# The Influence of the External Acidity of H-ZSM-5 on Its Shape Selective Properties in the Disproportionation of Ethylbenzene

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The shape selectivity of H-ZSM-5 in the disproportionation of ethylbenzene was investigated, using a set of samples with the same Si/Al ratio, but different particle sizes in the range from 0.1 to 80  $\mu$ m. The number of external acid sites of each sample was measured gravimetrically by the adsorption of 2,6-dimethylpyridine. The data were correlated with the results of catalytic experiments. Conversion and product distribution are strongly dependent on the external acidity which in turn correlates well with the particle size. An estimate for the diffusion coefficient could be obtained by fitting the effectiveness factor for the different particle sizes. © 1997 Academic Press

### INTRODUCTION

Para-substituted dialkylbenzenes serve as important raw materials in a number of industrial processes. Such compounds can be produced using the shape selective properties of zeolites such as ZSM-5. There are several investigations of the influence of the ZSM-5 crystal size on conversion and para-selectivity in reactions of alkylated benzenes. Also the effect of the framework aluminum content has been studied. However, there are no reports about the measurement of the external acidity and its correlation with activity and selectivity in the above-mentioned reactions. Paparatto et al. (1) concluded that isomerization of para-alkylated toluene over ZSM-5 and ZSM-11 proceeds on external acid sites, and that decreasing the concentration of external acid sites suppresses the activity, resulting in enhancement of para-alkylated product selectivity. The authors proposed a two-step mechanism: in the first step, the para-isomer is formed by toluene alkylation with high selectivity inside the zeolite channels. In the second step the isomerization of the three isomers toward the thermodynamic equilibrium distribution proceeds on the external surface only. In addition to these suggestions, Lonyi et al. (2) proposed that the primary para-product isomerizes first to meta- and then to ortho-diethyltoluene. Increasing conversion is often correlated with decreasing para-selectivity (3-6), since at high conversion consecutive isomerization reactions can occur easily.

In xylene isomerization over ZSM-5 it has been observed that the crystal size has a more prominent effect on the shape selectivity than the site density (7). The enhanced formation of *p*-xylene is attributed to the occurrence of diffusion limitations in the Al,B-MFI sample. Kaeding (8) states that for the disproportionation of ethylbenzene over ZSM-5 samples with large crystal sizes a higher concentration of para-diethylbenzene is formed than over smaller crystals. He attributes this effect to the lower amount of external surface sites which are responsible for nonselective reactions on the lager crystals as compared to the small crystal size sample. Similar results were obtained by Shiralkar et al. (9) and Beschmann et al.(10) in their studies of the methylation of toluene and Bhat et al. (11) for the ethylation of toluene. Also Csicsery (12) explains such an effect by the influence of the external surface: on small crystals with a high external surface area, the diffusion-controlled shape-selective transformations proceed at a lower rate than the unrestricted surface reactions. Therefore, the paraselectivity is increased for alkylation when the external crystal surface is coated with residues (13). The problem of the nonselective external surface can be reduced by inactivation of the external surface which results in a high para-selectivity, as for instance Hibino et al. (14) and Bhat et al.(11) observed for the alkylation of toluene over ZSM-5.

One problem of previous studies (1-14) with the exception of the recent work of Beschmann et al. (10). Arsenova et al. (15), and Bhat et al. (11) was the fact that no welldefined sample set of more than two samples with different crystal sizes and the same Si/Al ratio was available. In addition, there is a lack of data on the amount of acid sites on the external surface which was never measured in these studies. In the literature, conversion and shape selectivity have been correlated with the crystal size instead of the external acidity because the latter data were not available. Since the aluminum distribution over a crystal might be inhomogeneous (16), it is important to have also independent information on the number of external acid sites. The aluminum distribution within ZSM-5 crystals resulting from different synthesis systems has been investigated by Althoff et al. (17) with electron microprobing. It has been shown that in samples synthesized from tetrapropylammonium (TPA)-containing systems there is always a pronounced enrichment of aluminum in the crystal rim, the extent of which, however, can vary. Information on the amount of acid sites on the external surface is thus necessary to fully understand catalytic data. We chose the adsorption of 2,6-dimethylpyridine as a probe molecule to measure this property. This amine has been used before as an indicator of acidity in FTIR-spectroscopic experiments (18–20), and should be too bulky to enter the ZSM-5 pore system. A similar approach had been used already several years ago by Karge and co-workers who used 2,6-di-tert-butylpyridine to analyze the external acidity of other zeolite types (21). They found that catalytic activity in the dehydration of cyclohexanol correlated almost linearly with the absorbance of the IR-band characteristic for the *di-tert*-butylpyridinium ion for mordenites and clinoptilolites. Recently another bulky probe, 4-methylquinoline, was used to analyze the external acidity of ZSM-5 (22).

