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Toluene Ethylation on ZSM Zeolites

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The activity and selectivity to *para*-ethyltoluene in toluene alkylation with ethanol have been correlated to the structural and morphological features of the ZSM-5 and ZSM-11 zeolites employed as catalysts. In particular, as the particle size increases and correspondingly the surface area outside the zeolite channels decreases, lower activities and higher *para*-isomer selectivities (up to 90%) are obtained. This behavior has been interpreted by supposing a two-step mechanism: in the first step, *para*-isomer forms by toluene alkylation with high selectivity inside the zeolitic channels (shape selectivity), while in the second step the isomerization toward the thermodynamic equilibrium of the three isomers proceeds just on the external surface.

INTRODUCTION

Toluene alkylation to *para*-ethyltoluene (*p*-ET) is a reaction of great industrial interest. Subsequent dehydrogenation of the *p*-ET gives the corresponding *p*-methylstyrene (PMS), the monomer for poly(*p*-methylstyrene) (PPMS) production (*1*). According to the inventors, this polymer might capture in the near future a large proportion of the polystyrene market (*2–4*). Apart from the cost of the raw material, PPMS has physical advantages over polystyrene such as higher flash point and glass transition temperatures and lower specific gravity (*5*).

The keystone of this new process is the catalyst containing ZSM-5-modified zeolite which exhibits an extraordinary selectivity to the *para*-isomer (*6*). The unmodified catalyst gives a near-equilibrium mixture of isomers, while physical treatments of the ZSM-5 zeolite with steam or coking, or modifications with metal salts (containing particularly P and/or Mg), produce catalysts which give the entire spectrum of isomeric mixtures containing up to 99% *p*-ET in the product (*7–9*).

While the patent literature is broad (*10* and Refs. therein), scientific papers in journals are rather scarce. Kaeding *et al.* (*11*) explain the dramatic increase of *para*-isomer selectivity when the zeolite is modified by supposing that this modification produces a magnification of the difference in diffusion rates between the smaller *para*-isomer and the *ortho*- and *meta*-isomers.

In this work we have studied the effect of the composition (SiO_2/Al_2O_3 ratios) and the crystal properties of the unmodified ZSM catalysts (H-form) on the *p*-ET selectivity in order to obtain additional information on the mechanism of this reaction inside the zeolitic framework. With the same purpose we have compared the toluene ethylation results with those obtained on the same catalysts in the isomerization of *m*-xylene.

EXPERIMENTAL

Catalyst Preparation

Zeolites of the ZSM-5 family (ZSM-5 and ZSM-11) were prepared by hydrothermal crystallization in an autoclave (423 K for 48 h) of a mixture containing NaOH, $NaAlO_2$, silica-sol, and a specific organic salt, namely the tetrabutylammonium (TBA^+) iodide for ZSM-11 synthesis and both the traditional tetrapropylammonium (TPA^+) bromide for ZSM-5 and also triethanolamine (TEA) which is able to template the ZSM-5 framework cystallization, too (*12*).

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The products were filtered, washed free of extraneous salts with water, and dried at 393 K for 15 h. These samples ("as made" form) were transformed into the acid form by calcining them at 813 K for 10 h before and after three exchanges with NH_4Cl solution. The formed catalysts were obtained by extruding (1 mm diameter) the acid zeolites kneaded with 20% SiO_2, activating them at 813 K for 2 h, and, only for the alkylation reaction, grinding them to 18–60 mesh. To compare with zeolites, an amorphous commercial SiO_2–Al_2O_3 (Akzo La-3P) was used as catalyst in both reactions.

Structural and Morphological Characteristics

The zeolite structure was determined by XRD analysis performed with an X-ray powder diffractometer (Philips PW 1050/25) using Ni-filtered Cu$K\alpha$ radiation.

The average crystallite size of the ZSM-5 and ZSM-11 zeolites was estimated from line broadening of the (102) and (110 + 011) peaks, respectively. The shape and size of the crystals or of their aggregates were carried out using a conventional scanning electron microscope (Cambridge MK2c). The external (outside the zeolitic pores) surface area was determined by N_2 adsorption at 77 K following the t plot method of Lippens *et al.* (*13*) in the range 0.5–1.5 nm. The primary particle average size was estimated with the usual formula (*14*): $d = 6/\rho S$, where d, ρ, and S are the size, density, and external surface area of the primary particles, respectively.

