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SURFACE DEACIDIFICATION OF ZSM5 BY $SiCl_4$ TREATMENT: ASSESSMENT OF SURFACE SPECIFICITY BY METHYLENE BLUE ADSORPTION

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A study has been made of ZSM5 zeolite deacidification (dealumination) by high temperature treatment in $SiCl_4$ vapour, monitoring total acidity by Na^+-exchange, and external surface acidity by methylene blue adsorption (exchange), with comparative measurements of the N_{Si}/N_{Al} ratio (nominally external surface) by XPS.

Using H-ZSM5, the highest specificity for external surface deacidification was found at the lowest usable values of treatment temperature, time and p_{SiCl_4}. Using Na-ZSM5 in place of H-ZSM5 did not offer a useful improvement.

A steaming/HCl-leaching method was shown not to be suitable for selective external surface deacidification.

Values of N_{Si}/N_{Al} by XPS were dependent on the method of sample preparation, with mechanical stress (pelleting, pressing) tending to give abnormally low values due to crystal or aggregate fracture: this effect became more serious with increasing severity of $SiCl_4$ treatment. Even after correcting for XPS emission from subsurface layers, agreement between surface N_{Si}/N_{Al} values from XPS and acidity measurements was poor for samples with a low degree of bulk deacidification (mild $SiCl_4$ treatments), and is ascribed to non-acidic surface Al.

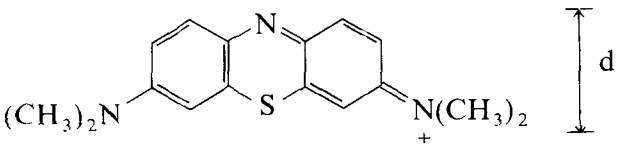
Acidic sites at the external surface of ZSM5 zeolite can be undesirable by allowing catalytic reactions free from size-shape selectivity restraints (e.g. ref. [1]). An inert coating on the external surface can selectively mask external sites [2,3], but the coating can also reduce the effective diameter of the channel entrances [2,3] and may lack adequate thermal or chemical stability. The present work deals with the removal of acidic sites from the surface of ZSM5 zeolite.

A Bronsted acidic site in an alumino-silicate zeolite is associated with an aluminium atom present substitutionally in the framework [4], so dealumination and deacidification are equivalent provided the latter refers to removal of the entire site (i.e. not merely to proton replacement). Nevertheless, a direct measurement of the Si/Al ratio in the external surface (e.g. by XPS [5–7]) is not necessarily a sound method of assessing surface acidity since zeolites may contain adventitious non-framework Al, particularly after dealumination treatment [8,9],

and the Si/Al ratio measured by XPS is sensitive to the method of sample preparation [7].

We have used methylene blue adsorption (exchange) as a direct measure of external surface acidity of ZSM5 [11], and have examined dealumination for the selective removal of external surface acidity. A comparison is also made with the surface Si/Al ratio measured by XPS.

The cationic form of methylene blue has the structure



and the minimum effective kinetic size (in the direction d above) is ca. 0.73–0.76 nm (0.73 from Catalin model, 0.76 quoted in ref. [10]). One would therefore expect the methylene blue cation to be unable to enter the channel structure of ZSM5 (channel diameter 0.55–0.59 nm).

Total acidity was measured by Na^+-ion exchange (exhaustive exchange at room temperature with 1M $NaNO_3$ solution, titration of liberated acid). External surface acidity was measured as the monolayer methylene blue adsorption (exchange) capacity [11] (equilibration with aqueous methylene blue solution at room temperature for 48 h with shaking, aqueous supernatent concentrations estimated spectrophotometrically; monolayer adsorption estimated from Langmuir isotherm plot). The accuracy of the monolayer methylene blue adsorption method was checked (for untreated H-ZSM5) by titration of the liberated acid, giving agreement to within 1%.

Using the total (N_T), external surface (N_S), and bulk (N_B) acidities (mmol/100 g; $N_T = N_S + N_B$; N_T, and N_S measured), it is convenient to define degrees of deacidification D_S and D_B for the external surface and bulk respectively by $D_S = (N_S^0 - N_S)/N_S^0$ and $D_B = (N_B^0 - N_B)/N_B^0$, where N_S^0 and N_B^0 are for the untreated H-ZSM5 ($N_S^0 = 1.75$; $N_B^0 = 38.55$ mmol/100 g). It is convenient also to define an index of specificity for external surface deacidification, S_{DA}, by $S_{DA} = D_S/(D_S + D_B)$.

