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On the External and Intracrystalline Surface Catalytic Activity of Pentasil Zeolites

Molecular shape-selective catalysis arises from the presence of active sites within the intracrystalline free volume of zeolites. Because of the constraints which may be imposed on the reagents and/or the products, at any time along their reaction pathways, certain conversions can be favored and deviations from equilibrium product distribution are sometime observed. Several recent and comprehensive reviews describe and discuss these effects (*1–4*).

A formal distinction should be made between the above intracrystalline catalytic sites and those present on the outer surface of the crystallites which will not cause molecular shape-selective effects. For pentasil materials, such as ZSM-5 and ZSM-11, the percentage of external surface tetrahedral sites, T_S (%), either Si or Al, can be estimated to be given approximately by

$$T_S(\%) = 181 \cdot (1/D)$$

where D is the mean crystallite size (in nm), i.e., a nonnegligible amount for catalyst particles with size of 100 nm or less. It is also known that aluminum distribution gradients can be found in such materials, depending on either their synthesis conditions (*5, 6*) or their subsequent modifications (*7*). Therefore, their outer surface composition often differs from the bulk composition. It has been shown that XPS was a suitable technique to estimate the external surface aluminum content (*7*) whereas prompt nuclear and atomic reactions were ideal tools to obtain bulk compositions (*8*).

n-Hexane (*n*-C6) is a molecule which is known to diffuse freely within the pentasil frameworks, thereby having access to all the active sites (*9*). In contrast, 1,3,5-trimethylbenzene (TMB) has a van der Waals diameter of 0.86 nm which should render it too bulky for probing the intracrystalline catalytic sites. The present note shows that the conversions of *n*-C6 and TMB can be used to probe, respectively, the overall and the outer surface activities, by drawing the attention to the direct proportionality which exists between aluminum content, surface or bulk, and catalytic activity.

Table 1 lists the samples used in the present study and the respective acidification or other pretreatments which apply. No significant amount of Na was present in their protonated forms. All the ZSM-5 catalysts had a mean crystal size of 1500–2000 nm whereas the ZSM-11 particles (ca. 1000 nm) were aggregates of smaller crystallites (100 nm or less) as reported elsewhere (*10*). Table 2 summarizes the reaction conditions. The catalysts were first calcined *in situ* at 773 K for 2 h in dry air before adjusting the microreactor reaction temperature. Dry air was replaced by dry nitrogen for sample C–ZSM-5(A) (used catalyst). The reactor was purged with dry nitrogen before introduction of the reagents. On-line gas chromatographic analysis was used to separate and identify the products. Other experimental details are described elsewhere (*11, 18*).

Table 3 lists the measured specific catalytic activities (SCA), i.e., the number of moles of reagent (*n*-C6 or TMB) converted per hour and per mole of aluminum, calculated assuming first-order kinetics. The percentage of external surface sites, T_S(%), evaluated from the aforementioned crystallite sizes was used in the evaluation of the

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TABLE 1

Catalyst Descriptions

Sample	[Al/(Al + Si)] (Bulk)[a]	[Al/(Al + Si)] (Surface)[b]	Remarks
ZSM-5(A)	3.72	2.49	H-Form from ion-exchange with HCl 0.5 *N*
ZSM-5(B1)	6.45	5.08	H-Form from NH_4NO_3 1 *N* ion-exchange, calcined at 773 K in air
ZSM-5(B2)	6.53	4.59	H-Form from pretreatment with NH_3 gas followed by NH_4NO_3 1 *N* ion-exchange, calcined at 773 K in air
B–ZSM-5(A)	3.50	2.39	H-Form from HCl 0.5 *N* ion-exchange, impregnated with aqueous H_3BO_3 (0.3 wt% B (*8*))
P–ZSM-5(C)	7.35	5.26	H-Form from ammonium exchange and calcination treated with $P(OCH_3)_3$ as described in Ref. (*11*) (2.06 wt% P(*8*))
C–ZSM-5(A)	3.72	4.76	ZSM-5(A) after 16 h on stream in CH_3OH conversion (643 K, WHSV = 2 h^{-1}, ca. 3 wt% C)
ZSM-11	2.65	4.00	H-Form from NH_4NO_3 1 *N* ion-exchange, calcined at 773 K

[a] Mean *T*-site Al atomic fraction (×100) measured by prompt nuclear analysis (*8*).
[b] Surface *T*-site Al atomic fraction (×100) measured by XPS (*7*).

specific activities for the conversion of TMB. A range of SCA is given for ZSM-11 for which the crystallite size cannot be specified as particles are aggregates.

