Acidity studies of titania–silica mixed oxides

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A series of titania–silica mixed oxides were prepared by co-precipitation and sol–gel methods. The mole fraction of titanium was varied from 0 to 1. The effects of preparation method and chemical composition on the physical properties and acidity profiles of mixed oxides were examined. While pure silica was non-acidic and titania contained only Lewis acid sites, Brønsted acidity was created by the Ti–O–Si interaction in the binary oxides. Samples containing a titania : silica mole ratio of 9 : 1 possessed the largest amount of Brønsted acidity. The generation of acid sites and the stability of the oxide was a strong function of preparation method. With all preparation methods, higher calcination temperatures increased crystallinity and decreased the total number of acid sites.

Keywords: TiO_2 / SiO_2; mixed metal oxides; acidity; TGA; DRIFTS

1. Introduction

Mixed oxides frequently possess unique catalytic properties in comparison to those of the pure oxide components [1–3]. The most notable case, silica–alumina, has been widely used for many acid catalyzed reactions [4,5]. Silica–alumina is a stronger acid than either pure silica or alumina [6]. Acid centers are created by a charge imbalance which results from substitution of Al(III) into the SiO_2 structure. Recently, there has been increasing interest in titania–silica mixed oxides. Materials belonging to this system have acidity comparable to silica–alumina [7]. Moreover, titania–silica mixed oxides are used as supports for several catalysts such as nickel for CO hydrogenation [8], chromia for polymerization [9], and more recently, as supports for vanadia-based catalysts for NO_x reduction by ammonia [10,11]. Unlike silica–alumina, simple substitution of Ti(IV) for Si(IV) in the oxide structure does not create an obvious charge imbalance. Several theories have been developed to justify the enhanced acidity of these mixed oxides [12–14].

Tanabe [12] suggests acidity is generated by a charge imbalance caused by substituting a metal atom into the structure of the host oxide. His model is based on two hypotheses: (i) positive metal atoms retain the coordination number found in

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its pure oxide; and (ii) oxygen assumes the coordination number of the major component. Therefore, when oxides possessing different structures combine, a charge imbalance is created which leads to the generation of new acid centers. When Tanabe's model is applied to the TiO_2–SiO_2 system, it would predict that in titanium-rich binary oxides, Lewis acidity is generated while in silicon-rich systems new Brønsted sites are created.

Seiyama [13] predicts that new acid sites will form at the boundary of two oxides. In TiO_2–SiO_2, oxygen bridging between titanium and silicon will develop a net negative charge. At the interface, oxygen develops a negative charge resulting in the formation of Brønsted acidity. Thus, regardless of composition, Seiyama's model predicts the new acid centers on TiO_2–SiO_2 mixed oxides will be Brønsted sites.

The goal of this study is to evaluate the acidity profile of a series of titania–silica mixed oxides in an attempt to further our understanding of this system. Prediction of the impact of modifying solid acidity on the catalytic properties of mixed oxide requires a comprehensive knowledge of acid density, type, and strength distribution. A multi-technique approach is used in this study to analyze the acidity of TiO_2–SiO_2 mixed oxides. Thermogravimetry of pyridine is used to determine the population of acid sites. Total acidity is determined by measuring the pyridine adsorption at 150°C, while the number of strong acid sites is determined by pyridine adsorption at 350°C. Diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS) of adsorbed pyridine is used to determine the relative amounts of Lewis and Brønsted acid sites. Methanol dehydration is used to probe the catalytic activity of TiO_2–SiO_2 mixed oxides.

Because interaction of titania and silica is critical to the creation of acid sites, preparation method is expected to have a strong influence on acidity. Therefore, titania–silica samples prepared by various routes are examined.

2. Experimental

2.1. SAMPLE PREPARATION

Co-precipitation method. Mixed oxides of titania and silica were prepared by co-precipitation of titanium and silicate salts according to the method of Itoh et al. [15]. Aqueous solutions of $TiCl_4$ and $(C_2H_5)_4SiO_4$ were mixed to give the desired chemical composition. The mixture was treated with HCl, heated to 95°C, and held at this temperature for 1 h. Titania–silica mixed oxides were precipitated by slowly adding ammonium hydroxide (14.5 M) until the solution was neutralized. The precipitate was filtered and washed repeatedly with distilled water until no chloride ions were detected in the filtrate using the silver nitrate test. Samples prepared by this method are referred to as co-precipitated (CP) mixed oxides.

