

Synthesis, characterization and catalytic properties of titania–silica catalysts

Mohamed Mokhtar Mohamed^{a,*}, T.M. Salama^b, T. Yamaguchi^c

^a Chemistry Department, Faculty of Science, Benha University, Benha, Egypt

^b Chemistry Department, Faculty of Science, Al-Azhar University, Naser City, Cairo, Egypt

^c Department of Applied Chemistry, Faculty of Engineering, Ehime University, Matsuyama, Japan

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Abstract

The preparation of titania doped ($0.63\text{--}3.2\text{ mmol g}^{-1}$) silica ($\text{TiO}_2/\text{SiO}_2$) was described together with a mixed oxide sample ($\text{TiO}_2\text{--SiO}_2$) at a nominal molar ratio near to 1. These materials were thoroughly characterized by XRD, N_2 adsorption at 76 K and ammonia adsorption measurements as well as FTIR spectroscopy. The activity of the materials towards 1-butene isomerization was also tested. FTIR results showed a band at 612 cm^{-1} attributed to bulk TiO_2 phase, in the doped 3.2 mmol g^{-1} $\text{TiO}_2/\text{SiO}_2$ sample, that was paralleled to an exhibited perturbation for the SiO_2 bands in the low frequency region, specifically those at 470 and 808 cm^{-1} . The former band was similarly obtained in the $\text{TiO}_2\text{--SiO}_2$ sample, with a lower decrease in intensity, together with the appearance of a new band at 948 cm^{-1} attributed to Ti–O–Si linkages. This deed indicated the decrease in population of Ti–O–Ti bridges in the mixed oxide sample. FTIR spectra of adsorbed D_2O established the presence of different types of titania hydroxyl groups (3615 and 3520 cm^{-1}) that were composed during desorption of water from the titania surface. The activity towards 1-butene isomerization was found to increase gradually, in the doped samples, to achieve its maximum at the titania loading 3.2 mmol g^{-1} , however, a tremendous decrease was obtained for the mixed oxide sample. This behavior was correlated with the acidity of the samples. The dependence of the reaction on either Ti–O–Ti or Ti–O–Si sites was evaluated and discussed. © 2002 Published by Elsevier Science B.V.

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1. Introduction

The most important class of oxides and mixed oxides widely used in catalysis are those of transition metal oxides. It has been acknowledged, in

the last two decades that TiO_2 attracted a great deal of attention as a support material. For example, doping the TiO_2 support with Rh enhances the catalytic reduction of NO [1]. TiO_2 supported V_2O_3 (WO_3) catalysts have also been used as a commercial selective catalytic reduction (SCR) for NO by ammonia [2,3].

TiO_2 can be added in small amounts or mixed with some other oxides so as to improving surface

* Corresponding author

E-mail address: mohmok2000@yahoo.com (M.M. Mohamed).

characteristics (surface area and porosity), thermal stability and surface acidity of the composite catalysts and consequently their catalytic performances. For instance, Rh dispersed on TiO₂ doped SiO₂ carrier was used to enhance CO dissociation as well as improving the selectivity to ethanol formation in the CO hydrogenation reaction [4,5]. The presence of titanium enhances the active sites number for the latter reaction if compared with that of titanium free Rh/SiO₂ catalyst. The well dispersion of TiO₂ particles in SiO₂ supported Ni increased the rate of ethane hydrogenolysis and CO hydrogenation reactions [6]. Lisitsyn et al. have established that the presence of Ti ions into silicate skeleton enhanced the dispersion of CO that led to the increase in the relative yield of light hydrocarbons and ethanol in the CO hydrogenation reaction [7].

