-1 [3].

TiO_2 and SiO_2 form a large number of different materials, in both the amorphous and crystalline phases. The materials have been described in many articles and review papers. The most informative are: Tanabe [4], Bellussi and Rigutto [5], Notari [3], Vayssilov [6], Saxton [7], Sheldon et al. [8], Dusi et al. [9], Ratnasamy et al. [10].

In 1974 Itoh et al. [1] reported on the catalytic activity of TiO_2–SiO_2 mixed oxides for some reactions such as 1-butene isomerization, phenol amination, and ethylene hydration. The catalytic activity was attributed to the formation of Brønsted acidity.

In 1975 Wulff [2] discovered that TiO_2 deposited on SiO_2 acts as a highly selective catalyst for the epoxidation of olefins. This catalyst, perfected during many years of industrial application, is currently used in the Shell industrial process for the production of propylene oxide and uses ethylbenzene hydroperoxide as the oxidant.

In 1983 Taramasso et al. [11] discovered a new Ti-containing crystalline material, titanium silicalite-1 (TS-1) in which Ti substitutes for Si in the framework of the crystalline silicalite-1. TS-1 catalyzes the selective oxidation of a large number of organic compounds by H_2O_2. Selectivities of 90% in the use of H_2O_2 and 85% or more in organic products are obtained. The economical and ecological advantages of having high selectivities and only H_2O as a byproduct are remarkable.

---

* Corresponding author. Tel.: +1 617 373 3962.
E-mail address: r.willey@neu.edu (R.J. Willey).

0920-5861/$ – see front matter © 2006 Elsevier B.V. All rights reserved.
doi:10.1016/j.cattod.2006.02.086

This discovery was rapidly put to industrial use by Enichem in two important applications: (1) the production of hydroquinone and catechol from hydrogen peroxide and phenol in a 10 kt/y plant built in 1986 in Ravenna, Italy and (2) the production of cyclohexanone oxime from hydrogen peroxide, cyclohexanone and ammonia in a 12 kt/y plant in Marghera, Italy. The same process is being applied by Sumitomo in combination with its own process of rearrangement of the cyclohexanone oxime for the industrial production of caprolactam [12].

Recently DOW, BASF, Krupps Uhde and Degussa announced the development of industrial plants for the production of propylene oxide (PO) from propylene and hydrogen peroxide. The process of DOW–BASF is based on Enichem technology and TS-1 as catalyst [13,14].

The impact of the discovery of TS-1 on the science of catalysis and zeolites has also been remarkable. New research efforts have been directed to the discovery of materials with similar structures in the hope of obtaining even better performances. Many molecular sieves with Ti substituting Si have been synthesized and their chemical, physical and catalytic properties investigated (TS-2, Ti-ZSM-48, Ti-beta, Ti-ZSM-12, RiMCM-41, Ti-HMS, Ti-MCM-48, Ti-MSU, Ti-SBA-15, Ti-MMM, Ti-MWW, Ti-TUD-1 and Ti-NU-1). The search was also extended to the substitution of Si in many of these structures with other elements such as V, Fe, Ta. While many interesting materials have been obtained and described in the literature, TS-1 appears to be the catalyst of choice for industrial applications due to its resistance to aging and its ability to withstand repetitive high temperature regeneration.

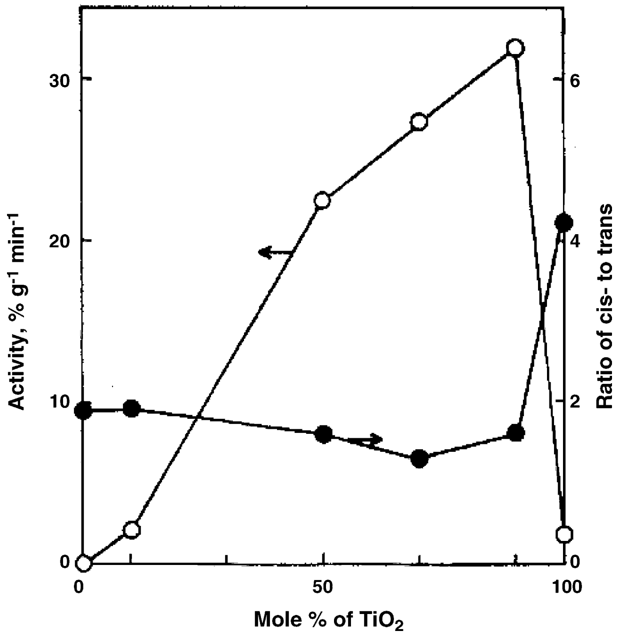

Fig. 1. Isomerization of 1-butene by TiO_2–SiO_2 mixed oxides of different TiO_2 content. Reprinted from [1] with permission of Elsevier.

2. Literature data on Brønsted acidity of TiO_2–SiO_2

While for the oxidation reactions with H_2O_2 there is general consensus now that the active sites are the tetrahedrally coordinated Ti^{4+} isolated in a SiO_2 matrix [10,15], less clear is the source of the activity in the previously mentioned reactions described by Itoh et al., such as the isomerization of 1-butene to *cis*-2-butene and *trans*-2-butene (Fig. 1).

The catalytic activity could not be attributed to the properties of the pure oxides: in fact pure TiO_2 has only Lewis acid properties and the silanol groups Si–OH of SiO_2 are so weakly acidic that the material is generally classified as inert.

In the attempt to find a plausible explanation Tanabe proposed that new Brønsted acid sites are formed upon interaction of TiO_2 and SiO_2 at the molecular level, and extended this proposal formulating a hypothesis that should be able to predict the presence of acidity in mixed oxides in general [4,16,17]. According to his hypothesis, the substitution of a metal ion into the structure of the host oxide follows these rules: (i) all cations maintain the coordination they have in their most stable oxide; (ii) all anions have the coordination they have in the majority component. In the specific case of TiO_2–SiO_2, in the SiO_2 rich region Brønsted acidity would develop while in the TiO_2 rich region Lewis acidity would develop (Fig. 2).

A different hypothesis has been proposed by Seiyama [18]: according to his hypothesis the oxygen bridging between Ti and Si develops a negative charge as a consequence of the different coordination of the two cations, and this charge is neutralized by H^+ originating Brønsted acidity. In this hypothesis Brønsted acidity is predicted regardless of composition, while the extension of the acidity depends on the degree of dispersion and mixing of the two oxides.

In the following years several papers were published in which the experimental results were interpreted as evidence for the presence of Brønsted acidity in TiO_2–SiO_2.

It is necessary to make a distinction between reactions carried out in the presence of H_2O_2 and those in the absence of H_2O_2. Several papers have described secondary reactions attributed to Brønsted acidity in the course of oxidation reactions with H_2O_2 as the oxidant. There is a plausible

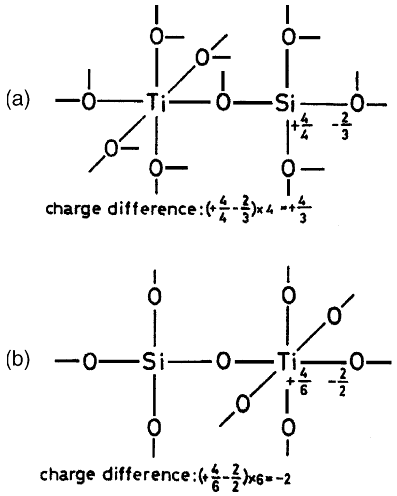

Fig. 2. Brønsted and Lewis acidity in TiO_2–SiO_2 according to Tanabe model. Reproduced from [4] with kind permission of Springer Science and Business Media.