Apparatus and Procedure

Toluene alkylation. The apparatus consisted of a fixed-bed stainless-steel downflow microreactor (10 ml capacity) packed with 0.5 g of ground catalyst diluted with 5 g inert corundum. A mixture of He, toluene, and ethanol in the molar ratio 20 : 4 : 1 was fed to the microreactor at 623 K and atmospheric pressure for 6 h. Gas chromatographic analyses were performed directly on the effluent vapor by using a column of Bentone 34 (C. Erba). There is no substantial difference using ethanol rather than ethylene as alkylating agent because ethanol is dehydrated very rapidly into ethylene at a relatively low temperature (*11*).

m-Xylene isomerization. The apparatus consisted of a stainless-steel downflow reactor (100 ml capacity) packed with 15 ml of extrudate catalyst and 85 ml of corundum. A mixture of H_2 and *m*-xylene (5 : 1 molar ratio) was passed over the catalyst at 598 K, 15 atm, and at a space velocity of 6 h^{-1} (LHSV) for 4 h. The effluent vapors from the reactor was passed through a cold-water trap. No significant amounts of uncondensed gases were detected in the effluent hydrogen. The condensed liquids were analyzed by using a gas chromatographic column of Bentone 34.

RESULTS

The characteristics of the catalysts employed are summarized in Table 1. The symbols TPA, TBA, and TEA refer to the type of organic cation used in the synthesis and R refers to the SiO_2/Al_2O_3 molar ratio of the zeolitic samples. In the same table some main features of the zeolite crystals are summarized: these are the crystalline structure, the crystallite size (d_{XRD}), the shape and the dimension range (d_{SEM}) of the crystals or their aggregates, the size of the primary particles (d_S), and the surface area outside the zeolitic pores (S_{ex}).

m-Xylene Isomerization

Generally the *p*-xylene selectivity increases as the activity decreases (Fig. 1). The *p*-xylene selectivity is near the expected thermodynamic equilibrium value in the most active crystalline samples (about 50% at 46% conversion) and in the amorphous one. As the activity decreases, the selectivity moves away from the thermodynamic value, increasing to as much as 75%, emphasizing the known kinetic effect of the zeolitic pores (shape selectivity).

TABLE 1

Summary of the Characteristics of the Catalysts in Comparison with Their Performances in *m*-Xylene Isomerization and Toluene Alkylation with Ethanol

Sample	Structural and morphological properties							*m*-Xylene isomerization		Toluene ethylation	
	Organic cation	SiO_2/Al_2O_3 mol/mol	Structure	d_{XRD} (nm)	d_{SEM} (μm)	d_S (nm)	S_{ex} (m^2/g)	Conversion (%)	*p*-Xylene selectivity (%)	Conversion (%)	*p*-ET selectivity (%)
1	TPA	25	ZSM-5	34	0.5	36	88	44	54	74	31
2	TPA	25	ZSM-5	64	1–2	640	5	25	76	44	85
3	TPA	58	ZSM-5	87	1–4	160	20	46	52	65	41
4	TPA	63	ZSM-5	90	1–4	320	10	40	59	61	48
5	TEA	25	ZSM-5	83	1	145	22	46	52	71	46
6	TEA	25	ZSM-5	63	1	400	8	39	59	65	57
7	TEA	25	ZSM-5	145	3–7	460	7	36	62	61	57
8	TEA	25	ZSM-5	77	3–7	530	6	35	65	55	75
9	TEA	48	ZSM-5	300	4–8	750	4	21	75	50	87
10	TEA	63	ZSM-5	300	4–8	700	4–5	22	73	46	92
11	TBA	40	ZSM-11	50	1	35	90	46	50	54	33
12	TBA	80	ZSM-11	58	1	40	80	45	54	45	45
13	—	—	Amorphous	—	—	—	485	4	50	13	27

A comparison of the catalytic activities to the structural and morphological properties of the samples shows that the determining factor is the primary particle size (d_S) rather than d_{XRD} and d_{SEM} (Fig. 2). Moreover, the activity values are scarcely dependent on the zeolitic structure (ZSM-5 or ZSM-11) or on the type of organic cation used in the synthesis and the SiO_2/Al_2O_3 molar ratio (R), at least in our experimental range.

