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Modification of HZSM-5 by CVD of Various Silicon Compounds and Generation of Para-Selectivity

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The modification of HZSM-5 zeolite was carried out by a method of chemical vapor deposition of various silicon alkoxides. We thus obtained the HZSM-5 zeolites with the different pore-opening sizes and with the varied extents of inactivation of acid sites on the external surface. Among the various silicon compounds used in this study, the $SiOCH_3(C_3H_7)_3$ was effective in selective inactivation of acid sites on the external surface of HZSM-5 zeolite without affecting its intracrystalline void space. From the characterization of the modified HZSM-5 zeolites, and its relationship with the shape selectivity, we concluded that the enhancement of para-selectivity in the methylation of toluene was ascribable more closely to controlling the pore-opening size than to the inactivation of acid sites on the external surface.

INTRODUCTION

The para-alkylbenzenes are important starting materials for many commercial processes. These compounds can be produced by alkylations (1–10), disproportionations (11–13), isomerization (12), or transalkylation (14) of monoalkylbenzenes using zeolite catalysts. The function of the catalyst utilized in these reactions is a shape selectivity of the zeolites. The para-selective formation is obviously the most important reaction on zeolites. The modifications of HZSM-5 zeolite for producing para-alkylbenzene selectively have been reported, for example, loading with oxide of P, Mg, or B (1–3, 5, 7, 11, 12), coking with methanol (12), silanation with silicon alkoxide (6, 8, 14), using HZSM-5 zeolites of different crystal sizes (4), and metallosilicate zeolites with MFI structure (9). Furthermore, the reasons for the improvement of para-selectivities of the modified HZSM-5 zeolites have been reported. Kaeding *et al.* proposed that the high para-selectivity of modified HZSM-5 zeolites for the alkylation or disproportionation was due to product shape selectivity, that is, the intracrystalline diffusivity of the *p*-isomer was much higher than that of the other two isomers (2, 3, 11). Recently, Mirth *et al.* reported the evidence for diffusion control of para-selectivity in the methylation of toluene by IR measurements (10). Paparatto *et al.* reported that the *p*-isomer was formed selectively inside the HZSM-5 channels in the ethylation of toluene, while the isomerization of the *p*-isomer proceeded just on the external surfaces and that the improvement in para-selectivity by the modification was due to the inactivation of the acid sites on the external surfaces (4). On the other hand, Yashima *et al.* proposed that the primary product in the alkylation was only the *p*-isomer due to restricted transition-state shape selectivity and that the improvement in para-selectivity by the modification of HZSM-5 was due to the suppression of the isomerization of primarily produced *p*-isomer (1, 5, 9). This transition-state shape selectivity was first described by Haag *et al.* in the cracking of hydrocarbons using HZSM-5 zeolites of different sizes and activities (15).

In general, the modifications of HZSM-5 give rise to control of the pore-opening size and simultaneously inactivation of acid sites on the external surface (1–3, 5, 7, 11, 12). The silanation with $Si(OCH_3)_4$ [Tetra] also brings out the reduction of pore-opening size and inactivation of the external surface (6, 8, 14, 16–20). In order to clarify the reason the modifies HZSM-5 zeolites exhibit high para-selectivity, we therefore need to know not only the reduction in pore-opening size but also the inactivation of acid sites on the external surface.

In this study, we tried to modify HZSM-5 by the silanation with various silicon alkoxides in order to gain HZSM-5 zeolites with the different pore-opening size and with the varied extent of inactivation of acid sites on the external surface. Furthermore, we aimed to clarify the reason the modified HZSM-5 zeolites with silica exhibit higher para-selectivity for the methylation of toluene.

EXPERIMENTAL

Catalysts

HZSM-5 ($SiO_2/Al_2O_3 = 76$) was obtained from Mobile Catalysts Co. Ltd. of Japan. The crystal size of the HZSM-5 was a uniform 500 nm in diameter. Its external surface area, measured by the benzene-filled pore method (21), was 10.8 $m^2\,g^{-1}$. The silane compounds used here are $SiOCH_3(CH_3)_3$ [Mono], $Si(OCH_3)_2(CH_3)_2$ [Di], $Si(OCH_3)_3(CH_3)$ [Tri], Tetra, or $SiOCH_3(C_3H_7)_3$ [MTPS]. Abbreviations in the

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brackets will be used in the following description. The apparatus consisted of a vacuum system equipped with a conventional quartz spring balance. The sample was set in a basket hung on the balance and evacuated at 673 K until the decrease of weight was not observed. Then, the alkoxide was deposited at 593 K (Mono, Di, Tri, or Tetra) or 343 K (MTPS). After the deposition, the sample was calcined with 200 Torr (1 Torr = 133.3 N m^{-2}) of oxygen at 673 K to remove carbonaceous residues formed on the sample during the deposition.

