# Boroaluminosilicate Catalysts with the ZSM-5 Structure Synthesized in Nonalkaline Media

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Aluminosilicate and borosilicate (containing up to 3.80 B atoms per unit cell) zeolites with the ZSM-5 structure have been prepared by the "fluoride route" and studied by a range of techniques. Contrary to numerous studies (which investigated the conversion of methanol at much higher temperatures), *trans*-but-2-ene and not ethylene is the first hydrocarbon desorbed from the catalyst at temperatures below 200 °C. We propose a mechanism for this reaction which does not require the formation and desorption of ethylene to the gas phase. The reaction of the methoxy intermediate formed on an acid site with the  $CH_3OH$ molecule gives surface ethoxy groups, which are alkylated by further methanol molecules to give propoxy and butoxy groups.

# Introduction

In naturally occurring borosilicates boron is normally present in trigonal coordination, but 4-coordinated boron is found in rare minerals such as datolite, garrelsite, and reedmergnerite.<sup>1</sup> However, many crystalline synthetic borosilicates and boroaluminosilicates with 4-coordinated framework boron and structures of various zeolites, including the structure of ZSM-5,<sup>3-5</sup> have been prepared. The substitution of boron into the zeolitic framework is reflected in (i) the gradual decrease of the unit cell volume and the increase of intensity of the infrared band at 920 cm<sup>-1</sup> (B–O–Si symmetric stretching) with increasing boron content and (ii) the presence of the sharp <sup>11</sup>B NMR signal at between -3 and -4 ppm from BF<sub>3</sub>-Et<sub>2</sub>O found in magic angle spinning (MAS) NMR spectra of hydrated samples, characteristic of framework boron in the BO<sub>4</sub> tetrahedra.

In a novel synthetic route to ZSM-5 zeolites,<sup>6</sup> fluoride ions are used to solubilize the sources of silicon and aluminum, and crystallization proceeds at pH < 7. The advantages of this method are that the product is obtained as large crystals directly in the TPA<sup>+</sup>/NH<sub>4</sub><sup>+</sup> form, so that the hydrogen form, essential in catalysis, is formed directly by calcination in air, thus avoiding tedious ion exchange with ammonium salts. Furthermore, sodium, a catalyst poison, is absent from the synthesis gel. Metal-containing zeolites can also be prepared by the "fluoride route", which yields more perfect, defect-free crystals than conventional synthesis.<sup>7</sup> The objective of this work is to study the properties of boron- and aluminum-substituted MFI-type zeolites prepared by the fluoride route.

## **Experimental Section**

Sample Preparation. The synthesis of boroaluminosilicates was as follows.<sup>8</sup> Fumed silica (Cab-O-Sil), tetrapropylammonium bromide (TPA-Br), ammonium fluoride, orthoboric acid, and aluminum nitrate were used as starting materials. TPA-Br was dissolved in water and mixed with the source of silica. A suspension was aged under vigorous stirring for 3 h at room temperature, and then a solution of ammonium fluoride, orthoboric acid, and aluminum nitrate was added. Typically, the samples a gel of composition prepared were from  $2.27 \text{SiO}_2$ :  $1.00 \text{H}_3 \text{BO}_3$ :  $0.28 \text{TPA} - \text{Br}: 0.51 \text{NH}_4 \text{F}: 73 \text{H}_2 \text{O}$ . The amount of aluminum nitrate in the gel was adjusted according to the desired level of Al substitution. The gel was homogenized for 1 h and transferred into a Teflon-lined stainless steel autoclave, which was then heated without stirring at 200 °C for 14-20 days. Zeolitic crystals were washed, dried at 60 °C, and calcined at 450 °C in air to remove the template. Pure [Si]-ZSM-5 (silicalite) and [Si,B]-ZSM-5 were prepared using a similar procedure. Analytical grade reagents were used to avoid contamination with aluminum. Atomic absorption analysis showed that silcalite and [Si,B]-ZSM-5 are completely aluminum free, and <sup>27</sup>Al MAS

NMR detected no aluminum in either material. The composition of the samples is listed in Table I. The "ZSM-5" label will from now on be omitted in the text for brevity.