From the foregoing survey, it becomes clear the promising potential of TiO_x on SiO₂ in controlling and enhancing the catalytic performance (activity and selectivity) of some supported metal catalysts towards specific reactions [8,9]. However, a scarce attention has been paid for investigating the nature of dispersed TiO₂ particles on the SiO₂ support that exhibited major differences from that of the bulk TiO₂ [10]. For example, the effect of adding TiO₂ onto SiO₂ extensively induced higher acidic properties than that for the bulk TiO₂ [11]. Recent studies [12,13] of synthesized TiO_x/SiO₂ catalysts showed through Raman study that both structural and coordination changes of TiO₂ in TiO_x/SiO₂ were confirmed as a result of the influence of preparation parameters. The nature and the oxidation states of titania in the TiO_x/SiO₂ catalyst were also determined by Fernandez et al. [14]. Nevertheless, the relation between the catalytic properties of the TiO_x/SiO₂ system and the structure transformation of TiO₂ ions following its incorporation into silica is still not yet clarified.

In this work, infrared (IR) spectroscopy is used to study the TiO_x/SiO₂ system at varying titania loadings (0.63–3.3 mmol g⁻¹), with giving attention to the high frequency region together with the low frequency one. The dispersion state, surface properties, acidity and their effects on the catalytic activity towards 1-butene isomerization were evoked and discussed.

2. Experimental

2.1. Catalyst preparation

The parent silica used in the present study was obtained from Degussa Aerosil 200 (200 m² g⁻¹). To prepare TiO₂ doped SiO₂ carrier; weighed amounts of titanium tetra-isopropoxide were refluxed, in toluene solution, at 380 K with the SiO₂ support under a N₂ atmosphere. These samples were then dried under vacuum and calcined at 823 K for 5 h. Four series of TiO₂/SiO₂ were prepared and denoted by S_I, S_{II}, S_{III} and S_{IV} representing 3, 6, 9 and 15 wt.% Ti loadings, respectively. Each deposition process was repeated four times. The TiO₂-SiO₂ mixed oxide sample (molar ratio near to 1) was prepared by co-hydrolysis of the ethanol solution of titanium isopropoxide and silicon ethoxide under continuous stirring at 373 K. The residue was washed repeatedly with water and ethanol and dried at 383 K for 24 h. The dried material was then heated to 823 K for 5 h and then slowly cooled to room temperature.

2.2. Catalyst characterization

Powder diffraction patterns of the samples were obtained using a Philips PW213/00, using nickel-filtered CuK α radiation ($\lambda = 1.5405$) at 35 kV and 20 mA at a scanning rate of $2\theta = 2^\circ \text{ min}^{-1}$.

The specific surface areas were determined using the BET equation from physical adsorption of N₂ at $T = 77 \text{ K}$. The BET equation was applied on the part of the adsorption isotherm in the $0.05 < p/p^\circ < 0.35$ range. The solids were outgassed at 473 K to a residual pressure of 10^{-4} torr, and the weight of the outgassed sample was that used in calculations.

The amount of acid sites was determined for ammonia coated samples through subjecting to TG analysis over the temperature range from ambient to 873 K at a heating rate of 2.5 K min⁻¹ under dry N₂ (40 cm³ min⁻¹). The TG curves were automatically recorded on a model Shimadzu DT 40 unit. The weight loss was measured as well as the derivative weight loss as a function of temperature. This was to determine

the amounts of ammonia irreversibly adsorbed. More details concerning ammonia adsorption can be seen elsewhere [15]. The enthalpy change (ΔH) during ammonia desorption over a given temperature range was derived from a power compensated DSC model Setaram 131 unit. This value is considered to show the relative strength of acid sites involved together with temperature ranges in which the peak maximum is occurred.

FTIR spectra of the samples were recorded on a JASCO FTIR 5300 spectrometer at room temperature with 40 co-added scans at 2 cm^{-1} resolution. The sample was pressed into a self-supporting wafer and mounted in a quartz IR cell with CaF_2 windows that connected to a vacuum (10^{-4} torr) closed circulating Pyrex system with a dead volume of 189 cm^3 . The D_2O was admitted onto the samples at 373–573 K and was desorbed at same temperatures prior the measurements. The IR cell was equipped with an electric furnace.

