Acidic and Catalytic Properties of SiO$_2$–Ta$_2$O$_5$ Mixed Oxides Prepared by the Sol-Gel Method

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The acidic and catalytic properties of a series of silicon–tantalum mixed oxides containing between 0 and 30 at% tantalum were characterized by temperature-programmed desorption of ammonia, by FTIR spectra of adsorbed pyridine, and by the test reaction of 1-butanol dehydration at 250–300°C. Probe molecule adsorption and catalytic testing show an acid site generation in silicon–tantalum mixed oxides compared to pure tantalum oxide. Both Brønsted and Lewis acid sites are present on the mixed oxide surface. Brønsted and Lewis acid sites seem to be weaker in SiO$_2$–Ta$_2$O$_5$ mixed oxide than in analogous SiO$_2$–Al$_2$O$_3$, since a greater reaction temperature is required to achieve the same conversion in the above test reaction. However, a great advantage of this new solid acid is the production of butenes with 100% selectivity. © 1995 Academic Press, Inc.

INTRODUCTION

Binary mixed oxides, including SiO$_2$, Al$_2$O$_3$, or TiO$_2$, are well known to possess surface acid sites which often lead to interesting catalytic properties. The origin of these catalytic properties has been explained by the creation of new types of acid sites by the combination of two single oxides. In order to investigate general rules of acidity generation, many binary oxide systems were subjected to acidity measurements (1).

A great number of these mixed oxides have been synthesised by the sol-gel method (2, 3). Indeed, extremely pure and homogeneous multicomponent oxides can be synthesized following the sol-gel route. In the field of catalysis this method has answered, in part, the demand for new high surface area catalysts.

Silica–alumina is a representative silica-containing binary oxide which has been extensively studied (4); however, nowadays considerable attention is being paid to silica-containing binary oxides of different metals, e.g., SiO$_2$–Nb$_2$O$_2$ (5), SiO$_2$–V$_2$O$_5$ (6), SiO$_2$–TiO$_2$ (7), SiO$_2$–ZrO$_2$, TiO$_2$–ZrO$_2$ (8). Several comprehensive reviews have been published (3, 9).

The acid–base properties of tantalum oxide have been studied recently, particularly those of hydrated tantalum oxide. Much interest is shown in Ta$_2$O$_5$ due to its unusual properties as a solid acid catalyst (10, 11).

In the present work, the acidic properties of a series of Ta$_2$O$_5$–SiO$_2$ mixed oxides with different Ta/(Ta + Si) atomic ratios have been studied, as well as their catalytic activities in butanol dehydration. The mechanism of acidity generation by mixing Ta$_2$O$_5$ and SiO$_2$ is discussed.

METHODS

Preparation of SiO$_2$–Ta$_2$O$_5$ Mixed Oxides

The SiO$_2$–Ta$_2$O$_5$ mixed oxides were prepared, as previously described (12), using the sol-gel method (13) by mixing tetraethylorthosilicate (TEOS) and tantalum pentaethoxide in methanol.

All the hydrolysis and condensation processes were carried out at room temperature. The final alkoxide molecular concentration (Si(OEt)$_4$ + Ta(OEt)$_5$) was 0.09 M.

Thermal analysis of pure tantalum oxide synthesised by this method shows that the prepared sample, in contrast to pure silica and silicon–tantalum mixed oxides, possesses a large percentage of carbon species on the catalyst surface which cannot be eliminated by thermal treatment below 700°C (14). For this reason an alternative synthesis method was employed in the preparation of Ta$_2$O$_5$ (SiTa100). Tantalum pentaethoxide was dissolved in ethanol and allowed to mature for 2 h. The suspension was then dried in a rotary evaporator. The resulting solid was suspended in boiling 1 M HCl. The final suspension was filtered and washed until chlorine was no longer detected.

Table 1 presents the nomenclature of the synthesised samples with their corresponding Ta/(Ta + Si) atomic ratios and BET surface area after calcination at 500°C.