In the above experimental conditions, SCAs for the nonmodified (ZSM-5(A,B1, B2)) and the boric acid impregnated (B–ZSM-5(A)) ZSM-5 catalysts are found to be nearly constant for both the *n*-C6 and TMB conversions, relative to the mean bulk and surface aluminum concentrations, respectively. Whereas the correlation of the specific activities is good (within 10%) for the cracking of *n*-C6, a somewhat larger scattering (≈25%) is observed for the conversion of TMB. It is attributed to the fact that

TABLE 2

Reaction Conditions

Variable	*n*-C6	TMB
Temperature (K)	588	723
Pressure (atm)	1.0	1.0
WHSV (h^{-1})	0.185	0.100
Time-on-stream (h)	1.0	0.33

TABLE 3

Specific Catalytic Activities[a]

Sample	k_{C6}[b]	k_{TMB}[c]
ZSM-5(A)	3.39	718
ZSM-5(B1)	2.67	485
ZSM-5(B2)	3.07	475
B–ZSM-5(A)	3.00	437
P–ZSM-5(C)	1.12	68
C–ZSM-5(A)	0.89	68
ZSM-11	0.30	65–646

[a] Assuming first-order kinetics.

[b] Moles *n*-hexane/(mole bulk Al × h) at a WHSV of 0.185 h^{-1}. Product distributions were characteristic of those observed in the alpha-test (*12, 20*) and were essentially identical for all catalysts.

[c] Moles 1,3,5-trimethylbenzene/(mole surface Al × h) at a WHSV of 0.1 h^{-1}. For all catalysts, the isomerization of TMB was the prevailing reaction (>80%) with some contribution of transalkylation to the total conversion. The TMB isomers distribution was close to equilibrium.

XPS measures a surface Al concentration averaged over the outer layer (ca. 2–4 nm) of the crystallites rather than the Al concentration on the very external surface. In addition, the TMB isomers distribution was close to equilibrium for all catalysts. These results indicate that catalytic activity is directly proportional to the number of accessible aluminum acidic sites, in agreement with earlier data (*12*). It also demonstrates that the conversion of TMB is a suitable reaction to probe the external catalytic activity of pentasil (medium pore) catalysts.

ZSM-5(A) acidified by HCl has for both reactions a SCA somewhat higher than observed for the catalysts acidified through ammonium-exchange. Its surface aluminum content is also severely depleted (67% only of the mean bulk content). Both observations concur to support earlier views, namely that acidification by HCl can cause partial dealumination and impart a higher acid activity to the zeolite (*13*). Impregnation with boric acid (B-ZSM-5(A)) barely affects the catalyst activity at low boron content (0.3 wt%), only reducing slightly the SCA for the conversion of TMB. Pretreating the zeolite by gaseous ammonia prior to NH_4NO_3 ion-exchange does not appear to modify extensively its intrinsic catalytic activity contrarily to earlier thoughts (*18*).

In contrast, the catalyst modified by phosphorus (P–ZSM-5(C)) shows a decrease in SCA by a factor of about 3 in the conversion of *n*-C6 and of about 7 in that of TMB. It indicates that phosphorus which may be present in the zeolite channels (*14*) deactivates to an even larger extent the external surface of the catalyst. Comparing the SCAs of P–ZSM-5(C) to those of the used coked catalyst C–ZSM-5(A) confirms this point. Indeed, similar specific catalytic activities are observed and it is known that the deposition of carbonaceous residues on ZSM-5 is essentially restricted to the external surface and pore mouths of the crystallites (*15, 16*). The present catalytic data hence support the proposal that phosphorus poisons primarily acidic sites at the crystallite pore mouths, based on microcalorimetry (*13, 17*) and XPS (*17*) results.

Our ZSM-11 catalyst shows when compared to nonmodified ZSM-5 materials, a lower SCA for the *n*-C6 conversion. It is attributed tentatively to the fact that ZSM-11 appears to have a lower acid strength than ZSM-5, as discussed by several authors (*13, 18, 19*).

To conclude, we have shown that the conversion of 1,3,5-trimethylbenzene is a suitable reaction to probe the outer surface activity of pentasil, and probably other medium pore size, zeolites. Their acid catalytic activity, in appropriate conditions, is directly proportional to the number of accessible acidic aluminum sites. The comparison of specific catalytic activities for the *n*-hexane and 1,3,5-trimethylbenzene conversions enables the evaluation of the relative roles played by the intracrystalline and external surface sites.

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