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NOTE

Coke Induced Stabilization of Catalytic Activity of Silylated ZSM-5 Zeolite

One of the ways to synthesize dialkylbenzenes is to alkylate monoalkylbenzene with an alkylating agent such as alcohol or olefin over a Friedel–Crafts or zeolite catalyst. The latter is gaining importance as it is an environmentally friendly system. Dialkylbenzenes like *para*-xylene, *para*-ethyltoluene, and *para*-diethylbenzene are sources for various monomers.

Several techniques have been reported in the literature to modify the zeolite characteristics in such a way that the dialkylbenzenes formed during monoalkylbenzene alkylation contain more *para* isomer. Among these techniques, the chemical vapor deposition of silica (CVD) is drawing the attention of researchers (1, 2). The silylation results in fine control of pore opening size with the silica deposited on the external surface. The internal structure remains unaffected; only the pore entrance is narrowed (3).

It was observed that the silylated zeolite used for synthesizing *para*-dialkylbenzene by monoalkylbenzene alkylation deactivates with increased time on stream. This paper deals with the coke-induced stabilization of of catalytic activity of ZSM-5 zeolite during alkylation of ethylbenzene with ethanol.

ZSM-5 zeolites used were synthesized according to the method described in the well-known Mobil patent (4). The zeolites were characterized by XRD for phase purity, by SEM for crystallite size and morphology, by MAS NMR for framework composition, and by a combination of wet chemical analysis and atomic absorption spectrometry for Si/Al ratio and by TPD of ammonia for acidity.

The zeolite powder is of a high Si/Al ratio, 310. The XRD pattern indicated that the material contains 100% ZSM-5 phase. The morphology of the crystallite is pseudocubic with two flat surfaces, the rest of the four faces being joined by curved edges. The average size is about 5.5 × 5.5 × 4.4 cubic micrometers. The total acidity as estimated by TPD is 0.177 millimoles of ammonia per gram. ^{27}Al NMR spectrum indicated the absence of any extra framework aluminum.

One to two grams of zeolite in proton form was used in the catalytic run. The run was carried out in a continuous, fixed-bed, glass reactor at atmospheric pressure. The reactant mixture was fed by a syringe pump, vaporized in a preheater, and passed through the catalyst bed maintained at the reaction temperature. The products were condensed in a chilled water circulated condenser at the reactor outlet and analyzed in a Varian Vista 6000 gas chromatograph equipped with a 0.25 mm × 50 m LB-550 capillary column.

The silica deposition of the zeolite was done *in situ* by chemical vapor deposition of bulky silicon compound, tetraethyl orthosilicate (5). A 6.5% $Si(O\ C_2H_5)$ solution in 50 : 50 toluene and methanol was vaporized at 473 K and passed through the catalyst bed maintained at 503 K. The silica precursor solution was fed at a rate of 8 ml/h, and a flow of hydrogen was maintained to ensure uniform contact between the vapor and the catalyst. After the vapor was contacted for the desired period of time, the hydrogen flow was changed to nitrogen. The nitrogen gas was further replaced with air and the reactor temperature was raised to 815 K. This temperature was maintained for 10 h to decompose $Si(O\ C_2H_5)$ to SiO_2.

The coking of the catalyst was also done *in situ* by contacting with appropriate quantity of ethylbenzene vapor at 623 K.

Table 1 presents the results of ethylbenzene ethylation with ethanol over ZSM-5 zeolite at three different temperatures, viz. 300, 350, and 400° C. The main products of alkylation are diethylbenzenes, while ethylbenzene dealkylation takes place as a parallel reaction. There is formation of other products like toluene, xylenes, C_9 aromatics, and lighter hydrocarbons.

During ethylation over ZSM-5 zeolite, the ethyl group attached to the benzene ring activates the *ortho* and *para* positions for alkylation. However, due to the spatial constraint inside the zeolite channel, ethylation occurs only at the para position (6). The alkylation can take place at the *ortho* position on the external surface sites and this occurs to a negligible extent due to steric hindrance.

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TABLE 1

Effect of Temperature on Alkylation Activity

	Temp °C		
	300	350	400
EB conversion (%)	15.12	29.73	41.28
Ethanol conversion (%)	100	100	100
Selectivity (wt%)			
Benzene	6.58	24.78	35.29
Diethylbenzene	80.00	57.31	39.73
Other	13.42	17.91	25.00
Rate of reaction (g mol/g cat h)	0.0036	0.0066	0.0092
Diethylbenzene isomers (%)			
Para	70.82	54.39	39.34
Meta	29.18	45.14	59.81
Ortho	0.00	0.47	0.85

Note. EB: ethanol = 4 : 1; WHSV = 2.2 h^{-1}.

Hence *para*-diethylbenzene is formed as the primary product of ethylation and can isomerize to *meta*-diethylbenzene inside the channel intersection as well as on the external surface sites.