Sol–gel method. Titania–silica mixed oxides were also prepared using sol–gel principles from the hydrolysis of tetraethoxy orthosilicate (TEOS) and tetraisopropoxy orthotitanate (TIOT) [16,17]. Two different hydrolysis techniques were used. Fully hydrolyzed (FH) mixed oxides were prepared by completely hydrolyzing orthotitanate and orthosilicate in separate vessels prior to mixing and neutralizing. Staged hydrolyzed (SH) samples were prepared by slowly adding a controlled amount of distilled water to TEOS. The amount of water was sufficient to hydrolyze only about half of the silicate. TIOT was added dropwise to the 50% hydrolyzed silicate mixture before additional water and HCl were added to complete the hydrolysis reaction. Samples were then precipitated, filtered, and washed with distilled water until the filtrate was free of chloride ions. For brevity, the two sol–gel methods will be referred to as "full" (FH) and "staged" (SH) hydrolysis.

Calcination procedure. The titania–silica samples were dried at 100°C for at least 5 h and separated into two batches. One portion of the catalyst was calcined at 350°C while the remaining portion was calcined in flowing air at 650°C for 16 h.

2.2. CHARACTERIZATION OF PHYSICAL AND CHEMICAL PROPERTIES

Chemical analyses were obtained after lithium tetraborate fusion on a Phillips PW1480 XRF. XRD analyses were performed on a standard Phillips XRG 3100. Trace aluminium contents were determined by ICP mass spectrometry after nitric acid digestion. Scandium at mass 45 was used as an internal standard. Nitrogen BET surface areas were measured on a Quantachrome Autosorb-6 instrument. A summary of the catalysts with some characteristic properties are listed in table 1.

2.3. ACIDITY MEASUREMENTS

The total number of acid sites and strength distribution were measured by thermogravimetric analysis (TGA) of pyridine [18]. A 30–50 mg sample of the oxide was placed in the aluminum pan of a DuPont 951 TGA. The sample was heated under a nitrogen flow at 20°C/min to the final calcination temperature (350 or 650°C) and held for 2 h, or until no further weight loss was detected. After cooling to 150°C, pyridine was adsorbed onto the surface until a constant weight was obtained. Pyridine adsorption was discontinued and sample was purged with nitrogen for at least 4 h until no further desorption of pyridine was noted. The latter step removed all pyridine physically bound to non-acidic sites. Total acidity was determined from the weight gain and expressed in terms of μmoles per gram of sample. Heating the oxide to 350°C desorbed pyridine from the weak sites and allowed the determination of strong acid sites. Acidity values were also calculated on a surface area basis.

Diffuse reflectance infrared spectroscopy (DRIFTS) was used to identify the type of acid sites and the relative amounts of Brønsted and Lewis acidity [19]. The DRIFTS cell (Harrick Scientific Corporation) used for this purpose was equipped with a heater and connected to a vacuum system. An additional thermocouple was

Table 1
Acidity and physical properties of silica–titania samples

Sample I.D. [a]	Calcination temperature (°C)	Ti/(Ti + Si) (measured)	Surface area (m^2/g)	Total acidity (μmol/g)	Brønsted abs. $\times 10^3$	Lewis abs. $\times 10^3$	Methanol dehydration	
							%conversion	activity (μ mol/g min)
SiO_2-P-1	350	0.00	347	9	0.00	0.00	0.3	0.1
TiO_2-P-1	350	1.00	150	336	0.00	27.38	21.5	9.2
TiSi-CP-1	350	0.20	352	181	1.77	3.02	19.4	7.9
TiSi-CP-2	350	0.44	422	349	6.06	10.74	36.8	14.9
TiSi-CP-3	350	0.87	371	564	7.84	16.00	42.3	16.2
TiSi-CP-4	350	0.92	292	473	3.14	14.80	56.5	21.4
SiO_2-FH-1	350	0.00	342	26	0.00	0.00	0.8	0.3
TiSi-FH-1	350	0.09	525	127	1.60	2.18	8.1	3.2
TiSi-FH-2	350	0.48	415	192	1.85	6.00	13.4	5.2
TiSi-FH-3	350	0.90	318	538	2.90	10.12	36.9	14.0
TiO_2-FH-4	350	1.00	150	377	0.00	2.25	31.7	12.5
SiTi-SH-1	350	0.47	467	478	7.83	11.21	35.9	13.9
SiO_2-P-2	650	0.00	210	0	0.00	0.00	0.0	0.00
TiSi-CP-5	650	0.21	325	141	0.75	2.81	18.1	7.35
TiSi-CP-6	650	0.44	335	246	5.19	13.72	15.8	6.33
TiSi-CP-7	650	0.87	170	265	4.32	20.55	17.1	6.46
TiSi-CP-8	650	0.92	131	215	3.81	31.12	14.8	5.50
TiO_2-P-2	650	1.00	52	138	0.00	13.05	6.6	2.46
SiO_2-FH-2	650	0.00	348	33	0.00	0.00	1.1	0.00
TiSi-FH-6	650	0.09	507	153	0.24	2.80	4.5	1.72
TiSi-FH-7	650	0.48	342	146	0.50	1.30	7.2	2.71
TiSi-FH-8	650	0.90	152	238	4.64	16.64	16.1	6.24
TiO_2-FH-2	650	1.00	0.75	0	0.00	0.00	0.0	0.00
TiSi-SH-2	650	0.47	123	72	1.12	2.84	9.8	3.77

