

An investigation on the catalytic properties of titania–silica materials

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Abstract

Binary TiO_2 – SiO_2 mixed oxides display interesting catalytic properties which have not been attributed to the pure TiO_2 and SiO_2 . Many authors have proposed that Brønsted acidity is generated upon interaction of the two oxides. Recent results from our laboratories have demonstrated that high-purity crystalline and amorphous TiO_2 – SiO_2 mixed oxides do not possess Brønsted acidity, only Lewis acidity. We have investigated the catalytic properties for 1-butene isomerization up to 340 °C. High-purity TiO_2 , prepared with low temperature supercritical drying, has a high catalytic activity, close to that of the TiO_2 – SiO_2 . The reaction products obtained from TiO_2 and from TiO_2 – SiO_2 are identical and consist of linear butenes only, while Brønsted acid catalysts give rise to isobutylene and C_3 – C_5 hydrocarbons. These results suggest that nanoparticles of TiO_2 stabilized by SiO_2 are the active components of TiO_2 – SiO_2 . No evidence for Brønsted acidity in TiO_2 – SiO_2 has been found.

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1. Introduction

Many physical and chemical properties of a metal oxide can be modified by interaction with a second oxide. Silica–alumina, for example, has stronger acidity than both silica and alumina [1], and has been widely used for many acid-catalyzed reactions [2,3]. Thomas in 1949 suggested that binary oxides' acidity originated from the isomorphous substitution of cations in the crystal structure of one oxide by cations of different elements. For silica–alumina, when a Si^{4+} is replaced by an Al^{3+} , an additional cation is necessary to establish electrical neutrality. When the cation is H^+ , the solid exhibits activity of an acid [4].

TiO_2 – SiO_2 mixed oxides have been reported to have higher catalytic activity with respect to pure TiO_2 and SiO_2 for a number of different reactions such as phenol amination [5], olefin epoxidation [6], ethene hydration [5], butene isomerization [5,7,8], cumene dealkylation, 2-propanol dehydration [9], and 1,2-dichloroethane decomposition [10]. Tanabe [11] attributed these catalytic properties to the formation of Brønsted acid sites. According to his hypothesis, the substitution of a metal ion into the structure of the host oxide follows these rules: (i) All the cations maintain the co-

ordination they have in their most stable oxide, and (ii) all the 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. Some support for this hypothesis has come from the titration of acid sites with *n*-butylamine and Hammett indicators [5,12] or potentiometric titration [13].

The Tanabe hypothesis has been found in disagreement with a number of experimental facts: (i) 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 [14,15]; (ii) in the crystalline material titanium silicalite-1 (TS-1), Ti has tetrahedral coordination, not octahedral as required by one of the Tanabe rules and no Brønsted acidity [16,17]; (iii) tetrahedral coordination for Ti has also been reported in the SiO_2 -rich region of the amorphous TiO_2 – SiO_2 mixed oxides [18–21]; (iv) under reducing conditions, such as those of a catalytic reaction, reduced Ti oxides are formed, with different coordinations and structures [22,23].

In order to resolve this conflict between hypothesis and experimental results, a modification of the Tanabe hypothesis was proposed which considered the possibility of two different coordinations for Ti, tetrahedral in the SiO_2 -rich region and octahedral in the TiO_2 -rich region. According to

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this modified hypothesis, Brønsted acidity should form only in the TiO₂-rich region [14].

A different hypothesis has been proposed by Seiyama [24]. According to this 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. Only Brønsted acidity is predicted by this hypothesis regardless of composition, while the extension of the acidity depends on the degree of dispersion and mixing of the two oxides.

The presence of Brønsted acidity in TiO₂-SiO₂ has already been questioned [15,25]. More recently a study of the surface properties of crystalline TS-1 and amorphous TiO₂-SiO₂ demonstrated that no Brønsted acidity is present in these materials, only Lewis acidity [26]. This result stimulated our interest to learn more about the properties of TiO₂-SiO₂ mixed oxides, and the catalytic activity for 1-butene isomerization. The materials selected for our study are: crystalline TS-1 of different Ti content, amorphous TiO₂-SiO₂ of different compositions, and pure TiO₂. In this paper we present new experimental evidence on the catalytic properties of high-purity TiO₂.

2. Experimental and methods

2.1. Sample preparation

Raw materials of the highest purity available have been used in this study. Traces of trivalent cations can impart acid properties to both amorphous and crystalline silicas and interfere with the interpretation of the results. For this reason, great care was taken in the selection and handling of the materials at all stages, in order to avoid contamination during manipulation. Table 1 lists the materials used in the preparations. All of the operations were carried out in Teflon or plastic containers for both gel formation and crystallization, and in quartz ampoules for the high-temperature treatments.