Isomerization of 1-butene was carried out in the above mentioned closed circulating system that connected with a U type reactor, in which the samples were charged. The ratios of *cis/trans*-2-butene were obtained by extrapolating to zero conversion. The sample was pretreated in air at 823 K followed by degassing at 673 in vacuum prior to the admission of the reacting gas. The product gas mixture was withdrawn periodically for the gas chromatographic (Tracor-540) analysis over chromosorb W AW column coated with 20% dimethylsulfolane operated at 273 K. More informations on the steps during and prior the catalytic measurements can be seen elsewhere [16].

3. Results and discussion

3.1. Surface and morphology

Table 1 revealed the changes in S_{BET} surface areas of silica as a function of increasing the Ti loading. Apparently, the presence of small amounts of TiO_2 in SiO_2 does not significantly alter the catalyst surface area. Small changes in the area was perceived at the 9 wt.% Ti loading (the S_{III} sample) after which a marked reduction in the area for the S_{IV} sample was obtained, that comprised 45% from that of silica support. An increase in the crystallite size of titania particles was obtained as the titania loading reached 9 wt.%, confirming the possibility of sintering titania particles as a result of calcination at 823 K i.e. bulk expansion took place. The latter phenomenon was more clarified in the S_{IV} sample that showed particles size enhancement into 5.0 nm and as a result a marked decrease in the BET surface area was depicted. This indicates that titania content in the latter sample is above limit for monolayer coverage, as can be calculated from the surface area of the SiO_2 support and the lattice parameters of TiO_2 . An amorphous feature was depicted for all samples except S_{III} and S_{IV} ones, which showed crystallite features as a result of exposing the diffraction line at $2\theta = 23.4$ due to (101) phase of TiO_2 anatase. Fig. 1 also shows the changes in crystallinity and surface areas versus Ti contents in the doped $\text{TiO}_2/\text{SiO}_2$ samples. The crystallinity growth of titania particles beyond the 9 wt.% loading while decreasing the surface areas

Table 1
Molar compositions, surface properties and morphologies of the studied samples

| Sample | Ti content | | V_p (ml g^{-1}) | S_{BET} ($\text{m}^2 \text{g}^{-1}$) | r_{H} (Å) | XRD analysis, average particle size (nm) |
|--|----------------------|------|---------------------------------|--|-----------------------|---|
| | mmol g^{-1} | wt.% | | | | |
| TiO_2 | 15.8 | 72.5 | | 20 | | 15% rutile, 85% anatase |
| $\text{TiO}_2\text{-SiO}_2$ (mixed) | 9.3 | 44.6 | 0.33 | 305 | 11.12 | Amorphous |
| $\text{TiO}_2/\text{SiO}_2$ (S_{I}) | 0.63 | 3.0 | 0.38 | 165 | 23.0 | Amorphous |
| $\text{TiO}_2/\text{SiO}_2$ (S_{II}) | 1.3 | 6.0 | 0.35 | 157 | 22.4 | Amorphous |
| $\text{TiO}_2/\text{SiO}_2$ (S_{III}) | 1.9 | 9.0 | 0.32 | 151 | 21.2 | 2.7 |
| $\text{TiO}_2/\text{SiO}_2$ (S_{IV}) | 3.2 | 15.0 | 0.22 | 116 | 19.1 | 5.0 |

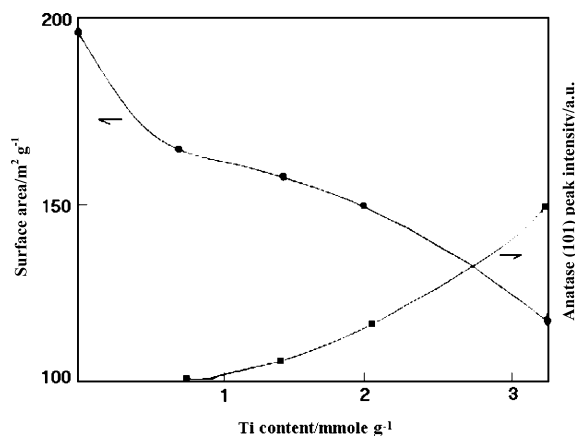


Fig. 1. Changes of crystallinity and surface areas as a function of Ti contents in the doped $\text{TiO}_2/\text{SiO}_2$ samples.