X-ray Diffraction. X-ray diffraction (XRD) patterns of the as-prepared samples were acquired in the range  $3^{\circ} \le 2\theta \le 60^{\circ}$ on a Philips PW1710 automatic powder diffractometer using Cu K $\alpha$  radiation at a scanning rate of 1° min<sup>-1</sup>. All samples were fully hydrated in order to avoid sorption of water vapor during the acquisition of data. Silicon powder was used as an internal standard, and peak positions were determined by a computerized peak-search program. A refinement program was used for calculating the lattice parameters. All samples were highly crystalline to X-rays and contained pure phase with the ZSM-5 structure. No amorphous material was found (see Figures 1 and 2).

**Transmission (TEM) and Scanning (SEM) Electron Microscopies.** TEM was performed with Hitachi H-7000 and Jeol JEM 200 CX electron microscopes at 75 and 200 kV, respectively, and SEM was performed with Jeol-840 at 25 kV.

MAS NMR. Short pulses are necessary if quantitative spectra of quadrupolar nuclei are to be obtained.<sup>9</sup> The samples were hydrated in the desiccator over saturated NH<sub>4</sub>NO<sub>3</sub> solution prior to obtaining NMR spectra. <sup>11</sup>B MAS spectra were measured at 128.33 MHz using a Bruker MSL-400 multinuclear spectrometer. Samples were spun in Vespel rotors at 4–5 kHz using air as the spinning gas. <sup>11</sup>B radio-frequency pluses of 1- $\mu$ s duration were applied with a 300-ms recycle delay. Chemical shifts are quoted in ppm from external BF<sub>3</sub>·Et<sub>2</sub>O. <sup>27</sup>Al MAS spectra were measured at 104.2 MHz by using 0.6- $\mu$ s ( $\pi$ /20 pulse angle) pulses with a 200-ms recycle delay. Chemical shifts are given in ppm from external Al(H<sub>2</sub>O)<sub>6</sub><sup>3+</sup>.

Adsorption. The adsorption/desorption isotherms of nitrogen were obtained using a Micromeritics ASAP 2400 apparatus. All samples were outgassed at 400 °C under vacuum prior to experiment.

Catalytic Measurements. For catalytic measurements crystals were pressed into binder-free wafers, crushed, and sieved to 30-60 mesh. A 50-mg sample was diluted with 0.5 cm<sup>3</sup> of quartz chips (30-60 mesh) and packed in a stainless steel down-flow microreactor (10-mm i.d.) placed in a tube furnace. Additional amounts of quartz chips were placed before and after the catalyst bed to give a total volume of ca. 3 cm<sup>3</sup>. The thermocouple well was located centrally in the microreactor connected to a gas chromatograph. The catalyst was activated overnight in situ at 450 °C in a helium flow. Measurements were carried out in a pulse mode, which makes possible a quick comparison of activity and selectivity within a series of samples. Also, catalyst coking is significantly suppressed. All the reaction parameters were kept constant during the experiment in order to maintain maximum reproducibility of the results. The samples had approximately the same sorption properties (see Table II); hence, the result of catalytic experiments could be directly compared. Methanol (5  $\mu$ L) was injected into the microreactor, and the reaction products were conveyed by a heated tubing into gas sample valve. Products

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TABLE I: Composition and Unit Cell Parameters of [Si]-ZSM-5 (Silicalite) and Boron- and Aluminum-Substituted Samples with the ZSM-5 Structure

						unit cell parameters, A		
	B/uc	Al/uc	Si/(Al + B)	Si/B	Si/Al	a	ь	с
[Si,B]-ZSM-5	3.80		24.3	24.3		19.89	19.71	13.34
[Si,B,Al]-ZSM-5 I	3.10	0.69	24.3	29.8	133.6	19.93	19.82	13.32
[Si,B,Al]-ZSM-5 II	3.72	1.07	19.0	24.5	85.2	19.94	19.81	13.31
[Si,B,Al]-ZSM-5 III	2.34	2.12	20.5	39.1	43.2	19.99	19.82	13.34
silicalite						20.01	19.88	13.35



Figure 1. SEM photograph of silicalite.