Toluene Ethylation

Under our experimental conditions (high dilution of the reactants in the feed) the only exhibited products were the three isomers of ethyltoluene. Moreover, the activity and the selectivity remained constant during the experimental runs (6 h).

When operating with ethanol-deficient feed, only 25% of toluene conversion was expected; in this work the conversions are

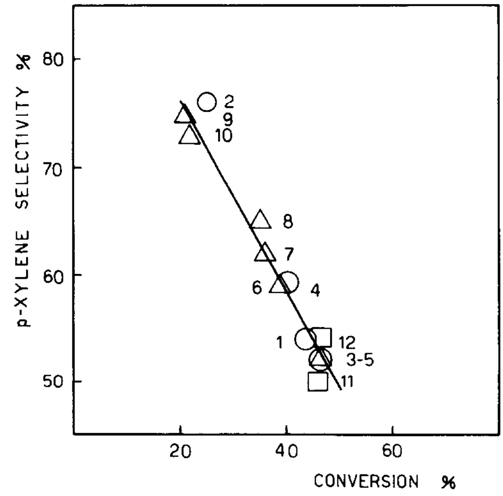

FIG. 1. *m*-Xylene isomerization: selectivity to *p*-xylene versus conversion.

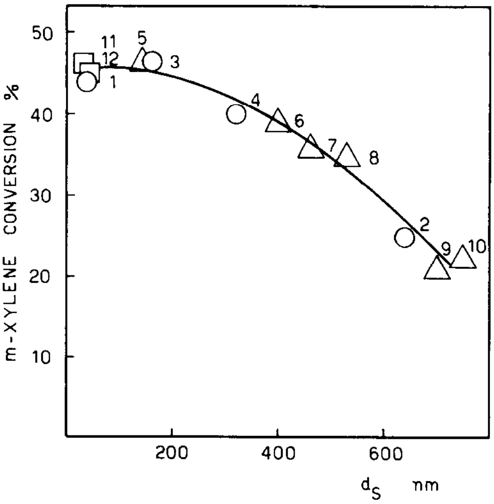

FIG. 2. *m*-Xylene isomerization: conversion versus primary particle size (d_S) of the zeolite samples.

expressed as percentages of the theoretical conversion. In order to obtain information on the performance of the samples when the conversion changes, the activities were measured at increasing space velocities (WHSV). The results as a whole are shown in Figs. 3–5. With the aim of making a significant comparison among the catalysts, the conversion of toluene and the selectivity to *p*-ET at WHSV = 50 h^{-1} have been interpolated from each curve.

The trends obtained (Fig. 6) are similar to those of *m*-xylene isomerization: the *p*-ET selectivity rises remarkably as the activity decreases, moving away from the equilibrium value (~30%), which is the case of the most active crystalline samples and of the amorphous one. However, the most peculiar feature in the alkylation case is the effect of the structure and of the organic cation used in their synthesis: ZSM-11 (TBA samples) appears less active and/or selective than ZSM-5 (TPA, TEA samples). Fur-

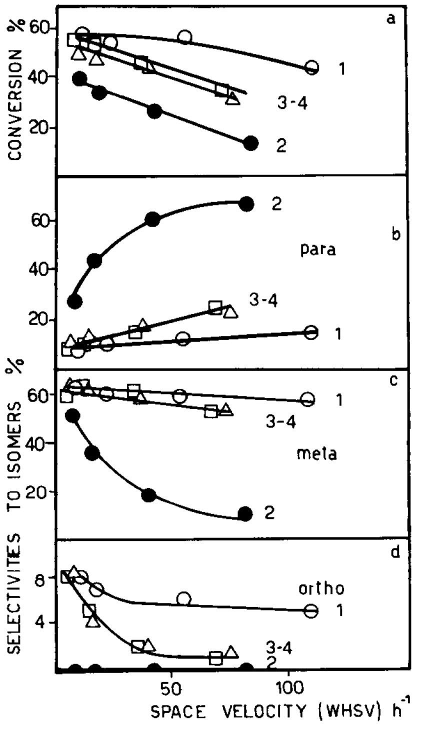

FIG. 3. Toluene ethylation: activities and selectivities for TPA-prepared zeolite samples.