Determination of Acid Sites on the External Surfaces

The cracking of 1,3,5-triisopropylbenzene (1,3,5-TIPB) was performed to confirm the extent of inactivation of the external acid sites of zeolites (20, 22). This reaction was performed by a usual pulse method. Helium was used as a carrier gas. The catalyst was pretreated at 773 K for 1 h. The reaction temperature was 573 K, the weight of sample was 5 mg, the flow rate of helium was 27 cm^3 min^{-1}, and the conversion was less than 6% in order to reveal the catalytic activity in differential conditions.

Determination of Pore-Opening Size

Gravimetric measurements of *o*- or *p*-xylene adsorption were performed on a highly sensitive thermal microbalance. After samples (0.1 g) were evacuated at 673 K until the decrease of weight was not observed, the measurements were performed at 393 K and at the *o*- or *p*-xylene pressure of 4.0 Torr.

Determination of Acidic Property

The temperature-programmed desorption (TPD) measurement was performed by a method described in previous literature (23). Samples (0.1 g) were evacuated in a quartz tube at 773 K for 1 h, and then exposed to 100 Torr of ammonia for 30 min at 373 K; it was then evacuated at 373 K for 30 min. The NH_3-TPD measurement was carried out from 373 to 973 K at a heating rate of 10 K min^{-1}. Helium was used as a carrier gas with a flow rate of 60 cm^3 min^{-1}. Ammonia desorbed was detected with a thermal-conductivity detector.

IR Measurement

The IR measurement was carried out with an FT-IR JASCO-5300 spectrometer with a quartz cell. The samples were pressed into self-supporting wafers. The samples were evacuated at 773 K for 1 h. The IR spectra were measured at room temperature.

Alkylation of Toluene with Methanol

The alkylation of toluene with methanol at 673 K was carried out with a continuous flow method under atmospheric pressure. Before the reaction, the sample was activated at 773 K for 1 h with helium as a carrier gas. The reactant (toluene/methanol = 1/1 mol/mol) was fed with a microfeeder.

RESULTS

Cracking of 1,3,5-Triisopropylbenzene

The extent of inactivation of acid sites on the external surfaces of the modified HZSM-5 zeolites with silica was measured by a test reaction of the cracking of 1,3,5-TIPB. The 1,3,5-TIPB is a suitable probe molecule for determining the activities of the external surfaces of zeolites (22), because the molecular dimension of 1,3,5-TIPB was too large to enter into the pores of HZSM-5 (20, 22) or H–mordenite zeolite (20).

Figure 1 shows the effect of the amount of silica deposited on HZSM-5 zeolite on the conversions of the cracking of 1,3,5-TIPB. All conversions decreased with increasing silica content deposited, indicating that the acid sites on the external surfaces were deactivated by the modification of silica. However, the extent of inactivation of the external acid sites on the modified HZSM-5 zeolites depends on the type of silane compounds used. In the case of the deposition of Tetra, about 5.7 wt% of silica (Tetra-5.7; number in the figure indicates the amount of silica deposited in weight percent) was required for inhibiting the cracking of 1,3,5-TIPB. The conversions of 1,3,5-TIPB on Tri–HZSM-5 zeolites also decreased with increasing amount of silica deposited, and completely inactivated at 6.9 wt% of the deposited silica (Tri-6.9). In the case of the deposition of Di, the amount of silica required for complete inactivation of external acid sites of HZSM-5 was more than twice that of Tetra. On the other hand, 3.0 wt% of Mono (Mono-3.0) was required for complete inactivation of the acid sites on the external surfaces. Furthermore, in the case of MTPS, the conversion of the cracking of 1,3,5-TIPB reached an almost zero value at silica deposition of 1.0 wt%. These facts indicate that