[a] The suffix found in sample I.D. refers to the preparation method used: P: precipitation; CP: co-precipitation; FH: full hydrolysis; SH: staged hydrolysis.

installed directly above the sample cup and in direct contact with the sample to accurately control the sample temperature. Other modifications made to both the cell and diffuse reflectance accessory (praying mantis mirror assembly) were similar to those reported by Venter and Vannice [20]. Experiments were performed using 20–25 mg sample of the solid acid placed in the DRIFTS cell. The sample was pretreated in a dry nitrogen purge while heating the sample to a final temperature of 350 or 400°C and maintained for 2 h before cooling to 40°C and collecting a reference spectrum. After reheating to 150°C under a nitrogen purge, the sample was exposed to pyridine for ten minutes. Pyridine adsorption was accomplished by directing the nitrogen flow through a pyridine saturator and flowing the nitrogen–pyridine mixture over the sample. To remove physically bound pyridine, the sample was purged with nitrogen at 150°C for an additional 2 h period. After cooling the sample to 40°C , a spectrum was collected. The sample was purged with dry nitrogen for 3 h at 350°C to remove weakly adsorbed pyridine. At the conclusion of this step, the sample was again cooled to 40°C and a final spectrum was recorded. The reference spectrum recorded from the calcined sample was subtracted from the spectra collected following the desorption at 150 and 350°C. Baseline corrections were performed on spectra and relative populations of Brønsted and Lewis acid sites were determined from the absorbance of bands observed at 1542–1545 and 1448–1455 cm^{-1}, respectively. Other bands corresponding to pyridine adsorbed on Lewis acid sites were found at 1490 and 1577 cm^{-1} and the remaining bands corresponding to pyridine adsorbed on Brønsted sites were found at 1490 and 1635 cm^{-1}. Fig. 1 shows a representative DRIFTS spectrum of titania–silica (TiSi-CP-4) after desorbing pyridine at 150°C.

Methanol dehydration experiments were performed in a continuous-flow fixed bed quartz reactor with an internal diameter of 1.0 cm. A sample weight of 0.8 g

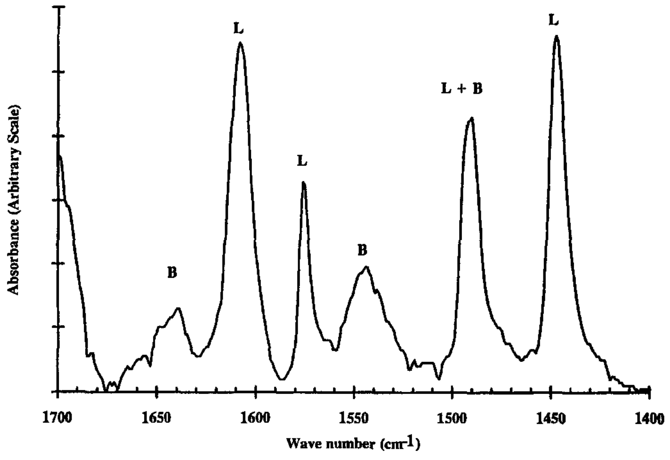

Fig. 1. Pyridine adsorption DRIFTS spectrum after baseline correction of TiO_2–SiO_2 mixed oxide (0.92 mole fraction titanium) prepared by co-precipitation (CP) and calcined at 350°C.

was placed in the reactor and pretreated in flowing helium (20 ml/min) at 350°C for 2 h. The helium flow was directed through a saturator containing methanol before entering the reactor. The saturator was held at 0°C to maintain a constant methanol vapor pressure. The reaction products were analyzed by a gas chromatograph equipped with a flame ionization detector and a Porapak N column. Conversion, activity (μmol methanol reacted)/[(g catalyst) (min)], and turnover frequency (TOF) of each catalyst were calculated at steady state conditions. This was normally achieved after 20 min on stream.

