Toluene ethylation over metallosilicates of MFI structure. Effects of acidity and crystal size on para-selectivity

P.A. Parikh, N. Subrahmanyam

Chemical Engineering Department, Faculty of Technology and Engineering, Kalabhavan,
The M.S. University of Baroda, Baroda 390 001, India

Y.S. Bhat and A.B. Halgeri *

Research Centre, Indian Petrochemicals Corporation Ltd., Baroda 391 346, India

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Toluene ethylation with ethanol over Al-MFI and B-, Fe-, Ga-isomorphously substituted zeolites of MFI structure was carried out. The acid properties of the metallosilicates increased in the order B < Fe < Ga < Al. This order is reflected in the activity of the zeolites in terms of toluene conversion. The separate effects of crystal size variation and acidity change by isomorphous substitution on para product selectivity have been established.

Keywords: Acidity; crystal size; ethylation; metallosilicates; para-selectivity

1. Introduction

Para substituted dialkylbenzenes serve as important raw materials for producing various polymers. As a result, a lot of attention is being given to the synthesis of para-ethyltoluene on zeolites of MFI structure. After dehydrogenation to para-methylstyrene, this compound can be polymerised to its polystyrene analogue which has got certain advantageous properties over polystyrene in terms of lower density, better heat resistance, faster moulding cycles, etc. [1].

Studies reported so far on toluene alkylation have been carried out on ZSM-5 with and without modifications. Kaeding et al. [2] have pointed out that the high para-selectivity on MgO, P_2O_5, B_2O_3 or SiO_2 modified ZSM-5 is due to higher

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* To whom correspondence should be addressed.

diffusivity of the para isomer than that of the other two isomers in modified zeolites. Paparatto et al. [3] had concluded that isomerization of para alkylated toluene proceeds on external surface sites and modification of zeolite suppresses the activity of external surface sites resulting in enhancement of para alkylated product selectivity. However, Kim et al. [4] and Lonyi et al. [5] have reported that the number of Brønsted acid sites decreases with zeolite modifications and that this decelerates the side reactions more effectively than the formation of primary product, para-ethyltoluene.

Acid properties of zeolites are modified by isomorphous substitution of Ga, Fe, B, etc. For Al [6,7] Kim et al. [6] have shown that para-selectivity is higher on zeolite with lower acidity. However, the role of crystal size was not considered by them. In order to establish the relationship between acidity and para-selectivity, experiments have to be carried out in the absence of crystal size effects. Influences of acidity and crystal size of metallosilicates on primary product selectivity in the alkylation reaction have not been reported so far. Keeping this background in view, the present study was aimed at differentiating the effects of variation of crystal size and acid properties by isomorphous substitution in MFI zeolite on para-ethyltoluene formation during toluene ethylation.

2. Experimental

Al-, Ga-, B-, Fe-MFI were synthesized by hydrothermal technique as reported earlier [7]. Atomic ratios of Si to metal were determined by atomic absorption spectrophotometry. The zeolites were characterized by X-ray diffraction for MFI structure, scanning electron microscopy for crystal size, ESCA for elemental detection and temperature programmed desorption of ammonia for acidity. All the zeolites were transformed into the H-form by exchanging three times with 1 M NH_4NO_3 followed by calcining at 773 K.

Alkylation of toluene with ethanol was carried out in a fixed-bed, continuous-flow glass reactor at atmospheric pressure. The feed mixture of toluene and ethanol was vaporized before it was contacted with the catalyst bed. Before collecting the data points used in this paper the zeolites were tested for 10 h to see the time on stream behaviour. The product samples, collected at time intervals of 1 h, were analysed in the gas chromatograph. No change in activity and selectivity with time on stream from the second to the tenth hour was observed. As there was no change in catalyst behaviour during the tested period of 10 h, the runs for data collection were carried out only for 6 h. The results presented are the average of second to sixth hour data. Analysis of product mixture was carried out in a Varian Vista 6000 gas chromatograph using a 50 m LB-550 capillary column.