can be illustrated in this figure. This can be due to blocking of silica fine pores and even rather narrowing the wide ones as can be estimated from the monotonous decrease in both area and pore volume (Table 1), which were paralleled to a consecutive decrease in r_H values at the time of increasing the titania contents.

3.2. IR spectroscopy

The IR spectrum of the parent silica (heated at 823 K) (Fig. 2(a)) displays in the low frequency region bands at 1110, 808 and 470 cm^{-1} due to asymmetric stretching, symmetric stretching and bending modes of bulk SiOSi, respectively [17]. The small sharp band at 980 cm^{-1} is due to Si–OH stretching of surface silanol groups [18]. The IR spectra of the doped $\text{TiO}_x/\text{SiO}_2$ samples (from S_I to S_{III}) showed no change neither in intensity nor in position for the 1110 cm^{-1} band. However, the spectrum of the S_{IV} sample showed multiple spectral changes as a result of increasing the titania loadings into 15 wt.%. The 980 cm^{-1} band showed a marked decrease in intensity the same as the 808 cm^{-1} band that lost its symmetry. An evolution of a new band at 612 cm^{-1} was depicted in addition to a significant decrease in intensity for the 470 cm^{-1} band that was inferred from its relative intensity in comparison with the most intense band at 1110 cm^{-1} .

The involvement of silica surface hydroxyls in interaction with titanium ions, is manifested by the marked decrease in intensity of the 980 cm^{-1} band. As a consequence of this interaction, a Si–O–Ti linkage of a band in the $960\text{--}940\text{ cm}^{-1}$ region should be formed but, however, it could be masked due to the presence of the 980 cm^{-1} ($\nu\text{Si-OH}$) band. This suggestion is further confirmed by the developed band at 612 cm^{-1} , attributed to the TiO_2 bulk phase [19], due to the fact that the formation of Ti–O–Si linkages are prerequisite for the generation of the latter phase. More interestingly, the remarkable loss in intensity of the bending mode (SiOSi) at 470 cm^{-1} in the S_{IV} sample might infer the engagement of Ti atoms into siloxane bridges. The sharpening behavior observed for the latter band could be resulted from the condensation of hydroxyls that are too near to each other as distinct from changes in the Si–O–Si angle (144°) and the

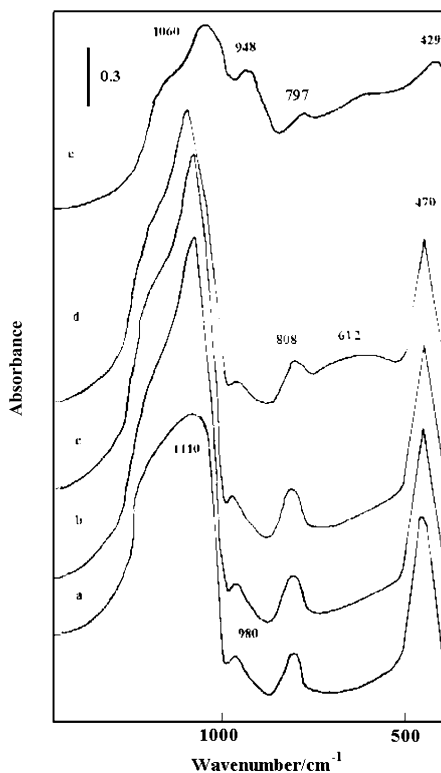


Fig. 2. FTIR spectra, in the $1400\text{--}400\text{ cm}^{-1}$ range, of: (a) parent silica; (b) S_I ; (c) S_{III} ; (d) S_{IV} ; (e) $\text{TiO}_2\text{--SiO}_2$.