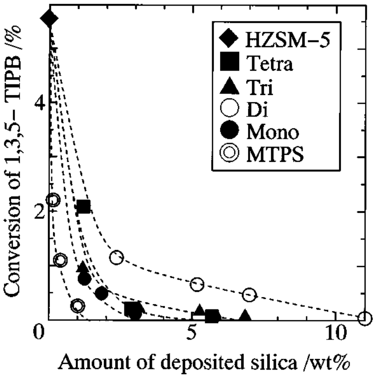

FIG. 1. Relationship between the amount of silica deposited on the HZSM-5 zeolite and the conversion of 1,3,5-TIPB.

TABLE 1

Effect of the Modification of Silicon Alkoxide on Adsorption Properties and Para-Selectivity

Catalyst[a]	Ao[b] (μmol g^{-1})	Ap[c] (μmol g^{-1})	Ao/Ap[d]	Para-selectivity (%)[e]
HZSM-5	251	250	1.00	58.1
Mono-1.2	212	249	0.85	65.1
Mono-3.0	129	250	0.51	72.1
Mono-5.8	83	218	0.38	77.7
Di-2.5	217	249	0.87	67.8
Di-7.0	85	213	0.40	71.3
Di-11.0	36	124	0.29	77.5
Tri-3.1	202	250	0.81	72.6
Tri-6.9	112	213	0.53	78.7
Tetra-2.8	155	253	0.61	74.0
Tetra-5.7	107	250	0.43	86.0
Tetra-11.3	23	246	0.09	99.6
MTPS-0.1	251	250	1.00	62.1
MTPS-0.4	254	252	1.01	62.9
MTPS-1.0	209	249	0.84	70.0

[a] Number indicates the amount of silica deposited in weight percent.
[b] Amount of *o*-xylene adsorbed at 5000 sec.
[c] Equilibrium amount of *p*-xylene.
[d] Relative *o*-xylene adsorption rate.
[e] Reaction temperature; 673 K.

among various silane compounds used in this study, MTPS is effective in inactivation of acid sites on the external surface of HZSM-5 zeolite. Thus, we were able to prepare the HZSM-5 zeolites with varied amount of acid sites on the external surfaces.

Adsorption Measurements of p- and o-xylenes

The adsorption measurement of *o*-xylene was then carried out on the modified HZSM-5 zeolites with silica. The findings are summarized in Table 1. Figure 2 shows the typical *o*-xylene uptake curves for the modified HZSM-5 zeolites with silica using Tetra. When the Tetra was deposited on HZSM-5, the adsorbed amount of *o*-xylene remarkably decreased with increasing silica content, as shown in Fig. 2. Similar phenomena were observed on every series of the HZSM-5 deposited with silane compounds. However, it took too long to obtain the equilibrium amount of *o*-xylene on the modified HZSM-5 zeolites with large amounts of silica, for example Tetra-11.3 (Fig. 2), Di-11.0, and Mono-5.8 zeolites. Thus, the adsorption measurement of *p*-xylene with a smaller molecular size than *o*-xylene was carried out.

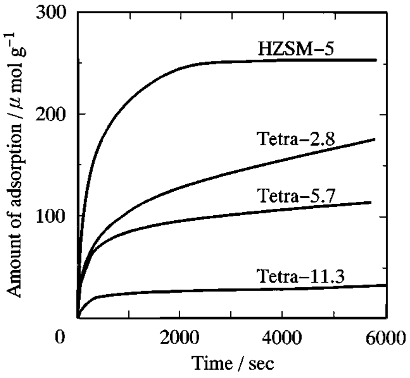

FIG. 2. Typical *o*-xylene uptake curves on the HZSM-5 zeolites modified with Tetra.

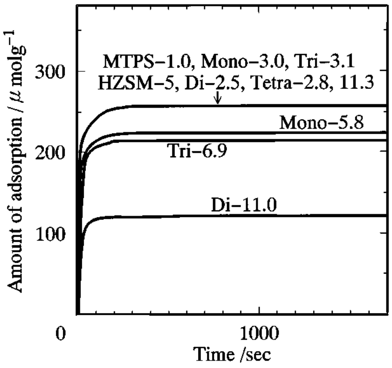

FIG. 3. Typical *p*-xylene uptake curves on the HZSM-5 zeolites modified with silica.