3. Results and discussion

Table 1 summarizes Si/metal ratios and crystal sizes of metallosilicates. Activity and selectivity of various metallosilicates for toluene ethylation are presented in table 2. As it is evident from table 2, all zeolites have shown good ethyltoluene selectivity (90–94%). The conversion and selectivity terms referred to in table 2 are defined as

$$\%\ \text{toluene conversion} = \frac{\text{toluene consumed}}{\text{toluene fed}} \times 100,$$

$$\%\ \text{ethyltoluene (ET) selectivity} = \frac{\text{wt\% ethyltoluene in product}}{\text{wt\% toluene conversion}} \times 100,$$

$$\%\ \text{para-ethyltoluene } (p\text{-ET}) \text{ selectivity} = \frac{\text{wt\% para-ethyltoluene in product}}{\text{wt\% ethyltoluenes in product}} \times 100.$$

The thermodynamic composition of ethyltoluene isomers at reaction conditions is given in parentheses. The activity in terms of toluene conversion was highest with Al-MFI followed by Ga-, and Fe-MFI. This trend is in accordance with the acidity of metallosilicates (SC) as depicted in fig. 1. The acidity of zeolites decreases in the order Al-MFI > Ga-MFI > Fe-MFI > B-MFI. A similar trend was observed for metallosilicates having larger crystals. The selectivity for ethyltoluene was lower (90–91%) with metallosilicates of higher acidity whereas it was higher (94%) on metallosilicates of lower acidity. In other words, extent of side reactions was lower on zeolites of lower acidity.

The small crystals of Ga-, Fe- and Al-MFI gave para product concentration near thermodynamic equilibrium value. A small difference in these values may be attributed to slight variation in crystal size. This leads to a very important observation that the change in acidity by isomorphous substitution enhances para-selectivity only to a little extent. Without taking into account the effect of

Table 1
Crystal size, morphology and SiO_2 to M_2O_3 ratio of metallosilicates

Zeolite [a]		Crystal size (μm)	Morphology	SiO_2/M_2O_3
Al-MFI	(SC)	0.5–1	spheroidal	64
	(LC)	30	oblong	58
Ga-MFI	(SC)	2.5	spheroidal	54
	(LC)	20	oblong	62
Fe-MFI	(SC)	0.2–0.6	spheroidal	61
	(LC)	21	oblong	51
B-MFI	(LC)	20	cubic	50

[a] SC = small crystal, LC = large crystal.

Table 2
Catalytic performance of metallosilicates for toluene ethylation (623 K, 6.83/h, toluene/ethanol = 6)

Components (wt%)	Zeolite		
	Fe-MFI (SC)	Ga-MFI (SC)	Al-ZSM-5 (SC)
lighters	0.00	0.00	1.06
toluene	88.89	85.92	81.72
C_8 aromatics	0.00	0.00	0.51
p-ET	3.75	4.68	5.4
m-ET	6.60	7.77	10.1
o-ET	0.07	0.22	1.12
C_{9+} aromatics	0.00	0.00	0.09
tol. conv. (wt%)	11.11	14.08	18.28
ET selectivity (wt%)	94	90	91
ET composition (%)			
p- (33.43)	35.99	36.95	32.49
m- (49.70)	63.34	61.35	60.77
o- (16.80)	0.67	1.70	6.74

Table 3
Product distribution of toluene ethylation at a single temperature and comparable conversions over metallosilicates

Component (wt%)	Zeolites		
	Fe-MFI [a] (SC)	Ga-MFI [b] (SC)	Al-MFI [c] (SC)
lighters	0.57	0.40	1.27
toluene	90.83	91.89	91.58
C_8 aromatics	0.00	0.23	0.35
p-ET	3.42	2.53	2.28
m-ET	5.09	4.13	4.03
o-ET	0.09	0.07	0.09
C_{9+} aromatics	0.00	0.75	0.40
tol. conv. (wt%)	9.17	8.11	8.42
ET selectivity (wt%)	94	83	76
ET composition (%)			
p-	39.77	37.69	35.64
m-	59.19	61.32	63.02
o-	1.04	0.99	1.34

[a] 623 K, 8.53/h, toluene/ethanol = 6.
[b] 623 K, 9.60/h, toluene/ethanol = 6.
[c] 623 K, 12.00/h, toluene/ethanol = 6.

