Applied Catalysis B: Environmental 235 (2018) 45–55

Contents lists available at ScienceDirect

Applied Catalysis B: Environmental

journal homepage: www.elsevier.com/locate/apcatb

Catalytic pyrolysis of crude glycerol over shaped ZSM-5/bentonite catalysts for bio-BTX synthesis

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ARTICLE INFO

Keywords:
Bio-aromatics
Glycerol
ZSM-5
Bentonite
Pyrolysis

ABSTRACT

Ex-situ catalytic pyrolysis of crude glycerol for the synthesis of bio-based benzene, toluene and xylenes (bio-BTX) was performed in a tandem micro-reactor (TMR), a batch gram scale reactor and a continuous integrated bench scale unit using ZSM-5/bentonite extrudates. A bio-BTX yield of 8.1 wt.% (14.6% carbon yield) based on crude glycerol was obtained over the fresh catalysts (Cat-F) in the bench scale unit (crude glycerol feed rate of 200 g h^{-1}, pyrolysis temperature of 520 °C and catalytic upgrading temperature of 536 °C). Catalyst activity was shown to be a function of the time on stream (TOS) and after 4.7 h the activity dropped with about 8%. After an oxidative regeneration step to remove coke, the activity of the regenerated catalysts (Cat-R1) was recovered to 95% of the original catalyst activity. After 11 reaction-regeneration cycles, the bio-BTX yield decreased to 5.4 wt.% (9.7% carbon yield) over Cat-R11. The fresh, deactivated and regenerated ZSM-5/bentonite catalysts were characterized in detail using nitrogen physisorption, XRD, ICP-AES, EA, TEM-EDX, TGA, NH_3-TPD, pyridine-IR and solid MAS NMR. Coke (10.5 wt.% over Cat-D) was mostly deposited on ZSM-5 planes, and not only decreased the number of Lewis and Brönsted acid sites, but also blocked the pores, resulting in catalyst deactivation. Coke removal was effectively performed using an oxidative treatment. However, exchange of cations (*e.g.*, Na) of the bentonite and possibly also from the crude glycerol feed with protons of ZSM-5 was observed, leading to irreversible deactivation. Furthermore, the layered structure of bentonite collapsed due to the removal of interlamellar water and dehydroxylation.

1. Introduction

The biodiesel industry has grown substantially in the last two decades [1]. However, its production inevitably leads to the formation of glycerol (*ca.* 10% (wt./wt.)). The worldwide crude glycerol production is expected to grow further to 6 million ton in 2025 [2]. The identification of high value applications of glycerol would significantly improve the profitability and sustainablity of the biodiesel industry.

Glycerol has been recognized as an interesting 'green building' block for the chemical industry. Various examples [3,4] have been reported for the conversion of glycerol by oxidation, hydrogenolysis, dehydration, esterification/etherification, pyrolysis/gasification and steam reforming, *etc*. In addition, glycerol pyrolysis has also been studied in detail. Thermogravimetric analysis (TGA) revealed that pyrolysis products are generated at temperatures between 150 and 500 °C [5]. Thermal (non-catalytic) pyrolysis of glycerol mainly leads to the formation of non-condensable gases (*e.g.*, H_2, CO, CH_4 and C_2H_4) when performed at relatively long residence times (*e.g.*, 22 s) [6] and condensable gases (*e.g.*, acrolein and acetaldehyde) using very short residence times (*e.g.*, 0.1 s) [7].

An interesting option is the conversion of glycerol using catalytic pyrolysis to produce bio-based low molecular weight aromatics (benzene, toluene and xylenes, termed as bio-BTX), which are intermediates for the synthesis of a wide range of polymers. This may be achieved by using both *in situ* and *ex-situ* approaches. In the latter case, proper catalysts are used to upgrade the glycerol pyrolysis vapors. It has been shown that glycerol is first dehydrated into oxygenates (mainly acrolein and acetaldehyde), followed by a series of acid-catalyzed aldol condensation, dissociation, cyclization and oligomerization, *etc*., to form aromatics [6–10]. Hoang *et al.* [11] were the first to report on the catalytic pyrolysis of glycerol over a series of zeolites in a fixed bed reactor. It was shown that aromatics are favorably formed on zeolites with three-dimensional medium sized pores (*e.g.*, ZSM-5, BTX carbon yield of 7.4%). Lowering the SiO_2/Al_2O_3 mole ratio, leading to higher Brönsted acidity, favored aromatization [9] resulting in a higher BTX yield [9,12]. However, simultaneously, the hydrophilicity is also

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https://doi.org/10.1016/j.apcatb.2018.04.047
Received 28 December 2017; Received in revised form 1 April 2018; Accepted 18 April 2018
Available online 21 April 2018

increased which inhibits acid-catalysed dehydration reactions [9]. A maximum BTX yield was obtained using ZSM-5 with a SiO_2/Al_2O_3 mole ratio of 30 [9,12]. The co-feeding of H_2, which is referred as catalytic hydro-pyrolysis, has a positive effect on BTX yields. For instance, carbon yields of 18.1% over a tandem Pt/ZnO and ZSM-5 catalyst [11] and carbon yields of 42.9% over bi-functional Pd/ZSM-5 catalysts have been reported [13].