Figure 2. SEM photograph of (a, top) [Si,B]-ZSM-5 and (b, bottom) [Si,B,A1]-ZSM-5 I.

were analyzed by use of a high-resolution gas chromatograph (Carlo Erba 5340 Mega Series) equipped with a flame-ionization detector. Two fused silica capillary columns (30 m long, 0.32-mm i.d.; J&W Scientific) with DB-1 and DB-WAX liquid phases, respectively, were used for analysis. Analytical grade hydrocarbons and MeOH supplied by Aldrich were used without further purification to estimate molar response factors of the detector.

## **Results and Discussion**

The characterization of all the catalysts is given in Table I. In samples [Si,B,AI]-I and [Si,B,AI]-II the amount of boron was

#### TABLE II: Surface Area and Pore Volume of the Catalysts

		pore volume, cm <sup>3</sup> /g			
	BET surface area, m <sup>2</sup> /g	micropore (t plot) <sup>a</sup>	mesopore (BJH) <sup>b</sup>		
[Si,B]-ZSM-5	378	0.159	0.056		
[Si,B,Al]-ZSM-5 I	387	0.162	0.062		
[Si,B,Al]-ZSM-5 II	402	0.144	0.059		
[Si,B,Al]-ZSM-5 III	391	0.171	0.061		
silicalite	341	0.160	0.126		

<sup>a</sup>de Boer, J. H.; Lippern, B. C. J. Catal. **1965**, *4*, 319. <sup>b</sup>Barrett, E. P.; Joyner, L. G.; Halenda, P. P. J. Am. Chem. Soc. **1951**, 73, 373.

relatively high (above 3 B/uc), while sample [Si,B,A1]-III contained 2.34 B/uc. The amount of aluminum increases from 0.69 Al/uc in sample I to 2.12 Al/uc in sample III. It was found impossible to introduce more than 2 Al/uc while maintaining the high level of boron substitution.

The unit cell parameters of silicalite (Table I) are similar to those of the sample prepared under alkaline conditions: a = 20.1, b = 19.9, c = 13.4 Å.<sup>10</sup> Substitution with boron leads to a contraction of the unit cell (unit cell volumes of 5230 Å<sup>3</sup> for [Si,B]-ZSM-5 and 5311 Å<sup>3</sup> for silicalite) because the B atom is smaller than the Al atom (0.20 and 0.50 Å). A steady increase of the aluminum content results in a small increase of the unit cell parameters, especially along the a and b axes. The size of the unit cell is intermediate between pure silicalite and a pure borosilicate, as the two heteroatoms have an opposite influence on the unit cell size.

SEM pictures given in Figures 1 and 2 show that the products are completely crystalline and that the crystals have a characteristic elongated prismatic morphology typical of ZSM-5. The crystals of silicalite and [Si,B]-ZSM-5 are ca. 50  $\mu$ m long; those of [Si,B,AI]-ZSM-5 I are ca. 150  $\mu$ m long. No amorphous material is found in either sample.

The <sup>27</sup>Al MAS NMR spectra (not shown) of samples I, II, and III contain a single signal assigned to 4-coordinated framework aluminum. This proves that all the aluminum is substituted into the framework sites and that there is no extra framework aluminum in any as-prepared sample. Tetrahedral framework boron in borosilicates and boroaluminosilicates gives rise to a sharp signal with a chemical shift in the range -3.3 to -4.0 ppm from BF<sub>3</sub>. Et<sub>2</sub>O.<sup>5,6,11-13</sup> In minerals such as kernite and inderite, BO<sub>3</sub> and BO<sub>4</sub> units can be unambiguously distinguished by NMR spectroscopy. Relative spectral intensities are in excellent agreement with the X-ray studies and chemical composition.<sup>14</sup> In all boron-containing samples we have found a single sharp <sup>11</sup>B signal at ca. -4 ppm (spectrum not shown) unambiguously corresponding to 4-coordinated framework boron.