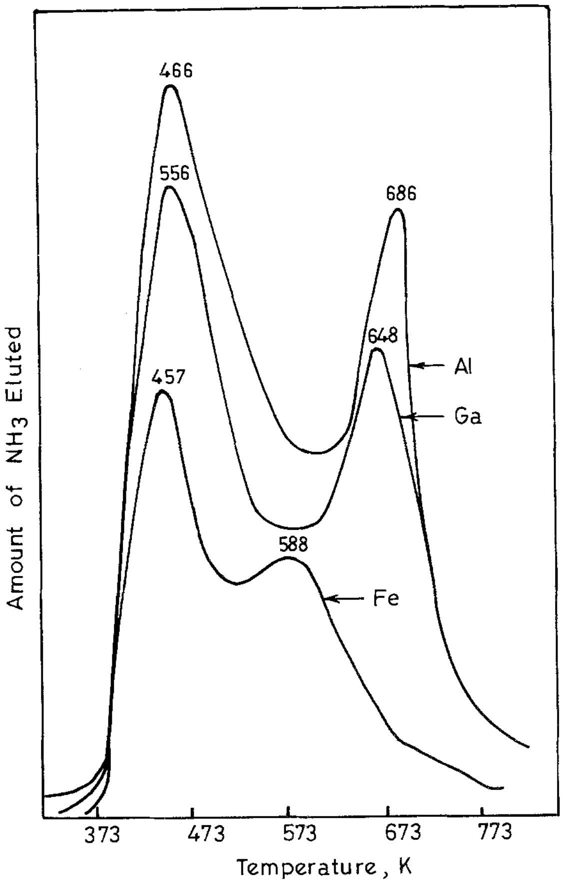

Fig. 1. Ammonia TPD of isomorphously substituted MFI zeolites (small crystals).

crystal size, Kim et al. [6] have shown that para-selectivity was more on metallosilicate having lower acidity.

The ortho alkylated product formation was very low on all the zeolites. This can be attributed to the fact that the alkyl group already present on the benzene ring sterically hinders the substitution of an ethyl group at the ortho position. This observation is in confirmation with that of Kim et al. [6] and Halgeri et al. [8].

It is always appropriate to compare para-selectivity of various zeolites at similar alkylation activity, i.e. toluene conversion, at a fixed temperature. Toluene conversion in the range of 7–9% was obtained by adjusting the space velocity for different metallosilicates and their performance is reported in table 3. Here again para-selectivities are comparable and follow the trend Al-MFI < Ga-MFI < Fe-MFI. In order to confirm this, experimental runs were carried out on larger crystals of Al-, Ga- and B-MFI zeolites. Details of the results are given in table 4. It is quite evident that para-selectivity is higher on all metallosilicates

Table 4
Performance comparison of large-crystal metallosilicates for toluene ethylation (623 K, 6.83/h, toluene/ethanol = 6)

Component (wt%)	B-MFI (LC)	Ga-MFI (LC)	Al-MFI (LC)
lighters	0.25	0.15	0.15
toluene	91.33	85.31	84.87
C_8 aromatics	0.00	0.27	0.26
p-ET	5.74	10.43	11.00
m-ET	2.38	3.67	3.62
o-ET	0.06	0.01	0.01
C_{9+} aromatics	0.25	0.16	0.09
tol. conv. (wt%)	8.67	14.69	15.13
ET selectivity (wt%)	94	96	97
ET composition (%)			
p-	70.17	73.90	75.19
m-	29.10	26.00	29.71
o-	0.73	0.10	0.10

irrespective of their acidity. With increasing crystal size, the number of sites on the external surface decreases which results in lowering of isomerization of the primary product of the reaction, para-ethyltoluene.

4. Conclusion

The results presented and discussed above lead to the following important conclusions: Variation in crystal size and change in acidity by isomorphous substitution affect the para-selectivity to different extents. With smaller crystal size the metallosilicates of different acidity showed an increase in alkylation activity with increase in acidity, while para-selectivity decreased in a narrow range. Metallosilicates of larger crystal size but different in acidity gave very high para-selectivity. Influence of crystal size variation on para-selectivity was much more than the change in acidity by isomorphous substitution.

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