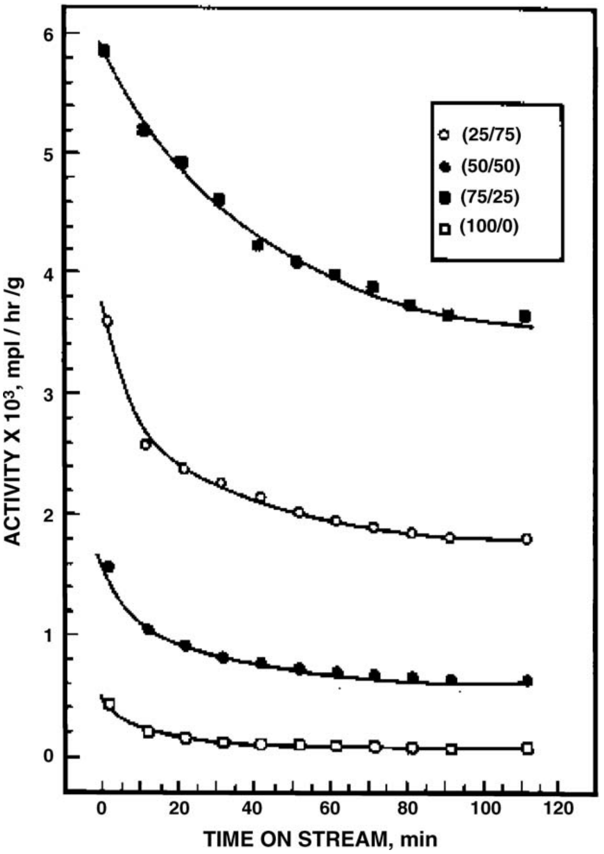

Fig. 3. 1-Butene isomerization on TiO_2 and TiO_2–SiO_2 catalysts. Reprinted from [19] with permission of Elsevier.

explanation for this, the formation of Ti–OOH species which have a Brønsted acid character similar to that of formic acid. The effects are more pronounced when an excess of H_2O_2 is present [5]. Since we are discussing here the intrinsic acidity of the TiO_2–SiO_2 mixed oxides themselves, we will not deal with the induced acidity caused by H_2O_2 and limit the scope of this review to the cases in which Brønsted acidity has been claimed in the absence of H_2O_2.

Ko et al. studied the properties of TiO_2–SiO_2 mixed oxides of different compositions and attributed the catalytic activity to the presence of Brønsted acidity [19] (Fig. 3).

Connell and Dumesic [20] and Kataoka and Dumesic [21] studied the adsorption of pyridine on samples of 1% TiO_2 on Cabot SiO_2 by IR. They reported that Lewis acidity was detected upon evacuation at 420 K. However, when H_2O was admitted, Brønsted acid sites formed as evidenced by the appearance of an absorption band at 1545 cm^{-1} attributed to pyridinium ions being adsorbed on Brønsted acid sites. They also reported that the strength of the acidity appears weak, since evacuation at 420 K decreased the intensity of the 1545 cm^{-1} absorption band. However, on samples reduced in H_2 at 720 K no pyridinium ions were detected, even after H_2O was admitted.

Sohn and Jang [22] studied TiO_2–SiO_2 materials in a wide range of compositions and proposed a correlation between the IR frequency of Si–OH bending vibration and activity for acid catalyzed reactions such as cumene dealkylation and 2-propanol dehydration which are assumed to be acid catalyzed.

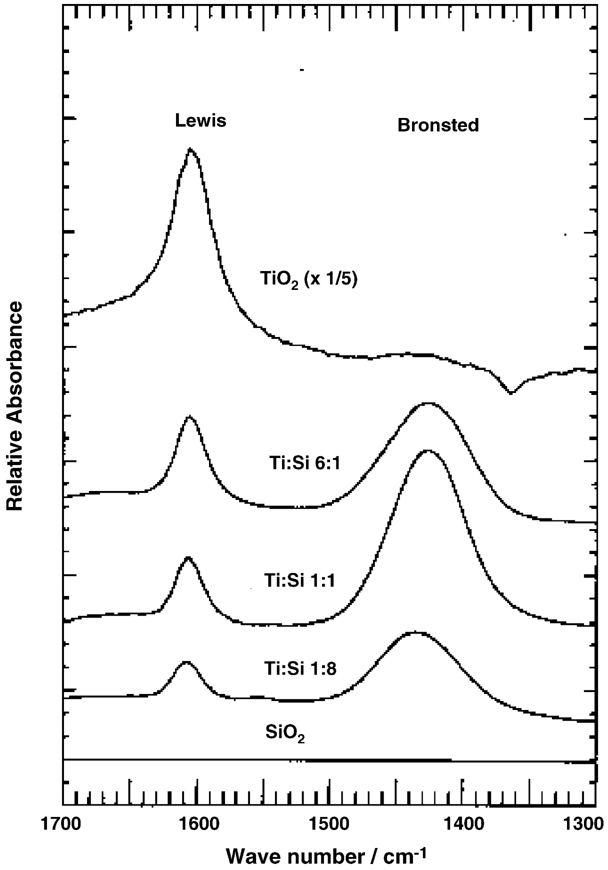

Fig. 4. Evidence of Brønsted acidity on TiO_2–SiO_2 by NH_4^+ ions formation. Reprinted from [23] with permission of Elsevier.

They also detected the formation of pyridinium ions in the IR spectra of adsorbed pyridine and Brønsted acid sites by titration with *n*-butylamine and Hammett indicators.

Liu et al. [23] reported that when NH_3 is adsorbed on TiO_2–SiO_2, NH_4^+ ions are formed, which they attributed to Brønsted acidity. No evidence of NH_4^+ ions was found on pure TiO_2 or SiO_2 (Fig. 4).

Doolin et al. [24] investigated the properties of TiO_2–SiO_2 by the rate of CH_3OH dehydration, and by thermogravimetry/IR absorption of pyridine. Both these methods were assumed to

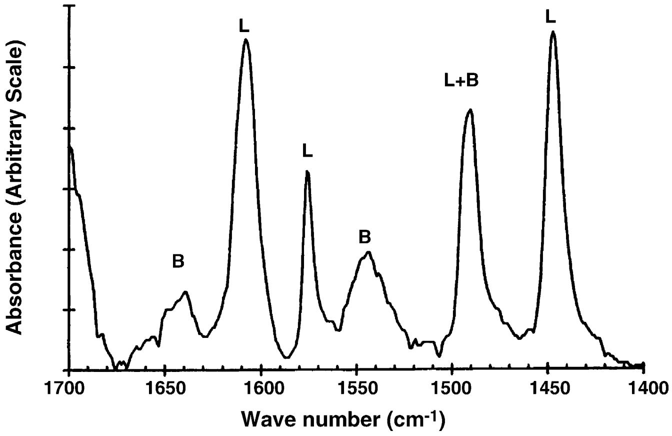

Fig. 5. Brønsted and Lewis acidity in TiO_2–SiO_2 by IR pyridine band.

measure Brønsted acidity. They reported that Brønsted acidity is present in TiO_2–SiO_2 with maximum values in compositions having a molar ratio TiO_2:SiO_2 of 9:1 because materials with these compositions had a maximum value of CH_3OH dehydration and IR pyridinium band intensity (Fig. 5). They also reported that pure TiO_2 has a significant catalytic activity for the CH_3OH dehydration reaction.

Liu et al. [23] also studied the isomerization of 1-butene and reported results similar to those reported by Itoh et al. [1] with a maximum of activity in the compositions rich in TiO_2 (Fig. 6). Also in this case *cis*- and *trans*-2-butenes were the only reaction products detected.

Miller et al. [25] studied the properties of TiO_2–SiO_2 materials dried with the low temperature supercritical procedure using CO_2. They also found that the 1-butene isomerization rate has a maximum in the TiO_2 rich region and evaluated the "fractional Brønsted site population" for different compositions (Fig. 7).

Contescu et al. [26] reported that the activity for 1-butene isomerization is linearly related to the density of a particular type of Brønsted acid site determined by potentiometric titration. The source of Brønsted acidity could be either a Si–OH group adjacent to a Ti or a Ti–OH group (Fig. 8).

Gao and Wachs [27] reviewed the previous literature and the evidence for acidity and alcohol dehydration reactivities as a function of Ti coordination for TiO_2–SiO_2 materials and presented many results in the compacted form of Fig. 9, where the 2-propanol reactivity is given as percentage of propanol reacted from [23], the methanol dehydration reactivity as rate of reaction from [24], and the Acidities from measurements of pyridine and ammonia absorption from [24]. They concluded that the Brønsted acidity follows the same trend as the activity for CH_3OH and 2-propanol dehydration, both increasing with the increase of the TiO_2 content in the TiO_2–SiO_2 mixed oxides composition (Fig. 9).