Characterization

A detailed description of acid surface properties would include the determination of the amount, nature (Lewis or Brønsted), and strength of the acid and base sites. In seeking this information, two methods were used: (i) ad-

TABLE 1

Characteristics of Silicon–Tantalum Mixed Oxides

Sample	$\dfrac{Ta}{(Ta + Si)} \times 100$	S_{BET} (m²/g)
SiTa0	0	106
SiTa5	5	442
SiTa10	10	449
SiTa20	20	353
SiTa100	100	56

TABLE 2

Chemisorbed Ammonia Desorbed from Mixed Oxides Precalcined at 500°C and Exposed to NH_3 at 120°C

Sample	Quantity of NH_3 desorbed	
	$\mu mol \cdot g^{-1}$	$\mu mol \cdot m^{-2}$
SiTa0	0	0
SiTa5	482	1.09
SiTa10	596	1.33
SiTa20	636	1.80
SiTa100	175	3.12

sorption of a gaseous probe molecule (temperature-programmed desorption (TPD) of ammonia and FTIR of adsorbed pyridine) (15, 16) and (ii) catalytic activity in a model reaction (1-butanol dehydration) (17).

Temperature-programmed desorption of NH_3 was carried out using samples calcined at 500°C. Before ammonia adsorption, the samples were treated at atmospheric pressure in a flow of helium at 500°C for 1 h. Ammonia adsorption was carried out at 120°C for 15 min. The physisorbed ammonia was eliminated by maintaining the samples in a flow of helium at the adsorption temperature for 1 h. The linear temperature increase from 120 to 500°C, at a rate of 4°C/min, results in the desorption of ammonia. The ammonia desorbed with increase in temperature was continuously recorded by a thermal conductivity detector. In addition, the desorbed ammonia was collected in a boric acid solution and titrated with sulfuric acid according to the Kjeldahl method (18).

Pyridine FTIR spectra were recorded using a Bruker FT 88 spectrometer. Samples were calcined at 500°C before analysis. In preparation for pyridine adsorption, samples were pressed into self-supported disks, placed in an IR cell and treated under vacuum (10^{-6} Torr) at 400°C for 4 h. After cooling to room temperature, spectrum (a) was recorded. The samples were then exposed to pyridine vapour for 5 min. After evacuation (5×10^{-5} Torr) at room temperature for 1 h, spectrum (b) was recorded. Spectra (c), (d), and (e) correspond to subsequent successive outgassing of samples at 150, 250, and 400°C, respectively.

The test reaction, 1-butanol dehydration, was carried out at atmospheric pressure and 250–300°C in a fixed bed reactor (i.d. 4 mm). Before reaction the catalysts were sieved and the particle size fraction of 100–200 μm was used. The catalyst mass was 60 mg and the corresponding bed height was adjusted to 14 mm. Catalyst activation was carried out in a helium flow at the reaction temperature for 1 h. Helium, the carrier gas, was used to entrain 1-butanol into the vapour phase from a saturator held at 53°C (5.5 kPa butanol partial pressure). This helium/1-butanol gas reaction mixture passed through the reactor at a rate of 60 ml/min flow (LHSV = 9.8 h⁻¹).

Depending on the nature of catalyst active sites, the reaction products are butyraldehyde, dibutylether, and 1-butene. Simultaneously, under the reaction conditions, the 1-butene formed isomerizes to cis- and trans-2-butene.

To prevent 1-butanol, butyraldehyde, and dibutylether condensation, all lines from the saturator to the chromatograph were heated to 100°C.

The dehydration products and 1-butanol were analyzed by gas chromatography using a Shimadzu GC-8A chromatograph equipped with a thermal conductivity detector.

A 20% Reoflex/400 Embacel column, 2 m long, was used in the analysis of 1-butanol and the dehydration products, butyraldehyde and dibutylether. Isomerisation products, cis- and trans-2-butene and 1-butene, were analyzed by a 2-m octane/Porasil column. Both columns operated isothermally at 60°C and the carrier gas was helium.