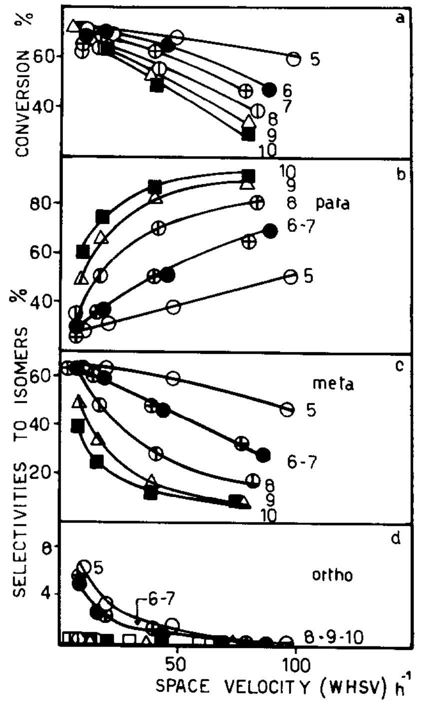

FIG. 4. Toluene ethylation: activities and selectivities for TEA-prepared zeolite samples.

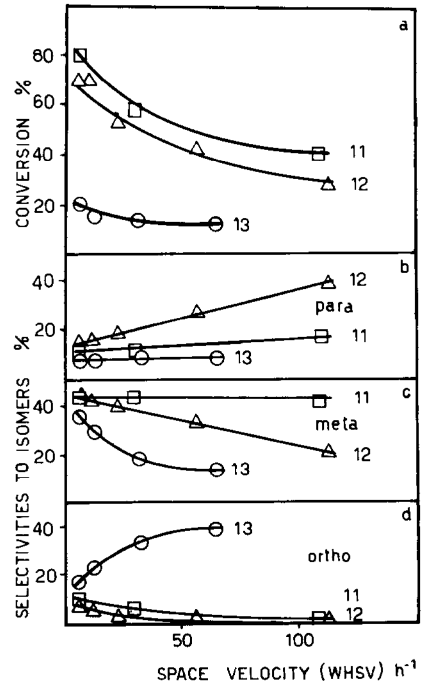

FIG. 5. Toluene ethylation: activities and selectivities for TBA-prepared zeolite samples and for amorphous SiO_2–Al_2O_3.

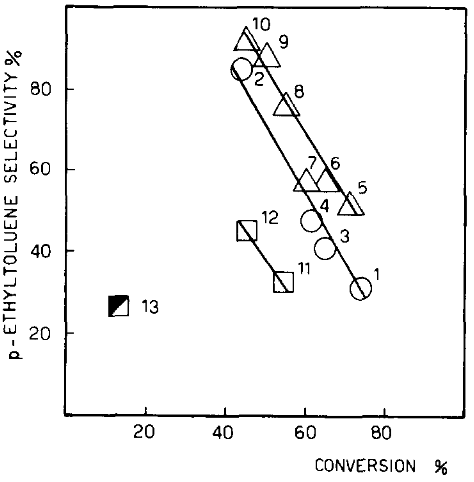

FIG. 6. Toluene ethylation: selectivity to *p*-ethyltoluene versus conversion.

thermore, the TEA-ZSM-5 catalysts show better performance than the TPA-ZSM-5 catalysts. As observed in *m*-xylene isomerization, the activity values are better correlated to the primary particle size (Fig. 7) than to d_{XRD}, d_{SEM}, and R (the latter at least in the experimental range). From this point of view, the activities have the following sequence:

TEA > TPA > TBA > SiO_2–Al_2O_3

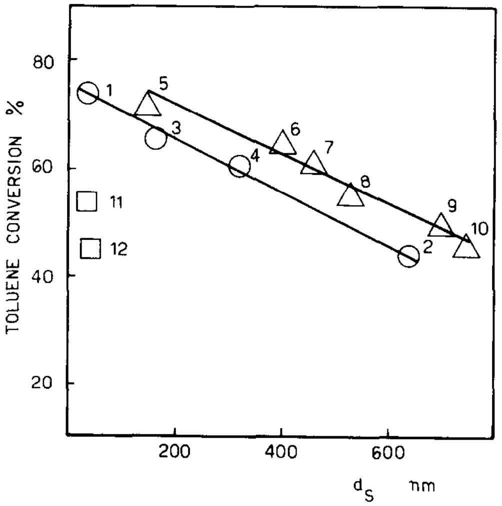

FIG. 7. Toluene ethylation: conversion versus primary particle size (d_S) of the zeolite samples.

