

# Solid State Chemistry in Two Dimensions

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Acidic properties (acid sites strength and concentration) of three series of mixed oxide catalysts (titania-silica, zirconia-silica, and alumina-silica) were analyzed by proton affinity distributions. Catalytic properties under mild dehydration conditions (but-1-ene isomerization at 423 K) of these materials were also evaluated. A Brønsted-type correlation was found between first-order apparent isomerization rate constants and acid strengths of certain components of the  $pK$  spectra of the catalysts. This was explained in terms of proton transfer processes that take place at both wet and dry interfaces, *i.e.* at the surface hydroxyl layer. The results were discussed on the basis of the presence of large surface hydroxyl populations on all catalysts under the reaction conditions.

Under ambient conditions, many solids and oxides, in particular, are covered with surface hydroxyl groups. These groups are ampholytes, *i.e.* they are available for both adsorption or desorption of protons. A large influx of research papers has recently dealt with the modeling, prediction, and characterization of proton-binding properties of surface hydroxyls at the oxide/solution interface. This has resulted in a clearer understanding that the proton binding/releasing propensity is an intrinsic crystallochemical property of the solid. In other words, it is intrinsically linked to the **Solid State Chemistry** of the oxide.

For many solid surfaces, data from infrared spectroscopy reveal the presence of different types of surface hydroxyls; their occurrence was explained based on crystal structure considerations, due to the fact that surface hydroxyls or oxygen ions may be bound to a different number of lattice metal atoms. The order of acid strengths of surface hydroxyls on different oxides (or of different hydroxyls on the same oxide, viewed as a heterogeneous surface) measured either by methods of surface chemistry and catalysis, or by methods of solution chemistry, should be the same or, at least, in close agreement. In this paper, the use of proton affinity distributions (PADs) determined from potentiometric titration and its relation to **Two Dimensional Chemistry** will be described.

Quantitative information on the Brønsted acidity, revealed by their PADs, of several mixed oxide systems will be presented. It will be demonstrated that a linear relationship exists between the surface den-

sity of specific proton-binding sites of a particular acid strength at the hydrated oxide surface and the catalytic activity for but-1-ene isomerization of the same samples. First-order apparent rate constants for the *cis* and *trans* products were evaluated from the laboratory data. It is shown that Brønsted-type plots of apparent rate constants,  $k_{cis}$  and  $k_{trans}$ , against characteristic  $pK$ s for the active sites previously identified for each catalyst series are linear over three orders of magnitude for  $k$  and four units on the  $pK$  scale.

## BACKGROUND

### Distribution Function Characterizing Heterogeneity of Surface Sites on Oxide Catalysts

In general terms, a distribution function of proton lability for a nonuniform oxide surface,  $f(pK)$ , can be defined as the mole fraction of surface sites with acidity constants in the interval ( $pK$ ,  $pK + dpK$ ). For a system composed of several groups of proton-binding sites, the total concentration of deprotonated sites is given by

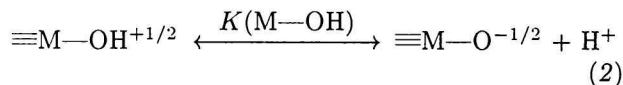
$$\Theta = \int_{pK_1}^{pK_2} [\Theta([H], pK)] f(pK) dpK \quad (1)$$

where the bracketed term in the integral takes the form of a Langmuir local isotherm with the corresponding proton binding constant,  $K^{-1}$ . It corresponds to proton transfer processes between amphoteric surface hydroxyls and the aqueous electrolyte

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solution, usually described by simple local equilibria which are structurally dependent



The proton transfer process described above is pH-dependent. In accordance with the above description, it appears that there is a simple and versatile experimental method which is well suited for evaluation of surface structures on solid samples which undergo proton transfer to or from the aqueous environment: potentiometric titration. The advantages of the potentiometric titration method over other methods in current use for characterization of acid properties of catalysts are: 1. direct access to Brønsted acidity and other charge-developing phenomena, and 2. surface sensitivity.