A major reason of concern about all these experimental data is due to the fact that the properties of the materials are highly dependent on purity and especially on methods of preparation: to name a few, deposition of one component on the preformed second oxide, separate hydrolysis, staged hydrolysis, coprecipitation, flame pyrolysis, thermal treatments. Furthermore, when reference is made to reaction rate per unit surface area (SA), it should be considered that the SiO_2 component gives a substantial contribution to the total SA but presumably very little to the activity, and it has not been possible up to now to satisfactorily measure the SA of the two oxides independently. The chemical interactions between the two oxides depend on the degree of dispersions and the thermal treatments. As a consequence of all these variables it is difficult to compare results obtained in different studies in which presumably different materials were tested.

These papers, and many others that are omitted for brevity, have diffused in the catalysis community the impression that

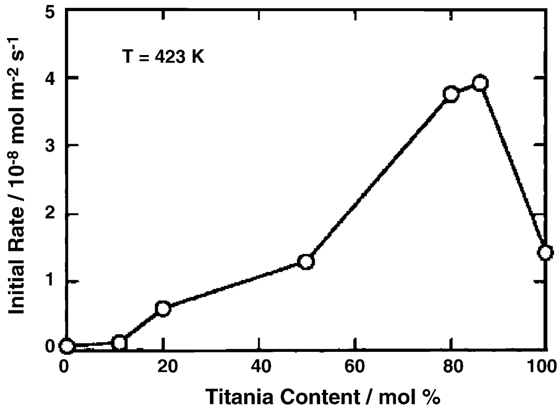

Fig. 6. 1-Butene isomerization on TiO_2–SiO_2 catalysts. Reprinted from [23] with permission of Elsevier.

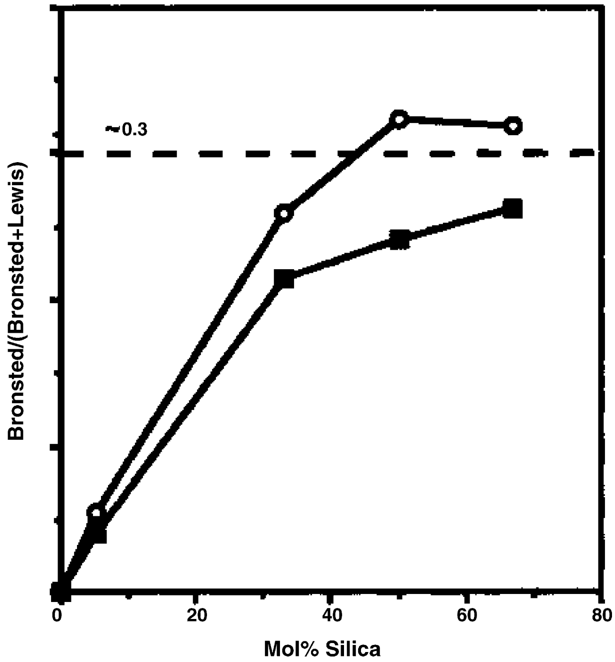

Fig. 7. Fractional Brønsted site population TiO_2–SiO_2 catalysts.

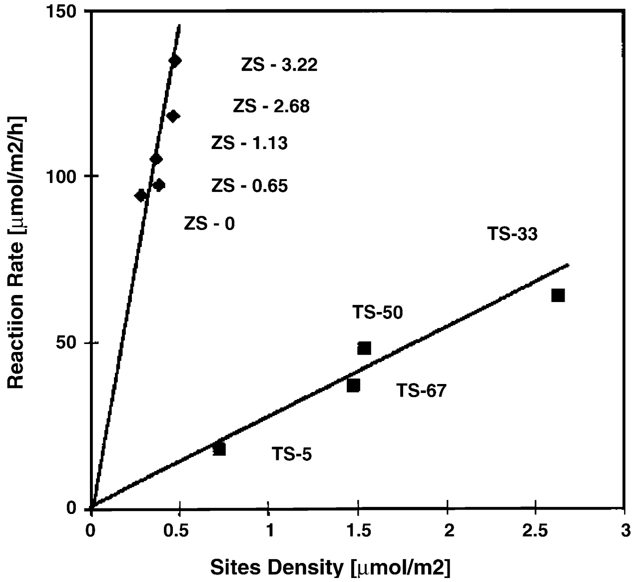

Fig. 8. Linear relationship between isomerization rates and Brønsted acid sites. Reprinted from [26] with permission of Elsevier.

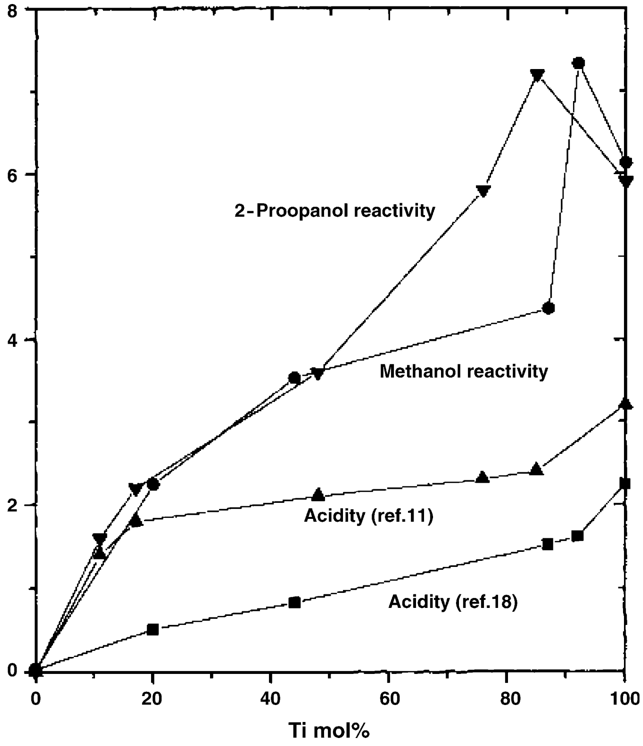

Fig. 9. Acidity and alcohol dehydration reactivities as a function of Ti concentration for TiO_2–SiO_2 mixed oxides.

indeed TiO_2–SiO_2 mixed oxides possess Brønsted acidity, thus supporting the Tanabe hypothesis: And no doubt the experimental evidence at first glance appears overwhelming.

3. Objections to Brønsted acidity

A number of experimental facts on which we acquired experience while working with TiO_2–SiO_2 materials appeared difficult to reconcile with the presence of Brønsted acidity:

(i) Very sensitive molecules such as epoxides are obtained on TS-1 in the presence of H_2O and/or solvents without significant hydrolysis or solvolysis. These side reactions would be expected should Brønsted acidity be present.

(ii) The coordination of Ti in TiO_2–SiO_2 is not always octahedral as postulated by Tanabe. It is tetrahedral in crystalline TS-1, as proposed since its discovery [3,11] (Fig. 10).

In amorphous materials different coordinations have been identified by X-ray absorption near edge structure (XANES) as shown in Fig. 11 [28]. As can be seen there is a marked difference between Ti in octahedral coordination, as in anatase and rutile, and Ti in mixed oxides (bottom lines). At high SiO_2 content (Ti:Si = 1:8) the pre-edge peak is greater in intensity, indicating that Ti has a different coordination, very likely tetrahedral as in TS-1 or 5-coordinated. The intensity of this peak further increases upon dehydration (not shown). As the Ti content is increased, the XANES spectra indicate a shift to a different coordination, more similar to that of anatase and rutile.

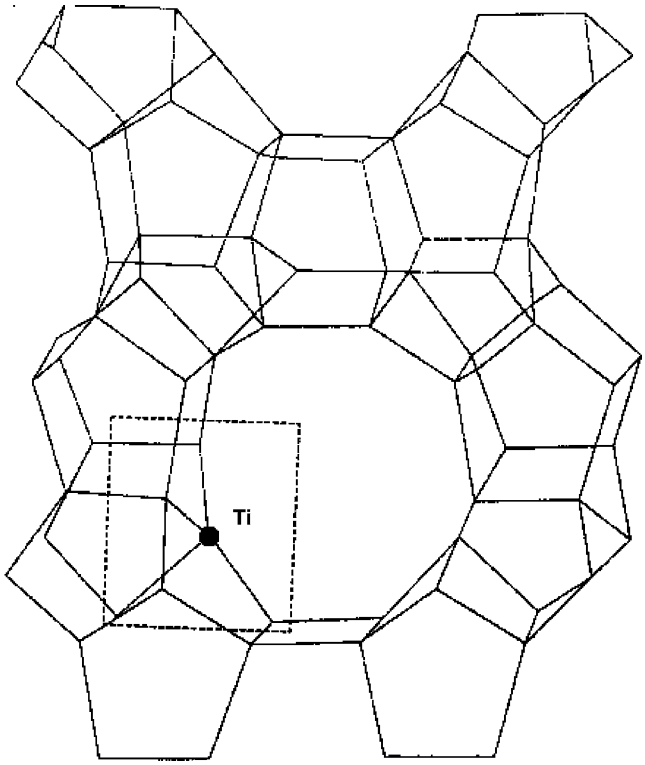

Fig. 10. Tetrahedral coordination of Ti in TS-1. Reprinted from [3] with permission of Elsevier.