The equilibrium amount of *p*-xylene adsorbed on the zeolites used in this study is also summarized in Table 1. Figure 3 shows the typical *p*-xylene uptake curves for the modified HZSM-5 with silica. The adsorption of *p*-xylene attained its equilibrium within 5 min (Fig. 3). The equilibrium amount of *p*-xylene may correspond to the pore volume. The pore volume of the modified HZSM-5 zeolite with a large amount of Mono, Di, or Tri was remarkably reduced. On the other hand, in the cases of the modified HZSM-5 zeolites with Tetra or MTPS, the pore volumes were the same as that of HZSM-5. Especially, the adsorbed amount of *p*-xylene for Tetra-11.3 zeolite was the same as that of HZSM-5, in spite of the modification of large amount of silica.

From the adsorption experiments of *o*- and *p*-xylenes, we determined the "relative *o*-xylene adsorption rate" as a parameter of the narrowing of pore size. Olson *et al.* have reported that "$t_{0.3}$; a parameter of the critical mass transfer property" was obtained from the measurement of the time to reach 30% of the equilibrium amount of *o*-xylene (12). In this study, we used the relative *o*-xylene adsorption rate (Ao/Ap) which was defined as

$$Ao/Ap = (\text{Amount of } o\text{-xylene adsorbed at 5000 sec})/(\text{Equilibrium amount of } p\text{-xylene}).$$

The values of Ao/Ap are summarized in Table 1. The Ao/Ap became smaller as the silica amount increased. On the other hand, the Ao/Ap for the modified HZSM-5 zeolites with MTPS were much higher than those for HZSM-5 zeolites modified with other silane compounds.

TABLE 2

Effect of the Modification of Silicon Alkoxide on Acidic Property

Catalyst	Heat of adsorption of ammonia (kJ mol^{-1})	Amount of desorbed ammonia (mmol g^{-1})
HZSM-5	133	0.448
Tetra-11.3	133	0.398[a]
Di-11.0	133	0.169[b]

[a] 0.449 mmol (g-zeolite)$^{-1}$: Amount of acid sites divided by the weight of only zeolite for the Tetra-11.3.

[b] 0.190 mmol (g-zeolite)$^{-1}$: Amount of acid sites divided by the weight of only zeolite for the Di-11.0.

Determination of Acidic Property

In order to clarify the change of the acidic property by deposition of silica, the measurements of NH_3–TPD for the HZSM-5, Tetra-11.3, and Di-11.0 zeolites were carried out. The NH_3–TPD spectra of these zeolites consist of two desorption peaks (l and h peaks at low and high temperature, respectively). The amount of acid sites of zeolite was related to the amount of ammonia desorbed from the h peak, since the l peak had been assigned to very weakly and/or physically adsorbed ammonia in the literature (23). We determined the heat of adsorption of ammonia as a parameter of the acidic strength from the h peak. The findings are summarized in Table 2. Both the acidic strength and the amount of acid sites divided by the weight of zeolite for the Tetra-11.3 were the same as those of HZSM-5 zeolite. On the other hand, the amount of acid sites of Di-11.0 zeolite were reduced by the modification of silica, but the acidic strength of this zeolite was not changed.

IR Measurement of the Modified HZSM-5 with Various Silane Compounds

To characterize the variation of the acidic OH group of HZSM-5 zeolite by the modification of various silane compounds, we carried out the IR measurements of HZSM-5 and the modified HZSM-5 zeolites with a large amount of silica (Fig. 4). The bands at 3743 and 3611 cm^{-1} are due to silanol and acidic OH groups of HZSM-5 zeolite, respectively. The intensity of the IR band of the silanol group on HZSM-5 zeolite was significantly changed by the modification of every silane compound. The 3611 cm^{-1} band of the acidic OH group after the modification of Mono, Di, or Tri almost disappeared. On the other hand, the band at 3611 cm^{-1} on the modified HZSM-5 zeolite with Tetra or MTPS was little affected.