The ZSM5 was prepared by standard methods [12], had $SiO_2/Al_2O_3 = 46/1$, and consisted of hexagonally terminated lath-like crystals (average size ca. 2 μm) associated into aggregates (scanning electron microscopy). The specific pore volume was 0.15 $cm^3\ g^{-1}$ from nitrogen sorption data at 77 K (Carlo-Erba Sorptomatic 1800) using a t-plot method [13], and the external surface area was ca. 3 m^2g^{-1} (from nitrogen BET after blocking the pores with organic component).

The most thoroughly studied methods for zeolite dealumination are treatment with, (i) $SiCl_4$ [14,15], (ii) steam with HCl leaching [16,17], (iii) $(NH_4)_2SiF_5$ (aqueous) [18,19], and (iv) EDTA (aqueous) [20]. Of these, (iii) and (iv) can give

extension defect formation and poor crystallinity [8,21], and thus were not examined further for external surface dealumination of ZSM5. This report refers mainly to selective external surface deacidification by method (i) ($SiCl_4$), with some supplementary information by method (ii) (steam with HCl leaching). Namba et al. [22] have previously reported on a degree of surface selective dealumination of Na-ZSM5 with $SiCl_4$, but with the analysis confined to XPS methods.

Exploratory studies with the steaming-HCl leaching method, using both H-ZSM5 and Na-ZSM5 (steaming at 1073 K up to 96 h, followed by leaching in 0.5M HCl and 373 K for 12 h, H_2O washing until Cl-free), gave substantial bulk deacidification (e.g. 51% for Na-ZSM5 steamed for 96 h, 90% for H-ZSM5 steamed for 70 h), but the acid site content of the external surface was not necessarily reduced, and could even be higher than that of the starting material. The accumulation of some aluminium in a zeolite surface consequent upon the steaming-HCl leaching treatment has been reported previously [8,9] although not necessarily as framework aluminium. The lower reactivity of Na-ZSM5 compared to H-ZSM5 to steaming agrees with previous work [23]. We conclude that this treatment is not suitable for selective external surface deacidification (dealumination).

Treatment with $SiCl_4$ was carried out in a vertical fused silica reactor with the ZSM5 (1 g) carried as a thin layer on a frit. Dry argon (80 cm^3 min^{-1}, zeolite dehydration) was used for preliminary sample dehydration (2 h at treatment temperature) and to carry $SiCl_4$ vapour (1.04 kPa–53.3 kPa) for treatment. After $SiCl_4$ treatment the sample was quenched to room temperature in argon and swept for 30 min at room temperature, followed by treatment with 0.5M HCl at 373 K for 12 h, H_2O washing until Cl-free, and air drying at 373 K. The XRD patterns from the treated and untreated ZSM5 samples were essentially unchanged (Siemens D-500 diffractometer) with the average lattice spacings varying by less than 0.05%. Scanning electron micrographs also showed that the $SiCl_4$ treatments were without effect on the zeolite crystal morphology and aggregate morphology.

$SiCl_4$ has an estimated kinetic diameter at 600–700 K of ca. 0.57 nm (from molecular diameter data from gas viscosity, ref. [24]), and is thus expected to be able to enter ZSM5 channels, although possibly less readily with Na-ZSM5 than with H-ZSM5 [22]. A preliminary comparison (table 1) was made between $SiCl_4$ treatment of Na-ZSM5 and H-ZSM5, the former having been previously postulated in preferable [22]. The use of Na-ZSM5 at short treatment times resulted in lower D_S and D_B values than H-ZSM5, although S_{DA} was much the same (cf. expts. 1 and 9). At longer treatment times, D_S, D_B and S_{DA} were comparable for both forms of zeolite (cf. expts. 2 and 10). We conclude that, at least with our ZSM5 samples, there is little to be gained by using Na-ZSM5 rather than H-ZSM5 for selective external surface deacidification, and the fact that a good S_{DA} may be obtained more readily at a relatively high D_S with H-ZSM5 makes this the preferred starting material.