3. Results and discussion

The physical properties of titania–silica mixed oxides calcined at 350 and 650°C are presented in table 1. Properties of pure titania and silica oxides are listed for comparison.

3.1. SURFACE AREA

Titania–silica mixed oxides calcined at 350°C possessed higher surface areas than those calculated from a linear combination of titania and silica oxide as shown in fig. 2. The surface areas of mixed oxides prepared by staged hydrolysis (SH) method were slightly higher than those prepared by the other methods.

Increasing calcination temperature from 350 to 650°C resulted in a loss of surface area. Samples prepared by staged hydrolysis (SH) experienced the greatest decline in surface areas with almost two-thirds reduction in area after calcination

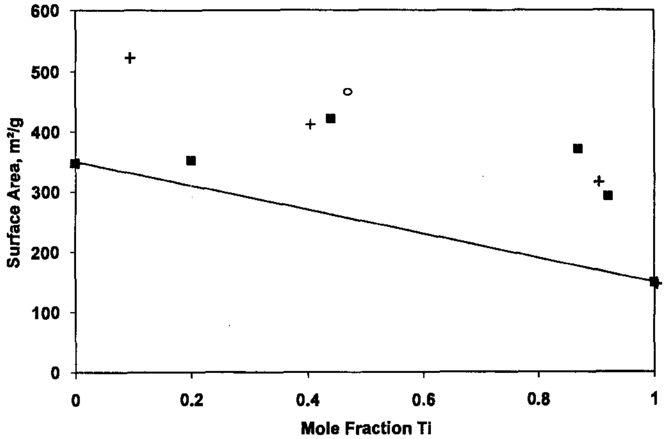

Fig. 2. Dependence of surface area on titanium mole fraction for TiO_2–SiO_2 mixed oxides prepared by co-precipitation (■), full hydrolysis (+), staged hydrolysis (○) and physical mixing (–) calcined at 350°C.

at 650°C. Co-precipitated (CP) sample was the most thermally stable, retaining 79% of its surface area after calcination at 650°C. The FH sample had moderate stability, retaining 48% of its surface area. As the titanium content was increased, a marked drop in surface area was observed for the samples calcined at 650°C. The observed trend was seen for all three preparation methods which confirms that crystallization occurs more readily on samples rich in TiO_2.

3.2. X-RAY DIFFRACTION

XRD spectra for the pure titania samples calcined at 650°C reveal sharp, intense anatase and rutile peaks. XRD spectra for co-precipitated (CP) 9 : 1 TiO_2-SiO_2 calcined at 350 and 650°C are shown in fig. 3. The XRD pattern of the sample calcined at 350°C contains broad low intensity peaks assigned to an anatase phase. This broad feature indicates the poor crystallinity of the mixed oxide. After calcination at 650°C, anatase XRD peaks become sharper and more intense. Even though phase transition from anatase to rutile is known to occur on pure titania, the rutile phase was seldom found on the TiO_2-SiO_2 mixed oxides even after calcination at 650°C. The presence of a small amount of silicon (10%) in the mixed oxides inhibited crystallization and transition to the rutile phases. XRD studies indicate that pure silica remained amorphous at the calcination temperatures used in this study.

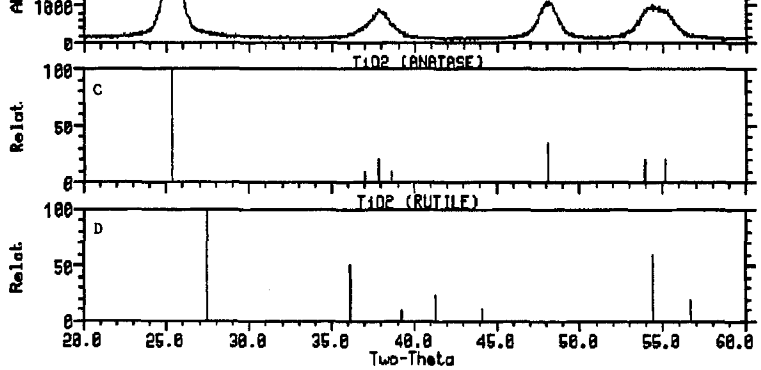

Fig. 3. XRD spectra of 9 : 1 CP TiO_2–SiO_2 calcined at 350 and 650°C showing low intensity, broad peaks for anatase only.