RESULTS

TPD of NH_3

The total amount of chemisorbed NH_3 desorbed from the samples during TPD is given in Table 2. The profiles
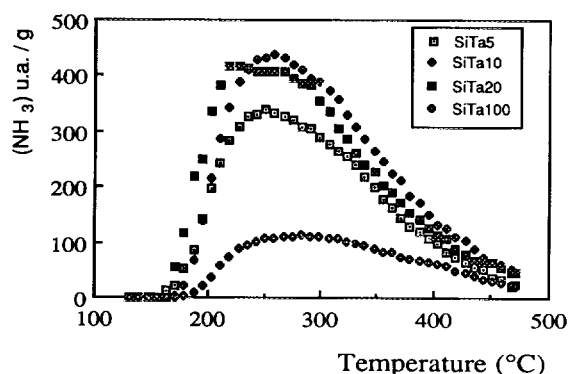

FIG. 1. Recorded response of desorbed NH_3 (arbitrary units)/g of catalyst as a function of temperature.
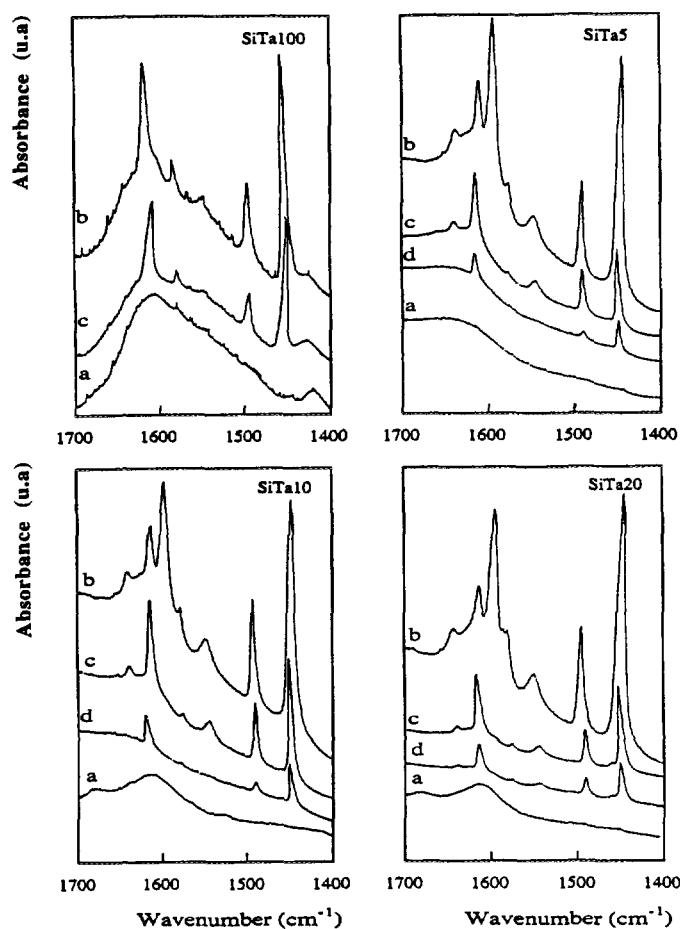
FIG. 2. FTIR spectra of pyridine adsorbed on pure tantalum and on mixed oxides. Spectra before pyridine adsorption (a) and sample exposed to pyridine and outgassed at room temperature (b), 150°C (c), and 250°C (d).

of the desorbed NH₃ with desorption temperature are presented in Fig. 1.

Ammonia desorption profiles for pure and mixed oxides are quite similar. These profiles typically consist of a very wide desorption band with a maximum between 250 and 300°C. The NH₃ desorption signal starts at approximately 170°C and returns to its baseline at 500°C.

According to Fig. 1 and Table 2, column (i), the amount of NH₃ chemisorbed on silicon–tantalum mixed oxides is proportional to the tantalum content and greater than that obtained for pure tantalum oxide. However, acid site concentration expressed per unit surface (m²) is greatest for the pure tantalum oxide and decreases in the order SiTa20 > SiTa10 > SiTa5.

FTIR Spectra of Adsorbed Pyridine

The spectroscopic study of adsorbed bases, such as pyridine, is a useful method for the characterisation of the nature of surface acidity (19, 20).

Figure 2 illustrates the spectra of adsorbed pyridine on various samples evacuated at different temperatures. Pure silica is not shown, since after outgassing at 150°C no characteristic bands of adsorbed pyridine were observed.

