Selective alkylation of alkylaromatics over HZSM-5 zeolite synthesised in fluoridemedium

Pushparaj Hemalatha, Kandan Venkatachalam, Mani Ganesh,
Peng Mei Mei, Joo Bo Lee, Hyun Tae Jang*
Department of Chemical Engineering, Hanseo University, Seosan-si 356 706, South Korea
*Corresponding author: htjang@hanseo.ac.kr

Fluoridemedium에서 HZSM-5 제올라이트를 이용한 알킬아로마틱의 선택적 알킬화

푸시파라지 헤마라다, 칸단 벤카타찰람, 마니가니쉬, 팽메이메이, 이주보, 장현태
한서대학교 화학공학과

Abstract

HZSM-5, synthesized in fluoride medium, showed high selectivity for the formation of 1,4-diethylbenzene (1,4-DEB) in the vapour phase ethylation of ethylbenzene (EB) with ethanol and hence becomes a convenient eco-friendly substitute for hazardous mineral acid catalysts. De-ethylation of EB to benzene was also minimized over this catalyst. As the medium pore size and presence of weak and medium acid sites might be the cause of such benefits, fluoride mediated synthesis of ZSM-5 is proven to be advantageous for *para*-selective alkylation of alkyl aromatics.

1. Introduction

Zeolite catalysts find applications in the field of petroleum refining and petrochemistry [1]. Among the zeolites, the medium pore ZSM-5 is important as it is extensively used in industries and production of fine chemicals. ZSM-5 zeolite was been synthesised with and without the aid of organic template. An unprecedented discovery in zeolite synthesis is the replacement of hydroxide ion mineralizer by fluoride. Several advantages have been reported for fluoride mediated synthesis [2] but there are disadvantages like occlusion of fluoride inside the cages [3] which reduces the acidity of proton [2] and reduces transport of aluminium from the gel to the framework due to formation of AlF_x^- species[4]. Incorporation of anadditional co-complexant(phosphate) to aluminium to compete with fluoride in the gel medium could be a cognizant solution to solve such problem. Hence in the present study it was one of the objectives to synthesise HZSM-5 in fluoride medium in the presence of phosphate and test its catalytic activity towards the vapour phase ethylation of ethylbenzene (EB) using ethanol as the alkylating agent.

2. Experimental

2.1. Synthesis of HZSM-5 (25, 50 and 75)

Synthesis of HZSM-5 with Si/Al = 25, 50 and 75 in fluoride medium was carried out using the reported procedure [2] along with the use of phosphoric acid. In a typical synthesis, appropriate amount of aluminum sulphate, 0.25 g phosphoric acid, 1.05 g tetrapropyl ammonium bromide, and water were mixed and stirred. To this solution, calculated amount of ammonium fluoride and tetraethylorthosilicate were added and then stirred for 3 h. The whole mother slurry was transferred

to a 100 ml Teflon-lined autoclave and hydrothermal crystallization was carried out at 170 ºC in an oven for 5 days. The crystallized product was recovered by filtration, washed repeatedly with water, dried at 110°C, and calcined at 550°C in air.

2.2. Catalyst characterization

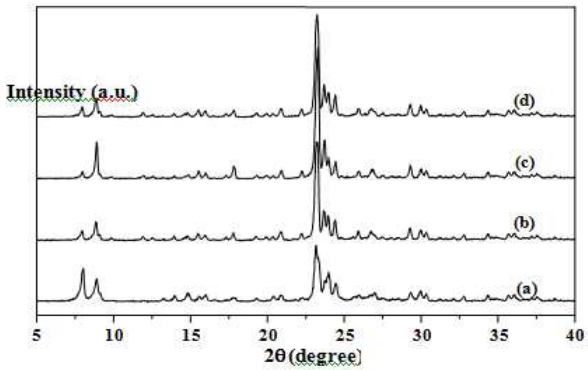
The X-ray diffraction (XRD) spectra were acquired on a PANalytical X'pert PRO diffractometer equipped with a CuKα (1.54 Å) radiation source and a liquid cooled germanium solid state detector. The samples were scanned from 5 to 40° (2Θ) in steps of 0.02 Å with a count time of 5 s at each point. The specific surface areas of the samples were measured by nitrogen adsorption at 77 K with a Micromeritics; ASAP 2420 instrument. Prior to measurements, the samples were heated for 4 h in vacuum at 400 ºC. The surface areas were determined by the Brauner-Emmet-Teller (BET) method. The morphology and size changes of the prepared zeolite crystals of the samples were studied by JEOL JSM 5600 scanning electron microscopy (SEM). The Si/Al ratio of the samples was determined using an energy dispersive X- ray analyzer (EDS) in the SEM chamber. The temperature programmed desorption (TPD) of ammonia was performed on a BELCAT-M catalyst analyzer. The sample cell was loaded with *ca.* 200 mg of the synthesized material and then heated in flowing helium at 500 °C for 2 h, followed by sorption of NH_3 at 100°C for 90min. Desorption of ammonia was done by purging with helium (80ml/min) atarate of 10°C/min from 100 to 500°C.