3.3. ACIDITY PROFILES

Total acidity values for the series of titania–silica mixed oxides are shown in fig. 4. These values are expressed on a mass basis and do not reflect changes in surface area. The highest total acidity was obtained on the 9 : 1 samples (TiSi-CP-3, TiSi-SH-3) calcined at 350°C. At Ti : Si of 1 : 1, the sample prepared by the staged hydrolysis method possessed a larger number of acid sites than samples prepared by either full hydrolysis (FH) or co-precipitation (CP) methods.

Increasing calcination temperature from 350 to 650°C resulted in an overall loss of acid sites. Total acidities of the low titania samples declined approximately 20%, while a decline of over 50% occurred with the high titania samples. The highest loss in acidity (85%) was observed with the 1 : 1 titania–silica prepared by the SH method, demonstrating the thermal instability of this preparation. Si–O–Ti bonds were weaker than either Si–O–Si or Ti–O–Ti bonds. Preparations that maximize the number of Si–O–Ti bonds produce mixed oxides which are less thermally stable.

For comparison purposes, physical mixtures (PM) of TiO_2 and SiO_2 were prepared. The titania precipitated from $TiCl_4$ was used in PM samples because it contained significantly higher acidity than the titania prepared from TIOT. Higher acidity was noted despite the fact that surface areas of both titania samples were comparable (table 1). For the three preparation methods, acidity values of titania–silica mixed oxides were greater than the physical mixtures, as shown in fig. 4. This indicates that the preparation methods produce true mixed oxides. The SH method produces the most Ti–O–Si interaction, but unfortunately SH mixed oxides are the least stable samples.

In order to determine if acid site population is a function of surface area, values of total acidity are divided by the catalyst surface area and expressed in terms

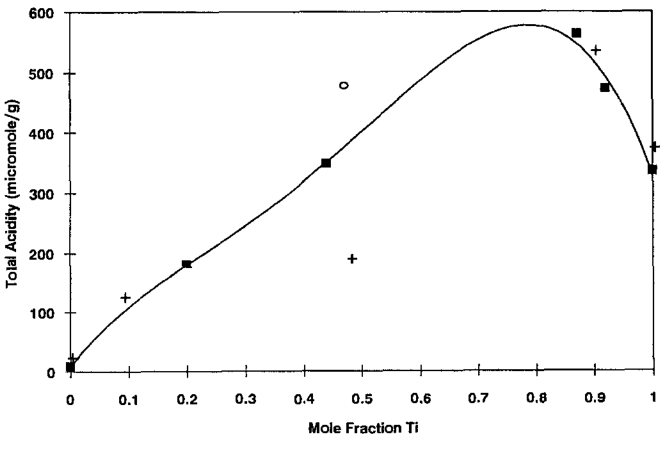

Fig. 4. Effect of preparation method on total acidity of TiO_2–SiO_2 samples calcined at 350°C: co-precipitation (■), full hydrolysis (+), and staged hydrolysis (O).

of acid density with units of μmol/m^2. The results for samples prepared by co-precipitation, along with data obtained by Tanabe et al. [15], are shown in fig. 5. Acid density increases with increasing titania content at both calcination temperatures. With the exception of the 9 : 1 titania–silica sample (calcined at 350°C) the same trend was reported by Tanabe. Increasing the calcination temperature reduces both surface area and acidity while the acid density (μmol/m^2) remains fairly constant. When comparing properties of a titania–silica calcined at 350 and 650°C, surface area and acidity are lost at the same rate. As the temperature increases, oxide crystallinity begins to occur. The unstable Ti–O–Si bonds break and Si–O–Si and Ti–O–Ti bonds reform resulting in a loss of acidity. The titania rich regions begin to crystallize to form the tetragonal phase of TiO_2.

As the titania content of the TiO_2–SiO_2 mixed oxide increased, a corresponding increase in the acid site population was observed. Acidity increased to a greater extent than surface area for all preparation methods (table 1). In a homogeneous mixed oxide, the maximum number of Ti–O–Si bonds would be expected to occur at a Ti:Si ratio of 1 : 1. However, XPS and XAES investigations [21] of TiO_2–SiO_2 found homogeneous solid solutions only at low TiO_2 concentrations (TiO_2 $\leqslant$10 wt%). At least two phases (silica-rich phase and titania-rich phase) were found at intermediate TiO_2 concentrations. At high titania content ($\geqslant$85%), silicon formed titanium silicate coating on TiO_2 particles. Therefore, the surface of TiO_2 rich mixed oxides are expected to have a large number of Ti–O–Si interactions which will result in a high acid density due to dispersed TiO_2–SiO_2 mixed oxide phase on titania support.