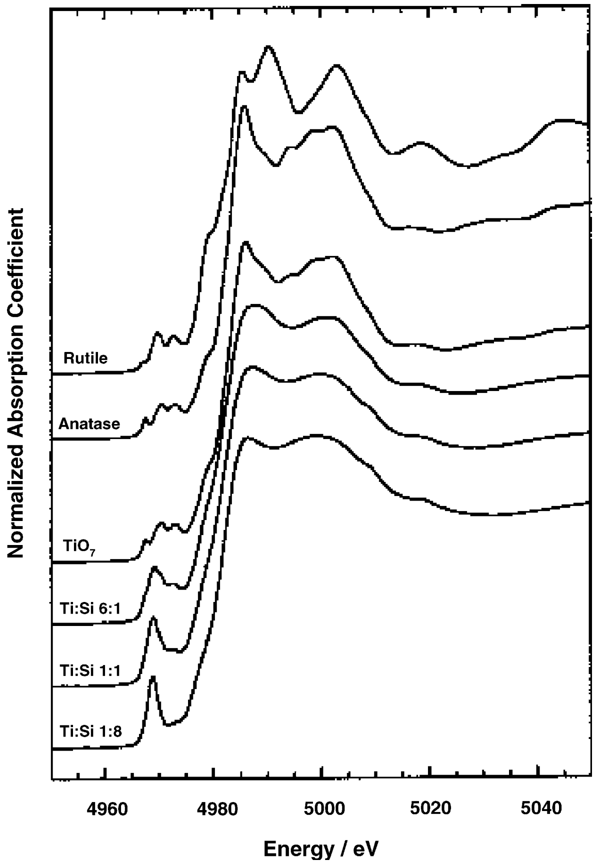

Fig. 11. In TiO_2–SiO_2 mixed oxides Ti has different coordinations. Reprinted from [28] with permission of the American Chemical Society.

(iii) The catalytic activity in 1-butene isomerization has a very low value in the SiO_2 rich region, where the Tanabe hypothesis predicts Brønsted acidity and therefore, high activity is expected. Because of these conflicts with the original Tanabe hypothesis, and the observation that the coordination of Ti is not constant in the whole composition range, Liu et al. [23] proposed a modified Tanabe model, in which Ti is tetrahedrally coordinated in the SiO_2 rich region and octahedrally coordinated in the TiO_2 rich region.

(iv) Under reducing conditions, such as those of a catalytic reaction, reduced Ti oxides are formed, with the consequence that new and different coordinations and structures are formed.

The complex chemistry of these materials and the elements of conflict between previous reports and the present knowledge of the properties of these materials convinced us that a reexamination of the properties of TiO_2–SiO_2 mixed oxides was mandatory.

4. Experimental and methods

4.1. Sample preparation

High purity raw materials were used for the preparation of all the catalysts. It is known from the literature that traces of trivalent cations, particularly Al^{3+}, can drastically change the catalytic activity of SiO_2 based materials. One example has been reported by West et al. [29]: 120 ppm of Al^{3+} in pure SiO_2 increase the rate of 1-hexene isomerization by a factor of 10,000. We have therefore selected high purity raw materials [30] as indicated in Table 1.

Crystalline materials. TS-1 of different Ti content prepared as previously described [31].

Amorphous TiO_2–SiO_2 materials. Several materials with different compositions were prepared. The list of catalysts with their composition and drying procedure is presented in Table 2. The drying was carried out with the supercritical drying method (SCD) either at high temperature (2-propanol) or at low temperature (CO_2).

The detailed preparation of Aerogel 496, Tigel 29, Tigel 31 and Ti80Si20 has been described [30]. Aerogels A502-TiO2, A503-80/20, A504-90/10 and A505-70/30 have been prepared according to the following procedure. Two solutions are prepared, one containing the Ti and Si alcoholates in 2-butanol, the second containing the proper amount of distilled water and nitric acid in methanol. The solutions are cooled to 0 °C and then rapidly mixed in a Teflon container. No immediate precipitation occurs, and within a short time homogeneous gels are formed. The gels are covered and aged for 24 h, then dryed with the low temperature SCD. The amounts of chemicals used are given in Table 3.

Table 2
Catalyst notation, composition, method of drying

Catalyst notation	Ti/Ti + Si (mol%)	Drying procedure
Aerogel 496	100	High temperature SCD
Tigel 29	100	Low temperature SCD
Tigel 31	100	Low temperature SCD
Ti80Si20	80	Low temperature SCD
A502-TiO2	100	Low temperature SCD
A503-80/20	80	Low temperature SCD
A504-90/10	90	Low temperature SCD
A505-70/30	70	Low temperature SCD

Table 3
Amount of chemicals used for Aerogels 502, 503, 504, 505

	A502-TiO2	A503-80/20	A504-90/10	A505-70/30
Ti-isopropoxide (g)	36.6	30.32	34.11	28.43
2-Butanol (ml)	80	80	80	80
Tetraethylorthosilicate (g)		5.56	2.78	8.95
Nitric acid 70% (g)	0.871	0.604	0.604	0.648
Water (g)	9.6	9.6	9.6	9.6
Methanol (ml)	40.0	40.0	40.0	40.0

4.2. IR spectra of crystalline and amorphous materials

The FT-IR spectra have been recorded using a Nicolet Magna 750 Fourier transform instrument as described in [31].

4.3. Activity test

The activity tests were carried out by measuring the conversion of 1-butene at different temperatures under closely controlled and identical conditions for all catalysts. Details of the apparatus are given in [30]. In short, 200 mg catalyst 20/50 mesh was loaded in a tubular down-flow reactor. A mixture of 1-butene

Table 1
Raw materials used in catalyst preparations

Name	Grade	Catalog no.	Remarks
Methanol	99.9%	A412-4	Fisher
2-Propanol	99.5+%	44342-5	Aldrich
Tetrapropylammonium hydroxide	1 M	23453-3	Aldrich
Titanium isopropoxide	99.999%	37799-6	Aldrich
Tetraethylorthosilicate	99.999%	33385-9	Aldrich
Nitric acid	70%	43807-3	Aldrich
Carbon dioxide	99.8%		Med-Tech Gases
Nitrogen	99.9%		Med-Tech Gases
Triple distilled water			Northeastern University

(13.5 cm^3/min) and helium (180 cm^3/min) flowed through the reactor and the temperature was controlled to the desired value. Inlet and outlet streams passed through a sampling valve and analyzed on line with a HP5890A gas chromatograph with thermal detector using a 2 m 1/8 in. o.d. SS packed column (Supelco 80/100 Carbopack c/0.19% picric acid). No products other than linear butanes were observed. Second runs were carried out to check the reproducibility of the results. Most catalysts gave reproducible results, others showed a deactivation. When tests were made with ZSM-5, the same amount of catalyst was charged and many reaction products were observed.

5. Results

5.1. Surface areas of materials and effect of SiO_2

The SA values of TiO_2 and of TiO_2–SiO_2 mixed oxides having the indicated compositions after treatment at the indicated temperatures are shown in Fig. 12. It is clear that SiO_2 has a strong effect in preventing the sintering of TiO_2.

5.2. Composition of reaction products

The reaction products reported in previous studies are *cis*-2-butene and *trans*-2-butene. Our results confirm these findings. We have observed that at very low conversions where primary products are obtained, the 2-butenes *cis*:*trans* ratio is about 2 with TiO_2 and 1.6–1.8 with TiO_2–SiO_2 materials. The values decrease at higher temperatures indicating a fast *cis*–*trans* isomerization. The high values of the *cis*:*trans* ratio reported in the literature (4–6) were not observed in our experiments. When we have extended the temperature range investigated from the 150–200 up to 340 °C we have found that also at high temperatures the only reaction products are the linear butenes, for both TiO_2 and TiO_2–SiO_2 as shown in Figs. 13 and 14. Brønsted acid catalysts at this temperature give rise to different reaction products as shown in Fig. 15.