However, one should bear in mind in this connection that the term "external surface" or "external acidity" is not easy to define on a molecular level. The approach chosen here is clearly an operational definition, i.e., it is assumed that 2,6-dimethylpyridine is too bulky to enter the pores which is based on estimates using van der Waals radii, and then external surface is defined as that part of the sample which can react with the probe under the conditions of the sorption experiment. The probe was chosen so that it resembles the molecules under investigation in the catalytic experiments. We chose dimethylbenzene instead of diethylbenzene because this molecule proved to be more suitable for IR-spectroscopic analysis, the results of which will be reported in a forthcoming communication.

In order to clarify the influence of the external acidity in a reaction where shape selectivity has been observed, we used a well-defined set of four H-ZSM-5 samples with a Si/Al ratio of 35 in a crystal size range from 0.1 to 80  $\mu$ m, resulting from an alkali-based and an alkali-free synthesis system. The crystals have a good morphology with little intergrowth and a narrow crystal size distribution and are thus very well suited for this investigation. For all samples the amount of the external acid sites has been measured and correlated with the catalytic performance of the materials in the disproportionation of ethylbenzene.

# EXPERIMENTAL

*Materials.* A collection of well-defined H-ZSM-5 samples with identical Si/Al ratio, but different crystal sizes was synthesized with organic templates following well-known procedures in alkali-containing (samples A, B, C) (23, 24) and alkali-free (sample D) (25) systems. The crystals exhibit a regular morphology and show little intergrowth (Fig. 1). The zeolites were calcined in air by heating at 3 K/min to 774 K for 20 h and then exchanged four times with 1 *M* 

 $\rm NH_4NO_3$  solution for 24 h, washed, and dried at 394 K. By calcination at 774 K for 10 h the ammonium form was converted to H-ZSM-5. XRD of the samples showed 100% crystalline MFI-structure. No amorphous material was observed.

Characterization. The Si/Al ratios were measured by X-ray fluorescence (XRF). The crystal size was determined from scanning electron micrographs shown in Fig. 1. In order to obtain a direct measure of the external surface of the crystals, a method following the procedure of Grillet et al. (26) was employed: The pores of the ZSM-5-samples were first filled by preadsorption of n-nonane. For this preadsorption the zeolites had been evacuated to  $1 \times 10^{-5}$  Torr and activated at 623 K for 8 h. At room temperature n-nonane was dosed for 24 h. These samples were transfered to a Micromeritics ASAP 2000 volumetric sorption system and activated at 363 K for 3 h. Variation of the activation conditions for the preloaded samples did not change the results of the analysis. By N<sub>2</sub> adsorption at 77 K the nonmicropore surface of the samples could be measured. This procedure, however, was only possible for the samples with small crystal size (see below).

Adsorption measurements of the amines were performed employing a magnetic suspension balance (27). The sample was activated by evacuation to  $5 \times 10^{-6}$  Torr and then heated at 3 K/min to 623 K and kept at that temperature for 8 h. After cooling to room temperature the sample was exposed to pyridine at  $1 \times 10^{-3}$  Torr for 4 h. After this exposure time no further uptake of pyridine could be observed. Physisorbed pyridine was removed by heating under vacuum at 400 K for 2 h. Readsorption after this heating did not result in additional irreversible uptake. The results obtained agree very well with the Si/Al ratios determined via XRF so that complete saturation of the samples can be assumed.

The number of the external acid sites was measured gravimetrically by using instead of pyridine the probe 2,6dimethylpyridine. Adsorption and removal of physisorbed 2,6-dimethylpyridine was carried out under the same conditions as for pyridine. In parallel FTIR spectroscopic measurements it was shown that evacuation for 2 h at 400 K was sufficient to remove physisorbed pyridine and 2,6dimethylpyridine. Both Brønsted and Lewis acid sites were present in all samples on the internal and on the external surface. Quantification of the fractions, however, is difficult. Investigations are under way to obtain reliable estimates on the relative amounts of the different species.