Figure 2, spectrum c, of pyridine adsorbed on mixed oxides after degassing at 150°C exhibits Brønsted BPy bands at 1491, 1547, 1578, and 1640 cm⁻¹ and Lewis acid LPy bands at 1451, 1491, 1578, and 1614 cm⁻¹. Spectrum b, of pyridine adsorbed on mixed oxides after degassing at room temperature, shows in addition to these bands the characteristic band of physisorbed pyridine at ≈1600 cm⁻¹. Pure silica evacuated at 150°C presents no Brønsted and no Lewis acid sites. Tantalum oxide, evacuated at the same temperature, shows only Lewis LPy bands at 1448, 1489, 1577, and 1611 cm⁻¹. This implies that the addition of tantalum to the initial silica gel results in the formation of Brønsted acid sites in all the mixed oxides.

Bands typical of Brønsted acidity in the mixed oxides are eliminated after outgassing above 150°C. However, characteristic Lewis acidity bands are still observed even after outgassing at 250°C, see Fig. 2. Increasing the outgassing temperature from 150 to 250°C results in an upward shift of the LPy 8a and LPy 19b bands to a maximum of 1615 and 1451 cm⁻¹, respectively. At a given temperature the wavenumber of coordinates pyridine increases in mixed oxides with respect to pure tantalum oxide, e.g., the LPy 8a band, which presents the largest shift, exhibits a value of 1611 cm⁻¹ for SiTa100 and 1614 cm⁻¹ for silicon–tantalum mixed oxides.
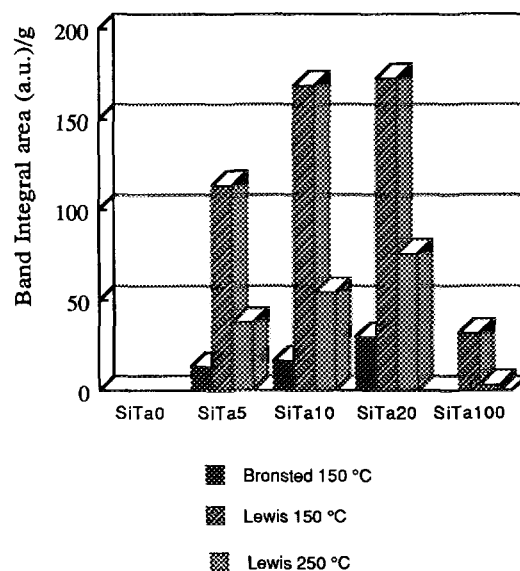
A semiquantitative analysis of the Lewis and Brønsted

FIG. 3. Lewis acid band (1450 cm⁻¹) integral areas after outgassing at 150 and 250°C and Brønsted acid band (1545 cm⁻¹) integral area after outgassing at 150°C for different pure and mixed oxides.

TABLE 3

Test Results of 1-Butanol Dehydration Using Pure Tantalum and Silica–Tantalum Mixed Oxides, Calcined at 500 and 300°C, at Steady-State and after 2 h Reaction

Sample	Reaction temperature (°C)	Butanol conversion (%)	Selectivity		
			1-butene	*cis* 2-butene	*trans* 2-butene
(SiTa5)$_{500°C}$	250	7.1	37.3	35.8	26.9
	275	15.7	38.1	34.7	27.2
	300	31.2	36.1	37.8	26.0
(SiTa10)$_{500°C}$	250	8.6	35.3	36.6	28.0
	275	17.4	35.2	37.6	27.3
	300	35.7	34.5	38.6	26.8
(SiTa20)$_{500°C}$	250	10.2	35.1	38.1	26.8
	275	25.5	33.5	39.2	27.3
	300	48.0	33.4	39.2	27.4
(SiTa100)$_{500°C}$	250	0.7	63.4	22.1	14.5
	275	2.3	62.0	23.3	14.7
	300	6.6	61.2	24.1	14.4
(SiTa20)$_{300°C}$	250	28.5	38.1	36.8	25.1
	275	55.5	36.2	38.6	25.2
	300	85.0	33.8	40.6	25.6
(SiTa100)$_{300°C}$	250	1.5	63.1	20.0	16.9
	275	3.2	61.8	22.6	15.6
	300	7.4	61.9	23.1	15.0

acid sites was carried out using the developed IR band intensities. The intensity of Lewis and Brønsted acid bands was calculated from the band integral area (a.u.) and wafer density (mg/cm^2). Calculated intensities of Brønsted acid bands (BPy $\approx$ 1545 cm^{-1}) after outgassing at 150°C and Lewis acid bands (LPy $\approx$ 1450 cm^{-1}) after outgassing at 150 and 250°C, are plotted against the tantalum content of mixed oxides in Fig. 3.