With an increase in temperature from 300 to 400°C, ethylbenzene conversion, as well as its dealkylation, increased, while selectivity for diethylbenzene and *para*-diethylbenzene decreased. The decrease in diethylbenzene's selectivity at elevated temperatures is due to the enhanced extent of dealkylation.

The modification of ZSM-5 zeolite was carried out by chemical vapor deposition of bulky molecule tetraethyl orthosilicate. The silica deposition enhances the *para* selectivity feature of the zeolite. The product shape selectivities in the alkylation reactions are controlled by the primary product formation inside the pore, diffusional constraint in the channel, and isomerization on the external surface sites. As the molecular size of tetraethyl orthosilicate is larger than the zeolite pore dimension, the chemical vapor deposition (CVD) results in a fine control of pore opening size, with the silica deposited on the external surface. The silylation narrows down the pore dimension without affecting the internal structure. The change in the reduction of pore opening size after CVD was monitored by a standard test reaction (7).

The results of the runs in which the zeolite was deposited with silica to different extents are depicted in Table 2. With an increase in silica deposition from 0.7 to 1.8 wt% ethylbenzene conversion decreased from 20 to 2% while *para*-diethylbenzene selectivity was enhanced to 100%. Around 1.5% silica deposition ethylbenzene conversion was appreciable, with *para*-selectivity around 99%. Higher than 1.5% silica deposition narrows the channel entrance considerably, which affects the diffusivity of both reactant and product in the channel, with the result that ethylbenzene conversion decreased.

Paparatto *et al.* (8) have reported that the *para* isomer formed selectively inside ZSM-5 channels while isomerization 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. On the other hand, Kim *et al.* (9) have suggested that the improvement in *para* selectivity by the modification of HZSM-5 with oxides was due to the suppression of the isomerization of the primarily produced *para* isomer. A conclusion similar to theirs was also reported (10).

Vayssilov *et al.* (11) have reported *para*-selective alkylation of toluene with methanol over ZSM-5 zeolites. The reactions of toluene alkylation and xylene isomerization are considered on both the external and the internal surface catalytic centers of the zeolite crystals.

Murakami (12) has investigated super-selective catalysis by CVD zeolites. This study reports deposition of ultrathin layer of silica to cover the external surface of zeolites and the thin layer of silica is effective in controlling the pore opening size without changing the internal structure.

The time-on-stream behavior of ZSM-5 zeolite deposited with different amounts of silica were studied. Results of the run using 1% silica deposited on ZSM-5 zeolite are presented in Fig. 1. The run was carried out for 20 h. The zeolite showed signs of deactivation, ethylbenzene conversion decreased steadily from 16 to 4%, and *para*-diethylbenzene selectivity increased from 88% to nearly 100%. This behaviour can be ascribed to steady coke

TABLE 2

Effect of Progressive Silylation of Zeolite on Catalytic Activity

	% silica deposited on 1 g zeolite				
Performance	0	0.7	1.0	1.5	1.8
EB conversion (%)	24.18	20.64	16.21	14.63	2.36
Selectivity wt (%)					
Benzene	21.96	23.47	26.87	19.05	17.29
Diethybenzene	64.45	60.21	55.18	58.26	57.67
Others	13.59	16.32	17.95	22.69	25.04
Rate of reaction (g mol/g cat h)	0.0066	0.0051	0.0040	0.0033	*
Diethylbenzene isomers (%)					
para	54.41	89.43	95.37	99.78	100
meta	45.08	10.57	4.63	0.22	0.00
ortho	0.51	0.00	0.00	0.00	0.00

Note. Temperature = 350°C; WHSV = 2.5 h^{-1}; EB: ethanol = 4 : 1; * = very low.

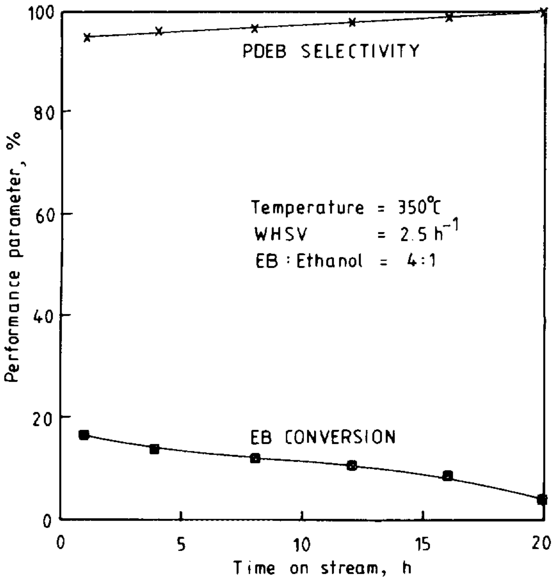

FIG. 1. Time-on-stream behaviour of 1% silica deposited on ZSM-5 zeolite.