Estimates of absolute numbers of acid sites on catalysts are needed. The raw data from potentiometric titration results can be easily converted to proton-binding curves that show the extent of proton transfer processes as a function of pH. Thus all information contained in the left hand term of eqn (1) is in principle available from experiment. This method should enable detection of acid sites on the catalyst surface, including those which were weakened by hydration and confined to the 0–14 p*K* range. It is required only that an accurate and reliable method for analysis of acid site heterogeneity at the solid/aqueous solution interface is available. In other words, a mathematical algorithm which would provide the solution to the integral eqn (1) in terms of a distribution function or p*K* spectrum,  $f(\text{p}K)$ , is needed. Work from our laboratory over the past five years has developed the mathematical machinery necessary to deconvolute eqn (1) and to access,  $f(\text{p}K)$ , the distribution function [1, 2].

### The Brønsted Relationship

In homogeneous catalysis, the Brønsted relationship relates the effectiveness of a general acid catalyst to its acid strength

$$k_A = g_A K_A^\alpha \quad (3)$$

where  $k_A$  is the specific rate constant for reactions catalyzed by acids, the acid dissociation constants of which are  $K_A$ ;  $g_A$  and  $\alpha$  ( $0 < \alpha < 1$ ) are constants for a series of similar catalysts, but depend on the reaction type (reaction mechanism) and experimental conditions (temperature, solvent).

In heterogeneously catalyzed reactions by solid acids linear correlations were found between the reaction rate at constant pressure and temperature and the concentration of Brønsted acid sites, for example, in zeolites and silica-aluminas. However, when attempts were made to quantify different active sites

in terms of their acid strength a general relationship between activity and acidity was more difficult to establish.

In this paper we show that the use of an aqueous titration method for the measurement of catalyst surface acidity can provide useful information when combined with other results. We demonstrate that a Brønsted-type relationship between dry reaction rate constants and wet proton-binding equilibrium constants could be identified for *certain* acid sites revealed by PADs. The correlation is established for the *same reaction* (but-1-ene isomerization) carried out on *various oxide systems* under conditions where the population of surface hydroxyls was not completely depleted by extensive dehydration.

### EXPERIMENTAL

The following experimental systems were studied (Table 1):

1. Titania-silica aerogels with variable molar proportion of the components (SiTi- $x$  % series);
2. Zirconia-silica aerogels with variable molar composition (SiZr- $x$  % series);
3. Zirconia-silica aerogels with constant molar composition and variable degree of homogeneity of the components at the molecular level, achieved by varying the prehydrolysis parameter during their preparation (SiZr-50 %-P series); and
4. Alumina-silica xerogels with variable molar composition (SiAl- $x$  % series).

For details on preparation and characterization of SiTi- $x$  %, SiZr-50 %-P, and SiZr- $x$  % series the reader is referred to several papers by *Ko et al.* [3–6]. All titania-silica samples came from preparation batches similar to those of prehydrolyzed titania-silica aerogels described recently by *Miller et al.* [3]. The starting chemicals were tetraethyl orthosilicate, titanium butoxide, zirconium propoxide, and methanol or propanol as solvents. To improve the intimacy of component oxide mixing in the SiZr-50 %-P series, the silicate precursor was prehydrolyzed with variable amounts of water before adding the zirconium precursor. The samples in the SiZr- $x$  % series were obtained in the same way as the SiZr-50 %-P sample with the same prehydrolysis ratio as the SiZr-50-d sample. The preparation of SiAl- $x$  % samples was described elsewhere [7]. For this series the sol-gel xerogel technique was used and the starting compounds were tetraethyl orthosilicate, aluminium isopropoxide, and ethanol.

The experimental setup and procedures used for characterizing the acid-base properties of surface hydroxyl groups in an aqueous environment were described in detail elsewhere [1, 8]. It consists of collecting a large number of potentiometric titration data over a pH interval as broad as allowed for by the sample solubility, but not exceeding the pH 3–11 range, wherein the proton concentration consumed or