Lewis acidity is predominant in all the multicomponent oxides. The intensity of the LPy bands increases significantly in mixed oxides compared to pure tantalum oxide. The intensity of these Lewis acidity bands increases with an increase in tantalum content.

1-Butanol Dehydration Test Reaction

Table 3 presents the results of the 1-butanol dehydration reaction (conversion and selectivity at steady state and after 2 h reaction using catalysts calcined at 300 and 500°C). Selectivity for produced butenes is defined as the molar ratio of each product to 1-butanol converted. In the range of temperatures tested, pure silica does not catalyze 1-butanol dehydration. Indeed, SiTa0 shows the first sign of catalytic activity at temperatures above 350°C. On tantalum oxide and silicon–tantalum mixed oxides, no sign of deactivation was observed even after 5 h on stream.

On these catalysts the cis-/trans-2-butene ratio in the reaction products was close to 1.5 at all reaction temperatures. In the 250–300°C reaction temperature range, conversion of 1-butene to cis- and trans-2-butene is constant and equal to 62–68% for all silicon–tantalum mixed oxides. On the other hand, pure tantalum oxide isomerizes to 34–38% 1-butene.

As shown in Table 3 for SiTa20 and SiTa100, 1-butanol conversion is more important when the catalysts are calcined at lower temperatures. Conversion of 1-butanol using SiTa20 calcined at 300°C is twice that obtained when the catalyst is calcined at 500°C.

DISCUSSION

Base Molecule Adsorption

From the analysis of the TPD of ammonia and information obtained from FTIR bands of adsorbed pyridine (LPy = 1490 cm^{-1}), a large increase in the number of acid sites is noted in the mixed oxides compared to pure silica or tantalum oxide.

The increase in the acidity of the mixed oxides, as can be seen in Fig. 4, is not only a result of the synthesis of solids with a higher specific area. The number of acid sites
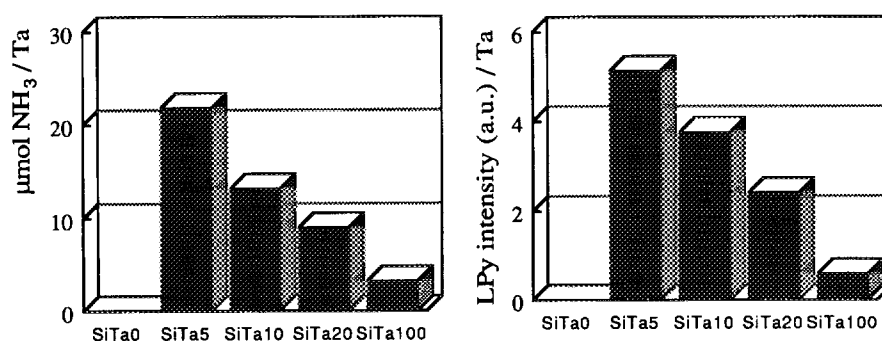
FIG. 4. Ammonia TPD and pyridine FTIR (1490 cm^{-1}) evaluation of acid sites per mol tantalum on catalyst surface.

per tantalum on the catalyst surface increases in the mixed oxides compared to pure tantalum oxide.

The number of acid sites per tantalum on the catalyst surface is a semiquantitative evalvation, calculated from the LPy band integral area and from the amount of NH_3 chemisorbed, taking into account the specific surface area of each sample and the percentage tantalum on the catalyst surface: acid sites per $Ta_{surface}$ = (μmol NH_3 or LPy band integral area)/($S_{BET} \cdot$ (Ta/Ta + Si)). The method of calculation is based on our finding (12) that there is a homogeneous distribution of the two components, silicon and tantalum, in the bulk as well as on the surface of the mixed oxides.