5.2.1. Catalytic activity tests

The catalytic activity tests performed on pure TiO_2 materials of different SA correlate well with the SA, as shown in Fig. 16.

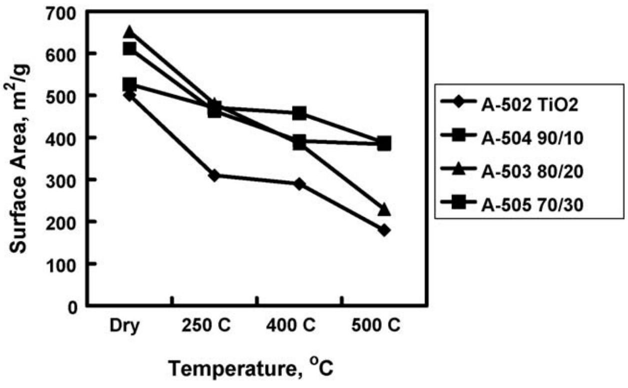

Fig. 12. Surface areas of pure TiO_2 and TiO_2–SiO_2 after treatment at the indicated temperatures.

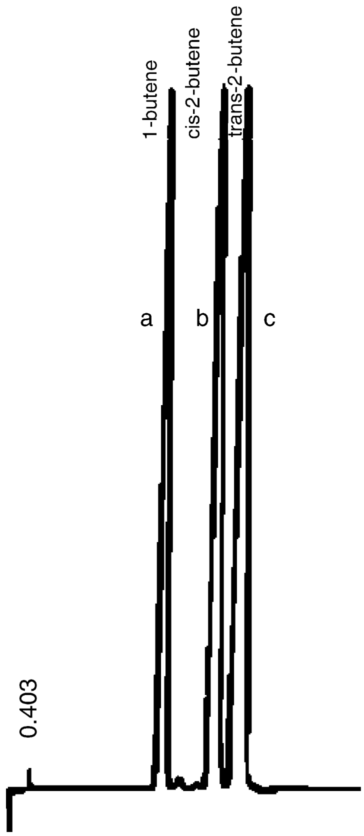

Fig. 13. Composition of reaction products with TiO_2. Reprinted from [30] with permission of Elsevier.

The catalytic activity of the most active TiO_2–SiO_2 and TiO_2 catalysts are compared in Fig. 17. It can be seen that the higher activity of TiO_2–SiO_2 is limited to the low temperature range.

Upon performing a second run it is observed that both activities are lower, but the differences between the two are now very limited, as seen in Fig. 18.

5.3. IR spectra of crystalline and amorphous materials

The IR spectra of TiO_2–SiO_2 materials are shown in Fig. 19.

6. Discussion

It can be seen from the data reported that high purity TiO_2 in the absence of any SiO_2 and prepared according to the low temperature CO_2 supercritical drying method has high surface area and high activity for 1-butene isomerization, and that the activity correlates with the SA of the different TiO_2 samples. The reaction products obtained consist only of the linear butenes up to a reaction temperature of 340 °C. It can also be seen that high purity TiO_2–SiO_2 mixed oxides obtained with the same procedure have slightly higher activity with respect to TiO_2 for 1-butene isomerization, but the differences become smaller in successive runs and disappear above 300 °C. Also for these materials the reaction products consist of linear butenes only, up to 340 °C. The difference between the results obtained with TiO_2 containing catalysts and ZSM-5 is clear: materials

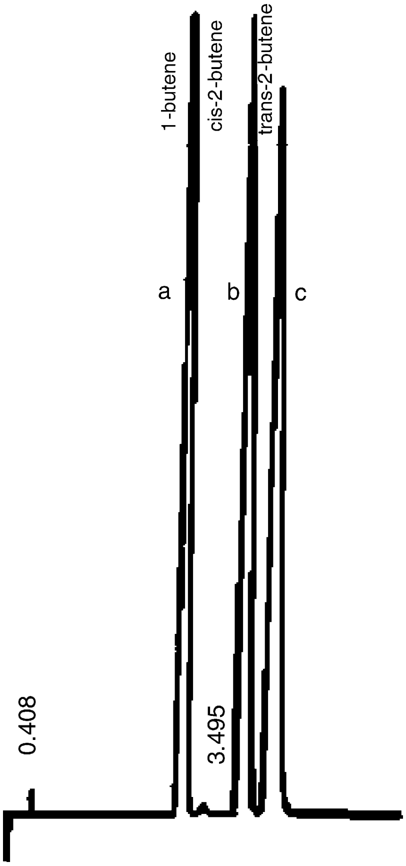

Fig. 14. Composition of reaction products with TiO_2–SiO_2. Reprinted from [30] with permission of Elsevier.

with Brønsted acid properties give rise to a number of reaction products, which have been ascribed to reactions of skeletal isomerization and other reactions including oligomerization and cracking. The previous studies were limited to temperatures of about 200 °C, and therefore little attention was paid to the lack of skeletal isomerization. The evidence here provided that skeletal isomerization and all other reactions typical of acid catalysis are absent even at 340 °C is evidence that there is no Brønsted acidity in TiO_2–SiO_2 materials.

Crystalline and amorphous TiO_2–SiO_2 materials have also been analyzed for Brønsted acidity by recording the IR spectra in the O–H stretching bond region. No absorption band typical of Brønsted acids is present, as seen in Fig. 19, where the spectrum of ZSM-5 is given as reference The wavenumber shift upon adsorption of acetonitrile is identical with that observed on pure SiO_2, indicating that the presence of Ti in all samples does not generate new OH groups nor does induce detectable Brønsted acidity in the Si–OH groups of SiO_2 [31]. Very different results are obtained from the absorption of nitriles on MFI [32].

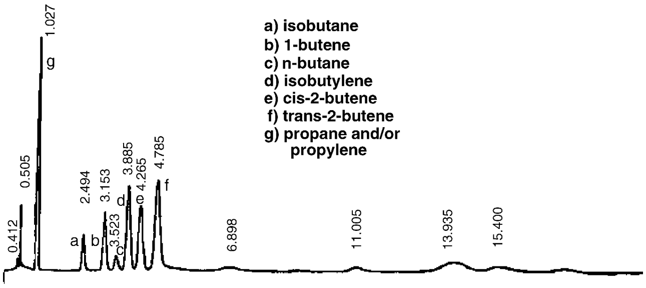

Fig. 15. Composition of reaction products with ZSM-5. Reprinted from [30] with permission of Elsevier.

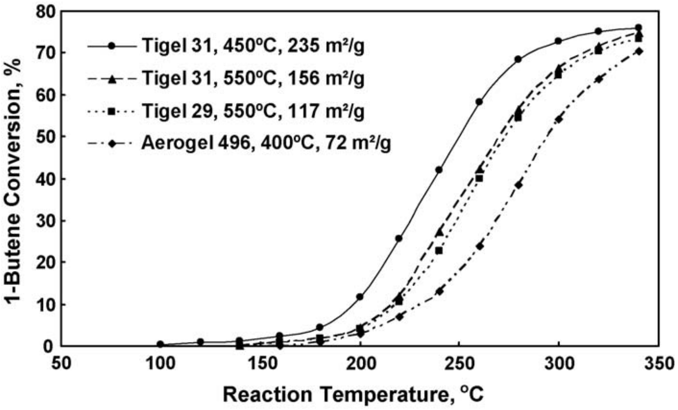

Fig. 16. Catalytic activity of TiO_2 correlates with Surface Areas. Reprinted from [30] with permission of Elsevier.

