Alkylation of Ethylbenzene with Ethanol with Different Modified Catalyst

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ABSTRACT

Alkylation of Ethylbenzene with ethanol was done previously with conventional catalysts but they are not reusable and creating pollution. After wards zeolite was used instead of conventional catalysts. Here, describe the different modification techniques over Zeolites and there comparison among them.

Keyword : - *alkylation, zeolite, ethanol, ethylbenzene*

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1. Introduction

Alkylation is the transfer of an alkyl group from one molecule to another. Substitution of atom attached benzene ring by an alkyl group is called aromatic alkylation. Electrophilic alkylation reactions producing below listed chemicals required acid catalysts. Different types of the acid catalysts have been reported for the alkylation reactions [12]. They include Lewis acids (metal halides) which is electron pair acceptor to increase reactivity of a subtracte, Bronsted (protonic) acids, acidic oxides or sulfides, supported acids, acidic resins, etc. Common Lewis acids or Friedel – Crafts catalysts are based on main group of metals such as aluminum, boron, silicon, tin as well as many early titanium, zirconiumand late ion, copper, zinc d-blockmetals. Along with that $AlCl_3$, BF_3, BCl_3, $BBr3$, $BeCl_2$, $CdCl_2$, $ZnCl_2$, $GaCl_3$, $GaBr_3$, $FeCl_3$, $SbCl_3$, $BiCl_3$, $TiCl_4$, $ZrCl_4$, $SnCl_4$ andUCl_4, $SbCl_5$ are capable of attracting electrons from basic reagentmaking it active species to alkylate the aromatic hydrocarbons. $AlCl_3$ and BF_3 are widely used due to their low cost and easily availability. Similar use of protonic acids H_2SO_4, HF, HCl and H_3PO_4 either alone or in combination with Lewis acids forming conjugate super acids.

ZSM -5 Zeolite is the largely exploited catalyst in Petrochemical industries. Medium pore size, thermal and hydrothermal stabilities and strong acidity are some of the important characteristics for their main catalytic applications. The acidity can be tuned to desired extents altering by Si/Al ratios. This zeolite has been synthesized in alkaline medium and subjected to ion exchange to get H-form. Alkaline medium was reported to yield reduced crystallinity and surface area. In contrast, synthesis of ZSM-5 in fluoride medium was reported to yield large crystal size and high crystallinity2. High crystallinity precludes external acid sites which are commonly observed over ZSM-5, synthesized in alkaline medium [3].

Alkylation of Ethylbenzene with ethanol to the discovery of para – selectivity of zeolite catalysts preparation of p – diethylbenzene (PDEB) was achieved which is most desirable. In past, complex synthesis procedure has been required. High-purity PDEB has been prepared by reduction of p-ethylacetophenone and by selective sorption of the para isomer from an isomeric mixture. In the latter process, X or Y zeolites, containing barium and/or potassium, were used. The sorbed PDEB was displaced and diluted with toluene to give a mixture easily separated by distillation [1].

DEBs are the main source of manufacturing of the divinylbenzene. Small quantity of divinylbenzene add to styrene markedly modifies the liner styrene polymers. para – DEB isomer is used to desorb the para – xylene from isomeric C8 aromatic mixtures. Conventionally it is produce by reduction of the diacetophenone. Instead, it can be prepared by shape selective ethylbenzene with ethylene, ethyl chloride, or ethanol. Ethanol use as alkylating agent seems to be more interesting because of its huge industrial availability compare to other feed stocks.

In this paper we will report para – selectivity of Diethylbenzene with different modified catalysts, for ethylbenzene with ethanol.

2. Synthesis of Zeolite

Zeolites of the ZSM-5 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-5 and also triethanolamine (TEA) which is able to template the ZSM-5 framework cystallization, too. The products were filtered, washed free of extraneous salts with water, and dried at 20 ºC for 15 hr. These samples ("as made" form) were transformed into the acid form by calcining them at 540 ºC for 10 hr 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 540 ºC for 2 hr, and, only for the alkylation reaction, grinding them to 18-60 mesh. To compare with zeolites, an amorphous commercial SiO_2-$A1_2O_3$ (Akzo La- 3P) was used as catalyst in both reactions [6].

