Short communication

Conversion of levulinic acid to BTX over different zeolite catalysts

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1. Introduction

Currently, the majority of the aromatics (BTX) production uses fossil sources, and is based on catalytic reforming and naphtha pyrolysis [1]. Recently, a few sustainable approaches were identified and one such option is to produce BTX from biomass using heterogeneous catalytic processes [1,2]. Particularly, lignocellulosic biomass is identified as economically viable and carbon neutral feedstock for the production of biofuels and chemicals through heterogeneous catalytic routes [3,4,5].

Levulinic acid has been identified as a promising biomass-derived chemical, whose production is economically viable, by the higher yield- ing acid hydrolysis of lignocellulosic biomass [6]. Many companies such as Biofine [7], DSM [8], Segetis [9] and GF biochemicals have developed the technology based on this concept. GF biochemicals started the world’s largest commercial production of levulinic acid in 2015 at a production scale of 2000 MT/a in Caserta, Italy [10,11]. Several reviews have been published describing the potential industrial applications of LA [12–14]. However, the use of LA as raw material for the production of BTX is still not well explored, especially through heterogeneous routes.

Catalytic pyrolysis of biomass using zeolite catalyst is considered as one of the most promising technology to produce BTX [15], however, through pyrolysis, it is difficult to control the selectivity and yield of different products. Tsutsui et al. have investigated the conversion of levulinic acid to BTX over ZSM-5 zeolite [16]. It can be expected that the interplay of chemical and textural properties of zeolites controls their performances in the conversion of LA to BTX [17]. In particular, BTX selectivity is a result of size, shape and connectivity of zeolite channels together with the concentration, type, and location of active sites.

Therefore the selection of the zeolite with a specific composition possessing required acid site density and strength, structure and pore size distribution for optimal transport of molecules is needed to achieve high aromatic yields.

The relationship between textural and chemical parameters and catalytic performance of zeolite in any catalytic reaction is of critical importance for the performance of such zeolite catalyst. Generally, reaction parameters can be divided into 2 groups: i) variables of catalytic reaction (reaction temperature, space velocity, concentration and molar ratio of reactants, and thermodynamic equilibrium), and ii) properties of the zeolite catalysts (channel size and dimensionality of the channel system, type and strength of acid sites, their location and density, as well as the rate of coking). We undertook the study to explore the impact of i) amount of acid sites and its strength ii) pore size and iii) pore geometry on the conversion of LA and selectivity to BTX. The effects of catalyst loading, reaction temperature, and reaction time on the formation of BTX were also investigated.

2. Experimental

Zeolite supports with SiO₂/Al₂O₃ ratios in the range 23–280 were procured from zeolyst and their structural properties are given in Table 1.

The acidity of catalysts was measured by NH₃-TPD by using a BELCAT-B system (BEL Japan, Inc.). Each sample (100 mg) was loaded into a quartz tube and preheated at 550 °C for 1 h in 50 ml/min He flow. The sample was then allowed to cool to 50 °C and saturated with 5% NH₃/He gas mixture at a rate of 50 ml/min for 1 h and then purged at 50 °C for 0.5 h with He gas. Desorption of NH₃ was carried out by increasing the temperature from 50 to 700 °C at 10 °C/min rate under
order: ZSM-5(25)

30 ml/min He flow and measured using an on-line thermal conductivity detector.

Catalytic reactions were carried out at atmospheric pressure in a fixed-bed, continuous-flow reactor equipped with a quartz tube using 0.5 g of catalyst pellets. The catalyst was activated at 500 °C for 30 min and cooled to 450 °C in N₂ (50 ml/min) and then the N₂ gas is changed to H₂ flow (30 ml/min) and kept for 30 min before starting the reaction. A mixture of LA (98% assay purchased from Alfa Aesar) and water (50/50 wt%) mixture was pumped into the vaporizer maintained at 300 °C at a rate of 0.025 ml/min and driven through the catalyst bed by hydrogen at a flow rate of 30 ml/min. The reaction is carried out for 2 h. The product gas is collected in a gas bag and analyzed by online gas chromatography (Shimadzu GC-14A) with FID and TCD detectors equipped with RT-Alumina bond column and Shin carbon ST column respectively. The condensed liquid products are analyzed by gas chromatography (Shimadzu GC-14B) with FID equipped with capillary column DB-WAX using biphenyl as the internal standard material.

The yield of solid bio-char was determined by thermogravimetric analysis (TGA) and derivative thermogravimetric (DTG) using a Seiko instruments EXSTAR 6000 with 10 °C/min heating rate from 20 °C to 800 °C in air with a 200 ml/min flow rate. Approximately 20 mg of the used catalyst was loaded in an alumina crucible.