The absorption/desorption isotherms of nitrogen are shown in Figures 3 and 4, while the surface areas and pore volumes are given in Table II. It is clear that the overall sorptive properties of all the samples are similar. The BET surface areas for pure borosilicate as well as boroaluminosilicates are in the range  $380-400 \text{ m}^2/\text{g}$ . However, the shapes of the isotherms differ significantly. Thus for silicalite, [Si,B]-ZSM-5, and partly for [Si,B,AI]-I multistep adsorption isotherms were obtained. Jacobs et al.<sup>15</sup> offered a geometrical interpretation for a similar isotherm in H-ZSM-5. They assumed that the shape of the isotherm reflects the closest-density packing of an adsorbed monolayer and a bilayer at the channel intersections. The multistep isotherm became the usual type I isotherm for Na-ZSM-5. This implied that the



Figure 3. Adsorption/desorption isotherms of nitrogen on (a) [Si,B]-ZSM-5 and (b) silicalite.



Figure 4. Absorption/desorption isotherms of nitrogen on (a) [Si,B,-Al]-ZSM-5 I, (b) [Si,B,Al]-ZSM-5 II, and (c) [Si,B,Al]-ZSM-5 III.

nitrogen molecules entered a less homogeneous channel system during adsorption. Multistep isotherms have been observed for other highly homogeneous adsorbents, such as graphite.<sup>16</sup>

TABLE III: Distribution of the Products of Methanol Conversion (mol %) on Zeolite [Si,B]-ZSM-5 at Contact Time  $\tau = 0.4$  s

	temperature, °C							
	112	132	150	162	187	212		
methane ethylene ethane dimethyl ether methanol trans-but-2-ene $c_{s+}$ paraffins and olefins benzene	0.23 99.76	0.21 99.77 0.02	0.26 99.72 0.02 trace	0.45 99.51 0.03 0.01	0.11 0.52 99.21 0.05 0.11	3.27 trace trace 0.65 95.22 0.12 0.73 0.01		
ethane dimethyl ether methanol <i>trans</i> -but-2-ene <i>cis</i> -but-2-ene C <sub>5+</sub> paraffins and olefins benzene	0.23 99.76	0.21 99.77 0.02	0.26 99.72 0.02 trace	0.45 99.51 0.03 0.01	0.52 99.21 0.05 0.11	trace 0.65 95.22 0.12 0.73 0.01		

Atom-atom approximation (AAP) calculations performed for argon and nitrogen revealed that in the unit cell of ZSM-5 there are 24 minima of the potential energy, of which 8 are situated in the straight and 12 in the zigzag channels. The remaining four are located at channel intersections.<sup>17</sup>

The channels have similar cross sections (5.3  $\times$  5.6 and 5.1  $\times$ 5.5 Å), but more space is available at channel intersections. It is therefore clear that if the adsorption takes place first in the channels (where 20 minima are situated), the first step at the isotherm should occur at ca. 20  $N_2/uc$ . Indeed, Müller et al.<sup>17</sup> observed the step in this position for Na-ZSM-5, and the next at 24  $N_2/uc.\,$  We have observed the first step at 21  $N_2/uc$  followed by the next at 26 nitrogen molecules [Figure 3b]. On pure borosilicate the step at 24  $N_2/uc$  is less pronounced. Similarly, the inflection near 24 molecules was observed for samples [Si,B] and [Si,B,Al]-I [Figures 3a and 4a]. Experimental results are therefore in a good agreement with the AAP calculations. Further adsorption on the solids in the region between 24 and 28 N<sub>2</sub> molecules for [Si,B]-ZSM-5, 29 molecules for samples I-III, and 32 molecules for silicalite corresponds to the change of the density of liquid to solid nitrogen. A small difference between total adsorption capacity of aluminum and boron homologues of the ZSM-5 structure is partly due to the contraction of the unit cell (see Table I).

It is interesting to note that in the case of argon multistep adsorption is either less pronounced<sup>13</sup> or even absent.<sup>18</sup> This may be due to different behavior of the diatomic nitrogen molecule possessing a quadrupole moment and permitting additional adsorbate-adsorbate interactions. As aluminum is substituted in the framework, the samples lose their homogeneity which is clearly seen for silicalite and borosilicate. For small amounts of aluminum (below 1 atom/uc) small steps are still seen in the isotherm, while samples with higher substitution levels do not show multistep adsorption patterns.