DISCUSSION

In order to clarify the toluene ethylation mechanism, it is interesting to consider the trends of the distribution of the ethyltoluene isomers obtained at different space velocities on amorphous SiO_2–Al_2O_3 and on crystalline ZSM-5 catalysts, respectively, and among the latter on samples with different primary particle size. On the amorphous catalyst at low contact time (i.e., at high WHSV) a mixture slightly enriched with *o*-isomer is obtained because of the inductive effect of the methyl group on the toluene molecule, while the *p*-isomer is near the thermodynamic equilibrium. On the contrary, on the zeolite catalysts, under the same conditions, a high content of *p*-isomer (particularly on the less active catalysts) is found, while the *o*-isomer is practically absent. The different behavior of crystalline ZSM samples with respect to the amorphous catalyst, particularly the lack of *o*-isomer in the mixture, suggests that ethylation proceeds practically only in the zeolite channels, while the contribution of alkylation on the external surface, which should give also the *o*-isomer, is negligible, at least under these conditions. Maximum conversion values are reached on the samples with smallest primary particle size and as the size increases the activity decreases because of diffusional transport inhibition inside the zeolite channels.

As the contact time increases the composition of products approaches the thermodynamic equilibrium distribution, both on amorphous and zeolite catalysts. On the former, the *m*-isomer rises at the expense of the *o*-isomer, while the *p*-isomer remains constant. On the latter, lowering WHSV, the mixture becomes progressively deficient in *p*-isomer and rich in *m*-isomer. Since the *o*-isomer is always absent on the zeolitic samples with large primary particle size, that is, with low external surface area, it is confirmed that on such catalysts the toluene ethylation reaction takes place almost entirely in the zeolite channels. The mixture of products obtained on the zeolitic catalysts with wider external surface area contains a significant amount of *o*-isomer, which means that, at high contact times, the contribution of the isomerization and/or of the non-shape-selective alkylation cannot be neglected because such reactions mainly take place on the external surface. However, also on these latter catalysts the concentration of *o*-isomer in the mixture is far from the thermodynamic equilibrium value, implying that the alkylation occurring inside the zeolitic channels is prevailing.

The behavior of ZSM catalysts can be summarized by the following two-step mechanism. The first reaction is the shape-selective alkylation which proceeds on the acid sites inside the zeolite channels, where the formation of *p*-isomer is favored. When the *p*-isomer passes through the windows of the ZSM pores, it comes into contact with the acid sites of the external surface, i.e., with those around the entrance of the channels. Under these new conditions it quickly isomerizes toward *m*- and *o*-ET as far as the thermodynamic equilibrium. Obviously this second step of isomerization is favored by high contact times and large external surface areas.

The behavior in *m*-xylene isomerization of the catalysts is quite similar to that observed in the toluene ethylation. The *m*-xylene conversion decreases and the *p*-xylene selectivity rises on increasing the primary particle size, i.e., on lowering the external surface area of the catalysts.

In the *m*-xylene isomerization no meaningful differences were observed between the zeolite samples prepared starting from different organic cations. On the contrary, in the toluene ethylation the reaction proceeds with a higher conversion and selectivity on ZSM-5 (TPA, TEA samples) than on ZSM-11 (TBA samples) and, as for ZSM-5 catalysts, the best performance was obtained on TEA samples.

On the basis of our results the optimum zeolite catalyst for the alkylation of toluene to *p*-ethyltoluene should have a very high internal surface area and a very low external surface, having at best no acid sites on it. This point of view suggests an alternative interpretation for the results reported by Kaeding *et al.* (*11*): the positive effect on the selectivity of modification with steam, coking, or metal salt deposition could be connected with modification or removal of the external acidity rather than to the tightening of the zeolite channels and subsequent improvement of the shape selectivity.

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