Table 1. Sample Characterization and Results

Sample name	Independent variable	BET Area $\text{m}^2 \text{g}^{-1}$	pK (Active sites)	N (Active sites) $\mu\text{mol m}^{-2}$	Conversion <i>cis</i> -but-2-ene/%	Conversion <i>trans</i> -but-2-ene/%	$k_{cis}$ kmol mol <sup>-1</sup> h <sup>-1</sup>	$k_{trans}$ kmol mol <sup>-1</sup> h <sup>-1</sup>
Series 1. Titania-silica aerogels (variable composition)								
	$w(\text{TiO}_2)/\%$							
SiTi-95	95	215	9.1	1.72	4.6	2.0	0.008	0.003
SiTi-67	67	318	8.6	2.63	18.5	14.8	0.019	0.015
SiTi-50	50	375	8.0	1.54	17.1	14.7	0.022	0.018
SiTi-33	33	405	8.2	1.48	12.2	10.7	0.014	0.012
Series 2. Zirconia-silica aerogels (variable composition)								
	$w(\text{ZrO}_2)/\%$							
SiZr-33	33	430	6.4	0.3	30.7	33.8	0.216	0.237
SiZr-50-d	50	186	6.5	0.47	16.8	14.5	0.151	0.126
SiZr-67	67	199	6.6	0.13	8.9	6.7	0.243	0.179
Series 3. Zirconia-silica aerogels (constant composition, various prehydrolysis conditions)								
	pH ratio							
SiZr-50-a	0	244	6.5	0.29	17.6	14.6	0.199	0.161
SiZr-50-b	0.65	262	6.4	0.39	18.4	15.5	0.152	0.124
SiZr-50-c	1.13	268	6.5	0.37	20.5	17.6	0.175	0.127
SiZr-50-d	2.68	186	6.5	0.47	16.8	14.5	0.151	0.126
SiZr-50-e	3.22	186	6.5	0.48	19.1	16.6	0.171	0.144
Series 4. Alumina-silica xerogels (variable composition)								
	$w(\text{Al}_2\text{O}_3)/\%$							
SiAl-3	3	320	5.4	0.181	31.2	51.5	0.435	0.846
SiAl-7	7	260	5.7	0.215	27.1	42.7	0.385	0.676
SiAl-10	10	271	5.7	0.380	31.8	57.3	0.261	0.592

released by the catalyst surface usually exceeds that caused by water autoprotolysis. Titration curves were then transformed into proton-binding isotherms *via* an appropriate balance equation.

Catalytic activity for but-1-ene isomerization was measured according to the procedure described by Miller *et al.* [3]. In standard experiments, the catalyst samples (0.2 g) were dried in a helium flow at 473 K for 1 h, then the temperature was reduced to the reaction temperature,  $T_r = 423$  K, and the reactant mixture (5 % but-1-ene in He) was fed at 100 STP  $\text{cm}^3 \text{min}^{-1}$  into the reactor. Table 1 collects the percent conversions to *cis*- and *trans*-but-2-ene after 90 min time-on-stream. Conversions measured in duplicate trials differ by no more than 5 %.

## DATA ANALYSIS

### Calculation of $pK$ Spectra of Brønsted Sites at the Oxide/Solution Interface

Overall proton-binding isotherms were interpreted as responses of nonuniform surfaces with continuously varying Langmuir local behaviour as described by eqn (1). The  $pK$  spectrum was calculated using the RJ approximation for the local solution of the adsorption integral equation [9]. A smoothing procedure [1] was applied to all experimental data which ensured that all significant information was retained and random errors were minimized. After subtracting the buffering effects of water at low and high pH, the resulting  $pK$  spectra were analyzed by decomposition into a sum of Gaussian functions using the Peakfit software which gives the  $N_i$  (surface density,  $\mu\text{mol m}^{-2}$ ) and  $pK_i$  (acidity constants) parameters for each kind of Brønsted acid site at the oxide/solution interface. Two constraints were imposed at this step: minimum number of components and limited widths (less than 0.8  $pK$  units) of Gaussian functions. The results of this analysis were further tested by recomposing the proton-binding curves and comparing with the experimental data.