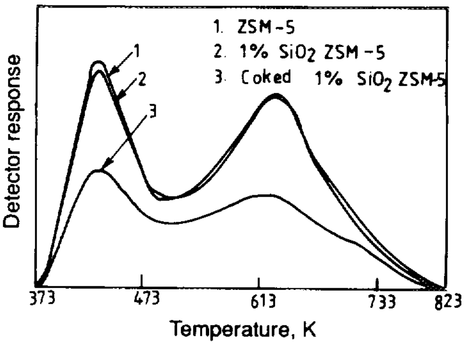

FIG. 2. TPD profiles of ZSM-5, silylated ZSM-5, and coked silylated ZSM-5 zeolites.

formation inside the channel, which affects the conversion and selectivity. The coke formation seems to be coming from the alcohol, which, being a smaller molecule than ethylbenzene, diffuses quickly inside the narrowed channel of ZSM-5 and participates in olefin formation. Further olefins oligomerize to coke precursors. This is in line with published information that finds that internal coke forms by the polymerization of small olefins (13).

An XPS study of coke distribution on ZSM-5 was made by Sexton *et al.* (14). This study provides strong evidence that on ZSM-5 coke fills the channel system initially before any significant amount of coke is formed on the external surface.

It has been reported by Derouane *et al.* (15) that when the pore system is constituted of interconnecting channels without cavities, like in HZSM-5, deactivation occurs initially through limitation of the access to the active sites, then through blockage of the access to the sites of the channel intersection in which the coke molecules are situated. Lastly, at high coke content coke molecules located on the outer surface of the crystallites can block access to the sites completely (16).

The acidity of the zeolite was measured by temperature-programmed desorption (TPD) and is presented in Fig. 2. The TPD profile consisted of a high and a low temperature peak corresponding to strong and weak acid sites. As silylation does not modify the internal structure, the total acidity and distribution of strong and weak acid sites remain the same. This is also evident from Fig. 2. Hence as soon as the alcohol enters the channel of silylated ZSM-5 it reacts readily on the strong acid sites and participates in coke precursor reaction with the result that the catalytic activity decreases and *para* selectivity increases due to the enhanced difference of diffusivity between *para* and *meta*-diethylbenzene. The coke is deposited continuously and ultimately deactivation occurs through limiting access to the active sites. At this juncture the catalyst shows negligible alkylation activity.

In order to stabilize the catalytic activity several methods were tried. Among the techniques which worked effectively was *in situ* coking of the zeolite. The *in situ* coking of the catalyst was done by contacting the catalyst with a known quantity of ethylbenzene vapor. The reactions taking place are ethylbenzene dealkylation to benzene and realkylation of ethylbenzene to diethylbenzene and a small quantity of ethylene. This ethylene will convert on the stronger acid sites to coke precursor. The

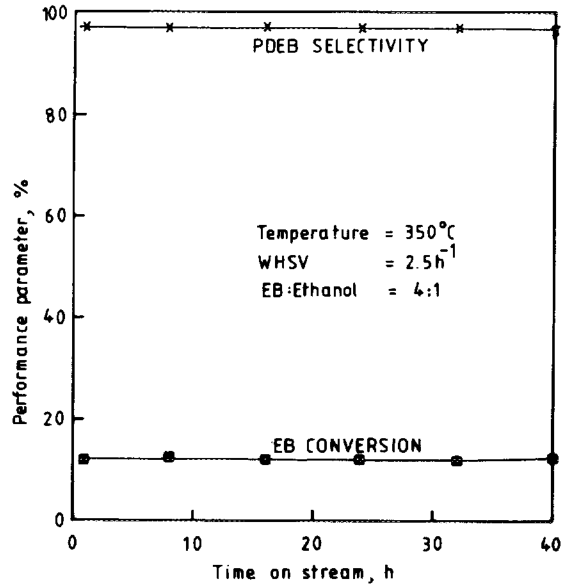

FIG. 3. Time-on-stream behaviour of coked 1% silica deposited on ZSM-5 zeolite.

extent of coke deposited is reflected by the distribution of diethylbenzene isomers. In the present case the catalyst was coked to achieve 97% selectivity of *para*-diethylbenzene. Soon after this ethanol was added along with ethylbenzene and alkylation was carried out. This catalyst shows steady activity in terms of consistent ethylbenzene conversion, 12 and 97% selectivity towards *para*-diethylbenze (Fig. 3). In other words, coking stabilizes the catalytic activity. This may be ascribed to the fact that coke suppresses some of the active sites leading to the decrease in total acidity. This is clearly evident in the NH_3 TPD results presented in Fig. 2. The total acidity of silylated zeolite before and after coking, in terms of equivalent millimoles of ammonia per gram of zeolite, was respectively 0.171 and 0.098. A combination of silica deposition by chemical vapor deposition and coking is a good technique for achieving *para* selectivity of ZSM-5 zeolite with extended time on stream.

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