3. Results and discussion

3.1. Characterisation of HZSM-5 zeolite

3.1.1. XRD

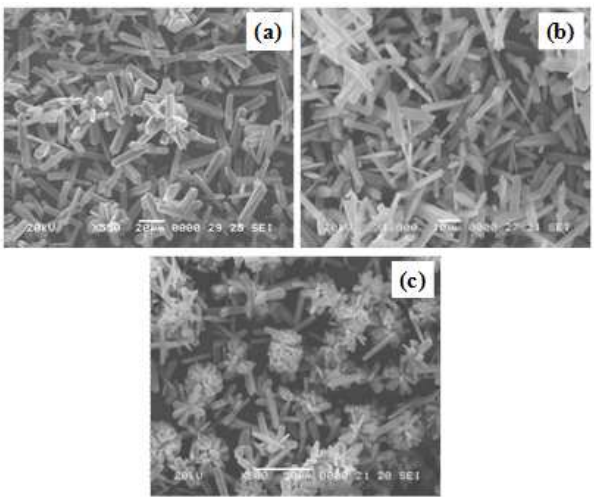
The XRD patterns of HZSM-5 (Si/Al = 25, 50 and 75) synthesized in fluoride medium and that of a commercial HZSM-5 (Si/Al = 25) are presented in Fig. 1. The intensities of the patterns of ZSM-5 synthesised in fluoride medium were higher than that of the commercial catalyst. This is due to the large crystal size, which was evident from SEM analysis, as discussed below. The intensities of the patterns at 2Θ = 7.92 and 7.98° were reversed compared to commercial catalyst.



[Fig. 1] XRD patterns of (a) commercial HZSM-5(25), (b) HZSM-5(25), (c) HZSM-5(50) and (d)HZSM-5(75)

3.1.2. SEM analysis

The SEM images of HZSM-5(25, 50 and 75) are shown in Fig.2. They showed elongated prismatic morphologies with sharp edges. However, their dimensions were not uniform. The crystals of HZSM-5(75) were slightly smaller than that of the others. Hence, the Si/Al ratios of the gel influenced the dimensions of the crystals. The tiny crystallites appeared over HZSM-5(75) reflect incomplete crystallisation.



[Fig. 2.] SEM images of (a) HZSM-5 (25), (b)HZSM-5(50)and(c)HZSM-5(75)

3.1.3. BET and EDS analysis

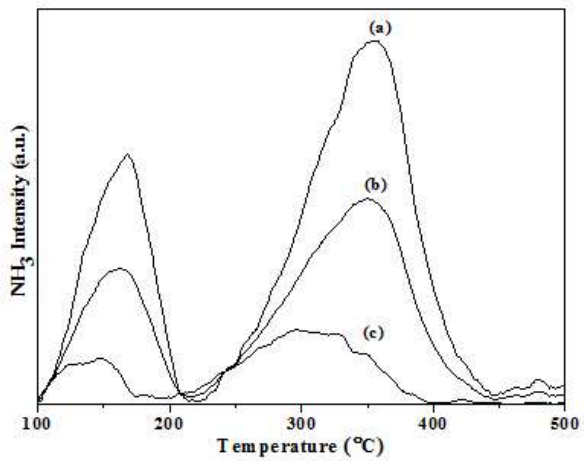
BET and EDS analysis results are presented in Table 1. The results illustrate that the synthesized materials possess high surface areas and pore volumes compared to the commercial HZSM-5. The Si/Al ratios of synthesised zeolites were slightly lower than the mother liquid. It clearly established the influence of phosphate on the AlF_x^- equilibria and in the transportation of aluminium from the gel to the framework.