Values of strong acidity obtained by measuring the pyridine adsorption capacity at 350°C are shown in table 1. The percentage of strong acid sites increased

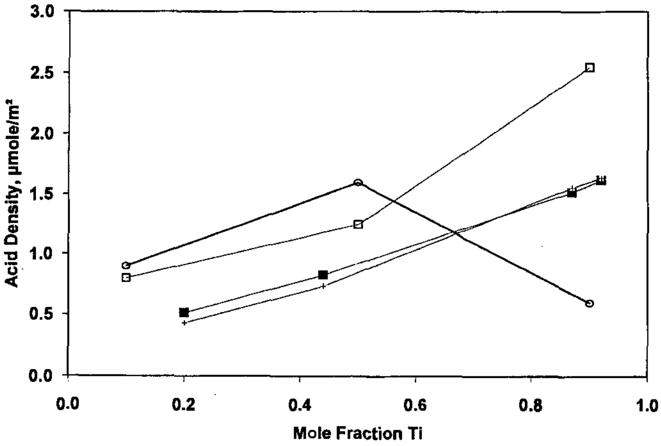

Fig. 5. Effect of titanium content and calcination temperature on acid density of TiO_2–SiO_2 samples prepared by co-precipitation: Tanabe [15] at 350°C (○); Tanabe [15] at 650°C (□); this work at 350°C (■); this work at 650°C (+).

with the titanium content. Mixed oxides with the highest mole fraction of titanium (0.9) calcined at 350°C had an acid density of 2.0 μmol/m^2, with only 0.5 μmol/m^2 strong acidity. Although this was the highest value of the series, it is significantly lower than that observed on Y zeolites. For instance, an HY zeolite with a unit cell of 24.7 Å has 1.2 μmol/m^2 of strong acidity when analyzed under similar conditions. However, titania–silica mixed oxides possess acidity characteristics similar to alumina–silica samples of comparable mole ratios.

3.4. METHANOL DEHYDRATION

Methanol dehydration activity obtained with titania–silica mixed oxides increased with total acidity as illustrated in fig. 6. These data further confirm the total acidity data obtained by pyridine adsorption at 150°C. Methanol dehydration is known to be catalyzed by weak to moderate strength acids [22]. The dehydration reaction is catalyzed by both Lewis and Brønsted acid sites and therefore is not a selective probe reaction for acid type. Although titania possesses only Lewis acidity, it exhibits a significant activity for this reaction. The activity is proportional to the total number of acid sites on the catalyst.

To further assess the catalytic activity of acid sites on titania–silica samples, the turnover frequency (TOF) was calculated and compared to samples of commercial silica–alumina. Fig. 7 shows that turnover frequency values obtained with titania–silica prepared by co-precipitation (CP) are similar to or higher than those of silica–alumina. Lower turnover frequencies were observed on samples prepared by sol–gel methods (SH and FH). Although turnover frequency is normally thought to be related to the strength of acid sites, TOF values did not increase with acid strength measured by pyridine adsorption at 350°C (table 1). Methanol dehydra-

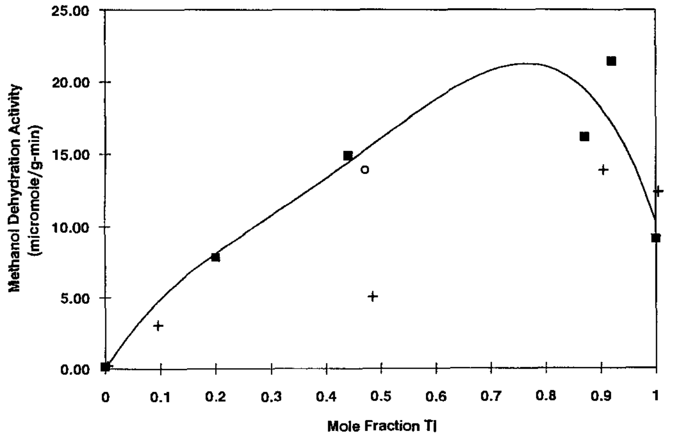

Fig. 6. Methanol dehydration activity of TiO_2–SiO_2 samples prepared by co-precipitation (■), full hydrolysis (+), and staged hydrolysis (○) after calcination at 350°C.