Table 1
Deacidification of ZSM5 with $SiCl_4$

Expt. No.	$SiCl_4$ treatment conditions [a]		parameters for treated zeolite [b]		
			D_S	D_B	S_{DA}/%
1	H-ZSM5	873 K; p_{SiCl_4} = 10.7 kPa; 1 min	0.63	0.08_6	88
2		10 min	0.65	0.37	64
3		30 min	0.69	0.41	63
4	H-ZSM5	p_{SiCl_4} = 10.7 kPa; 1 min; 973 K	0.83	0.27	75
5		1023 K	0.83	0.38	69
6	HZSM5	p_{SiCl_4} = 1.04 kPa; 1 min; 873 K	0.61	0.01_1	98
7		973 K	0.62	0.19	77
8	HZSM5	873 K; 1 min; p_{SiCl_4} = 53.3 kPa	0.67	0.20	77
9	Na-ZSM5	873 K, p_{SiCl_4} = 10.7 kPa; 1 min	0.39	0.03_4	92
10		10 min	0.53	0.37	59

[a] Treatment temperature; $SiCl_4$ pressure, treatment time.
[b] Errors on measurement of N_T and N_S estimated at ±1% and ±5% respectively.

For H-ZSM5 (table 1) S_{DA} is caused to increase by: (i) decreased treatment time (expts. 1–3); (ii) decreased treatment temperature (expts. 1, 4, 5 and 6, 7); decreased p_{SiCl_4} (expts. 1, 6, 8, and 4, 7). The best S_{DA} is thus found at the lowest usable values of treatment temperature, treatment time, and p_{SiCl_4}, and in the range of our experiments this was obtained in expt. 6 ($S_{DA} = 98\%$, $D_S = 61\%$, $D_B = 1.1\%$).

XPS measurements were made on a Vacuum Generators ESCALAB 5 (Al Kα excitation) at a working pressure of $\sim 10^{-8}$ Pa. Intensity ratios of Si/Al were obtained from the integral areas of the Si2p and Al2p peaks after a linear background subtraction, from which the atom number ratios N_{Si}/N_{Al} were obtained using cross-sections (σ) from the literature [25] ($\sigma_{Al2p}/\sigma_{Si2p} = 0.663$). Three types of specimen were examined: (i) Free powder; either adhered to scotch tape or settled from cyclohexane suspension onto a specimen holder; both methods gave similar results within the reproducibility limits of measurement: (ii) Pressed powder; ZSM5 powder was hand-pressed in a specimen holder with a flat spatula (applied pressure ca. 20 kPa): (iii) Pelletized powder; ZSM5 powder was pelletized in a pelleting die (applied pressure ca. 9000 kPa). Method (i) subjected the powder to negligible mechanical stress.

Table 2 presents XPS-derived N_{Si}/N_{Al} values (nominally for the external surface) together with corresponding values computed from acidity measurements (cf. Table 1) assuming each acidic site in the external surface is associated with one Al in the zeolite framework.

High mechanical stress (e.g. pelletization) resulted in reduced N_{Si}/N_{Al}, attributable to particle or aggregate fracture exposing fresh surface having a composition more characteristic of the bulk. This is increasingly serious with increasing

severity of $SiCl_4$ treatment. A relatively low mechanical stress (pressed powder) resulted in smaller depression of N_{Si}/N_{Al}, negligible for gentle $SiCl_4$ treatment (expts. 1, 2, table 2), significant for severe $SiCl_4$ treatment (expts. 3, 4, table 2).

There can be a significant difference in N_{Si}/N_{Al} values obtained by XPS for free powder and from acidity data (particularly expts. 1, 2, table 2). To examine if this discrepancy arises from the use of an inadequate XPS analytical model which does not take into account photoelectron emission from subsurface layers, we have computed corrected values for N_{Si}/N_{Al} from an attenuated emission model with contributions from subsurface layers [26,27], in which a 2.0 nm escape depth for Si2p and Al2p photoelectrons (Al K_α X-ray excitation) was adopted [28]. In the absence of detailed knowledge about the composition of the subsurface layers, two limiting models were assumed; (i) subsurface (bulk) dealumination propagated into the zeolite at a constant degree of dealumination equal to D_S and to a depth sufficient to generate the required value of D_B when averaged over the entire bulk, (ii) subsurface (bulk) dealumination was spread uniformly through the bulk at the required value of D_B. These corrected N_{Si}/N_{Al} values for the surface layer are also given in table 2.