Table 1
Raw materials used in catalyst preparations

Name	Grade	Catalog No.	Remarks
Methanol	99.9%	A412-4	Fisher
2-Propanol	99.5+%	44,342-5	Aldrich
Tetrapropylammonium hydroxide	1 M	23,453-3	Aldrich
Titanium isopropoxide	99.999%	37,799-6	Aldrich
Tetraethylorthosilicate	99.999%	33,385-9	Aldrich
Nitric acid	70%	43,807-3	Aldrich
Carbon dioxide	99.8%		Med-Tech Gases
Nitrogen	99.9%		Med-Tech Gases
Triple distilled water			Northeastern University

2.2. Preparation of TS-1

Three samples of TS-1 were prepared. They are identified by the value of $x = \text{Ti}/(\text{Ti} + \text{Si})$ which was 0.625, 1.25, and 2.5%. The preparation procedure has been previously described [26–28]. Table 2 gives the amount of chemicals used in the preparation of the three TS-1 samples.

The UV-vis spectra of these materials are shown in Fig. 1. The absorption at 210 nm is very sharp and no other absorption is present at higher values, indicating that all the Ti is incorporated into the framework and no extraframework TiO₂ is present. By comparison the UV-vis spectrum of a commercial sample of TS-1 having a slightly higher Ti content ($x = 2.63\%$) is shown in Fig. 2. It can be seen that, besides the major absorption at 210 nm, a shoulder is present at around 280 nm, which has been attributed to extraframework TiO₂ nanoparticles [15]. The analysis for TS-1 with $x = 1.25$ indicated a content of 82 ppm Na and 370 ppm K (see Table 3).

2.3. Preparation of TiO₂-SiO₂ with different compositions

Two materials have been prepared, one with 80% TiO₂ and the other with 70% TiO₂. The procedures closely followed those described in the literature [14,20,29]. The drying was carried out with the supercritical drying method (SCD) either at high temperature (2-propanol) or at low tem-

Table 2
Amounts of chemicals used for TS-1 synthesis

	TS-1		
	$x^a = 0.625$	$x = 1.25$	$x = 2.5$
Tetrapropylammonium hydroxide (1 M) (g)	60.00	60.00	60.32
Titanium isopropoxide (g)	0.490	0.905	1.773
Tetraethylorthosilicate (g)	57.110	49.900	50.052
Triple distilled water (g)	114.0	114.0	114.2

^a [$x = \text{Ti}/(\text{Ti} + \text{Si}) \times 100$].

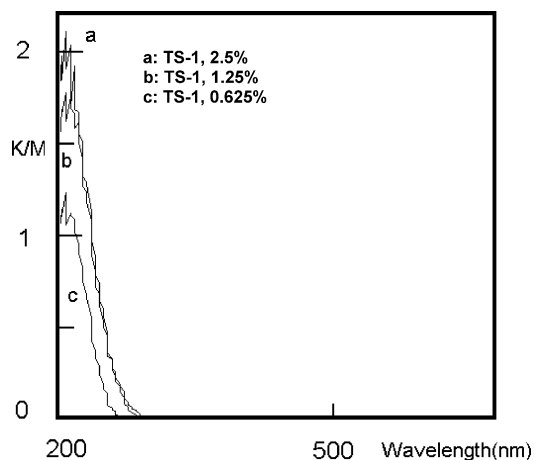


Fig. 1. UV-vis spectra of TS-1 ($x = 0.625, 1.25, \text{ and } 2.5\%$).

Table 3
List of catalysts evaluated for 1-butene isomerization

Catalyst name	Ti/(Ti + Si) (mol %)	Na (ppm)	K (ppm)	Calcination temp. (°C)	SA (m ² /g)	Remarks
Aerogel 477	0			550	673	High temperature SCD
Aerogel 479	1			550	669	High temperature SCD
Aerogel 481	10			550	522	High temperature SCD
Aerogel 496	100			350	72	High temperature SCD
Aerogel 496	100			400	75	High temperature SCD
Aerogel 496	100			450	69	High temperature SCD
Ti80Si20	80	45	500	550	349	Low temperature SCD
Ti70Si30	70			550	335	Low temperature SCD
Tigel 31	100			450	235	Low temperature SCD
Tigel 31	100			550	156	Low temperature SCD
Tigel 29	100			550	117	Low temperature SCD
TS-1 ($x = 0.625\%$)	0.625			550	358	Titanium silicalite
TS-1 ($x = 1.25\%$)	1.25	82	370	550	357	Titanium silicalite
TS-1 ($x = 2.5\%$)	2.5			550	400	Titanium silicalite
ZSM-5	SiO ₂ /Al ₂ O ₃ = 26.9				138	Reference test
Empty reactor						Reference test

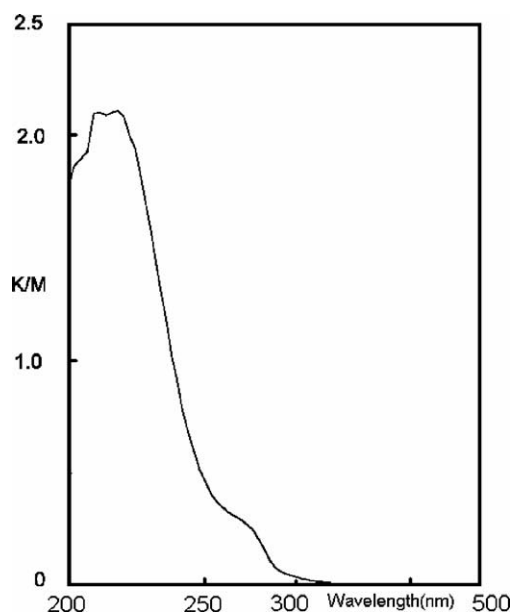


Fig. 2. UV-vis spectra of TS-1 ($x = 2.63\%$).

perature (CO₂) following the procedures described in the literature [30–32].