Si–O bond length (1.63 Å) [20]. It appears also that titanium atoms in the S_{IV} sample appear to engage the O–Si–O linkages (808 cm^{-1}) causing an effective decrease in its intensity.

On the other hand, the $\text{TiO}_2\text{-SiO}_2$ sample showed major spectral changes. The 1110 cm^{-1} band exhibited a shift to lower frequency (1060) with a significant decrease in intensity. An intense band at 948 cm^{-1} was observed at the expense of vanishing that at 980 cm^{-1} . The bands at 808 and 470 cm^{-1} showed severe loss and shift to lower frequencies to develop at 797 and 429 cm^{-1} , respectively. Besides, a marked decrease in intensity of the 612 cm^{-1} band was also depicted. The clear presence of the 948 cm^{-1} band (Ti–O–Si) with the increase in the Ti loading evidenced the enhanced increase in the interaction between Ti ions and silica. Moreover, the exhibited decrease in the 612 cm^{-1} band that belongs to TiO_2 bulk phase and assigned to $\nu\text{Ti-O}$, can be considered as evidence to the depletion of Ti–O–Ti linkages.

To account for this behavior, a pair of OH groups that are close together results in strongly held Ti species. However, a more widely separated pair causes the bonding in Ti–O–Si to be weak; at low Ti contents, and eligible for breaking during heating up to 823 K. This was the case in the S_{IV} sample that showed a significant decrease in intensity for the 980 cm^{-1} band during building up of the TiO_2 bulk phase that was represented by the broad band at 612 cm^{-1} . However, the chances of interaction between Ti and OH groups of silica are enhanced as the Ti loading reaches 48 wt.%, in the mixed sample, confirming that most of titania are consumed through the formation of Ti–O–Si linkages (948 cm^{-1}). As a consequence of the exhibited strong interaction between Ti and Si at such loading small amounts of Ti detach to form TiO_2 during the course of heating. It is interesting to note that the intensity of the 948 cm^{-1} band did not decrease after calcining the $\text{TiO}_2\text{-SiO}_2$ sample at 973 K for 2 h (not shown). This indicates that once titania ions were well incorporated into silica, it is difficult to remove it even at high temperatures. Fig. 3 depicts the IR spectra of the mixed oxide sample, $\text{TiO}_2\text{-SiO}_2$, after thermal treatment in air at 1173 K in comparison with that at 773 K. A separate phase of

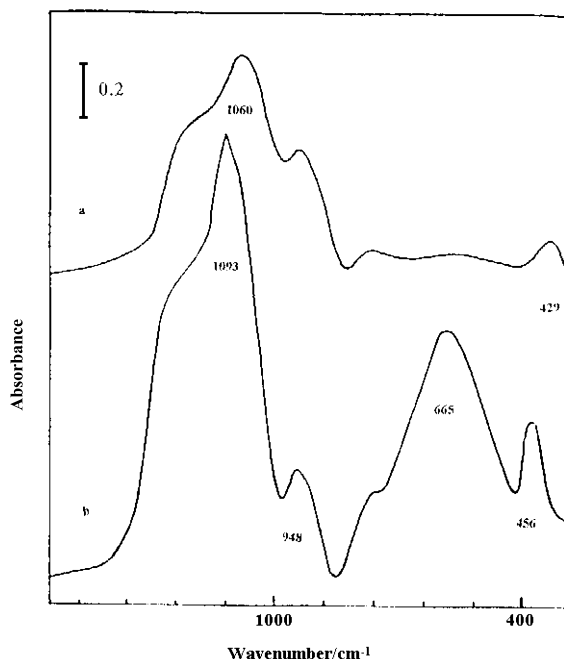


Fig. 3. FTIR spectra, in the $1400\text{--}400\text{ cm}^{-1}$ range, of the $\text{TiO}_2\text{-SiO}_2$ catalyst at: (a) 773 K; (b) 1173 K.