Ethylbenzene disproportionation was carried out on the powdered samples in a fixed-bed quartz reactor at 523 K with on-line GC analysis. No pellets were pressed in order to avoid crushing of the crystals. The samples were activated for 12 h in  $N_2$  atmosphere at 723 K prior to experiments. Selectivities were compared for identical



FIG. 1. Scanning electron micrographs of samples A-C and optical micrograph of sample D.

conversions by adjusting the space velocity, and the conversions for different samples were compared at identical space velocities.

# **RESULTS AND DISCUSSION**

The Si/Al ratio of all samples was determined by X-ray fluorescence to be 35. This is in excellent agreement with the gravimetrically measured uptake of pyridine of the zeolites, if a stoichiometry of one pyridine molecule per aluminum atom is assumed (see Table 1). Adsorption of 2,6-dimethylpyridine was carried out to analyze the number of acid sites accessible to sterically more demanding *di*-substituted benzene derivatives which are assumed to be formed mainly on the external surface in alkylation and isomerization reactions. The results of these experiments are also summarized in Table 1. As for pyridine, one acid site was assumed for every 2,6-dimethylpyridine molecule adsorbed. A clear dependence between crystal size and the amount of 2,6-dimethylpyridine adsorbed is obvious from the data. It should be pointed out here that this dependence is not a kinetic effect due to higher transport



FIG. 1-Continued

limitations on the larger crystals. Saturation of the sample with 2,6-dimethylpyridine was usually reached within 15 min. Long-term experiments over several days did not result in any additional uptake of 2,6-dimethylpyridine which proves that equilibrium had been reached. Crystals larger than 20  $\mu$ m with a correspondingly small external surface did not show any weight gain beyond the sensitivity limit of the balance and thus could not be analyzed gravimetrically.

The amount of 2,6-dimethylpyridine adsorbed is surprisingly high, if just the geometrical external surface is considered. Calculated external surface areas assuming the external surface to be well approximated by the geometric surface area of rectangular crystals are listed in Table 1. For sample A a spherical shape was assumed as the SEM photographs suggest. As can be derived from Table 1, the concentration of acid sites on the external surface is larger by a factor of around 10 than in the bulk, assuming a penetration depth of 2,6-dimethylpyridine of one unit cell. There are three possible explanations for this effect: (i) the calculated geometrical surface area could be too small due to

	TABLE 1a	
Summary of the	Results of Pyridine Adso	rption on all Samples

Sample	Crystal size ( $\mu$ m)	Si/Al ratio	Pyridine adsorbed (mg/g <sub>cat</sub> )	Acid site concentration (µmol/g)
А	0.1	35	36.2	458
В	5-10	35	36.5	462
С	15	35	36.0	456
D	80	35	36.1	457

*Note.* Si/Al ratio measured with X-ray fluorescence. One pyridine molecule assumed per acid site.

the presence of surface roughness and cracks, (ii) an enrichment of aluminum toward the edges of the crystals could be present, and (iii) 2,6-dimethlypyridine might penetrate deeper into the crystal than one unit cell.

In order to obtain a better estimate of the external surface area, N<sub>2</sub> adsorption measurements were performed on samples for which the micropore system had been blocked by preadsorption of nonane. Only samples A and B could be analyzed using this method, since the external surface area of the samples with larger crystal size (C and D) was too small to be reliably determined using this method. The external surface area obtained using this method is a factor of 3 larger than the calculated surface areas (52  $m^2/g$  for sample A and 2.7  $m^2/g$  for sample B). The N<sub>2</sub> isotherms of the samples completely filled with nonane showed no indication of the presence of micropores which proves that only the external surface has been measured in these experiments. The reason for the measured external surface being higher by a factor of 3 than the calculated external surface is most probably due to cracks formed during the calcination of the materials (clearly visible in the optical microscope on the large crystals) and to surface roughness.