2.3.1. Ti80Si20 Aerogel

Titanium isopropoxide (30 g) and tetraethylorthosilicate (5.49 g) were added to 100 ml of 2-propanol. Distilled water (11 ml) was added to this solution through a dripping funnel in about 20 min with stirring at room temperature. The gel which formed was aged for 1 week. The solvent was removed by extraction followed by low-temperature SCD. Extraction was carried out at room temperature with liquid CO₂. When no more liquid was flowing out, the temperature was increased to 49 °C and the CO₂ pressure increased to 104.4 bars. SCD was then obtained by depressurizing at 49 °C.

The gel was transferred to a quartz ampoule, positioned in a 1-inch quartz tube and calcined by heating slowly (1–2 °C/min) to 550 °C in 50 cc/min flowing nitrogen. Next 2.5 cc/min of oxygen was added (giving an oxygen concentration of 5%) and the calcination was continued at 550 °C for 2 h. Other samples shown below were calcined using the same method at the indicated calcination temperatures (Table 3). The analysis for Ti80Si20 indicated a content of 45 ppm Na and 500 ppm K.

2.3.2. Ti70Si30 Aerogel

Tetraethylorthosilicate (7.85 g) was mixed with methanol (40 ml) in a Teflon beaker with magnetic bar stirring. Distilled water (2.713 g) mixed with 70% nitric acid (0.395 g) was added to the above solution. The water and nitric acid were added according to the following molar ratios: H₂O/Si = 4, HNO₃/Si = 0.15. After 10 min of stirring, 25 g of titanium isopropoxide was added. Distilled water required for the hydrolysis of titanium isopropoxide was added under stirring (6.332 g water + 0.308 g nitric acid). Water and nitric acid were added according to the following molar ratio: H₂O/Ti = 4, HNO₃/Ti = 0.05. The gel was aged for 1 week. The solvent removal and calcinations followed the same procedure described for the Ti80Si20 Aerogel.

2.4. Preparation of pure TiO₂

Pure TiO₂ was prepared according to methods described in the literature [30,31,33,34] and dried according to the two methods of SCD.

2.4.1. Aerogel 496

Titanium isopropoxide (16.361 g) was added to isopropanol (84.42 g) and then distilled water (5.001 g) was added under stirring. The mixture was transferred to an autoclave and heated slowly to 270 °C and to a final pressure of 89.3 bar (the critical point of isopropanol is $T_c = 235.6$ °C

Table 4
1-Butene isomerization product composition at 200 °C over different catalysts

Product	ZSM-5	TiO ₂			TiO ₂ -SiO ₂			
		Tigel 31 (ca. 450 °C)	Tigel 29 (ca. 550 °C)	Aerogel 496 (ca. 450 °C)	Ti80Si20 (ca. 550 °C)	Ti70Si30 (ca. 550 °C)	Aerogel 481 (ca. 550 °C)	Aerogel 479 (ca. 550 °C)
C ₃ H ₈ and C ₃ H ₆	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
1-Butene	35.4	88.4	95.5	97.6	60.5	78.7	93.3	99.5
<i>cis</i> -2-C ₄ H ₈	24.9	7.6	2.7	1.3	23.9	13.1	3.6	0.0
<i>trans</i> -2-C ₄ H ₈	39.2	3.6	1.3	0.6	15.1	7.7	2.7	0.0
Isobutene	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
<i>n</i> -Butane	0.5 ^a	0.3 ^a	0.5 ^a	0.5 ^a	0.4 ^a	0.5 ^a	0.4 ^a	0.5 ^a
Isobutane	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
C ₅₊	0.0	0.1	0.0	0.0	0.1	0.0	0.0	0.0
Total	100	100	100	100	100	100	100	100

^a The same amount exists in the reactant stream.

and $P_c = 53.7$ bar). Then the autoclave was depressurized at constant temperature (260 °C). Next, nitrogen (1 ml/min) was used to flush the gel for 20 h to remove residual solvent. The calcination was done as described for Ti80Si20 Aerogel.

2.4.2. Tigel 29

The preparation method described in Ref. [30] was followed, modified by replacing tetrabutoxytitanium (IV) with the equimolar amount of Ti-isopropoxide. First two solutions were prepared: Solution A, 160 ml methanol + 35.25 g titanium isopropoxide; Solution B, 40 ml methanol + 9 g distilled water + 0.868 g nitric acid.