Table 2
N_{Si}/N_{Al} by XPS and by acidity measurement for surface of H-ZSM5 treated with $SiCl_4$

Expt. No.	$SiCl_4$ treatment conditions [a]	N_{Si}/N_{Al}				
		XPS [b]			from acidity measurements [c,d]	corrected XPS [e,f,g]
		free powder	pressed powder	pelletized powder		
1	873 K; $p_{SiCl_4}=1.04$ kPa; 1 min	38	42	26	60	46–49
2	973 K; $p_{SiCl_4}=1.04$ kPa; 1 min	52	48	34	62	39–57
3	973 K; $p_{SiCl_4}=1.04$ kPa; 10 min	74	40	33	> 400 [i]	–
4	973 K; $p_{SiCl_4}=10.7$ kPa; 90 min	139 [h]	–	29	–	–

[a] Treatment temperature, $SiCl_4$ pressure, treatment time.
[b] Except where stated otherwise, the average error on each figure is estimated at ±20%, with approximately equal contributions from the experimental intensity reproducibility and from the cross-sections (σ).
[c] Assuming each acidic site is associated with a framework Al, and using $N_{Si}/N_{Al}=[(N^0_{Si}/N^0_{Al})+D_S]/[1-D_S]$, derivable from conservation of total number of Si + Al surface atoms, where D_S is the degree of surface deacidification, and N^0_{Si}/N^0_{Al} is for the untreated zeolite and set at 23.0 from ZSM5 stoichiometry.
[d] Total likely error on each figure estimated at ±5% (from reproducibility of methylene blue adsorption measurements).
[e] Correction applied for exponentially depth-attenuated emission from subsurface layers (see text).
[f] First value in each pair assumes bulk dealumination is concentrated in surface region, second value assumes uniform spread of bulk dealumination (see text).
[g] Total likely error on each figure estimated at ±20%.
[h] Average error estimated at ±35% with main contribution from experimental intensity reproducibility, arising probably from sample non-uniformity.
[i] Lower limit from accuracy of measurement.

The estimated N_{Si}/N_{Al} values (table 2) from corrected XPS and from surface acidity for expts. 1, 2 barely overlap the extremes of their likely error ranges and real differences are likely. For the sample subjected to more severe $SiCl_4$ treatment (expt. 3), the corresponding difference is clearly very large. It is highly unlikely that these differences arise from an inability of methylene blue to pack sufficiently closely on the surface for all acidic sites to be counted (although this factor could be expected to operate if the acidic site density is high enough). Thus, with the present untreated H-ZSM5, the methylene blue adsorption (1.75 mmol/100 g) corresponds to ca. 0.3 nm^2 per methylene blue, while for the treated H-ZSM5 (expts. 1–3, table 2) the corresponding figures are in the range 0.75–5.0 nm^2 per methylene blue. These data should be compared with the minimum packing area per methylene blue of ca. 0.24 nm^2 per methylene blue [10] (for methylene blue molecules with the plane of the ring normal to the surface and the long axis vertical, thus bringing the formally positively charged nitrogen close to the surface).

On this basis, we attribute these differences in N_{Si}/N_{Al} by the two techniques to the presence of extra-framework Al (cf. [9] which contributes to the Al signal in XPS but which is not associated with acidic sites. On balance we suggest that methylene blue adsorption (exchange) is preferable to XPS for monitoring deacidification of the external surface of ZSM5. However, it should be noted that the use of methylene blue in this way is entirely dependent on the methylene blue molecule not being to enter the pores of the zeolite, and in any case the surface acid site density must be low enough to ensure that the methylene blue packing restrictions do not result in an underestimation of the number of acidic sites; for these reasons the method would be inapplicable to Y- or X-zeolite, for instance.

We have shown that $SiCl_4$ treatment of H-ZSM5 can yield a reasonably high S_{DA}. In practice, the choice of deacidification conditions may depend on what is required. If it is necessary to minimize deacidification of the ZSM5 interior, this can be achieved by sacrificing some surface deacidification (e.g. expt. 6, table 1). On the other hand, if it is necessary to obtain the maximum degree of surface deacidification, this requires accepting an increase in D_B and a decrease in S_{DA} (e.g. expts. 4, 5, table 1).

With respect to optimum treatment temperature, our conclusion for H-ZSM5 (minimum usable temperature) is opposite to that found by Namba et al. [22] for Na-ZSM5. It is not clear if this originates in the different forms of ZSM5 used in the two cases, or from some difference in the ZSM5 morphology, and this will be the subject of further work.

The observation that the effective N_{Si}/N_{Al} at the external surface of $SiCl_4$-treated ZSM5 can be drastically reduced by mechanical stress is of practical significance since it implies that if a ZSM5 catalyst is to be pelletized, this should be done before any $SiCl_4$ treatment is attempted for surface deacidification.

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