titania was observed through the existence of a strong band at 665 cm^{-1} attributed to TiO_2 species after calcination at 1173 K. In addition the bands at 1060 and 429 cm^{-1} of the calcined sample at 773 K were shifted to 1093 and 456 cm^{-1} , respectively with a concomitant increase in intensity after calcination at 1173 K. Resuming the intensities and wavenumbers of former bands to resemble those in SiO_2 support (Fig. 2(a)) emphasized the presence of unperturbed SiO_2 phase after the detachment of titania as TiO_2 phase. The presence of the 665 cm^{-1} band indicates that the majority of TiO_2 are in sixfold coordination [15].

In order to follow the hydroxyl groups of titania apart from those of silica, a D_2O adsorption on some representative samples was undertaken. Fig. 4(A1) presents the $\nu(\text{OH})$ bands, in the $4000\text{--}3000\text{ cm}^{-1}$ region, while Fig. 4(B1) represents the $\nu(\text{OD})$ bands in the $3000\text{--}2000\text{ cm}^{-1}$ range that resulted from D_2O adsorption on the S_{IV} sample. In comparison is shown the spectrum of the SiO_2 support, in section A, that indicated a

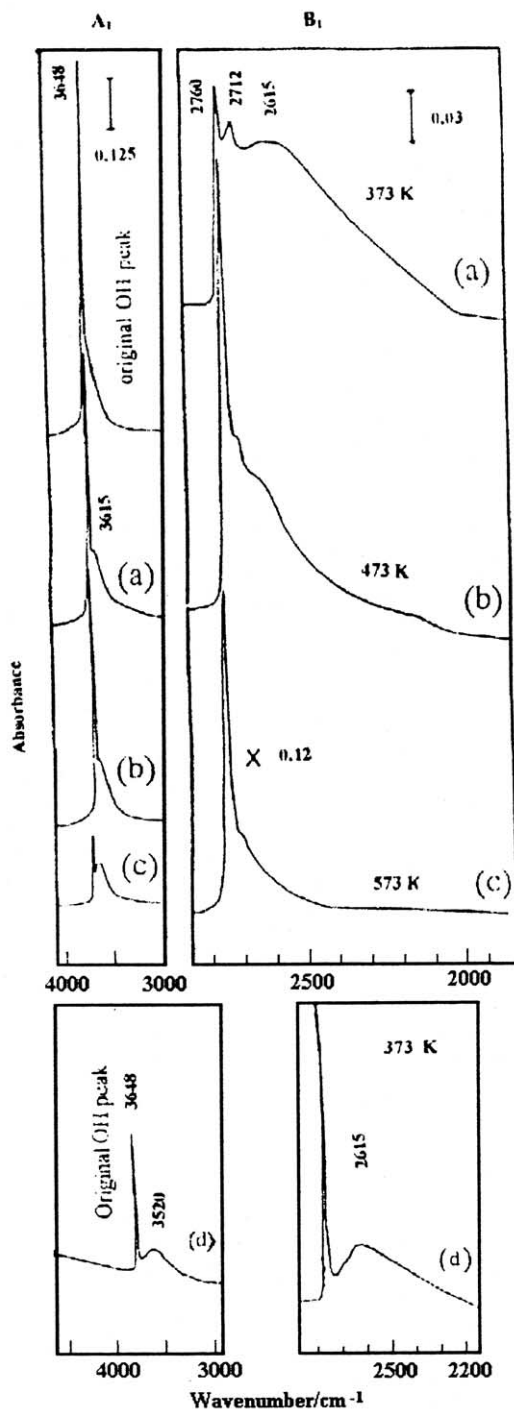


Fig. 4. OH and OD stretching bands of the doped S_{IV} and mixed TiO_2-SiO_2 samples at different adsorption–desorption temperatures: (a) S_{IV} at 373 K; (b) S_{IV} at 473 K; (c) S_{IV} at 573 K; (d) TiO_2-SiO_2 at 373 K. In comparison is shown the SiO_2 spectrum.