3. Modification of prepared zeolite

3.1 Modification with toluene methanol pre -coking

To avoid any interference with carbonaceous residues formed isomerization of HZSM-5 coke deposits from methanol conversion were used as pre-coke species on both nano-sized zeolites under study. After loading with methanol vapor at room temperature for 12 hr, pre-coking of HZSM-5 was performed in N_2 under static conditions at 450 ºC for 2 hr. Subsequently, these pre-coked samples were further subjected to a coke modification treatment with H2 at 460 ºC for 24 hr. The final coke content of both zeolites was about 0.5 wt% as determined by thermogravimetric and elementary analysis. Silanization treatments of HZSM-5 was carried out by chemical liquid deposition of TEOS while suspending the zeolites in acetone. For each run, silane hydrolysis was accelerate and accomplished by adding the stoichiometric amount of water acidified by maleic acid. The slurry was refluxed for 1 hr. After the withdrawn of acetone, the sample was calcined by heating to 550 ºC. As the result, the silanized zeolites were found to possess a SiO2 coverage of about 4 wt% [4].

3.2 Modification with Maganesium

ZSM – 5 type zeolite was synthesized by a similar method to that describe in mobil's patent usin tetrapropylammonium bromide, sodium silicate, aluminum sulfate, sulfuric acid and sodium chloride. The synthesized zeolite was calcined at 500 ºC for 3 hr in air. Its sodium cation was exchanged for proton by using mol dm $^{-3}$ hydrochloric acid at 60 ºC. The HZSM -5 (si/Al = 96) modified with magnesium oxide, designated as Mg – HZSM – 5 was prepared by impregnation of HZSM -5 with aqueous magnesium acetate solution followed by drying at 100 ºC and calcined at 550 ºC for 18 hr in an air stream. The weighted catalyst was set in a quartz reactor and dehydrated at 823 K for 1 hr in hydrogen before use [5,8-12].

3.3 Modification with Phosphorus

Modified zeolites, P – ZSM – 5 zeolite (60.5 g) having a crystallite size of approximately l-2 µm containing 35 wt% alumina binder, in the form of 1/16 in. extrudate, was steamed at 600°C for 1 h. It was thereafter impregnated with a solution of 38.7 g of diammonium acid phosphate in 100 ml of water, dried, and calcined at 500°C overnight in an open dish. The resulting product was cooled and impregnated overnight with a solution of 195 g aqueous phosphoric acid solution in 133 ml of water, dried, and calcined at 500°C for about 19 h. The final catalyst contained 3.48 wt% phosphorus, probably present as their corresponding oxides [1,8-12].

3.4 Modification with Boron

ZSM – 5 type zeolite was synthesized by a similar method to that describe in mobil's patent usin tetrapropylammonium bromide, sodium silicate, aluminum sulfate, sulfuric acid and sodium chloride. The synthesized zeolite was calcined at 500 ºC for 3 hr in air. Its sodium cation was exchanged for proton by using mol dm $^{-3}$ hydrochloric acid at 60 ºC. The HZSM -5 (si/Al = 96) modified with boron, designated as B – HZSM – 5 was prepared by impregnation of HZSM -5 aqueous boric acid solution followed by drying at 100 ºC and calcined at 550 ºC for 18 hr in an air stream. The weighted catalyst was set in a quartz reactor and dehydrated at 823 K for 1 hr in hydrogen before use [5,8-12].

3.5 Modification with silica vapor deposition

Surface modified, silylated samples were prepared by chemical vapor deposition of silica (Si-CVD), using TEOS as the silylation agent, following the procedures reported earlier. Pelletized parent HZSM5 zeolite (10–20 mesh; ca. 4 g) was first packed into a home-built reactor, followed by calcination at 723K in air (flow rate 100 ml/min) for 8 h, then brought to 413K under stream of N2 gas (100 ml/min). Silylation treatment of samples were conducted by passing mixture of 4 wt.% TEOS in
toluene through the catalyst bed at 413K under N_2 carrier gas (12 ml h−1) for various deposition time (*t*d), subsequently followed by calcination in flowing air (100 ml/min) at 823K for 4 h. The effectiveness of the treatment was monitored by analyzing the residual TEOS in the reactor effluent at various *t*d. Accordingly, samples with varied amount of deposited SiO2 were obtained (Table 1). They are identified by Si/HZSM5 followed by the duration of deposition *t*d, for example, Si/HZSM5-6 means the parent (HZSM5) zeolite was modified by one Si-CVD cycle for *t*d = 6 h. A sample modified with two Si CVD treatment cycles (denoted as Si/HZSM5-6/2) was prepared by a sample first silylated by one Si-CVD cycle with *t*d = 6 h, calcined and subsequently followed by second Si-CVD treatment for additional 2 h (i.e. *t*d = 6 + 2 h) and the calcination treatment [7].