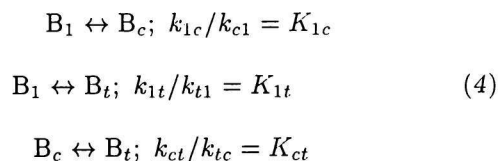
The errors that may affect data derived from potentiometric titration experiments were analyzed previously in detail [1]. These experimental errors depend on the accuracy of pH readings or may be caused by sample solubility. Both errors depend on pH and increase at the extremes of the pH scale. We have also shown [8] that the pH window whereby meaningful proton affinity spectra may be obtained from potentiometric titration depends on the properties of analyzed samples and the experimental conditions. The window of reliable information is broader for catalysts with large surface area than for low surface area samples. The increasing buffering effects due to the aqueous medium both in acidic and basic ranges were subtracted from the calculated PADs [8]. In a previous paper we have explained the criteria used in the Gaus-

sian analysis step of complex  $pK$  spectra; the correlation coefficients obtained for all decompositions were larger than 0.992, as already reported [8]. Based on these considerations and on several duplicated experiments, we estimate that the uncertainties that affect the values reported in columns 4 and 5 of Table 1 are not greater than 10 % for  $N_i$  and 0.2 units for  $pK_i$ .

### Kinetic Analysis of But-1-ene Isomerization

The mechanistic description involving proton transfer steps between the solid acid surface and the organic substrate, with additional steric contributions [10] in the stabilization of some intermediate carbenium ion, is widely accepted [11]. The idea that a coupled, kinetically inseparable surface process (transfer plus rearrangement) is rate-controlling is the reasonable extension of our argument. On the other hand, equilibrium solid-aqueous proton transfer is reflected in PADs. If our fundamental assumption that surface structural entities responsible for "dry" acidity and thus catalytic activity are preserved (even if somewhat transformed) in aqueous media and, moreover, resolvable through the PAD approach, a relationship such as Brønsted's is expected to link the dry *apparent* isomerization rate constants and *certain* wet equilibrium constants. This is actually demonstrated here by a more careful analysis of the previously reported [8] data.

The isomerization reaction was treated following a simplified procedure suggested by Hightower and Hall [12] and subsequently followed by others [13–16] within a reversible first-order mechanistic scheme



where  $k$  stands for kinetic and  $K$  for equilibrium constants, with subscripts 1,  $c$  and  $t$  denoting but-1-ene, *cis*- and *trans*-but-2-enes, respectively. For the above reaction scheme the principle of detailed balancing yields:  $k_{1c}k_{ct}k_{t1} = k_{c1}k_{tc}k_{1t}$  or  $K_{1c}K_{ct}/K_{1t} = 1$ . The above network was decomposed into its individual reversible first-order steps and *apparent* rate constants,  $k_i$ , under integral reactor operating conditions were expressed as [17]

$$k_i = \frac{\ln[1 - (1 + K_i^{-1})x]^{-1}}{\tau_R(1 + K_i^{-1})}; \quad i = 1c, 1t \quad (5)$$

where  $x$  is the fractional conversion and  $\tau_R$  represents the mass time ( $\text{g h mol}^{-1}$ ) [18]. Thermochemically estimated equilibrium constant values were 4.27 and 8.61 for the but-1-ene  $\rightleftharpoons$  *cis*-but-2-ene and but-1-ene