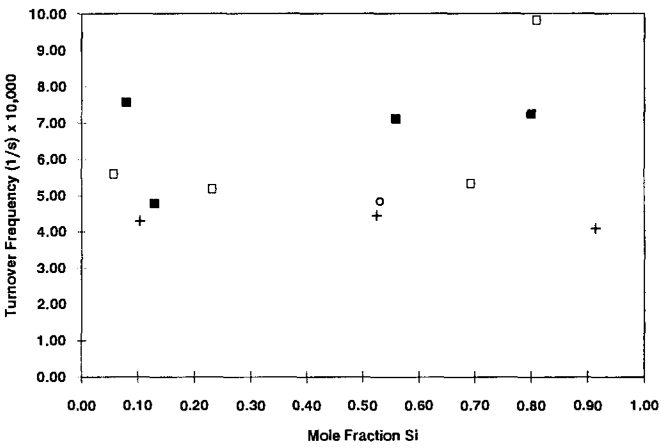

Fig. 7. Comparison of turnover frequencies on TiO_2–SiO_2 mixed oxides and Al_2O_3–SiO_2 for methanol dehydration reaction; (■) Ti–Si (CP), (+) Ti–Si (FH), (○) Ti–Si (SH), (□) Al–Si (Davison).

tion can be catalyzed by fairly weak sites. Dehydration occurs on both Brønsted and Lewis sites and may be further complicated by differences in minimum strength requirements for each acid type. For these reasons, TOF was not affected by the relatively narrow range of acidity found on the titania–silica samples.

3.5. TYPE OF ACIDITY

Diffuse reflectance infrared spectroscopy (DRIFTS) experiments with pyridine were used to identify the type of acid sites present on titania–silica binary oxides. Spectra recorded after pyridine adsorption at 150°C indicated the presence of surface Lewis and Brønsted acid sites. Lewis acidity was followed by monitoring the infrared band at 1448–1455 cm^{-1} corresponding to coordinately bound pyridine. Brønsted sites generated pyridinium ions (PyH^+) which exhibited a distinct band at 1540–1545 cm^{-1}. The ratio of Brønsted and Lewis sites was determined from the normalized absorbance of PyH^+ and PyL bands after adsorbing pyridine at 150°C. The relative populations of strong Brønsted and Lewis sites were determined after desorbing pyridine at 350°C. At this desorption temperature, only pyridine molecules adsorbed on stronger sites remained.

Lewis acidity was a function of the titanium content as shown in fig. 8. Lewis centers are thought to be associated with Ti(IV) species present on the surface of the mixed oxides. The amount of Lewis acidity was slightly higher than predicted based upon the physical mixtures of pure titania and silica. However, silica incorporation increased the overall surface area and, consequently, the number of incompletely coordinated titanium atoms on the surface. A second explanation for the increased Lewis acidity is through the generation of another type of Lewis site. Odenbrand [23] contends that two types of Lewis sites exist on the surface of tita-

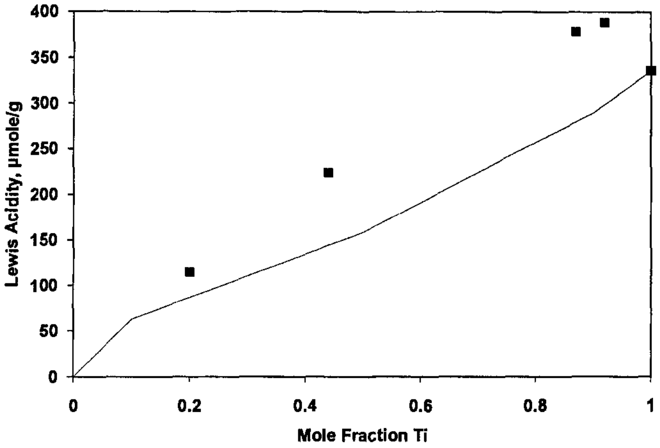

Fig. 8. Lewis acidity of co-precipitated (CP: (■)) and physical mixtures (PM: (–)) of TiO_2–SiO_2 as a function of titanium content.

nia–silica binary oxides in addition to the coordinately unsaturated octahedral titanium ions. Incorporation of silica into the titania structure results in the formation of surface tetrahedrally coordinated titanium atoms. These tetrahedral sites are thought to be considerably stronger Lewis acid sites than octahedral sites [24]. Although our work has shown the appearance of a new peak at 1457 cm^{-1} after desorbing pyridine at 350°C, the peak could not be definitively assigned. Further work would be required to verify the hypothesis of two types of Lewis sites.