#### TABLE 1b

#### Summary of the Characterization of the External Acidity

Sample	2,6-DMP adsorbed (mg/g <sub>cat</sub> )	Concentration of external acid sites (µmol/g)	External/ internal acidity	Calcd external surface area (m²/g)	Measured external surface area (m²/g)
А	29.7	277	1.53	16.5	52.0
В	2.0	18	0.04	1.1	2.7
С	0.8	8	0.02	0.4	*
D	*	*	*	0.1	*

*Note.* The number of external acid sites has been calculated from the adsorption of 2,6-dimethyl-pyridine (2,6-DMP) assuming one molecule per acid site. For the calculation of the external surface area rectangular crystals were assumed (for the 0.1  $\mu$ m crystal spheres). The measured external surface area was determined by BET analysis with nitrogen after pore filling with nonane.

\* Nonmeasurable values.

However, even taking into account that the measured external surface area is larger than the calculated surface area based on a smooth crystal surface, the amount of aluminum analyzed by 2,6-dimethylpyridine adsorption is still higher by a factor of about 4 than that expected from the bulk Si/Al ratio. Due to the fact that no additional uptake of 2.6-dimethylpyridine is observed even for long times, penetration of 2,6-dimethylpyridine into the pore system seems to be rather improbable. There is a report in the literature that 2,6-dimethylpyridine can be formed over ZSM-5 (28) and the formation is assumed to be taking place in the pore system. However, there is no information on the crystal size, and the reaction was carried out at 723 K where there might indeed be some penetration of the molecules into the pore system. Under the conditions of the adsorption experiments, however, we exclude this possibility. The high concentration of acid sites on the external surface can be better explained by an enrichment of aluminum towards the rims of the crystals. Since the crystals used were all synthesized using TPA as the template, enrichment of Al is to be expected. It can amount to a factor of 5 or more (16, 29, 30) which, together with the presence of surface roughness and cracks, explains the high concentration of acid sites measured by 2,6-dimethylpyridine.

If the density of acid sites on the external surface is calculated from the amount adsorbed and the measured external surface areas, one arrives at about three sites per square nanometer which in turn means that there is only a space of about 0.3 nm<sup>2</sup> per adsorbed molecule of 2,6dimethylpyridine. This is only about twice the space requirement assumed for a nitrogen molecule adsorbed on surfaces. Space requirements for the 2,6-dimethylpyridine can most probably not be based on the kinetic diameter. For pyridine, on-top adsorption on acid sites could be demonstrated (31), so that the space requirement is probably best described by the projection of the shape of the molecule along the  $C_2$  axis. This is difficult to estimate, but 0.3 nm<sup>2</sup> should be sufficient to accommodate a 2,6-dimethylpyridine molecule, if the estimate is simply based on van der Waals radii (approx. 0.14 nm<sup>2</sup>). However, it should be pointed out that substantially higher surface concentrations of acid sites than measured here could probably not be detected by this probe molecule due to packing constraints.

The difference between the number of external acid sites in the four samples is strongly reflected in their catalytic behavior. The conversion of ethylbenzene to benzene and the isomeric diethylbenzenes strongly increases with an increase of the number of external acid sites (Fig. 2). This is in agreement with published data mentioned in the Introduction in which the particle size instead of the amount of external acid sites had been correlated with the activity of the samples in reactions with different disubstituted benzenes.

On the other hand, the selectivity decreases with increasing external acidity (Fig. 3). This is in agreement with Chen



**FIG. 2.** Dependence of ethylbenzene conversion on the concentration of external acid sites at constant  $T_{\text{reactor}} = 523$  K, WHSV = 0.06 h<sup>-1</sup>. Concentration of external acid sites for sample D was estimated assuming an identical density as for sample C.

*et al.* (32, 33) who observed that the *para*-selectivity for reactions of toluene depends on the crystal size. Large crystals which have a correspondingly small external surface showed a high *para*-selectivity. The conversions and selectivities observed here are not linearly correlated with the amount of external acid sites, since both are governed by the interplay between reaction and diffusion, resulting in nonlinear dependences.