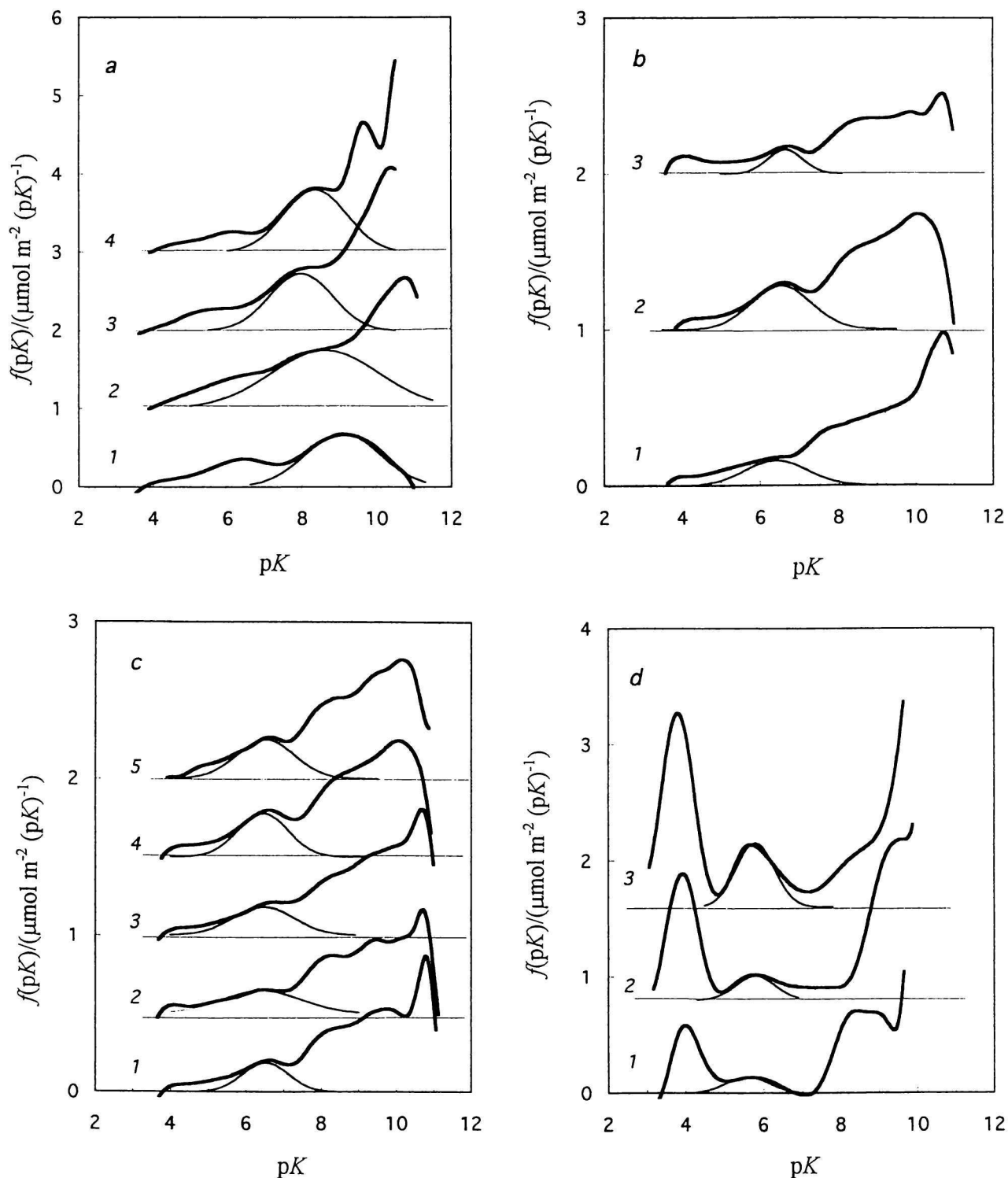


Fig. 1. Proton affinity distributions of catalyst samples. a) Titania-silica aerogels (variable composition): 1. SiTi-95, 2. SiTi-67, 3. SiTi-50, 4. SiTi-33; b) zirconia-silica aerogels (variable composition): 1. SiZr-33, 2. SiZr-50-d, 3. SiZr-67; c) zirconia-silica aerogels (constant composition, various prehydrolysis ratio): 1. SiZr-50-a, 2. SiZr-50-b, 3. SiZr-50-c, 4. SiZr-50-d, 5. SiZr-50-e; d) alumina-silica aerogels (variable composition): 1. SiAl-3, 2. SiAl-7, 3. SiAl-10.

$\rightleftharpoons$  *trans*-but-2-ene reactions at 423 K working temperature, respectively. Slightly lower values (3.36 and 6.58) at 448 K were obtained by *Garcia-Ochoa* and *Santos* using another database [18]; even if differences are larger than those corresponding to a 25 K temperature rise, this is of no consequence throughout the subsequent argument.

## RESULTS

Fig. 1 shows the proton affinity distributions of surface hydroxyls at the oxide/solution interface calculated from potentiometric titration data. They consist, in general, of several overlapping peaks that correspond to several kinds of Brønsted acid sites. For a quantitative analysis, the continuous distributions were deconvoluted in terms of Gaussian functions. In general, within a series of similar catalysts PADs are characterized by the existence of similar acid functionalities (at nearly identical  $pK_i$  values) present in different amounts (different  $N_i$ ) for different samples.