4. APPARATUS AND PROCEDURE

Experiments were carried out in a continuous – flow fixed bed reactor. The amount of the catalyst used in the reaction was around 2.0 g of 0.3 to 0.5 mm particles size. The loaded catalyst was pre- heated with air stream at 540 ºC for 2 hr. then a nitrogen stream was applied for 30 min to sweep out any residual air. Ethylbenzene and ethanol was delivered by syringe or metering pump along with hydrogen as carrier gas. The flow rate was measures and controlled by a mass flowmeter. In case of alkylation of ethylbenzene with ethanol, the mixture of EB and ethanol around 5 to 10 mol was deliverd by metering pump to vaporizer. The composition of the reactants and products were analyzed by gas chromatography.

5. DISCUSSION

Post synthetic modification of HZSM – 5 zeolites by pre – coking and silanization has been performed to enhance the selectivity of catalysts maintaining high reaction rates. For HZSM – 5 pre – coking treatment was found to facilitate selective passivation external acid sites in MAS NMR measurements. The decreased proportion of strong surface acid sites on the pre-coked HZSM-5 sample is consistent with the desired reduction of toluene.

The HZSM -5 loaded with oxide of magnesium, phosphorous or boron showed much higher selectivity for paea – diethylbenzene formation than the parent HZSM -5 catalyst as observed in the alkylation of toluene with methanol. On Mg – HZSM -5 the fraction of p – diethylbenzene increases and the conversion of ethylbenzene decreased with increased the amount of magnesium added. It reaches maximum 6 wt% of magnesium.

On P – HZSM -5 the fraction of diethylbenzene increased to 100% with increasing amounts of phosphorous up to 10 wt%. However, the conversion of ethylbenzene and the yield of diethylbenzene decreased notably with increasing amount of phosphorus, suggesting that the zeolite channels were rigoriously bloacked with phosphorous oxide and / or that the aacid sites on the zeolite disappeared on the additional phosphorous oxide.

On the B- HZSM -5, the fraction of p – diethylbenzene increased with increasing amounts of boron added, as well as magnesium and phosphorus. However, on B(10) HZSM -5 the fraction of p-diethylbenzene was 100% at a conversion of ethylbenzene and high activity. It is shows an extremely high para – selectivity compared with p –

HZSM – 5 and MG- HZSM -5. The activity and the para – selectivity of Mg – HZSM -5 and P – HZSM – 5 catalyst did not change with process time. However, in case of B – HZSM – 5 ,the conversion of ethylbenzene and the yield of diethylbenzene increased with process time, while the fraction of para – isomer in the diethylbenzene produced slightly decreased. This suggests the boron emerged from the catalyst system during the process time. Modified HZSM – 5 gives higher selectivity than parent HZSM -5.

The effects of coking and surface modification of HZSM5 zeolites on the performance of *para*-selective process during disproportionation of EB have been investigated by the correlation between conversion and *p*-DEB selectivity. While a slight increase in extra-framework Al was found during Si-CVD treatment, they have negligible effect during the *para*-selective process. Precluding such dealumination effect, surface silylation treatment effectively inactivate the external active sites without changing the internal acidity or the adsorption capacity and effective free volume of the zeolites. The *p*-DEB selective process for the unmodified HZSM5 samples is strictly kinetic control at low conversion. For Si-CVD modified samples, EB conversion was found to decrease with increasing coke content, which also favor the *p*-DEB selectivity enhancement regardless of the surface SiO_2 content. At a given conversion, notable increase in *p*-DEB selectivity with increasing SiO_2 content was observed. Coke deposits, which are found to locate mostly in the intracrystalline defect sites of the zeolite, play only a minor role during the *para*-selective process compare to inactivation of external active sites by silylation. Similar conclusion can be made for sample modified by surface adsorption of lepidine. Moreover, cyclic Si-CVD treatment of the zeolite sample was found to provoke non-selective deposition of silica on the external surface that create additional steric constraints for the DEB isomers to diffuse out of the channels, consequently, a leap increase in *p*-DEB selectivity was observed. Thus, inactivation of external active sites and diffusion limitations both play the decisive role in the enhancement of *para*-selectivity during disproportionation over HZSM5. Substantial inactivation of surface active sites is inevitable in provoking substantial relative increase in *p*- versus *m*-DEB diffusivity and thus, in turn, promoting the desirable *para*-selectivity enhancement.

6. References

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