Neither pure silica nor pure titania contain Brønsted sites. However, these acid sites were generated on all of the TiO_2–SiO_2 mixed oxides. Infrared absorbance values (1545 cm^{-1}) for titania–silica mixed oxides at varying Ti mole fractions are presented in fig. 9. Only trace amounts of Brønsted acidity were observed when the pure titania and silica were mechanically mulled and heated together. Brønsted acidity of true mixed oxides was significantly larger than those of the physical mixtures. Differences between Brønsted acidity of physical mixtures and binary oxides increased with the titania content. The maximum Brønsted acidity was generated with the 0.9 titanium mole fraction samples. All preparation methods showed the same relationship between acidity and titania content. The staged hydrolysis (SH) method produced highest concentration of Brønsted acid sites at comparable compositions of titania and silica (1 : 1). This was consistent with ^{29}Si NMR studies by Walther et al. [17] who found evidence for Ti–O–Si bridges on titania–silica mixed oxides prepared by SH method. Our attempts to prepare a titanium-rich sample by this method have thus far been unsuccessful. Due to the small amount of silica in this high titania sample, the controlled addition of water to achieve staged hydrolysis is difficult. Small quantities of water in the air react with the TEOS precursor and lead to its rapid hydrolysis. Because this method appears promising, further

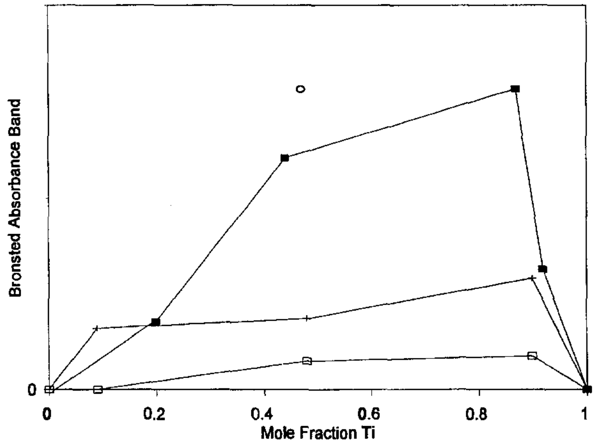

Fig. 9. Infrared absorbance of Brønsted acid band (1545 cm^{-1}) as a function of mole fraction of titanium for TiO_2–SiO_2 calcined at 350°C and prepared by co-precipitation (■), full hydrolysis (+), staged hydrolysis (○), and physical mixing (□).

attempts to prepare titania–silica mixed oxides with high titania content by staged hydrolysis methods will be made in a completely moisture-free environment.

The full hydrolysis (FH) method did not generate Ti–O–Si interaction to the extent of the other preparation methods. Low acidity values were found with samples prepared by full hydrolysis (FH) method. This finding was not surprising based on a recent study. Handy [16] found that preparing binary oxides by complete (single stage) hydrolysis of alkoxides (TEOS and TIOT) prior to mixing lead primarily to the formation of separate domains of TiO_2 and SiO_2 in the resulting mixed gels. Therefore, as expected this preparation method produces less Ti–O–Si interaction and less total acidity.

To ensure that the acidity found on the titania–silica mixed oxides was not the result of impurities in the silica and titania precursors used in preparation, trace metal analyses were performed. Aluminum contents of 45–70 ppm were detected by ICP mass spectroscopy. A qualitative XRF scan did not detect other impurities. Based on the assumption that one Brønsted site was created by a charge imbalance for each aluminum atom incorporated into titania, the contribution to acidity was negligible (1.6–2.6 μmol/g). A localized charge imbalance caused by the TiO_2–SiO_2 interaction is responsible for the generation of Brønsted acid sites. The formation of Brønsted acidity of the titania–silica binary oxides, despite the absence of such sites on pure titania and silica, is an interesting phenomenon. The interaction of Ti–O–Si resulted in formation of acidic bridging hydroxyl groups. A small amount of Brønsted acidity was even measured on physical mixtures of pure titania and silica. Apparently, during heating and mixing of the two oxides, a few Ti–O–Si bonds were formed. These findings would tend to support, but not confirm, Seiyama's hypothesis that the charge imbalance at the boundary between the two oxides results in the formation of new acid sites [13].

4. Conclusions

The purpose of this study was to gain further understanding of the titania–silica system. Surface area and XRD data indicate the mixed oxides have physical properties unlike either pure silica or titania. Brønsted and Lewis acidity were created and increased in strength and number with titania content reaching a maximum at titanium mole fraction of 0.9. The generation of these acid sites was a function of preparation method. Staged hydrolysis (SH) method produced the largest population of Brønsted acid centers at a titanium mole fraction of 0.5. Unfortunately, this sample was found to be the least thermally stable. The CP method produced the strongest acidity with the most stable Ti–O–Si bonds.

This study has provided additional insight into the effects of various preparation variables on the acidic properties of mixed oxides. However, increase in both Brønsted and Lewis acidity with titanium content found in this study would not have been predicted by any of the existing acidity generation models. More sophisticated models are needed to explain these findings.

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