Solution A was placed in a covered plastic container and then stirred with a magnetic stirring bar at room temperature. Solution B was placed in a dripping funnel and added to Solution A under vigorous stirring. A slight opalescent gel was formed. The gel was aged for 1 week, the solvent was removed with liquid CO₂, and the gel dried with low-temperature CO₂ SCD as described above.

2.4.3. Tigel 31

This recipe was roughly the same as the recipe of Tigel 29; the only difference was that a fraction of acid diluted with methanol was added to the Ti-isopropoxide: Solution A, 160 ml methanol + 34.05 g Ti-isopropoxide; Solution B, 5 ml methanol + 0.234 g nitric acid; Solution C, 9 g distilled water + 35 ml methanol + 0.65 g nitric acid.

Solution A was placed in a covered plastic container and then stirred with a magnetic stirring bar at room temperature. Solution B was added to Solution A. Then Solution C was placed in a dripping funnel and added to Solution A under vigorous stirring. A slight opalescent gel was formed. The solvent was removed with liquid CO₂ and the gel dried with low-temperature CO₂ SCD as described above.

2.5. Activity test

The isomerization of 1-butene was used to evaluate catalytic activity. Catalyst (200 mg) which was sieved between 20 and 50 mesh screens was loaded into a 3/8-inch o.d.

316SS tubular down flow reactor. A mixture of 180 cc/min helium and 13.5 cc/min 1-butene flowed through the reactor. The reactor was heated by an electrical oven (Lindberg, Model 55035-A), and the reaction temperature was controlled by an OMNI 2A 3590 Omega PID controller. The reaction temperature was controlled in steps from 50 to 340 °C. A Hewlett-Packard 5890A gas chromatograph with a thermal conductivity detector was used to analyze the reaction mixture composition with a Supelco column (80/100 Carbowax C/0.19% picric acid, 2 m in length, 1/8-inch o.d. S.S.), which was used to separate saturated and unsaturated C₃–C₅ hydrocarbons.

Table 3 lists all the catalysts evaluated.

The surface area (SA) of the materials range from 69 to 673 m²/g.

3. Results

3.1. Composition of reaction products

Previous studies have reported that when 1-butene is reacted over TiO₂-SiO₂ mixed oxide catalysts at temperatures of 150–200 °C, the reaction products consist of *cis*-2-butene and *trans*-2-butene [5,14,29]. Our results confirm these findings. Table 4 lists the products obtained at 200 °C with ZSM-5, TiO₂-SiO₂, and pure TiO₂ catalysts. Even with a Brønsted acid such as ZSM-5 only linear butenes are obtained.

We have extended the study to reaction temperatures up to 340 °C and found that even at this temperature the reaction products on all Ti catalysts consist of the linear butenes only (Table 5). This result is surprising because it is known that on Brønsted acid catalysts 1-butene undergoes a number of transformations besides the double bond shift, with formation of isobutylene, and also C₃ and C₅ hydrocarbons as a result of acid-catalyzed oligomerization followed by skeletal isomerization and cracking.

Typical analysis of the reaction products obtained with the Brønsted acid catalyst ZSM-5 at 340 °C are presented in

Table 5
1-Butene isomerization product composition at 340 °C over different catalysts

Product	ZSM-5	TiO ₂			TiO ₂ -SiO ₂			
		Tigel 31 (ca. 450 °C)	Tigel 29 (ca. 550 °C)	Aerogel 496 (ca. 450 °C)	Ti80Si20 (ca. 550 °C)	Ti70Si30 (ca. 550 °C)	Aerogel 481 (ca. 550 °C)	Aerogel 479 (ca. 550 °C)
C ₃ H ₈ and C ₃ H ₆	25.8	0.0	0.0	0.0	0.0	0.0	0.0	0.0
1-Butene	8.7	25.4	28.0	37.0	33.4	49.2	43.1	88.5
<i>cis</i> -2-C ₄ H ₈	13.1	33.3	35.0	35.6	32.5	26.7	28.9	3.7
<i>trans</i> -2-C ₄ H ₈	21.9	40.8	36.5	26.9	33.6	23.7	27.8	7.3
Isobutene	15.5	0.0	0.0	0.0	0.0	0.0	0.0	0.0
<i>n</i> -Butane	2.5	0.4 ^a	0.5 ^a	0.5 ^a	0.4 ^a	0.4 ^a	0.2 ^a	0.5 ^a
Isobutane	4.3	0.0	0.0	0.0	0.0	0.0	0.0	0.0
C ₅ +	8.2	0.1	0.0	0.0	0.1	0.0	0.0	0.0
Total	100	100	100	100	100	100	100	100

^a The same amount exists in the reactant stream.