We made several attempts to find a correlation between the activity for but-1-ene isomerization and the density of acid sites at various  $pK$  values for each series of catalysts. After the evaluation of possible combinations we concluded that among the surface sites identified in PADs there is only one type for each group of samples the surface density of which,  $N_i$ , ( $\mu\text{mol m}^{-2}$ ) correlates linearly with the areal rates ( $\text{mmol m}^{-2} \text{h}^{-1}$ ) of butene isomerization. The Gaussian profiles of only these peaks are shown in Fig. 1. Their characteristic parameters are given in columns 4 and 5 of Table 1. The surface site concentrations which were found to correlate with catalytic activity for butene isomerization are shown in Fig. 2. Straight lines exhibit fairly good correlation coefficients and intercepts increasing in the order SiTi < SiZr < SiAl, which coincides with the increase in overall activity. We can ascribe this "residual activity" to (partially) poisoned stronger acid sites.

Less acidic (more resistant to poisoning) sites are thus responsible for the majority of the catalytic activity after 90 min time-on-stream. The pH ranges and the corresponding  $pK_i$  values for these sites on fully hydrated samples are 8–9.1 for titania-silica, 6.4–6.5 for zirconia-silica, and 5.4–5.7 for alumina-silica. Note that there is one sample in Fig. 2 which deviates from the linear correlation, namely the silica-titania catalyst with 95 %  $\text{TiO}_2$ ; since this sample also shows a larger *cis/trans* ratio, we assume that the reaction mechanism on this particular sample may equally involve some basic sites of the titania component [8]. For that reason, the point pertaining to this sample was excluded from the linear fit.

Fractional conversions,  $x_i$ , and values of  $k_i$  expressed in amount of moles of product formed per 1 mol of active sites (given by PADs) per 1 h are presented in the last columns of Table 1; the latter can

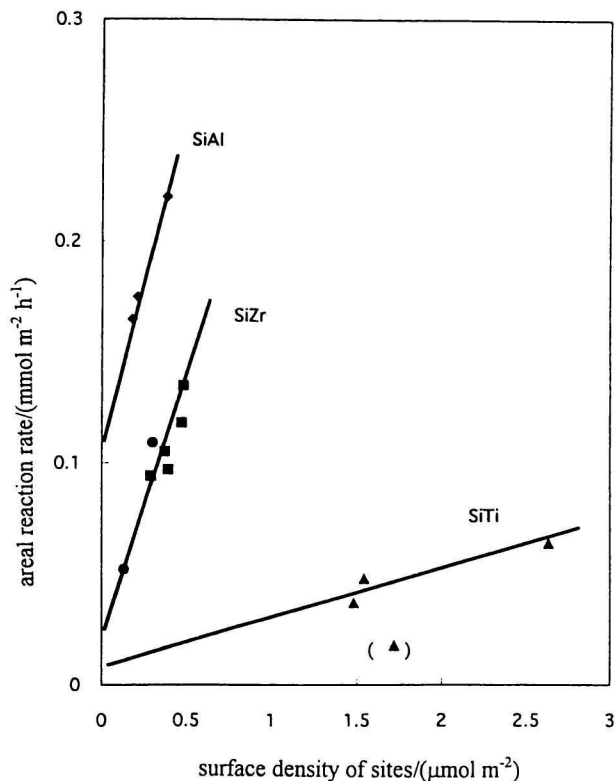


Fig. 2. Linear dependence of areal reaction rates for but-1-ene isomerization on surface density of active sites at  $8 < pK < 9.1$  (SiTi samples),  $6.4 < pK < 6.5$  (SiZr samples), and  $5.4 < pK < 5.7$  (SiAl) calculated from  $pK$  spectra. Correlation coefficients are 0.93 (SiTi), 0.92 (SiZr), and 0.99 (SiAl).

be viewed as turnover rate constants. Brønsted-type plots of these rate constants,  $k_{cis}$  and  $k_{trans}$  against characteristic  $pK$ s are illustrated in Fig. 3. Keeping in mind the approximations made in decomposing the reaction network and inherent experimental errors involved, the linearity over 3 or 4 orders of magnitude may be appreciated as more than satisfactory.

## DISCUSSION

Empirical correlations such as the Brønsted relationship are widely used as predictive tools in homogeneous catalysis. Analogous procedures in heterogeneous acid-base catalysis are greatly needed [19, 20]. The present contribution, which aims towards a correlation between wet (aqueous) acidity given by proton affinity distributions and dry catalytic activity of the same solid acids is, to our knowledge, the very first attempt.