*Para-* and *meta-*diethylbenzene are the only products observed in our study for low values of the external acidity. The formation of *m*-diethylbenzene increases and that of *p*-diethylbenzene decreases with increasing external acidity. *o*-Diethylbenzene can only be detected by GC when the thermodynamic equilibrium between *p*- and *m*-diethylbenzene has already been reached. (Equilibrium values calculated by Kaeding (8) for diethylbenzene at 523 K are p/m = 0.57; p/o = 1.95). Similar results were observed during the alkylation of ethylbenzene with ethanol which results in the primary formation of *p*-diethylbenzene



**FIG. 3.** Selectivity to *para-*, *meta-*, and *ortho*-diethylbenzene in ethylbenzene disproportionation over samples A–D in dependence on the concentration of external acid sites at a conversion of 4% and a reactor temperature of 523 K.  $\bigcirc$ , molar ratio p/m;  $\blacksquare$ , molar ratio p/o. The letters indicate the sample.



**FIG. 4.** Selectivity to the isomers at different conversions over sample A.  $\bigcirc$ , molar ratio *p*/*m*;  $\blacksquare$ , molar ratio *p*/*o*.

(13, 34). The product distribution is strongly dependent on the space velocity. Figure 4 shows the concentration of the products formed at different conversions achieved by varying the space velocity over sample A. The thermodynamic equilibrium between *para*- and *meta*-diethylbenzene is already reached at high space velocities while the conversion is still low. Decreasing the space velocity leads to the formation of increasing amounts of the *ortho*-isomer.

Two alternative explanations have been suggested to rationalize the selectivity in the isomerization of disubstituted benzenes, primarily for the xylene isomerization. The first was put forward by Wei (35) and Weisz *et al.* (36, 37). These authors assume that all isomers can enter the pore system. Shape selectivity then depends on the length of the intrazeolitic diffusion path and is therefore governed by the relation between intrinsic reactivities and diffusion coefficients of the different isomers. This in turn is dependent on the structure type, the modification, and the crystal size. In order to explain the lack of *para*-selectivity at high conversion, Wei (35) proposed product reentry into the zeolitic channel system for further reaction.

The other approach, put forward by Fraenkel (38), Derouane (39), and Nayak and Riekert (40), assumes that there are *para*-selective events in the pore system due to diffusional constraints while external acid sites are responsible for non-selective transformations.

Our results suggest that the *meta-* and *ortho-*isomers are produced mainly on the external surface of the crystals, which is in agreement with data of Karge *et al.* (41) who reported that *o*-diethylbenzene cannot enter the ZSM-5 pore system. If a major fraction of the acid sites is accessible for the reactants as well as for the product, isomerization until equilibrium is reached is easily understandable. The increase of *ortho*-diethylbenzene formation with decreasing space velocities can be rationalized by the fact that the reactants are in contact with the catalyst for a longer time, thus allowing the system to approach the equilibrium concentrations by isomerization on the non-shape-selective external surface. Lonyi et al. (2) discuss the formation of meta- and ortho-ethyltoluene in the ethylation of toluene in terms of a subsequent isomerization of the *p*-isomer formed first. Our data indicate that the isomerization of the primary product *p*-diethylbenzene proceeds on the external surface in a sequential reaction first to the *meta*-isomer, and finally from the meta- to the ortho-isomer. With increasing external acidity sufficient meta-diethylbenzene is produced from the *p*-diethylbenzene formed shape selectively in the pore system, which then reacts further to the ortho-isomer via a 1,2-alkyl-shift reaction. Allen and Yats (42) described that in the liquid phase *o*-xylene does not isomerize directly to p-xylene, or vice versa. Similar results were obtained for vapor phase reactions by Hanson and Engel (43). Although there seems to be some mobility of the ortho- and metaisomers of xylene in the pore system of ZSM-5, as Mirth et al. (44) determined (the ratio of the diffusion coefficients for the three xylene isomers by FTIR spectroscopy at  $100-200^{\circ}$ C is around *para*: ortho: meta = 1000:10:1), the contributions of meta- and even more so of ortho-xylenes should be negligible for the conversion in the pore system. This is even more important for the diethylbenzenes, where the molecules are bulkier.

From the dependence of the conversion on the particle size it is possible to obtain a rough estimate for the diffusion coefficient of ethylbenzene in ZSM-5. If a catalyst efficiency of 100% is assumed for sample A with very small particle sizes, the catalyst efficiency of the larger particle size materials can be fitted using the diffusion coefficient as the free parameter under the assumption of a constant turnover frequency (TOF) for all samples. The assumption of an efficiency of 100% seemed reasonable for a material, which has most of the active sites located at or near the external surface. A reasonable fit of the data could otherwise only be obtained, if very low catalyst efficiencies were assumed for sample A (below 10%) which did not seem plausible. The TOF has been calculated from the conversion over sample A to be  $3.4 \times 10^{-5}$  s<sup>-1</sup>, assuming that the concentration in the crystal did not substantially differ from the gas-phase concentration (catalyst efficiency assumed as 100%).