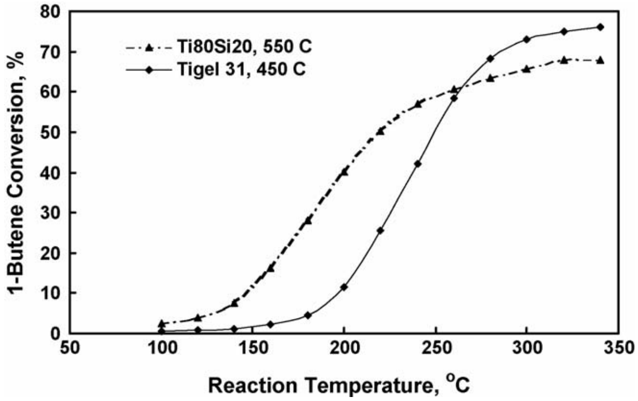

Fig. 17. Comparison of catalytic activity of TiO_2 and TiO_2–SiO_2. Reprinted from [30] with permission of Elsevier.

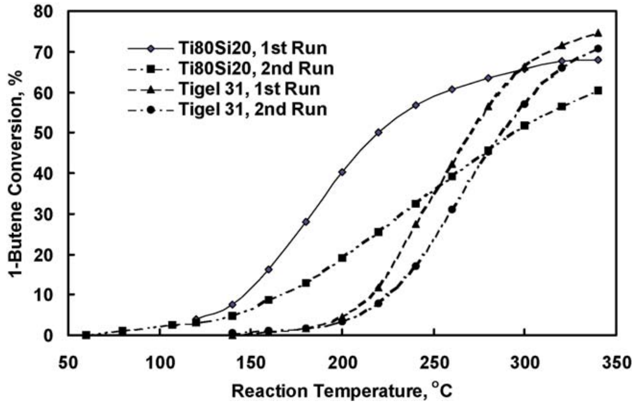

Fig. 18. Deactivation of TiO_2–SiO_2 and TiO_2 in second runs. Reprinted from [30] with permission of Elsevier.

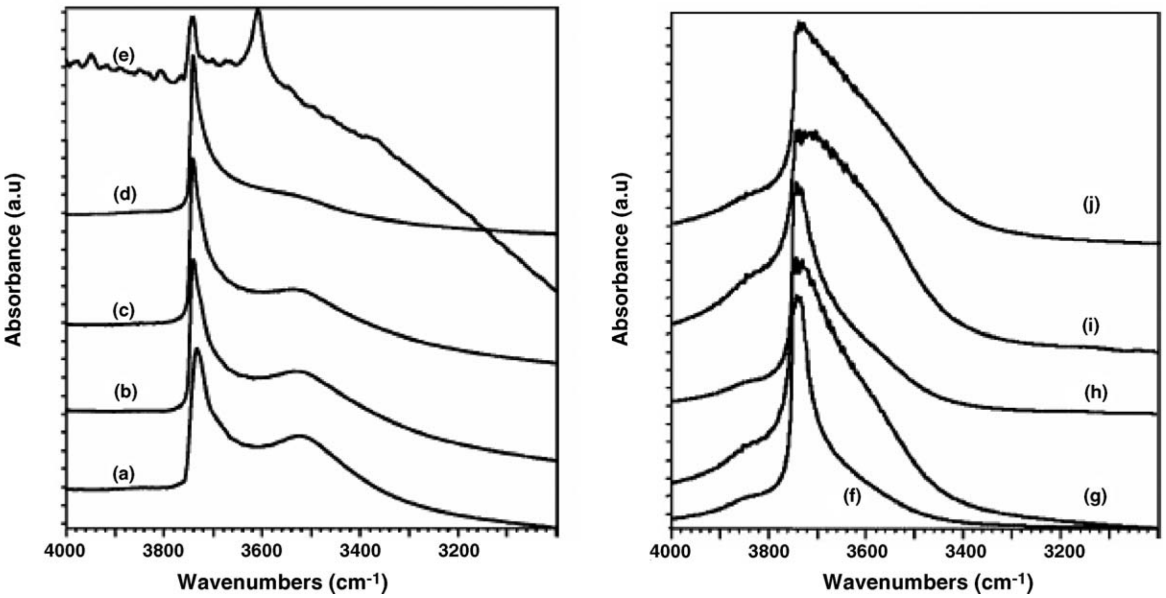

Fig. 19. IR spectra in the O–H region of TiO_2–SiO_2 materials in crystalline (a) and amorphous (b) form. ZSM-5 is given in trace (e) as reference. Reproduced from [31] with kind permission of Springer Science and Business Media.

The identity in the composition of reaction products obtained with TiO_2 and TiO_2–SiO_2 and the difference with reaction products obtained with Brønsted acids suggests that the reaction takes place on TiO_2 in both cases by an identical mechanism. It appears therefore that the high initial catalytic activity of TiO_2–SiO_2 is better explained with a very high degree of dispersion of the TiO_2 component that is obtained when SiO_2 is present during the preparation. The phenomenon is limited to the low temperature region, and the decreased activity already in the second run, as can be seen in Fig. 18 for Ti80Si20, indicates that at this high degree of dispersion the material undergoes some limited rearrangement.

These results are impossible to reconcile with the presence of Brønsted acidity and therefore with the Tanabe and/or Seiyama hypothesis.

A close examination of the validity of the evidence on which the claims were based shows that two major factors could be the cause of erroneous results:

- purity of the materials used,
- procedures selected for the detection of Brønsted acidity.

It is obviously impossible to accurately reproduce the materials that have been used in the studies reported in the literature, but the possibility that they were contaminated with acid-inducing elements such as Al^{3+} and/or Fe^{3+} is very plausible, especially for the early works. This would explain some cases in which Brønsted acidity was reported, but not all the cases.

As we have discussed above the catalytic activity in the 1-butene isomerization to the other linear butenes is not a valid proof for Brønsted acidity. Basic and radical catalysts also are active in the isomerization of linear butanes, and pure TiO_2 is also active. Only skeletal isomerization is diagnostic of Brønsted acidity, and it is absent.

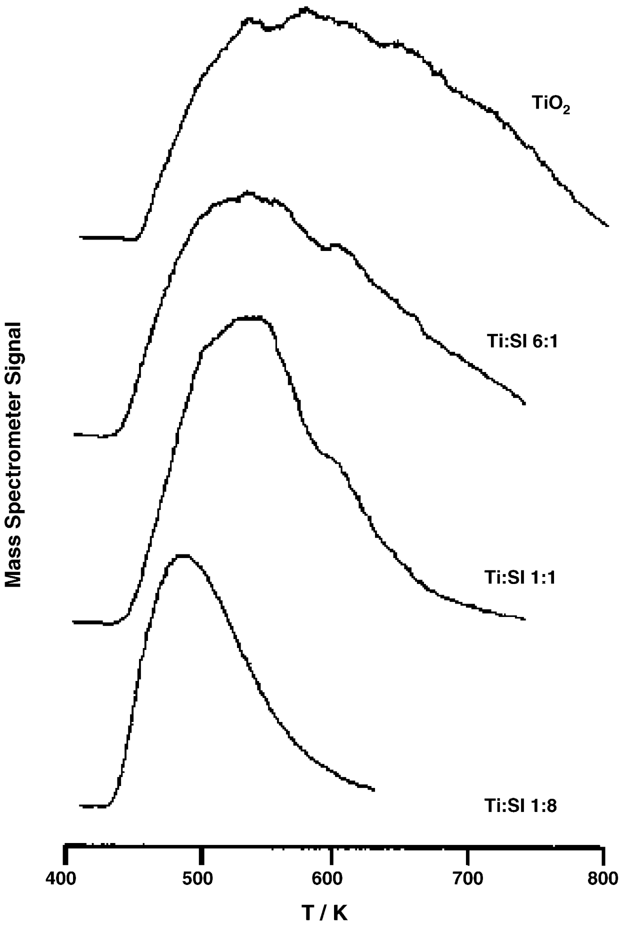

Fig. 20. TPD of NH_3 on TiO_2 and TiO_2–SiO_2 mixed oxides. Reprinted from [23] with permission of Elsevier.

The NH_3 absorption and temperature programmed desorption (TPD) has been used for the identification of Brønsted acid sites especially in the study of SiO_2–Al_2O_3 materials and the related zeolites, the rational being that the higher the desorption temperature, the strongest the acidity of the material. With this class of materials the results have been considered satisfactory. However, the application of this procedure to other materials has been challenged because NH_3 strongly interacts with many different oxides, not only with acid materials, and the results obtained by measuring acidity with NH_3 adsorption and desorption can be misleading [33]. In one reported case, the TPD of NH_3 from CaO shows that the release of NH_3 takes place in the same temperature range as with solid acid zeolites, which would imply that CaO is a strong acid [34]. Because the absorption of NH_3 on non-Brønsted sites may be stronger than on Brønsted sites, the recommendation has been made not to use NH_3 for probing acid sites [35].