single band at 3648 cm^{-1} . A sharp strong band at 3648 cm^{-1} due to stretching vibrations of the isolated (noninteracting) surface silanol and a very small shoulder at 3615 cm^{-1} , preceded by a tail in the range $3500\text{--}3300\text{ cm}^{-1}$ were observed at 373 K. On the other hand, intense OD absorption bands at 2760 and 2712 cm^{-1} were observed together with elaboration of a broad band at 2615 cm^{-1} . Comparison of spectra in (A1) and (B1) showed that homologous $\nu(OH)$ (3648 and 3615 cm^{-1}) and $\nu(OD)$ (2760 and 2712 cm^{-1}) bands were revealed, except the $\nu(OD)$ band at 2615 cm^{-1} that has no corresponding $\nu(OH)$ band. Thus, the latter band can be attributed to Ti–OD species. The 3615 cm^{-1} band was only revealed when titanium ions were incorporated into silica, thus it belongs to stretching mode of titania free hydroxyl $\nu(OH)$ groups.

Increasing the adsorption–desorption temperature of D_2O to 473 K showed a significant increase in intensity of the band at 2760 cm^{-1} and a marked reduction for the bands at 2712 and 2615 cm^{-1} . Resuming the intensity of the former band can be due to the perturbation of latter ones. At 573 K, a marked decrease in intensity of the $\nu(OH)$ band at 3648 cm^{-1} was observed that paralleled to a significant increase for the 3615 cm^{-1} band. This can be due to condensation of OH groups of silica that loses its hydration water at 473 K i.e. surface dehydroxylation begins (3648 cm^{-1}), whereas titania surface may retain molecular water up to 623 K [21]. The 2615 cm^{-1} band was completely vanished at 573 K admitting that the $\nu(OD)$ mode of Ti–OD; and more specifically to deuterium coordinated Ti^{4+} ions, was depleted.

Exposure of the TiO_2-SiO_2 sample to D_2O adsorption at 373 K, Fig. 4 spectrum d, leads to striking variation particularly vanishing the band at 3615 cm^{-1} , seen in the S_{IV} sample, and the appearance of a broad band at 3520 cm^{-1} . The disappearance of the $\nu(OH)$ band at 3615 cm^{-1} at such high loading of titania and the evolution of the 3520 cm^{-1} band implies the participation of the former band (active site) in the interaction with Si atoms whereas the latter probably stand for another Ti–OH groups. The presence of latter groups was further evidenced by D_2O through the

Table 2
Acidic properties and TOFs for the doped TiO₂/SiO₂ and mixed TiO₂-SiO₂ catalysts

| Sample | NH ₃ -TPD T _m /K NH ₃ ^a | Amount of acidic sites ^b (mmol g ⁻¹) | TOF molecule (min ⁻¹ per site) | Cis/trans ^c |
|--|--|--|--|------------------------|
| Bulk TiO ₂ | | 1.88 | 0.92 | 4.5 |
| Mixed TiO ₂ -SiO ₂ | 380 | 10.84 | 0.32 | 2.0 |
| Doped TiO ₂ /SiO ₂ | | | | |
| S _I | 393 | 1.85 | 0.92 | 2.60 |
| S _{II} | 405 | 3.0 | 1.50 | 3.2 |
| S _{III} | 417 | 3.5 | 1.76 | 3.4 |
| S _{IV} | 395 | 3.25 | 3.10 | 3.7 |

^a T_m is the maximum temperature observed during the temperature-programmed desorption of ammonia via DSC.

^b The amount of ammonia desorbed via temperature-programmed desorption using TG.