Methanol (MeOH) was reacted over a series of hydrogen forms of our samples. The distribution of products at constant contact time of 0.4 s and temperatures up to 212 °C is listed in Tables III-VI. These runs were carried out at relatively low temperatures in order to observe the *first* products desorbed from a catalyst bed.

Dimethyl ether (DME) is the first product at 87-112 °C. Figure 5 shows the plot of the yield of DME at 150 and 200 °C versus the number of Al atoms per unit cell. The relationship is clearly nonlinear: the higher the aluminum content, the higher the efficiency of dehydration of methanol. Interestingly, small amounts (up to ca. 1 Al/uc) of framework aluminum significantly influence the yield of DME.

Figure 6 shows the yield of DME versus the temperature. The amount of DME formed depends on the catalyst. Small amounts (below 1 mol %) of DME are formed over pure [Si,B] sample (Table III). We have shown that Lewis acid sites and weak Brønsted sites are inactive for the dehydration of methanol.<sup>19</sup> The reaction requires strong acid centers, and sodium forms of ZSM-5 up to 11% exchange level for hydrogen do not catalyze dehydration. A pure [Si,B] sample does not generate strong Brønsted acidity, and hence the formation of DME is negligible. Stepwise introduction of aluminum into the framework does generate Brøsted acidity, and the yield of DME increases dramatically.

TABLE IV: Distribution of the Products of Methanol Conversion (mol %) on [Si,B,Al]-ZSM-5 I at Contact Time  $\tau = 0.4$  s

	temperature, °C							
	87	112	139	148	166	179	201	
methane					trace	0.06	0.25	
ethvlene				1.74	0.52	0.30	0.11	
propylene				0.02	0.01	0.01	0.01	
DME	0.51	2.60	10.00	12.73	15.60	18.90	18.82	
methanol	99.49	97.39	89.95	81.97	82.16	79.87	80.43	
n-butane				0.02	0.01	0.01	0.01	
trans-but-2-ene	trace	0.01	0.04	0.43	0.42	0.26	0.08	
cis-but-2-ene		trace	trace	0.41	0.49	0.08	0.07	
C <sub>4</sub> paraffins and olefins		trace	0.01	2.68	0.79	0.51	0.22	
benzene			trace	trace	trace	trace	trace	

TABLE V: Distribution of the Products of Methanol Conversion (mol %) on [Si,B,A]-ZSM-5 II at Contact Time  $\tau = 0.4$  s

	temperature, °C							
	119	137	150	162	187	212		
methane					trace	0.53		
DME	2.21	11.55	15.54	17.93	22.42	23.41		
trans-but-2-ene	97.51 trace	88.39 0.01	87.79 0.04	82.00 0.01	0.01	0.01		
cis-but-2-ene C <sub>5+</sub> paraffins and olefins	trace trace	trace 0.01	trace 0.12	trace 0.05	trace 0.10	trace 0.22		

TABLE VI: Distribution of the Products of Methanol Conversion (mol %) on [Si,B,Al]-ZSM-5 III at Contact Time  $\tau = 0.4$  s

	temperature, °C						
	137	150	162	187	212		
methane				0.27	1.97		
ethylene				trace	0.03		
ethane					trace		
propylene					trace		
DMÉ	1 <b>2.99</b>	17.91	22.36	25.59	27.40		
methanol	86.99	81.78	77.47	73.93	70.43		
isobutane	trace	trace	trace				
trans-but-2-ene	trace	0.05	0.03	0.01	0.01		
cis-but-2-ene		trace	trace	trace	trace		
C <sub>1+</sub> paraffins and olefins	0.02	0.26	0.14	0.20	0.16		
benzene					trace		



Figure 5. Yield of DME versus the number of aluminum atoms per unit cell in samples [Si,B,Al]-ZSM-5 I, [Si,B,Al]-ZSM-5 II, and [Si,B,-Al]-ZSM-5 III at 150 and 200 °C.