Assuming plate geometry which is reasonable for the pore system of ZSM-5, the catalyst efficiency  $\eta$  is expressed as

$$\eta = \tanh \varphi / \varphi;$$

with  $\varphi$  being the Thiele modulus where

$$\varphi = L(r/D)^{1/2}$$

and *L* is the thickness of the crystal along [100], *r* is the reaction constant, and *D* is the diffusion coefficient.

Nonlinear regression of the catalyst efficiency yielded an effective diffusion coefficient for ethylbenzene of D=



FIG. 5. Dependence of the effectiveness factor on the crystal length along (100). Solid lines are fitted curves. Curve B:  $D=1.2 \times 10^{-12}$  cm<sup>2</sup>/s. For estimating the sensitivity of the analysis, curves are shown which are obtained using different values of the diffusion coefficient. (A)  $D=1.2 \times 10^{-13}$  cm<sup>2</sup>/s; (B)  $D=1.2 \times 10^{-12}$  cm<sup>2</sup>/s; (C)  $D=1.2 \times 10^{-11}$  cm<sup>2</sup>/s.

 $1.2 \times 10^{-12}$  cm<sup>2</sup>/s at 523 K (Fig. 5). This is somewhat lower than diffusion coefficients estimated for *para*-xylene by Mirth et al. (44)  $(6 \times 10^{-12} \text{ cm}^2/\text{s} \text{ at } 373 \text{ K})$  and appreciably lower than those reported by other authors (45-47) for ethylbenzene (around  $4 \times 10^{-9}$  cm<sup>2</sup>/s at 373 K). These data were obtained at low loadings from uptake measurements. However, even at higher loadings high mobilities have been reported (of the order of  $10^{-10}$  cm<sup>2</sup>/s (48)). One should bear in mind, however, that the diffusion coefficient obtained in this study is only an effective one, valid under reaction conditions in the ethylbenzene disproportionation, which can not easily be related to results from sorption experiments. Diffusion might be strongly hindered by the bulky isomers which can be present in the channel intersection, but not diffuse fast. Reduction of the diffusion rates by coking appears to be rather improbable, since no sign of coking of the catalysts was detected.

From Fig. 5 it can be deduced that the onset of diffusion limitations is expected for crystals in the size range of several micrometers. This agrees well with the findings of Arsenova *et al.* (15), who did not observe diffusion limitations for crystals up to 1  $\mu$ m in size, but at the slightly higher reaction temperature of 563 K.

#### CONCLUSIONS

By measuring the external acidity of a series of welldefined H-ZSM-5 samples using 2,6-dimethylpyridine as a probe molecule we could demonstrate that the activity as well as the shape-selective properties in the disproportionation of ethylbenzene are clearly correlated with the external acidity. Over large crystals (80  $\mu$ m) with a very low external acidity only *p*-diethylbenzene is formed in concentrations above the detection limit of the GC. With decreasing crystal size and thus an increasing number of external acid sites, first the *meta*-isomer, and only for very small crystals (100 nm) also the *ortho*-isomer, are observed as reaction products. The catalyst efficiency decreases from around 1 for the smallest crystals down to about 0.1 for the 80  $\mu$ m material. The measured external acidity is much higher than expected from the Si/Al ratio and the crystal size. The explanation for this fact is surface roughness and the presence of cracks on the one hand, and an enrichment of aluminum in the crystal rim on the other hand. The disproportionation of ethylbenzene most probably proceeds shape-selectively to *p*-diethylbenzene is then isomerized on the external surface of the crystals via 1,2-alkyl-shift reactions first to the *meta*-isomer and subsequently to *o*-diethylbenzene.

These results suggest that if a catalyst is desired which has a high *para*-selectivity as well as a high conversion, it is best to use crystals which are as small as possible, and block or remove the external acidic sites, following procedures which have been described in the literature (11, 49, 50).

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