3.1.4 TPD (ammonia)

The TPD (NH_3)resultsareillustratedin Fig.3. Only weak and medium acid sites with out strong acid sites were observed in all the catalysts whether phosphoric acid was used or not in the fluoride medium. Hence, phosphoric acid may not exert any effect on the acid strength of the catalysts.

Table 1. BET and EDS analysis results

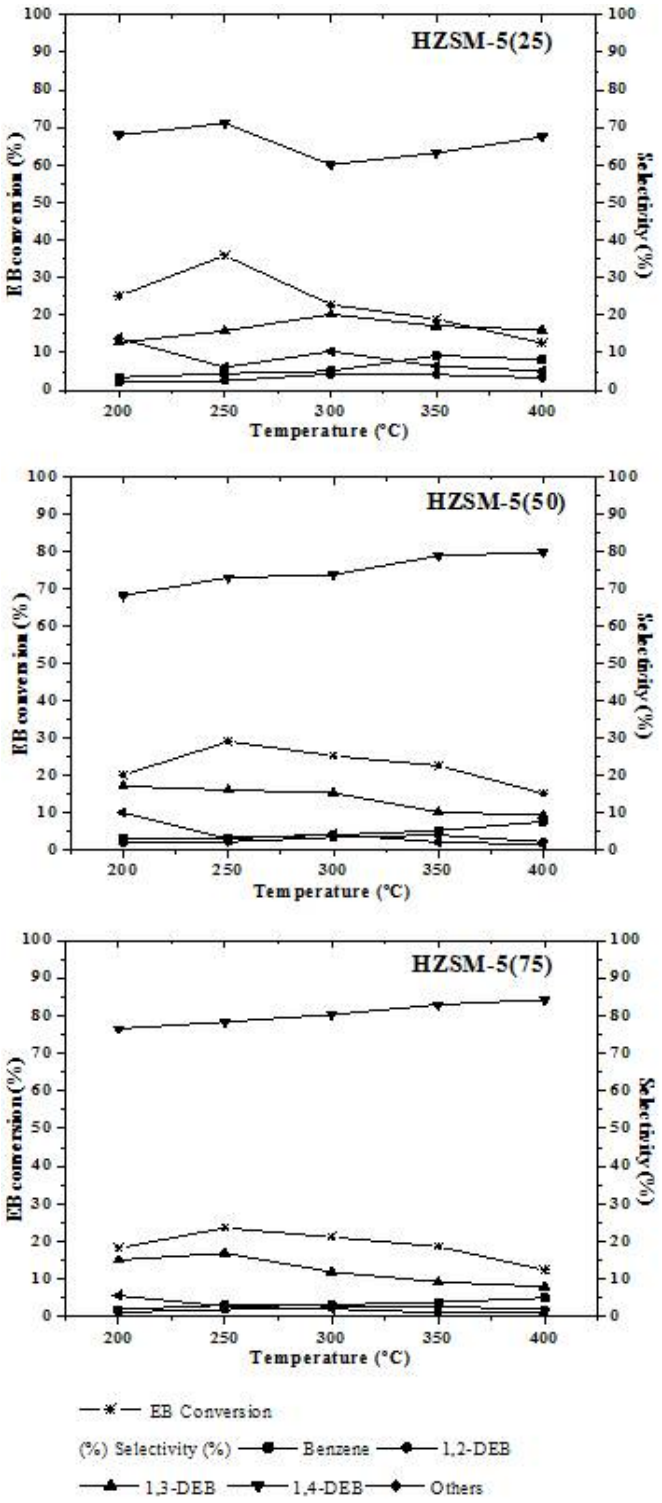
Catalyst	Si/Al (Mother liquid)	Si/Al (by EDS)	Atomic % (by EDS) Si	Al	O	P	Surface area (m^2/g)	Pore volume (ml/g)
HZSM-5(25) (Commercial)	25	-	-	-	-	-	430	0.163
HZSM-5(25)	25	22.0	14.7	0.7	84.6	0.0	750	0.259
HZSM-5(50)	50	38.0	21.0	0.6	78.5	0.0	790	0.280
HZSM-5(75)	75	52.7	20.0	0.4	79.5	0.0	634	0.214