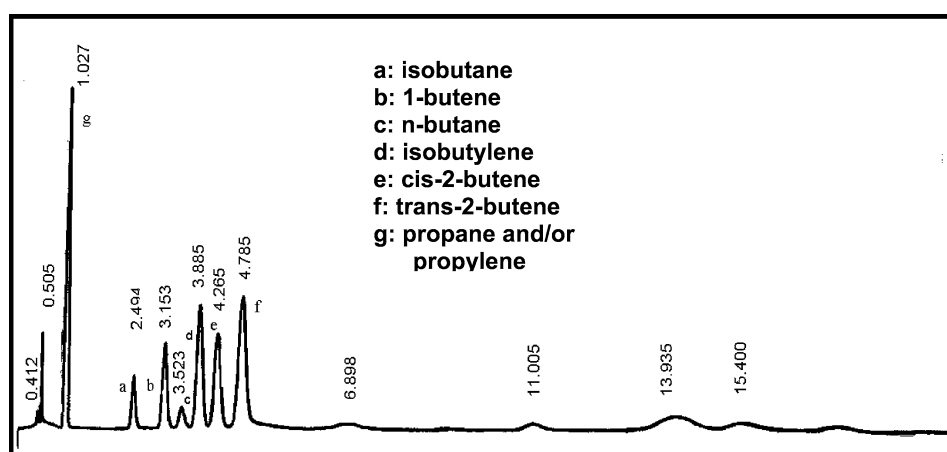


Fig. 3. 1-Butene isomerization products detected at 340 °C with ZSM-5.

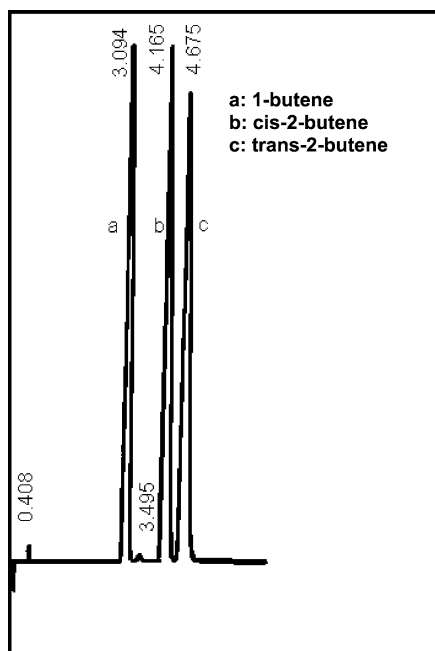


Fig. 4. 1-Butene isomerization products detected at 340 °C with Ti80Si20 calcined at 550 °C.

Table 5 and Fig. 3, while Fig. 4 presents the typical analysis of reaction products obtained with TiO₂-SiO₂ mixed oxides at the same temperature. The catalytic activity of pure TiO₂ of high SA for the isomerization of 1-butene is quite remarkable, and the reaction products obtained are also in this case the linear butenes, as shown in Fig. 5. These results differ significantly from previous reports which considered the catalytic activity of pure TiO₂ to be so low as to be irrelevant.

These results strongly suggest that pure TiO₂ could be the active component of the TiO₂-SiO₂ mixed oxides. To investigate this hypothesis the specific activity of the different catalysts has been studied.

3.2. 1-Butene isomerization activity tests

This system involves comparison of materials which have greatly different SA values, most of which is due to the SiO₂ which is not active. Citing the activity per unit SA would therefore be misleading. Methods of measuring the SA of TiO₂ in the presence of SiO₂ have been described but have not produced unequivocal results [35]. We therefore prefer to report the activity as the conversion of 1-butene to the sum of *cis*- and *trans*-2-butenes obtained for a constant weight of catalyst under a fixed value of reactant flow rate.

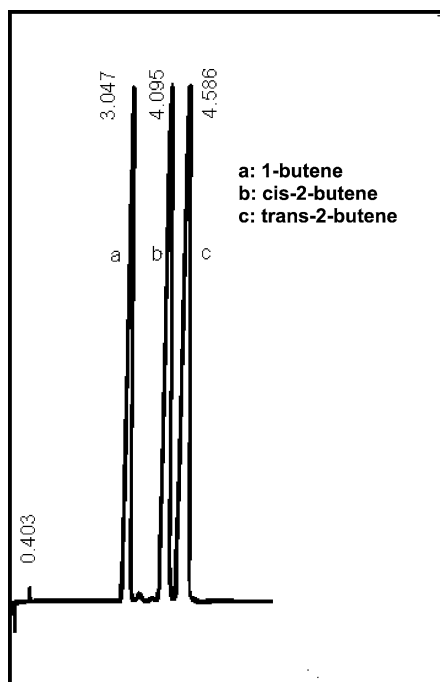


Fig. 5. 1-Butene isomerization products detected at 340 °C with Tigel 31 calcined at 450 °C.