Para-Selectivities for Methylation of Toluene

In the alkylation of toluene with methanol on the modified HZSM-5 zeolites with silica used in this study, the main aromatic products were three xylene isomers. Para-selectivity was defined as a fraction of *p*-isomer in the xylene isomers produced. To compare para-selectivities of the modified HZSM-5 zeolites with various silane compounds, para-selectivities at an almost constant conversion (20%) of toluene were measured and summarized in Table 1. The constant conversion was achieved by adjusting the contact time. Para-selectivities of the modified HZSM-5 zeolites with silica were higher than that of HZSM-5 zeolite. In particular, Tetra-11.3 zeolite exhibited very high para-selectivity of 99.6%. On the other hand, Di-11.0 zeolite had low para-selectivity compared with Tetra-11.3, in spite of the modification of almost the same amount of silica.

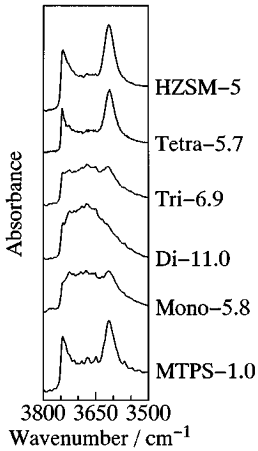

FIG. 4. IR spectra of silanol and acidic OH region on the HZSM-5 zeolites modified with large amounts of various silane compounds.

DISCUSSION

Modification of HZSM-5 Zeolite with Silane Compounds

The chemical vapor deposition of Tetra has attracted a lot of attention of researchers (6, 8, 14, 16–20). This technique gives rise to the reduction of the nonselective external surface and the narrowing of the pore-opening size. Thus, the shape selectivity on the modified HZSM-5 zeolite with Tetra would be enhanced either by the narrowing of the pore-opening size or by the inactivation of the external surface. The deposition mechanism and the structural analysis of deposited material were paid much attention by Niwa *et al.* (18–20). In this study, the various modifying agents were used for the modification of HZSM-5 zeolite, and then the effects of the deposition of silica on the activity of the acid sites on the external surfaces, the acidity of the acid sites, and the pore-opening size of the modified HZSM-5 zeolite with silica were studied.

As shown in Fig. 1, the inactivation of acid sites on the external surface of HZSM-5 depends on the kinds of silane compounds deposited. The amount of silica required to fully inactivate the acid sites on the external surface of HZSM-5 is ordered as Di > Tri > Tetra > Mono > MTPS. In the case of MTPS, only 1.0 wt% of silica was required for the complete inactivation of acid sites on the external surface; therefore, the deposition of this compound inactivates the acid sites most effectively. The value 1 wt% of silica corresponds to 9.3 Si nm^{-2} of the surface concentration, and it is close to 8.6 nm^{-2} of the monolayer.

As the findings from the IR observation and adsorption experiments indicate, the internal surface of HZSM-5 zeolite was not modified by the deposition of MTPS. Because of the large molecular size of MTPS, it cannot enter into the pore, and deposits only on the external surface of ZSM-5; even in the case of Tetra, a steric hindrance in the entrance of the pore is observed. As reported previously (20), Tetra is deposited nonselectively on the cation sites of the external surface. Because it has four functional groups of methoxide, it is easily polymerized into the siloxane network structure. On the other hand, MTPS has only one methoxide; thereby, it may be stabilized as an isolated species. Due to the attached alkyl group, the anion property of the Si–O-species could be enhanced. Based upon these considerations, it seems that MTPS deposits selectively on the acid sites to inactivate effectively the acid sites.

Mono also inactivates the acid sites on the external surface more readily than other silicon alkoxide compounds having a methyl substituent. However, Mono can enter into the interior of zeolite, as shown by the IR and adsorption experiments; the modification of the internal structure cannot be disregarded in the deposition of large amounts of silica. Furthermore, it was found that the compounds of Di and Tri entered into the pore easily to inactivate the internal acid sites. After all, these compounds are not effective reagents for the inactivation of the external surface.

From the adsorption experiment using xylene isomers, the extent of narrowing of the pore-opening size can be estimated. The values of *Ao/Ap* for the HZSM-5 zeolites modified with silica were smaller than that of HZSM-5 zeolite, and the pore-opening size was narrowed according to the extent of modification. The relationship between the amount of deposited silica and the *Ao/Ap* is summarized in Fig. 5; a close relationship between them was observed. Because the relationship was found simply for the modified zeolites with various silicon compounds, it is suggested that the pore-opening size is reduced in a similar extent by the silica deposited from any silicon compounds. The behavior was clearly contrasted from the finding of inactivation of the external surface. Because the internal structure of zeolite is completely kept, Tetra is the most effective silicon alkoxide for the control of the pore-opening size.