The bell-shaped curves are obtained with the maximum shifting gradually toward a higher temperature with the aluminum content in the sample. The maximum of 18.9% DME was observed at





180 °C for 0.69 Al/uc and nearly 30% at 242 °C for 2.12 Al/uc. A significant increase of the maximum DME yield from 18.9 to 30% indicates that the rate of DME formation is faster on those catalysts. Slower consecutive reactions lead to the buildup of DME. As the amount of acidic sites governed by the structural aluminum content increases, their strength slightly diminishes and consecutive reactions start to prevail at higher temperatures. Otherwise, the 60 °C shift in the position of the maximum would not be present. Intermediate electronegativity  $(S_{int})$  of the boroaluminosilicates was calculated and found to change slightly from 4.245 for sample I to 4.238 for sample III.<sup>20</sup> Electronegativity was therefore noticeably close to the maximum value of 4.256 and much higher than in the faujasite<sup>20</sup> or mordenite.<sup>21</sup> As the small change in electronegativity can be detected experimentally (Figure 6), it may be concluded that dehydration of methanol to dimethyl ether is extremely sensitive to overall change of  $S_{int}$  of the solids. The catalytic properties of ZSM-5 zeolites can be changed dramatically with a minute change of  $S_{int}$ . A variation of  $S_{int}$  by 0.03 leads to a significant increase of selectivity to olefins (up to 70%).<sup>22</sup> The situation found in boroaluminosilicates resembles closely the decrease in strength of the acid sites in the faujasitic catalysts (introduction of the next Al atom into the framework positions decreases simultaneously the strength of acid sites), but is less pronounced.<sup>23</sup>

The data given in Tables III-VI reveal that, after DME, trans-but-2-ene is the second product at temperatures below 200 °C. On zeolite [Si,B]-ZSM-5 the yield of trans-but-2-ene increases with the temperature up to the maximum at 212 °C, after which (data not shown) it steadily decreases. Similar behavior was found for samples I, II, and III, except that for these samples the maximum yield of trans-but-2-ene was shifted to 150 °C. However, there is no correlation between the amount of transbut-2-ene in the product and the aluminum content of the catalyst. We note that trans-but-2-ene is observed in the effluents long before even traces of ethylene are detected. The sensitivity of the GC analysis was sufficiently high for 0.005 mol %  $C_2H_4$  to be detected and integrated and traces (ca. 0.001 mol %) still to be qualitatively detected. We conclude that trans-but-2-ene is desorbed from the catalyst bed as the primary hydrocarbon product



Figure 6. Yield of DME versus temperature in samples [Si,B,A1]-ZSM-5 I, [Si,B,Al]-ZSM-5 II, and [Si,B,Al]-ZSM-5 III.

and suggest that ethoxy surface groups are formed at low temperatures inside the solid via alkylation of the methoxy species (see Schemes I and II). Those groups are alkylated further with methanol, and this is why ethylene is not detected among reaction products. Thus, carefully designed catalytic experiments provide substantial evidence that, contrary to numerous studies, ethylene is not the first hydrocarbon desorbed from the catalyst. We note that most earlier studies investigated the conversion of methanol at much higher temperatures, when various parallel and consecutive reactions take place and the analysis of reaction pathways becomes virtually impossible. Moreover, the absence of ethylene at the early stages of the reaction is in line with findings of van den Berg<sup>24</sup> and Novaková,<sup>25</sup> who demonstrated that ethylene is extremely reactive in the presence of zeolite catalysts. If the temperature of methanol conversion is raised further, ethylene can be found among the products produced by secondary cracking reactions of paraffins and olefins. Numerous hydrocarbons can be converted to ethylene at appreciable yields.<sup>26</sup>

The formation of methoxy groups on the surface of zeolites upon contact with methanol has been shown experimentally by means of catalytic tests<sup>27-29</sup> and IR studies<sup>30</sup> as well as <sup>13</sup>C NMR spectroscopy.<sup>31,32</sup> Recently, the phenomenon was investigated theoretically by Kazansky and Senchenya,<sup>33</sup> who carried out semiempirical and ab initio calculations of the electronic structure and geometry of surface alkoxy groups. These revealed that alkoxy groups are not as ionic as was previously believed. The electronic structure resembles rather closely those found in the alkyl fragments in liquid alcohols and esters.