3. Results and Discussion

Catalytic conversion of levulinic acid over different zeolites was carried out at 450 °C for 2 h. Uncatalyzed, empty reactor showed 72% of LA conversion which is assignable to the thermal cracking of LA molecules. The main liquid products of the uncatalyzed LA conversion are benzene, indane, naphthalenes, methyl benzenes (1, 2, 4 TMB and 1, 3, 4 TMB) and others (C9 and C10 hydrocarbons). The desired products toluene and xylene yields are less than 1%. More than 97% LA conversion is achieved over all the zeolites catalysts. The BTX formed under inert (absence of catalyst) and in the presence of zeolite catalysts are shown in Fig. 1. Among the different catalysts tested, ZSM-5 showed the highest BTX (24%) yield. The yield of BTX formation was found to be in the following order: ZSM-5 (25%) > FER (23%) > MOR (16%) > HY (13%) > Beta. Along with BTX, the other major products observed were nonane, ethylbenzene, ethyltoluene, indane, g-valerolactone, naphthalene, indene, 1,3,5-TMB and 1,2,4-TMB and C8, C9 and C10 hydrocarbons and other unidentified products.

In the presence of acid zeolites, LA can be deoxygenated and cracked. Deoxygenation may involve decarbonylation, decarboxylation, and dehydration which produce hydrocarbons, water, and carbon oxides. Cracking will give various carbon fragments which undergo oligomerization to produce a mixture of C2-C6 olefins [18]. These olefins undergo a series of reactions to produce different aromatic hydrocarbons [19,20]. Aromatization involves cyclization and hydrogen or hydride transfer. Some aromatics are polymerized to tar eventually to coke.

NH₃-TPD was carried out to identify potential correlations to the amount, strength and distribution of the acid sites and the selectivity to BTX (Fig.2). The curves corresponding to FAU and BEA display a desorption peak at relatively low temperature (below 200 °C), whereas FER, ZSM-5, and MOR shows two peaks one at a lower temperature (corresponding to weak acid sites) and another at a higher temperature (corresponding to strong acid sites). Among all the catalysts, ZSM-5 possesses the maximum number of weak and strong acid sites and produced maximum BTX yield of 24%. However, no straightforward relationship was observed among other zeolites acidity and BTX yield. For example, FER though possesses high amount of acidity showed the least selectivity for xylenes and formed mainly benzene. Due to the relatively smaller pores and unfavorable single file diffusion of larger LA molecule in FER, it is expected that significant amount of reaction in FER take place on the external acidic sites. Furthermore, if acid sites would be considered as decisive for achieving high BTX yields zeolite Beta possessing the much higher amount of acid sites compared to HY should provide the higher BTX yield, however, the BTX yield over beta is lower than HY. These results clearly show that the conversions LA to BTX cannot be directly related to the acidity of the zeolite catalyst.

Comparison of the kinetic diameters of the reactant and products directed that the majority of the aromatic products and the reactants can fit inside the zeolite pores of medium and large pore zeolites (Table 1). Among different catalysts, having different pore structures, medium pore zeolite ZSM-5 with three-dimensional pore structure showed the highest BTX yield of 25% at 450 °C. The high BTX selectivity over ZSM-5 is probably due to the good match between size and shape of the cage and the product size range. The small pore zeolite (FER) with one-dimensional structure also produced aromatics but mainly produced benzene and methyl benzenes as the major products. The lower yield of toluene and xylenes with a molecular size of 5.7 Å and 5.8–6.8 Å over FER with a pore size of 4.5 × 5.5 Å compared to ZSM-5 can be attributed to diffusional limitation. ZSM-5 with 10 ring windows of 5.4 × 5.6 Å diameter and three-dimensional structure allows the diffusion of reactant LA and products benzene, toluene and xylenes but
with different diffusional rates [21]. On the other hand, FER having relatively narrower pore and window size typically having single file diffusion of the molecule, did not allow the formation of xylenes. In the case of large pore zeolite, the primary reason for the lower activity compared to medium pore ZSM-5 and small pore FER is that larger pore size and void reaction volume leads to faster deactivation, which is clearly visible for Beta and HY zeolites. In contrast, medium pore ZSM-5 and small pore FER exhibited some stability against coking.

In addition to pore size, internal pore space and pore geometry also play a role in aromatics production and coke formation. Coking which is controlled by the pore structure and acidity of zeolites is a shape selective reaction. The medium pore ZSM-5 with moderate internal pore space and steric hindrance due to the three-dimensional geometry gave highest aromatic yield and the least amount of coke. In FER presence of acid sites inside the narrow pores and in small spaces and also the single file diffusion which restricts the degree of polymerization led to the least coke formation among the zeolites studied. High coke yield as determined by TGA and low aromatic yields were observed with large pore zeolite beta and HY both with three-dimensional structures, suggesting that the large pores with three-dimensional pore geometry facilitate the formation of coke.