Reactions such as but-1-ene isomerization or alcohol dehydration occur at moderate temperatures (300–350 K) and are frequently used to probe the acid-base properties of solid surfaces. They are classified at the low end of several acid strength scales that correlate qualitatively with activity and acidity

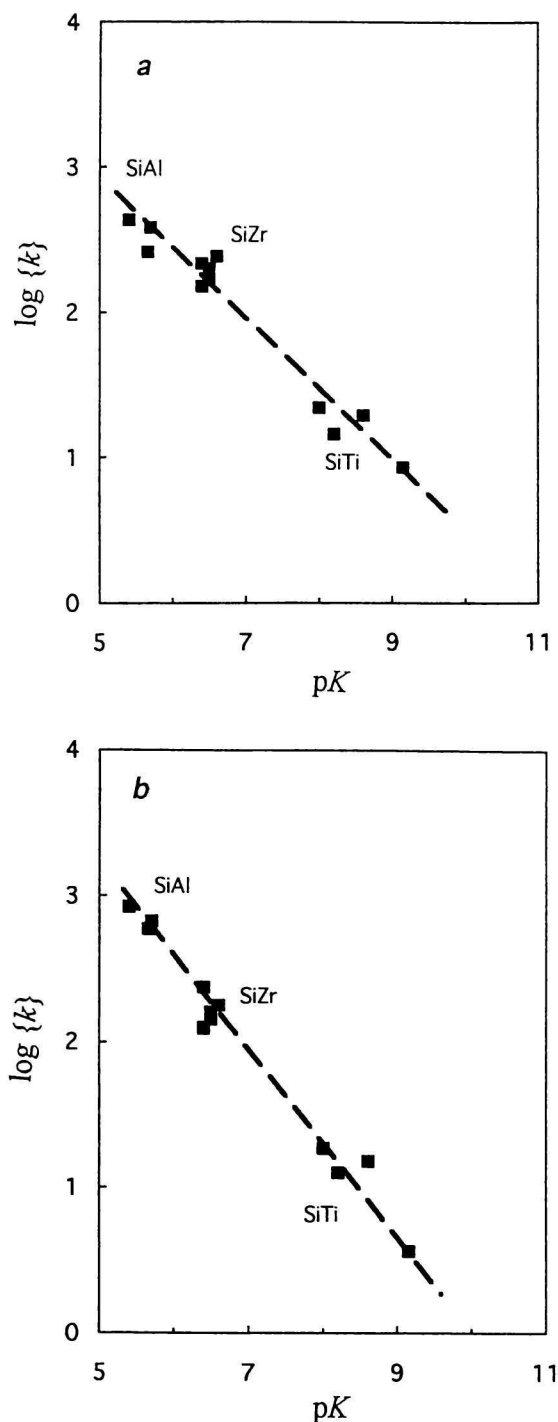


Fig. 3. Brønsted-type plots. a)  $k_{cis}$  ( $\alpha = 0.49$ ,  $r = 0.980$ ); b)  $k_{trans}$  ( $\alpha = 0.62$ ,  $r = 0.985$ ).

for various catalysts [21–23]. In their study of but-1-ene isomerization on various mixed oxides, including those studied in the present paper, *Ko et al.* [3–6] concluded that 1. the double-bond shift reaction at 423 K is catalyzed by weak Brønsted acid sites and 2. the isomerization activity measures the Brønsted acidity [24]. Lewis sites are ignored in view of not only

the fact that PADs are not able to resolve them, but also the *cis/trans* ratio of the but-2-ene formed which clearly points towards Brønsted sites as active centres [11].

Herein we analyze the catalytic properties of a series of mixed oxide aerogels and xerogels with different acid site distributions, as illustrated in Fig. 1 by the  $pK$  spectra obtained from potentiometric titration data in aqueous solution. The but-1-ene isomerization activity was measured on mildly dehydrated catalysts, as confirmed by infrared data [25]. In Fig. 2 we demonstrate that a linear relationship exists between the overall areal reaction rates and the surface density of a particular subset of the hydroxyl population, confined to a narrow  $pK$  range. This offered the basis for the estimation of turnover frequencies (TOFs) for the reaction studied on different catalysts. A significant result was that the TOFs were almost constant (within reasonable limits imposed by the experimental errors) for catalysts in a group of similar samples [8]. A simple kinetic analysis was possible for middle-range acid sites, the concentration of which was found to scale with overall catalytic activity: it allowed a more detailed, Brønsted-type correlation between aqueous equilibrium constants and isomerization rate constants. It is shown in Fig. 3.