The ionic properties of the alkoxy groups become more evident in the transition states, when the carbon-oxygen bonds are elongated. The excitation requires low activation energy. The surface methoxy groups are formed from methanol via interaction with the Brønsted acid site. The hydrogen marked with an asterisk in Scheme I may be hydrogen-bonded to a neighboring basic oxygen. The question arises how to explain the formation of the first carbon-carbon bond and then the presence of trans-but-2-ene, the first hydrocarbon desorbed. While for ethoxy or higher alkoxy groups the next elementary step may involve abstraction of the proton, restoring the acidic surface hydroxyl, and desorption of the corresponding olefin, the methoxy group would instead of olefin give ylide-like surface intermediates.

Low-temperature conversion of alcohols in the liquid phase by strong acids is known to proceed by carbenium ion mechanisms. Solvation is a necessary condition for the formation of carbenium ions in liquids.<sup>34</sup> The absence of such solvation in high-temperature conversions may prevent the formation of classical carbenium ions. However, solvation effects might be involved even over heterogeneous acidic catalysts at moderate temperatures, especially in light of the recent result<sup>35</sup> that a fraction of methanol molecules adsorbed on a ZSM-5 catalyst are protonated to methoxonium ions. Moreover, it has been shown that clusters of methanol molecules were associated with each Brønsted acid site. In this way up to six molecules of methanol may be associated with one Brønsted acid site by strong hydrogen bonding, and clusters consisting of four molecules were frequently observed. The rationalization of our results now becomes possible. Consider the methoxy group formed on an acid site and a cluster of several methanol molecules bonded via hydrogen bonding (Scheme II).

The reaction of the methoxy intermediate with the CH<sub>3</sub>OH molecule gives ethoxy groups on the zeolitic surface. These are extremely reactive, and hence ethylene is not detected in gaseous reaction products at low temperatures. The ethoxy groups are readily alkylated by the next methanol molecules from the cluster to give propoxy and then butoxy groupings. The latter decompose to trans-but-2-ene, the most thermodynamically stable of all n-butenes. cis-But-2-ene and but-1-ene are the products of consecutive double-bond isomerization of *trans*-but-2-ene at higher temperatures (see Tables III-VI). In this way the formation of trans-but-2-ene is explained without invoking the formation and desorption of ethylene to the gas phase, which would further readsorb and eventually dimerize to give a C4 olefin. The scheme suggested here is strongly supported by the catalytic experiments performed at low temperatures. As we have shown, ethylene is not a first hydrocarbon desorbing from the catalyst. Clusters of several molecules of methanol associated with a Brøsted acidic site in zeolite ZSM-5 play an essential role in the transformation and serve as a source of methanol. We suggest that the formation of trans-but-2-ene may proceed relatively fast by a concerted mechanism. The driving force in the rearrangement is undoubtedly a compensation of the energy of broken bonds by the energy of those newly formed. A high activation energy is therefore unnecessary.

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Registry No. OME, 115-10-6; MeOH, 67-56-1; methoxy, 2143-68-2; ethoxy, 2154-50-9; propoxy, 16499-18-6; butoxy, 19062-98-7; ethylene, 74-85-1; cis-2-butene, 590-18-1; trans-2-butene, 624-64-6.

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# Scanning Electrochemical Microscopy. 14. Scanning Electrochemical Microscope Induced Desorption: A New Technique for the Measurement of Adsorption/Desorption Kinetics and Surface Diffusion Rates at the Solid/Liquid Interface