As shown by the FTIR of pyridine, Fig. 2, the addition of tantalum to the initial silica gel leads to the formation of new Brønsted acid sites since this kind of acidity is not present in silica or in pure tantalum oxide.

The strength of Lewis acid sites, to which pyridine is coordinated, has been analysed according to the LPy 8a band wavenumber. The LPy 8a band of coordinated pyridine shifts from 1610 to 1640 cm^{-1} depending on the pyridine–Lewis centre interaction strength. In the analyzed samples, the LPy 8a band appears between 1611 and 1614 cm^{-1}, which corresponds to weak Lewis acid sites (21). The wavenumber at which this band appears in mixed oxides, 1614 cm^{-1}, is higher than for that of pure tantalum oxide, 1611 cm^{-1}. In the same way, the temperature required to eliminate all the adsorbed pyridine from Lewis acid sites is higher than for pure tantalum oxide. This would indicate that the strength of Lewis acid sites is higher in the mixed than in the pure oxides.

Test Reaction

1-Butanol dehydration using acid–base oxides takes place by elimination reaction mechanisms E1, E2, or E1cB (cB, conjugate base). These mechanisms have been modified to be adapted to acid–base catalysts (17).

The generally accepted mechanism for 1-butanol dehydration using acid–base catalysts is type E2 (22). This is

a one-step mechanism where the alcohol OH group is eliminated by an acid function and a proton in the β position is eliminated by a basic site. Therefore, 1-butanol dehydration by an E2 mechanism requires the existence of acid and base sites on the catalyst surface. For almost all solid catalysts, e.g., alumina and silica–alumina, the possibility of E2 elimination as the reaction mechanism is supported by the simultaneous production of butene and dibutylether, as products of the 1-butanol dehydration. The production of dibutylether from 1-butanol requires the existence of both acid- and base-active sites on the catalyst surface.

In the temperature range studied, for silicon–tantalum mixed oxides the selectivity to butenes is 100%; i.e., neither butyraldehyde nor dibutylether is formed. This indicates that 1-butanol dehydration takes place via the formation of a carbonium ion and implies an E1-type mechanism (23). That is, the catalytic active sites in the reaction conditions studied are acid sites. Base sites do not take part in the elimination mechanism.

In the reaction conditions employed, 1-butene obtained from 1-butanol dehydration is partially isomerized to cis- and trans-2-butene. Many studies have already been carried out concerning 1-butene isomerization as a test reaction to determine the nature of active centers on the catalyst surface. In fact, it has been shown that for solids which possess Brønsted acid sites the cis-/trans-2-butene ratio value is characteristically 1.5 (24–27), whereas on solids where the isomerization occurs by basic sites this ratio value is significantly higher (28, 29). The cis-/trans-2-butene ratio obtained for the isomerization of 1-butene for all mixed oxides tested and for the pure tantalum oxides is approximately 1.5 (1.4–1.5).

For mixed oxides at all reaction temperatures, the conversion of 1-butene to cis- and trans-2-butene is constant and equal to 62–68%, whereas pure tantalum oxide gives a conversion of 34–38%. Since with these solids 1-butanol dehydration proceeds via an E1 mechanism (Brønsted and Lewis acid sites) and 1-butene isomerization is catalysed
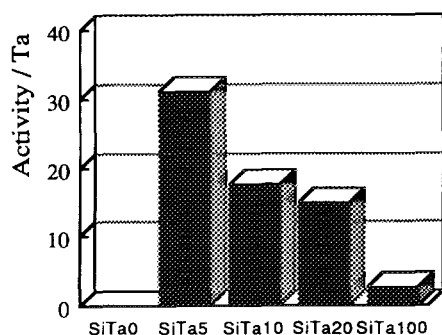
FIG. 5. Catalytic activity (μmol butene/min) per mol tantalum on catalyst surface, for the test carried out at 300°C using samples calcined at 500°C.

by Brønsted acid sites, the Brønsted/Lewis ratio must be higher in silicon–tantalum mixed oxides than in pure tantalum oxides. In addition this ratio is maintained constant for all mixed oxides.