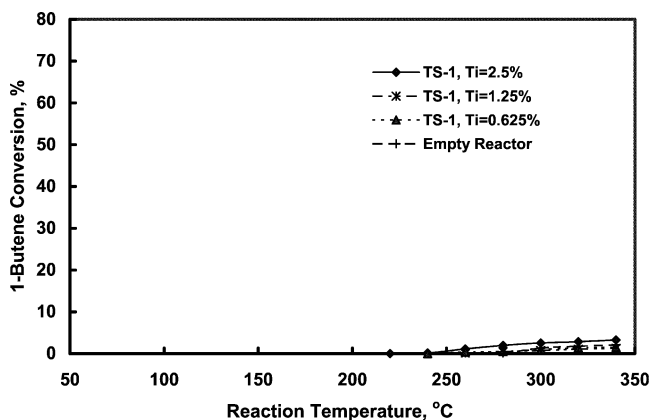


Fig. 6. 1-butene conversions as a function of temperature for TS-1 ($x = 2.5$, $x = 1.25$, and $x = 0.625$).

3.3. Crystalline materials (TS-1)

Fig. 6 shows the conversion of 1-butene as a function of temperature for pure TS-1 materials. It is clear that all TS-1 samples have almost no activity, the conversion values being similar to those obtained with an empty reactor. The Na (82 ppm) and K (370 ppm) content of the TS-1 sample with $x = 1.25$ cannot be responsible for poisoning any possible Brønsted acidity of this material, should any acidity be present. Their amount is far too low with respect to the atomically dispersed Ti present (10,000 ppm). Furthermore, there is consensus on the fact that only Lewis acidity is present in TS-1 [14]. This demonstrates that the Lewis acidity, which has been detected in previous studies in these samples, is not sufficient to catalyze the 1-butene isomerization.

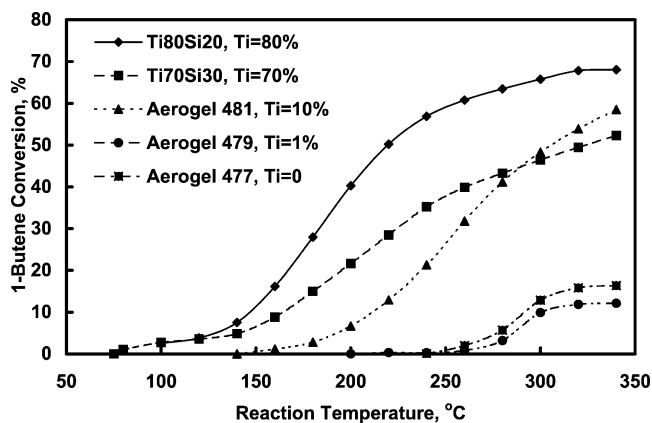


Fig. 7. 1-Butene conversions as a function of temperature for TiO_2 - SiO_2 mixed oxides.

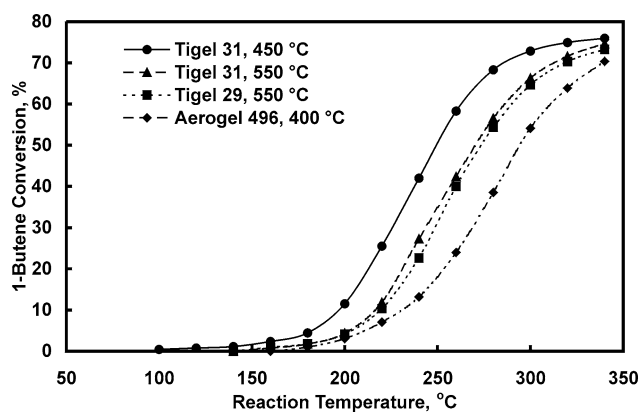


Fig. 8. 1-Butene conversions as a function of temperature for pure TiO_2 materials (Aerogel 496, Tigel 29, and Tigel 31).

3.4. TiO_2 - SiO_2 mixed oxide materials

It can be seen from Fig. 7 that Ti80Si20 has the highest activity of all materials tested and that the activity increases with the increase in Ti content of the mixed oxides, starting from Aerogel 481 (Ti = 10%). Aerogel 477 (Ti = 0) and Aerogel 479 (Ti = 1%) have very low activity. The Na (45 ppm) and K (500 ppm) content of the Ti80Si20 material apparently did not interfere with its catalytic activity. As previously noted, at low concentrations Ti is present in tetrahedral coordination substituting Si in the SiO_2 framework as found in crystalline TS-1. These results confirm the observation previously reported that activity is at a minimum in the high silica region of the mixed oxides [14].

3.5. Pure TiO_2 materials

Pure TiO_2 materials exhibit significant catalytic activity, as demonstrated by the results presented in Fig. 8. The activity depends on many factors which can influence the final value of the SA of TiO_2 . The low-temperature SCD with CO_2 produces a material (Tigel 31, 450 °C) with high SA ($235 \text{ m}^2/\text{g}$) and high activity, whereas high-temperature

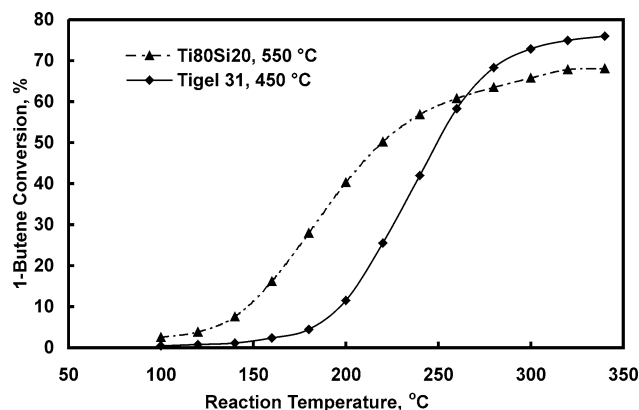


Fig. 9. 1-Butene conversions as a function of temperature for Tigel 31 and Ti80Si20.