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Scanning electrochemical microscope induced desorption (SECMID) is introduced as a new technique for the measurement of adsorption/desorption kinetics and surface diffusion rates at the solid/liquid interface, which is generally applicable to the study of reversible processes involving electroactive adsorbates. The method utilizes the ultramicroelectrode (UME) probe of a scanning electrochemical microscope, located close to the sample surface, to perturb the equilibrium of the solid/liquid interfacial adsorption/desorption process under investigation and to measure the resulting flux of adsorbate desorbing from the surface. This is achieved through the application of a potential step to the UME such that the solution component of the adsorbate is electrolyzed at a diffusion-limited rate. The resulting UME current is a measure of the rate of diffusion through solution, the adsorption/desorption kinetics, and the rate of surface diffusion. A theoretical treatment of the chronoamperometric (current-time) response of SECMID is developed, and experimental strategies for obtaining both adsorption/desorption kinetics and surface diffusion rates are delineated. Particular emphasis is given to the adsorption/desorption of H<sup>+</sup> on hydrous metal oxides. The applicability of the technique is illustrated with experiments on the adsorption/desorption of H<sup>+</sup> on rutile (001) and aluminosilicate, albite (NaAlSi<sub>3</sub>O<sub>8</sub>), (010) surfaces.

## Introduction

Adsorption/desorption processes and surface diffusion are key steps in the general scheme of reactions at the solid/liquid interface,<sup>1</sup> and thus dynamic measurements of their rates are of fundamental importance in understanding a variety of interfacial reactions in the physical<sup>2</sup> and biological<sup>3</sup> sciences. Although a number of techniques are available for measuring adsorption/ desorption kinetics at the electrode/electrolyte interface,<sup>4</sup> kinetic measurements of the elementary steps involved in such processes on insulating materials in contact with liquids are more difficult, and comparatively few studies in this area have therefore been reported.<sup>2g,5</sup> Notable exceptions include the use of relaxation methods,<sup>26,6</sup> employing either pressure jump or electric field pulses, and the stopped-flow technique<sup>7</sup> for kinetic measurements on suspensions of powdered material. Additionally, total internal reflection fluorescent methods have been used to study adsorption/desorption kinetics and surface diffusion rates of fluorescent-labeled molecules at the solid/liquid interface.<sup>3b,8</sup>

Relaxation methods have provided useful insights into the mechanisms of a number of rapid adsorption/desorption processes.<sup>2b,6</sup> However, since, in general, this approach can only be applied to adsorbents in the form of suspensions, which comprise various crystal faces (and amorphous material), the measured characteristics represent an average of the behavior of individual faces, possibly with very different adsorptive characteristics. This is in marked contrast to surface studies at both the electrode/ electrolyte<sup>9</sup> and gas/solid<sup>10</sup> interfaces, where well-defined surfaces (e.g., single crystals) are often used.

The aim of this paper is to introduce a new technique, scanning electrochemical microscope induced desorption (SECMID), which permits dynamic measurements of rapid adsorption/desorption processes involving an electroactive species at the solid/liquid interface and, in principle, adsorbate surface diffusion rates. The technique complements a recently proposed strategy for equilibrium adsorption measurements involving ultramicroelectrode voltammetry in small volumes of solution deposited on macroscopic adsorbents.11

The principles of SECMID are outlined, and a theoretical treatment of the method is developed. Particular emphasis is given to H<sup>+</sup> adsorption/desorption on hydrous metal oxides, since surface acidity is a significant field in solid/liquid interfacial adsorption.<sup>12</sup> Studies of  $H^+$  adsorption/desorption on both the (001) surface of rutile  $(TiO_2)$  and the (010) surface of the mineral albite (NaAlSi<sub>3</sub>O<sub>8</sub>) serve to illustrate the applicability of the technique. The generalization of the following treatment for other chemical systems should be straightforward.

#### Principles of SECMID

The scanning electrochemical microscope<sup>13</sup> (SECM) is a scanning probe instrument, employing an ultramicroelectrode tip (UME; a disk with a diameter typically in the range 1-25  $\mu$ m), which can provide local (micron or sub-micron resolution) information about the reactivity and topography of a variety sample substrates.14

In SECMID the tip UME is positioned close to the substrate (within an electrode radius), at which the adsorption/desorption process under study is initially at equilibrium. A potential step is then applied to the UME, such that the electrolysis of the solution component of the adsorbate (for example, the reduction of  $H^+$  to  $H_2$  in surface acidity studies) is diffusion-controlled. As illustrated schematically in Figure 1, the effect of this is to decrease the concentration of  $H^+$  in the tip-substrate gap. This perturbs the adsorption/desorption equilibrium, thereby inducing the de-

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