BTX can easily diffuse into the channels of all the large-pore zeolites such as Beta, MOR, and HY. The large pore size and pore volume in large pore zeolites (Beta, HY, MOR) allows easy alkylation of aromatics and these alkylaromatics cyclize or condense into polycyclics, which eventually dehydrogenate to coke. However, the diffusion of bulkier molecules such as 1,2,4-TMB and 1,2,4,5-tetramethylbenzene (1,2,4,5-TeMB) in these zeolites varies, these molecules can more easily diffuse into/out of the pores of MOR zeolite than of Beta and HY due to one-dimensional channel structure compared to three-dimensional structure of Beta and HY [22]. The faster diffusion of 1,2,4,5-TeMB in MOR than in USY and Beta indicates that bulky aromatic molecules can rapidly diffuse out of the MOR and HY channels more easily compared to beta zeolite, consequently, decreasing the coking rate and increasing the catalytic stability. Thus in addition to the size pore window, the steric hindrance of reacting molecules inside zeolite pores plays a role in this reaction.

Based on above results it seems that the aromatic yield and coke formation is a function of the pore size, pore volume and pore geometry of the zeolite catalyst.

In order to differentiate the effect of acidity and size of the pore on the production of BTX, ZSM-5 with different SiO$_2$/Al$_2$O$_3$ ratio was evaluated. The total number of acid sites decreased linearly with increase in the SiO$_2$/Al$_2$O$_3$ ratio of the zeolite (Fig. 1) and the catalytic activity followed the same trend (Fig. 3). ZSM-5 with SiO$_2$/Al$_2$O$_3$ ratio 23 with a maximum number of weak and strong acid sites showed the highest 25% BTX yield. The increase of aromatic yield with the decrease in SiO$_2$/Al$_2$O$_3$ could be due to an increase in density of acid sites in the catalyst with a low silica-to-alumina ratio. The above results indicate that a good combination of acidity and pore size is required to activate levulinic acid and its subsequent conversion to desired aromatics.

The effect of various reaction parameters such as temperature, catalyst amount and reaction time over HZSM-5 zeolite (SiO$_2$/Al$_2$O$_3$ = 23) was studied for obtaining the maximum BTX yield. The conversion of LA to BTX under different reaction temperatures (400–550 °C) is shown in Fig. 4. The BTX yield increased from 16 to 28% with the increase in temperature from 400 to 500 °C. Further increase in reaction temperature to 550 °C slightly decreased the BTX yield and this could be due to secondary cracking of products formed, giving a slight decrease of BTX yield from 28% at 500 °C to 26% at 550 °C. As the temperature is increased from 400 to 550 °C, the selectivity to benzene was decreased from 9 to 4%, while the selectivity for toluene increased from 2 to 9% and xylenes increased from 5 to 15%. This is probably due to initial cracking and diels–alder reaction taking place at low temperature leading to the formation of alkenes which combine to form benzene, toluene, and xylenes [23]. Huber and Corma [24] noticed that this aromatization may proceed via the diels–alder reaction in which olefins obtained by cracking combine with each other, forming cyclic and aromatic compounds.

The effect of varying feed rate of levulinic acid on BTX formation is shown Fig. 5. The maximum conversion of 31% is observed at a feed rate of 0.035 cm$^3$/min. On further increasing the feed rate to 0.05 cm$^3$/min showed a decrease in BTX yield to 28%. It is noticed that the high feed rate or low contact times results in the formation of more benzene and fewer xylenes. In order to optimize the catalyst amount for obtaining the high BTX yield, the reaction was carried out by varying the amount of catalyst from 0.05 g to 1 g and keeping constant the
other experimental conditions (Fig. 6). The BTX yield increased from 24% to 27% firstly with the increase of the catalyst amount from 0.5 to 0.75 g. However, higher catalyst amount of 1 g led to a slight decrease in BTX yield.

4. Conclusions

In the present endeavor, we have been trying to see the impact of 1) acidity, ii) pore size, iii) pore volume, iv) and pore geometry on the conversion of LA to BTX and coke formation. Among all the catalysts, ZSM-5 possesses the maximum number of weak and strong acid sites and produced a maximum BTX yield of 25%. However, no straightforward relationship was observed among other zeolites acidity and BTX yield indicating that pore size and pore structure are more important than acidity. ZSM-5 with three-dimensional pore geometry and moderate internal pore space gave the highest BTX yield and least coke. Large pore beta and HY with three-dimensional pore geometries gave lower BTX yields and high coke formation compared to MOR with one-dimensional pore geometry. Thus, by the proper choice of zeolite topology, it is possible to obtain excellent yield of BTX from LA.

References