^c At zero conversion.

appearance of the 2615 cm⁻¹ band of Ti-OD species. This band can tentatively be ascribed to hydrogen-bonded Ti-OH groups that existed on the surface due to excess titania, which retain molecular water to larger extent than that of silica. This hydrogen bonded OH groups (3520 cm⁻¹) were not appeared in the TiO₂/SiO₂ samples confirming that water molecules included in titania, at the loading margin 3–15 wt.%, were not able to form hydrogen bonded species but indeed promoted the formation of free Ti-OH groups (3615 cm⁻¹). From the foregoing results, one can suggest that at low loadings (doped samples) the interaction was apparently taken part in narrow pores of the SiO₂ substrate. However, at high titanium loading, a great part of the interaction occurs in the wide pores after filling off the smaller ones to show a high perturbation to the OH groups as has been occurred for the TiO₂-SiO₂ sample. Similar behavior was obtained as a result of molybdenum interaction with silica substrate at a 15 wt.% Mo loading [17,22].

3.3. Acid sites and the catalytic performance towards 1-butene isomerization

The amount of NH₃ desorbed (as determined from TG analysis) at the maximum temperature (as determined from DSC analysis, T_m) as well as the turn over frequencies (TOFs) for 1-butene isomerization for the samples are summarized in

Table 2. It can be seen that in the doped TiO₂/SiO₂ samples, the enhancement of acid site densities and their strengths was obtained. The amounts of acid sites for the TiO₂ sample were smaller than either those of doped (S_{II}-S_{IV}) or mixed oxide TiO₂-SiO₂ samples.

The catalytic activity of the doped TiO₂/SiO₂ samples was increased with the increase of Ti contents in silica. An abrupt increase of TOF for the S_{IV} sample is depicted that did not match to an increase in the amount of acid sites, i.e. fair amount of acid sites. Furthermore, the strength of latter sites in the S_{IV} sample was comparatively lower than that of the S_{III} sample. The cis/trans ratio was increased monotonically for doped samples, which was corresponding to the increase of Ti contents in silica. The mixed oxide sample revealed comparatively very low isomerization activity; although the higher amount of acid sites that showed lower strength than those of the doped samples.

From these results, it appears that the Ti-O-Ti linkages (S_{IV} sample) are rather important than the Ti-O-Si ones that rule in the TiO₂-SiO₂ sample. This states that bulk TiO₂ has the determining role for the isomerization of 1-butene, i.e. the oxide ion in the Ti-O-Ti bridge is of mechanistic importance. This can be due to the interaction of the double bond on the active sites via vinyl carbon atoms with exposing the corresponding unsaturated Ti atoms at the surface to form

allelic intermediate. Thus, the oxide ion plays as a medium for the transfer of a proton from the Π allelic carbon to the terminal olefinic carbon allowing the double bond isomerization. Such ion pair sites as those pointed by Peri (acid–base) [23] are very important, as they are the driving forces for 1-butene isomerization. According to this mechanism, the transfer requires the presence of Ti^{4+} and O^{2-} ions, forming acid–base pairs, and hydroxyl groups with a sufficiently mobile proton [24]. Accordingly, suppression of the activity of the mixed sample may be due to lowering the acid strength of OH groups when compared with those of doped ones. This strongly indicates the necessity of $\text{Ti}^{4+} - \text{O}^{2-}$ pairs in addition to appropriate amounts of acid sites.

4. Conclusions

The XRD analyses and the induced changes in the texture of silica due to doping or mixing with titania evidenced significant differences in titania morphology as well as surface structure. It was shown through employing the D_2O adsorption that different titania OH groups were formed as a result of retaining the water of hydration on the titania surface to high temperatures. The generation and domination of Ti–O–Ti linkages (active sites) in the doped 3.2 mmol g^{-1} ($\text{TiO}_2/\text{SiO}_2$) sample was responsible for exhibiting higher activity towards 1-butene isomerization rather than that of the mixed oxide one that exposed Ti–O–Si linkages. This was due to the presence of excess $\text{Ti}^{4+} - \text{O}^{2-}$ ion-pairs in the former sample besides the feasibility of hydrogen donation if compared with the latter.

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