The fact that stronger acid sites are not involved in the correlation, whereas weaker ones are, cannot be understood in view of solely homogeneous catalysis concepts. For heterogeneous catalysts, *Tanabe* [26] has shown that “the activity and selectivity (...) depend on the ‘acidic property’, *i.e.* the strength, the amount and the type of acid sites” Also, basic sites may act more or less in cooperation with active acid sites even for reactions that have been recognized to be catalyzed only by acidic sites. An example is the dehydration of butan-2-ol to but-1-ene which proceeds with higher selectivity on  $ZrO_2$  (a weak acid catalyst) than on  $Al_2O_3$  or  $SiO_2-Al_2O_3$  (more acidic) [26]. The “basic route” contribution was suspected, as already mentioned, for the 95 %  $TiO_2-SiO_2$  sample investigated in the present study, for which no correlation was found. The strongest acid sites contribution is more pronounced for silica/alumina samples: their relatively high concentration is evidenced in the corresponding PADs of Fig. 1, and corroborated with the highest intercept (residual activity) of Fig. 2. Poisoning, manifested in the marked decrease in activity within the first 20 min of each catalytic run, accounts for the fact that their concentration in fresh samples does not correlate with steady-state reaction rates (at 90 min time-on-stream).

Although apparent and not mechanistic kinetic quantities are involved in the Brønsted relationship shown in Fig. 3, the significant difference between *cis* and *trans*  $\alpha$  values obtained (0.49 and 0.62, respectively) deserves some comment.

Within the approximation used in evaluating ap-

parent rate constants we may assume a fast (quasi-equilibrated) protonation of but-1-ene yielding a single intermediate, be it a true secondary carbenium [12] or "carbenium-like" [11] ion. Reorganization of this intermediate (such as a "rollover" [14]) allows for methylenic H abstraction and thus but-2-ene formation. This reorganization is much less pronounced for the "cis" route than for the "trans" one. The obtained transfer coefficients appear to illustrate the above mechanistic argument:  $\alpha \approx 0.5$  ( $k_{cis}$ ) is consistent with a facile initiation step whereas  $\alpha > 0.5$  ( $k_{trans}$ ) for a more demanding steric requirement to produce the reaction intermediate.

## CONCLUSION

We have shown that the proton affinity distributions (or pK spectra) for the oxide/solution interface determined from potentiometric aqueous titration data give reliable information on the ability of surface sites to bind or release protons. When the same oxides were used as catalysts for double-bond isomerization of but-1-ene, a heterogeneous gas/solid reaction requiring weak Brønsted sites, the pK spectra of the hydrous oxides provided the means to identify and characterize those surface sites that may act as specific active sites under reaction conditions.

We report data on titania-silica, zirconia-silica, and alumina-silica mixed oxides that differ by their composition as well as preparation method. In all cases, a direct relationship was found between the areal reaction rates (at constant reaction conditions) and the surface density of only one particular type of site identified in the pK spectrum of the hydrous oxide surface.

For estimation of kinetic constants, the isomerization reaction of but-1-ene was treated following a simplified procedure within a reversible first-order mechanistic scheme and the first-order apparent rate constants were evaluated under integral reactor operating conditions. The Brønsted-type plots of apparent rate constants  $k_{cis}$  and  $k_{trans}$  against characteristic pKs for the active sites previously identified for each catalyst series were linear over 3 orders of magnitude for log  $k$  and 4 units on the pK scale.

The results were consistent with the assumption that proton abstraction by the but-1-ene reactant is mediated by the hydroxyls of the pseudo-dry surface and their acid strength and number are related to the pK spectra obtained from potentiometric titration measurements. This explains the observed correlation between apparent isomerization rate constants and aqueous-scale acid strength as revealed by proton affinity distributions.

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