[Fig. 3] TPD(ammonia) profiles of (a) HZSM-5(25), (b) HZSM-5(50) and (c) HZSM-5(75)

3.2. Catalytic activity

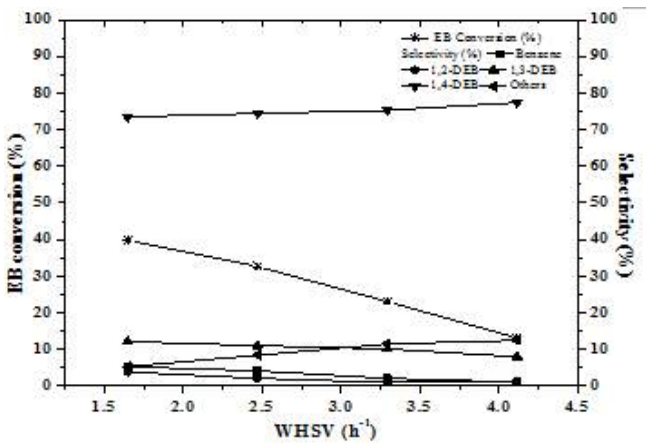
The results of effect on temperature on EB conversion and products selectivity are given in Fig.4. The EB conversion increased from 200 to 250 ºC and then decreased. The selectivity to benzene increased slightly as the temperature was increased from 200 to 350 °C, as dealkylation is an endothermic process.



[Fig 4] Effect of temperature on EB conversion and products selectivity

Among the diethylbenzene isomers, the selectivity of 1,4-diethylbenzene (1,4-DEB) was higher than others hence the optimum temperature was decided to be 250 ºC. HZSM-5(50) gave a higher selectivity for 1,4-DEB than HZSM-5(25), but less EB conversion. Similar results were also obtained with HZSM-5(75). Hence with the increase in the Si/Al ratio, the conversion decreased but selectivity of 1,4-DEB increased.

The effect of feed ratio study showed that at 1:2 feed ratio, the selectivity for 1,4-DEB was slightly higher than at 1:1, as the chance of isomerization might be slightly reduced due to enhanced blocking of the active acid sites by chemisorbed ethanol sites.. At 1:3 and 1:4 the conversion of EB decreased due to reduced accessibility of EB to the inside of the pore. So, 1:2 was chosen as the optimum feed ratio. The conversion decreased with the increase in WHSV due to reduced contact of reactants with the active sites (Fig.5). The selectivity for 1,4-DEB increased, as rapid diffusion suppressed isomerization to 1,3-DEB on the external acid The conversion and selectivity remained nearly the same for 6 h on stream. The absence of strong acid sites and the medium pore size of ZSM-5 might be the cause for the steady conversion without a high rate of blocking of acid sites by coke.



[Fig. 5.] Effect of WHSV on EB conversion and products selectivity

4. Conclusions

HZSM-5 zeolites, synthesized in fluoride medium, showed only weak and medium acid sites in their framework. Vapour phase ethylation of EB over these zeolites gave products with high selectivity for 1,4-DEB. As the selectivity for 1,3-DEB was less, there might be few external acid sites. Hence for selective alkylation to 1,4-dialkyl benzene products, catalysts without strong acid sites might be good, as they do not promote much isomerization of them to the more thermodynamically stable 1,3-DEB product. Hence, ZSM-5 zeolite synthesized in fluoride medium is a convenient substitute for mineral acid catalysts to make the alkylation process green and selective.

5. Acknowledgement

This study was supported by a grant (code CD3-201) from Carbon Dioxide Reduction & Sequestration Research Center, one of the 21st CenturyFrontierfundedbytheMinistryofSciencean dTechnologyofKoreanGovernment.

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