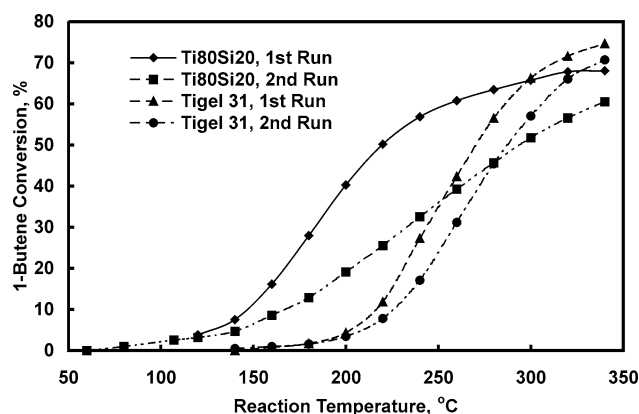


Fig. 10. Comparison of conversions for first and second run for Tigel 31 and Ti80Si20.

SCD with 2-propanol produces a material (Aerogel 496, 400 °C) with low SA (75 m²/g) and lower activity.

The activity of Tigel 31 calcined at 450 °C is higher than the activity of the same material calcined at 550 °C, consistent with a reduction of the SA from 235 to 156 m²/g. The activity of Tigel 29, 550 °C is intermediate and consistent with its SA value of 117 m²/g. In summary the catalytic activity data correlate with the SA values for these pure TiO₂ materials.

3.6. Relative activity of TiO₂ and TiO₂-SiO₂ materials

The activity of TiO₂ and TiO₂-SiO₂ materials are compared in Fig. 9. The activity of Tigel 31 is lower than that of the TiO₂-SiO₂ mixed oxides at temperatures up to 250 °C, but becomes comparable at higher temperatures. When tested in a second run, both activities are lower, but the differences between the two are now very limited, as can be seen from the data of Fig. 10.

It appears therefore that the high catalytic activity of TiO₂-SiO₂ is associated with a very high degree of dispersion of the TiO₂ component that is obtained when preparing the TiO₂ in the presence of SiO₂, but that this is a phenomenon present at low temperature that decreases for mi-

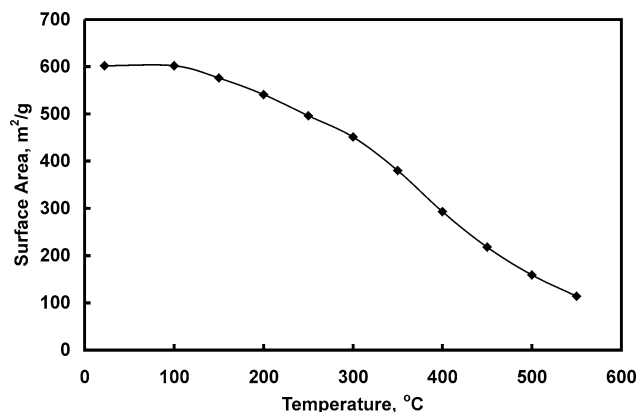


Fig. 11. Tigel 31 surface area after heat treatment under vacuum at different temperatures.

nor heat treatments as those encountered during reaction at 340 °C.

3.7. Study of thermal transformations of pure TiO₂

The unexpected catalytic activity of pure TiO₂ materials has prompted us to study the transformations of a TiO₂ gel with thermal treatment under vacuum. Tigel 31 was heated to different temperatures under vacuum at a heating rate of 1 °C/min, and then kept at the specific temperature for 2 h. Then, the SA was measured by the BET method. The results are shown in Fig. 11. Very high SA values were recorded at low temperatures, but decreased at higher temperatures, even though they always maintained values above 100 m²/g. When the heat treatment temperatures were higher than about 300 °C, the organic residues decomposed, but complete removal of the residues required oxidation at 450 °C. Since the heat treatment was done under vacuum, only the gas products were removed and some carbon deposits remained on the surface.