In the case of TiO_2, things appear even more complex. There is general agreement that pure TiO_2 is not a Brønsted acid, having only Lewis acidity. In spite of this pure TiO_2 absorbs NH_3 and releases it at a higher temperature than the TiO_2–SiO_2 mixed oxides, as can be seen from the results shown in Fig. 20 [23].

Not only NH_3 absorbs on TiO_2 and is strongly retained, but the temperature at which it is released depends on the dimensions of the TiO_2 particles: small particle sizes release NH_3 at a higher temperature than large particle sizes, as shown in Fig. 21 [36].

A further complication arises because of the ability of TiO_2 to oxidize many compounds, changing the simple acid–base chemistry into the more complex oxidation–reduction chemistry. Evidence for this can be observed in the case of TiO_2 used for the dehydration of ethanol: not only ethylene and water are obtained, also a substantial amount of butadiene is formed, necessarily via the oxidation to acetaldehyde followed by the aldol condensation between two molecules of acetaldehyde and dehydration to butadiene [37]. This oxidizing ability of TiO_2 will also affect surface probe molecules such as NH_3. The case of the pyridine absorption reported by Kataoka and Dumesic [21] with pyridinium ions identified upon absorption on the oxidized sample of TiO_2, but not present when TiO_2 samples were reduced with H_2, is most likely due to the fact that the reduction with H_2 modified the ability of TiO_2 to oxidize surface species which gave rise to the pyridinium bands which were in turn interpreted as evidence of Brønsted acidity. These phenomena sound an alarm on the usefulness, for the study of catalytic reactions, of results obtained from detection of surface species as in IR and TPD experiment, where a very limited amount of surface molecules is involved and chances of observing species that have nothing to do with catalysis are exceptionally high. Results obtained from real catalytic experiments, with a continuous flow of reactants, are therefore much more reliable and should be given preferential consideration.

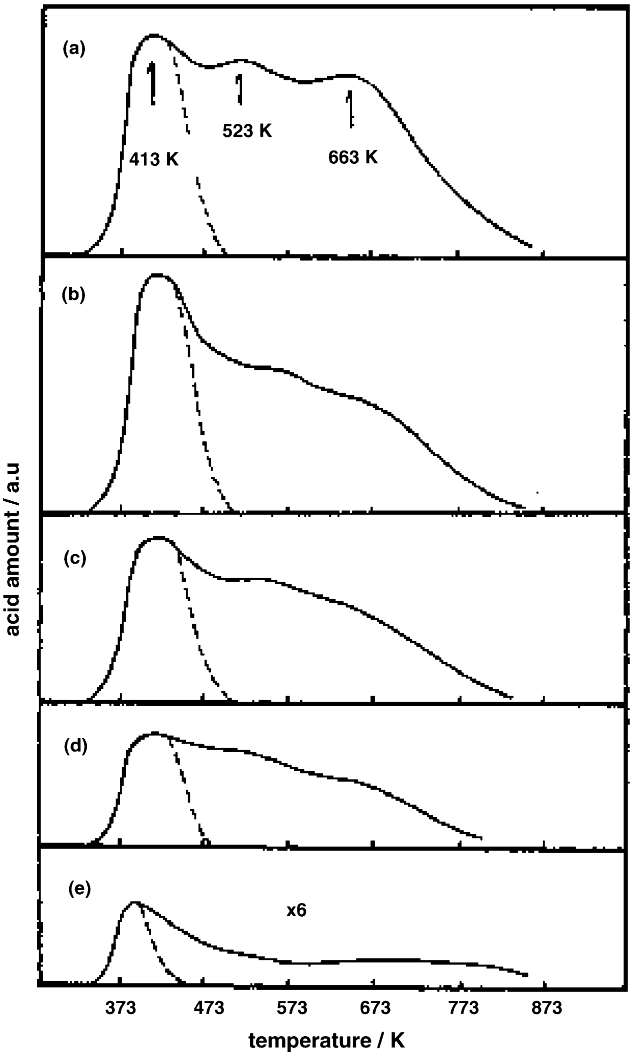

Fig. 21. TPD of NH_3 on TiO_2 with different particle size: (a) 75 Å, (b) 102 Å, (c) 125 Å and (d) 162 Å. Reprinted from [36] with permission of the Chemical Society of Japan.

The general conclusion is that evidence of Brønsted acidity obtained with NH_3 absorption and NH_3 TPD can produce erroneous results when applied to a number of materials, and this is the case of the TiO_2–SiO_2 mixed oxides.

Another method has bee used to identify Brønsted acidity in solids, the rate of alcohol dehydration. The catalytic activity in alcohol dehydration has been presented as evidence of Brønsted acidity for the TiO_2–SiO_2. No doubt Brønsted acids DO catalyze the dehydration of alcohols, but when Brønsted acidity is present, very low reaction temperatures are sufficient to carry out the reaction. Pertinent examples are the dehydration of alcohols with sulfuric acid at 50 °C or the dehydration of methanol on ZSM-5 at 130 °C [38]. But this fact has led to the generalization that ALL alcohol dehydration reactions are acid catalyzed and many authors have proposed to correlate the activity for alcohol dehydration to the acidity of catalysts [27,39]. This approach has recently been criticized [40]. Because dehydration of alcohols can proceed by mechanism different from acid catalysis, the correlation fails. Non acidic materials such as Al_2O_3 are the most active dehydration catalysts.

If Brønsted acidity is ruled out, then some other entity in the solid must be responsible for the catalytic activity and be compatible with the anion/radical mechanism observed. The search is made easier by the fact that we observe a very similar behavior for TiO_2 and TiO_2–SiO_2 mixed oxides, which allows us to start by considering the pure TiO_2. There are only Ti ions and O ions in pure TiO_2, and under reducing conditions reduced Ti species, known as defects, Ti^{3+}, Ti^{2+} are formed. Reduced species are accompanied by electrons, which are delocalized in the solid and could be responsible for anion/radical catalytic activity. Oxygen ions can have a more basic character when bound to cations of low valency, and they also could be the source of anion/radical catalytic activity, but this again requires the formation of Ti reduced species.

The formation of Ti^{3+} defects in TiO_2 has been detected with ESR already since 1967 by Che et al. [41]. Hattori et al. also measured the amounts of Ti^{3+} by the formation of nitrobenzene anion radical on both TiO_2 and TiO_2–SiO_2 evacuated at various temperatures [42]. Formation of Ti^{3+} on TiO_2–SiO_2 upon evacuation or heat treatment was later demonstrated by Fernandez et al. [43] from the IR spectra of CO adsorbed on TiO_2–SiO_2 and from ESR measurements.

More recently Haerudin et al. [44] reported that in the presence of H_2 the number of Ti^{+3} defects is in equilibrium with the gas phase according to the following relation:

$$Ti^{4+} + O^{2-} + H_2 = H_2O + V_O + Ti^{3+} + e^-$$

(where V_O represents an oxygen vacancy) and could distinguish between surface Ti^{3+} defects and bulk Ti^{3+} defects [44].

The search for the entity responsible for the catalytic activity of both TiO_2 and TiO_2–SiO_2 mixed oxides must therefore be directed at the elucidation of the properties of TiO_2 nanoparticles and the role played by Ti reduced species.

The role of SiO_2 can therefore be described as that of enhancing the degree of dispersion of TiO_2 during the preparation process, and stabilizing the nanoparticles of TiO_2 against thermal sintering.

7. Conclusions

Our results indicate that the 1-butene isomerization on TiO_2–SiO_2 does not proceed through an acid mechanism, but most likely through a radical or anion mechanism, the same mechanism that operates with highly divided pure TiO_2 materials. Evidence for this is the identity of reaction products with ALL Ti-containing materials and the difference with the reaction products obtained with known acid materials. Catalytic activity in the isomerization of 1-butene to linear butenes is not sufficient to prove Brønsted acidity: basic and radical catalysts are also active for this reaction. Only skeletal isomerization is diagnostic of Brønsted acidity.