Using identical reaction conditions, mixed and pure tantalum oxides calcined at lower temperatures, i.e., 300°C instead of 500°C, which lead to higher 1-butanol conversions. For SiTa20, conversion increases by 100% when the catalyst is calcined at 300°C, compared to the same catalyst calcined at 500°C. This higher conversion is not only due to a higher surface area. Indeed, the specific surface areas of SiTa20 are 450 and 353 m^2/g when calcined at 300 and 500°C, respectively.

This observation agrees with studies carried out on tantalum and niobium oxides (11). As a matter of fact, as stated by Tanabe et al. (16), tantalum and niobium oxides exhibit maximum acidity at low calcination temperatures (100–300°C) with a sharp decrease in activity observed with increase in calcination temperature.

Figure 5 presents the catalytic acitivity (μmol butene/min g) per mol tantalum on the catalyst surface, using samples calcined at 500°C.

In agreement with pyridine FTIR and ammonia TPD, 1-butanol dehydration shows that mixed oxides containing tantalum possess a greater number of acid sites than pure tantalum oxide. The increase in activity of the mixed oxides compared to the pure oxides can be explained using a proposed model of Tanabe et al. (30). According to this model the generation of acidity is explained by the existence of an excess positive or negative charge in the mixed oxide network.

The structural model proposed by Tanabe in studying the charge difference created in the mixed oxide matrix is based upon two postulates: (i) the coordination number of the two metals (silicon, tantalum) in the mixed oxide is maintained the same as in the pure oxides and (ii) the coordination number of the negative element (oxygen) of the main component is maintained for all the oxygen in

the mixed oxide. This model has been applied to many mixed oxide systems and has proved valid for 90% of them. For synthesized silicon–tantalum mixed oxides silica is the main component. Silicon coordination in silica is tetrahedral and the coordination of tantalum oxide is octahedral. According to Tanabe's model the proposed structure would be:
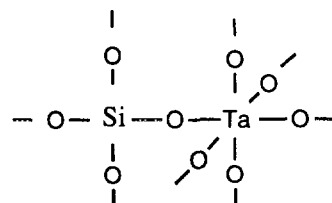
The charge difference by each Ta–O bond would be $[(5/6) - (2/2)] = -0.166$, and the unit charge would be $[6 \cdot (-0.166)] = -1.0$. Since the created charge difference is a negative unity, Tanabe's model assumes that a proton must be associated with the six oxygen surrounding tantalum to keep the structure electroneutrality. Therefore, the model implies that new hydroxyl groups be formed on the silicon–tantalum mixed oxide surface.

Tanabe's theory is in agreement with the catalytic test results. The proportion of Brønsted acid sites in the mixed oxides, which are able to isomerize 68% of 1-butene into 2-butenes, must be greater than in tantalum oxide which only isomerizes 30% of 1-butene. The FTIR results also seem to agree with Tanabe's theory. By FTIR a clear increase in the number of hydroxyl groups between 3000 and 3600 cm^{-1} is observed in the mixed oxides compared to silica (12). In addition, the pyridine FTIR spectra of the mixed oxides obtained after outgassing at 150°C show the creation of hydroxyl groups acidic enough to protonize the pyridine (BPy $8a = 1545$ cm^{-1}).

CONCLUSIONS

Probe molecule adsorption and catalytic testing show an acid site generation in silicon–tantalum mixed oxides compared to pure tantalum oxide. Both Brønsted and Lewis acid sites are present on the mixed oxide surface. In agreement with Tanabe's theory, the addition of tantalum to the initial silica gel generates Brønsted acid sites.

Brønsted and Lewis acid sites seem to be weaker in SiO_2–Ta_2O_5 mixed oxide than in analogous SiO_2–Al_2O_3, since a greater reaction temperature is required to achieve the same conversion. However, the great advantage of this new solid acid is the production of butenes with 100% selectivity. The absence of butyraldehyde and dibutylether in the product stream is probably due to the lack of basic sites.

ACKNOWLEDGMENTS

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