4. Discussion

The results reported here show that the catalytic activity of crystalline TS-1 for 1-butene isomerization is very low, indicating that the Lewis acidity of these materials is not sufficient to catalyze the transformation of 1-butene. The results also show that the products obtained at 340 °C from 1-butene with all Ti-containing catalysts consist only of the linear butenes, *cis*-2-butene and *trans*-2-butene. By contrast, with a typical Brønsted acid catalyst, ZSM-5, products beyond the linear butenes, isobutylene and C₃-C₅ hydrocarbons, are obtained as expected for a Brønsted acid catalyst. The catalytic activity of pure TiO₂ is significant and increases with the SA, a fact that has been overlooked in previous studies. The strong similarity between pure TiO₂ and TiO₂-SiO₂ and the difference in the reaction product composition with respect to Brønsted acid catalysts suggest that the active component

of the mixed oxides is a TiO_2 in the form of nanoparticles with SA higher than that obtained when SiO_2 is absent.

Our results are in such sharp contrast to what had been reported previously that we decided to undertake an examination of the experimental facts on which claims for Brønsted acidity for TiO_2 – SiO_2 have been based. They are:

Poisoning effects of NH_3 on the catalytic activity for 1-butene isomerization [5];

IR spectra of adsorbed NH_3 with formation of NH_4^+ ions [14];

IR spectra of adsorbed pyridine with formation of pyridinium ions [36];

Catalytic activity for some reactions such as 1-butene isomerization and alcohol dehydration [37].

The first three pieces of evidence can be discussed together. It has recently been shown that NH_3 gives strong absorption on many different oxides, not only on acid materials, and that the results can be misleading [38]. For example, the temperature-programmed desorption (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 [39]! Because the absorption of NH_3 on non-Brønsted sites may be stronger than on Brønsted sites, the recommendation has recently been made NOT to use NH_3 for probing acid sites [40]. This absorption of NH_3 on non-Brønsted acid sites could well be the reason for the observed reduction in 1-butene isomerization catalytic activity [5].

In the case of TiO_2 a further complication arises because of its ability to oxidize many compounds, changing the simple acid–base chemistry into the more complex oxidation–reduction chemistry. For example, on TiO_2 the dehydration of ethanol does not give rise only to ethylene and water: a substantial amount of butadiene is formed via the oxidation to acetaldehyde, aldol condensation, and dehydration [41]. Obviously surface probe molecules such as NH_3 can be changed by this oxidizing ability of TiO_2 . The case of the pyridine absorption provides some useful information. While pyridinium ions were identified upon absorption on the oxidized sample of TiO_2 – SiO_2 , no such ions were detected in the spectra obtained when TiO_2 – SiO_2 samples were reduced with H_2 , which led the authors to conclude that “no Brønsted acidity was observed for the reduced sample” [36]. Clearly the reduction with H_2 modified the ability of TiO_2 to oxidize surface species which gave rise to the pyridinium bands which were interpreted as evidence of Brønsted acidity.

The evidence concerning the catalytic activity for 1-butene isomerization has already been discussed: no evidence of Brønsted acidity has been found. Catalytic activity in alcohol dehydration has been associated with acidity of solid catalysts in the early theories on heterogeneous catalysis. No doubt Brønsted acids DO catalyze alcohol dehydration, but when Brønsted acidity is present, very low reaction tem-

peratures 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 [42]. This has led to the generalization that all alcohol dehydration reactions are acid catalyzed and some authors have proposed to correlate the activity for alcohol dehydration to the acidity of catalysts [43,44]. This correlation has been criticized [45]. For the specific case of the TiO_2 – SiO_2 mixed oxides we have already noted the case of ethanol which gives complex reaction mixtures. We plan to investigate other reactions on which claims of Brønsted acidity have been based, such as the dehydration of methanol on TiO_2 and TiO_2 – SiO_2 materials [37] and of alcohols in general.

In summary the claim for new Brønsted acidity [11,14, 43] is not supported by the results of this investigation. This also means that the hypotheses (Tanabe, Seiyama, etc.) to explain how Brønsted acidity is generated are not valid.

5. Conclusions

High-purity TiO_2 prepared according to the low-temperature CO_2 supercritical drying method has high surface area and high activity for 1-butene isomerization, and its activity increases with the surface area. The reaction products obtained consist ONLY of the linear butenes up to a reaction temperature of 340 °C.

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. This result is in sharp contrast with what is expected from a material with Brønsted acid properties. The similarity 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 suggest that the reaction takes place on TiO_2 in both cases. 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, when applied to materials that have oxidizing ability, produce unreliable results.

The activity of TiO_2 – SiO_2 mixed oxides in the double bond isomerization of 1-butene could be accounted for simply by a high degree of dispersion of the TiO_2 nanoparticles. In this hypothesis, the role of SiO_2 could be that of enhancing the degree of dispersion of TiO_2 during the preparation process, and stabilizing the nanoparticles of TiO_2 against thermal sintering. In the pure TiO_2 it is observed that sintering takes place at temperatures lower than those at which sintering of TiO_2 – SiO_2 mixed oxides takes place. This reduction in surface area of TiO_2 could be the cause of the low catalytic activity reported in previous studies.

In the absence of any Brønsted acid site for TiO₂–SiO₂, the Tanabe and Seiyama hypotheses to explain the formation of such acid sites applied to the TiO₂–SiO₂ are clearly unfounded.

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