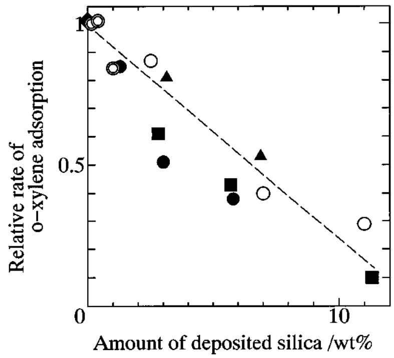

FIG. 5. Relationship between the amount of silica deposited on the HZSM-5 zeolite and the relative *o*-xylene adsorption rate *(Ao/Ap)*. Symbols, shown in Fig. 1.

Generation of Para-Selectivity

Para-selectivities of modified HZSM-5 zeolites were higher than that of inherent HZSM-5 zeolite (Table 1). The enhanced selectivity will be correlated with properties of the modified zeolites which were mentioned in the foregoing description. Because two important parameters, i.e., the external surface acidity and the pore-opening size, are taken into consideration with the shape selectivity, bi-dimensional plots are not appropriate. Tri-dimensional plots are shown in Fig. 6, therefore. In this figure, para-selectivity in the z axis is plotted against the extent of inactivation and the control of pore-opening size in the x and the y axis, respectively. The lowest selectivity was on the unmodified HZSM-5. Para-selectivity increased slightly along with the axis of the extent of inactivation. In this range, the acidity of the external surface of HZSM-5 zeolite decreased remarkably, but the pore-opening size was scarcely narrowed. The HZSM-5 zeolites modified with MTPS belong to this range.

On the other hand, para-selectivity increased significantly along with the axis of pore-opening size. In this range, the pore-opening size was largely narrowed, but the activities of acid sites on the external surface were not changed. It was remarkable that the deposition of Tetra was effective for the enhancement of para-selectivity due to the narrowing of the pore-opening size. Therefore, it is concluded that the enhancement of para-selectivity for the methylation of toluene on the HZSM-5 modified with silicon alkoxide is caused by the control of the pore-opening size. In other words, the selectivity is enhanced by the steric hindrance

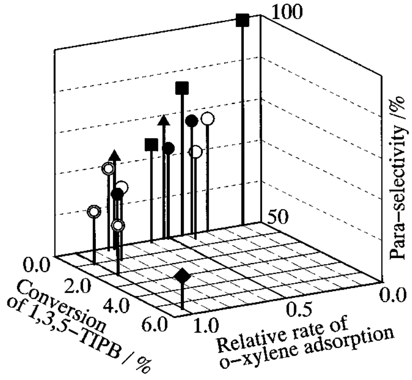

FIG. 6. Effect of the modification with silica on para-selectivity for methylation of toluene. Symbols, shown in Fig. 1.

of diffusion of the large compounds. So-called the product selectivity can explain the extremely high selectivity.

This conclusion is in agreement with the observation made by Mirth and Lercher (10), but not at all with the study by Paparatto *et al.* (4). It is not known exactly whether our conclusion is restricted to the zeolite modified with silicon alkoxides or not. The study on the selectivity enhanced by other methods will be a foregoing target.

CONCLUSION

We could obtain the HZSM-5 zeolites with different pore-opening sizes and with varied extents of inactivation of acid sites on the external surface by silanation using various silicon alkoxides. MTPS was effective in selective inactivation of acid sites on the external surface of the HZSM-5 zeolite. To clarify the reason why the modified HZSM-5 zeolites with silica exhibit high para-selectivity for the methylation of toluene, the effects of the activities of the external acid sites, the acidic strength, and the pore-opening size of the modified HZSM-5 zeolites on the enhancement of para-selectivity were studied. From the characterization of the modified HZSM-5 zeolites with silica and its relationship with para-selectivity, we concluded that the enhancement of para-selectivity for the methylation of toluene was ascribed more closely to controlling the pore-opening size rather than to the inactivation of acid sites on the external surface.

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