No Brønsted acid sites have been found in pure TiO_2–SiO_2 or in TS-1 by measuring the O–H absorption and the shift of the O–H stretching band upon contact with acetonitrile. The close examination of previous reports where Brønsted acidity was claimed for TiO_2–SiO_2 materials shows that there is no convincing experimental evidence for this claim, since they were based on methods that are not diagnostic of Brønsted acidity or, when applied to materials that have oxidizing ability, produce unreliable results.

The methods and techniques for the detection of Brønsted acidity that have been used in the past, including titration of acid sites with *n*-butylamine and Hammett indicators, TPD of NH_3 and rate of alcohol dehydration have provided erroneous results when applied to TiO_2–SiO_2 materials. A reexamination of the limits of their applicability is strongly recommended. This would also be important information for the catalysis and surface science community not only for the specific case of TiO_2–SiO_2 materials but also for the study of other catalysts that can undergo oxidation–reduction transformations upon contact with reactants.

References

[1] M. Itoh, H. Hattori, K. Tanabe, The acidic properties of TiO_2–SiO_2 and its catalytic activities for the amination of phenol, the hydration of ethylene and the isomerization of butene, J. Catal. 35 (1974) 225.

[2] H.P. Wulff, Expoxidation process with improved heterogeneous catalyst, 1975, U.S. Patent 3,923,843.

[3] B. Notari, Microporous crystalline titanium silicates, Adv. Catal. 41 (1996) 253–334. Academic Press.

[4] K. Tanabe, Solid acid and base catalysts, in: J.R. Anderson, M. Boudart (Eds.), Catalysis Science and Technology, vol. 2, Springer, Verlag, 1981, p. 255.

[5] G. Bellussi, M.S. Rigutto, Metal ions associated to the molecular sieve framework: possible catalytic oxidation sites, Stud. Surf. Sci. Catal. 85 (1994) 177. Elsevier.

[6] G.N. Vayssilov, Structural and physico-chemical features of titanium silicalites, Catal. Rev. Sci. Eng. 39 (1997) 209.

[7] R.J. Saxton, Crystalline microporous titanium silicates, Top. Catal. 9 (1) (1999) 43–57.

[8] R.A. Sheldon, I.W. Arends, A. Dijksman, New developments in catalytic alcohol oxidations for fine chemicals synthesis, Catal. Today 57 (2000) 157–166.

[9] M. Dusi, T. Mallat, A. Baiker, Epoxidation of functionalized olefins over solid catalysts, Catal. Rev. 42 (2000) 15.

[10] P. Ratnasamy, D. Srinivas, H. Knozinger, Active sites and reactive intermediates in titanium silicate molecular sieves, Adv. Catal. 48 (2004) 1–169.

[11] M. Taramasso, G. Perego, B. Notari, Preparation of porous crystalline synthetic material comprised of silicon and titanium oxides, 1983, U.S. Patent 4,410,501.

[12] T. Suzuki, Active site model of a high silica MFI zeolite for the vapor phase rearrangement of cyclohexanone oxime to caprolactam, in: Proceedings of the Fifth International Symposium on Acid Base Catalysis, July 1, Puerta Vallarte, Mexico, 2005, Paper O-14.

[13] M. McCoy, New routes to propylene oxide, C&EN 79 (2001) 19–20.

[14] A. Tullo, Chem. Eng. News 82 (36) (2004) 15.

[15] B. Notari, Synthesis and catalytic properties of Ti-containing zeolites, in: Innovation in Zeolites, Stud. Surf. Sci. Catal. 37 (1987) 413. Elsevier.

[16] K. Tanabe, T. Sumiyoshi, K. Shibata, T. Kiyoura, J. Kitagawa, A new hypothesis regarding the surface acidity of binary metal oxides, Bull. Chem. Soc. Jpn. 47 (1974) 1064.

[17] K. Tanabe, M. Itoh, M. Sato, Chem. Commun. (1973) 676.

[18] T. Seiyama, Metal Oxides and Their Catalytic Actions, Kodansha, Toyko, 1978.

[19] E.I. Ko, J.P. Chen, J.G. Weissman, A Study of acidic titania/silica mixed oxides and their use as supports for nickel catalysts, J. Catal. 105 (1987) 511.

[20] G. Connell, J.A. Dumesic, The generation of Brønsted and Lewis acid sites on the surface of silica by addition of dopant cations, J. Catal. 105 (1987) 285–298.

[21] T. Kataoka, J.A. Dumesic, Acidity of unsupported and silica-supported vanadia, molybdena and titania as studied by pyridine adsorption, J. Catal. 112 (1988) 66.

[22] J.R. Sohn, H.J. Jang, Correlation between the infrared band frequency of the silanol bending vibration in TiO_2–SiO_2 catalysts and activity for acid catalysis, J. Catal. 132 (1991) 563.

[23] Z. Liu, J. Tabora, R.J. Davis, Relationship between microstructure and surface acidity of Ti–Si mixed oxide catalysts, J. Catal. 149 (1994) 117–126.

[24] P.K. Doolin, S. Alerasool, D.J. Zalewski, J.F. Hoffman, Acidity studies of titania-silica mixed oxides, Catal. Lett. 25 (1994) 209–223.

[25] J.B. Miller, S.T. Johnston, E.I. Ko, Effect of prehydrolysis on the textural and catalytic properties of titania-silica aerogels, J. Catal. 150 (2) (1994) 311.

[26] C. Contescu, V.T. Popa, J.B. Miller, E.I. Ko, J.A. Schwarz, Proton affinity distributions of TiO_2–SiO_2 and ZrO_2–SiO_2 mixed oxides and their relationship to catalyst activities for 1-butene isomerization, J. Catal. 157 (1995) 244.

[27] X. Gao, I.E. Wachs, Titania-silica as catalysts: molecular structural characteristics and physico-chemical properties, Catal. Today 51 (1999) 233–254.

[28] Z. Liu, R.J. Davis, Investigation of the structure of microporous Ti–Si mixed oxides by X-ray, UV reflectance, FT-Raman, and FT-IR spectroscopies, J. Phys. Chem. 98 (4) (1994) 1253.

[29] J. West, G. Haller, R.L. Burwell, J. Catal. 29 (1973) 486.

[30] S. Hu, R. Willey, B. Notari, An investigation on the catalytic properties of titania-silica materials, J. Catal. 220 (2003) 240.

[31] T. Armaroli, F. Milella, B. Notari, R.J. Willey, G. Busca, A spectroscopic study of amorphous and crystalline Ti-containing silicas and their surface acidity, Top. Catal. 15 (2001) 63–71.

[32] T. Armaroli, M. Bevilacqua, M. Trombetta, F. Milella, A.G. Alejandre, J. Ramirez, B. Notari, R.J. Willey, G. Busca, A study of the external and internal sites of MFI-type zeolitic materials through the FT-IR investigation of the adsorption of nitriles, Appl. Catal. A 216 (2001) 59.

[33] R.J. Gorte, Catal. Today 28 (1996) 405.

[34] M.V. Juskelis, J.P. Slanga, T.G. Roberie, A.W. Peters, J. Catal. 138 (1992) 391.

[35] R.J. Gorte, Catal. Lett. 62 (1999) 1.

[36] H. Nakabayashi, N. Kakuta, A. Ueno, Bull. Chem. Soc. Jpn. 64 (1991) 2428.

[37] M. Niwa, N. Katada, Y. Murakami, J. Catal. 70 (1981) 275.

[38] M. Xu, J.H. Lunsford, D.W. Goodman, A. Bhattacharyya, Appl. Catal. A: Gen. 149 (1977) 289.

[39] A. Gervasini, A. Auroux, J. Catal. 131 (1991) 190.

[40] J.E. Rekoske, M.A. Barteau, J. Catal. 165 (1997) 57.

[41] M. Che, C. Naccache, R. Imelik, M. Prettre, Comptes Rendus 264C (1967) 1901.

[42] H. Hattori, M. Itoh, K. Tanabe, The nature of active sites on TiO_2 and SiO_2–TiO_2 for the isomerization of butenes, J. Catal. 38 (1975) 172.

[43] A. Fernandez, J. Leyrer, A.R. Gonzalez-Felipe, G. Munuera, H. Knozinger, J. Catal. 112 (1988) 489.

[44] H. Haerudin, S. Bertel, R. Kramer, JCS Faraday Trans. 94 (10) (1988) 1481.