Besides the use of hydrogen, higher BTX yields can also be obtained by introduction of metals in the framework of the ZSM-5 zeolite. For instance, the introduction of Zn ions by Zn-proton exchange enhanced the BTX yield considerably [10,12,14] by suppressing hydrogen transfer reactions favoring olefin formation and providing dehydrogenation sites for dehydrocyclization [9]. Similarly, higher BTX yields were also observed by the introduction of Ga [12], Mo [10,12], Cu [12], Ni [10], Ag [10] and Sn [10] in the zeolite framework. Furthermore, Xiao *et al.* [15] observed that NaOH treated ZSM-5 gives higher yields of BTX due to the generation of mesopores as well as the formation of a zeolite with an optimum ratio between Brönsted and Lewis acid sites. Besides ZSM-5 based catalysts, the use of Al_2O_3 [16] and Pd and Ru catalysts thereof [17] were also explored, though relatively low BTX yields (2 wt.%) were obtained [16].

Dilution of the glycerol, *e.g.,* with water, has also shown to lead to higher BTX yields [12]. For instance, Zhang *et al.* [11] obtained a BTX carbon yield of 16.5% for the catalytic pyrolysis of 12.5 wt.% glycerol/water over ZSM-5 catalysts. Co-feeding with lower alcohols (*e.g.*, CH_3OH [10,12,14,16,18–20] and CH_3CH_2OH [12,16]), low molecular weight aromatics (*e.g.*, benzene and toluene [19]) and alkanes (*e.g.*, hexane [17], dodecane and hexadecane [16]) have been intensively studied to obtain higher BTX yields, to tune the individual amounts of benzene, toluene and xylenes in the BTX mixture and to extend catalyst life-time.

Most investigations on the catalytic pyrolysis of glycerol focussed on the use of powdered catalysts or pressed pellets with small particle size (max. 40–60 mesh). However, when using *ex-situ* approaches with vapour phase upgrading using a packed at larger scale, these are not suitable and shaped catalysts with larger particle sizes are needed. Such larger catalysts (*e.g.*, extrudes and spheres) are typically made using a binder (*e.g.*, bentonite [14]). It has been reported that the addition of bentonite hardly affects the BTX yields, even at high bentonite amounts (82%) [14]. However, investigations on the use of larger mm sized ZSM-5/bentonite particles for the catalytic pyrolysis of glycerol with respect to catalyst performance (BTX yield), catalyst life-time (time on stream), catalyst deactivation, catalyst regenerability and reusability have not been reported to date.

In this manucript, we demonstrate the *ex-situ* catalytic pyrolysis of crude glycerol for bio-BTX synthesis in a continuous dedicated bench scale unit containing 200 g catalyst with dimension of relevance for industrial operation in packed bed reactors. For this purpose, we made ZSM-5/bentonite extrudates with particle size between 1–2 mm, and examined the catalyst performance with respect to BTX yield, carbon yield, mass and carbon balance closure. The activity and stability of the ZSM-5/bentonite catalysts was systemically investigated for 11 reaction/regeneration cycles to examine the regenerability and reusability. The deactivated and regenerated catalysts were analyzed in detail (BET, XRD, ICP-AES, EA, TEM-EDX, TGA, NH_3-TPD, pyridine-IR and solid MAS NMR) to obtain insight in both reversible and irreversible catalyst deactivation phenomena.

2. Experimental

2.1. Materials

ZSM-5(23) powder (Product number CBV2314) in the ammonium form was supplied by Zeolyst International (USA). Bentonite powder (Product number 285234, CAS number 1302-78-9) was obtained from Sigma-Aldrich Corporation (USA). Crude glycerol, which is a mixture of glycerol and fatty acids (Table 1), was commercially supplied by Sunoil Biodiesel B.V., The Netherlands.

Table 1
Composition of the crude glycerol used in this study.

H_2O[a] (wt.%)	CH_3OH[b] (wt.%)	Glycerol[c] (wt.%)	FAME[c] (wt.%)	FFA[c] (wt.%)	Na[d] (wt.%)	Mg[d] (wt.%)	Fe[d] (wt.%)
2.43	0.05	49	4.3	44.5	0.76	< 0.01	0.03

FAME: fatty acid methyl ester.
FFA: free fatty acids.
[a] Karl Fisher analysis.
[b] trace GC analysis.
[c] ^{1}H NMR.
[d] AAS.

2.2. Catalyst preparation

The as-received ZSM-5(23) and bentonite powders were pre-calcined separately at 550 °C for 8 h. For the ZSM-5(23) powder, this converts the ammonia form to the H-ZSM-5 form (termed as ZSM-5). The two calcined powders were then mixed with different weight ratios (90:10, 80:20 and 60:40, ZSM-5:bentonite) in a Multilab Mixer/Extruder/Spheronizer (Caleva, UK) followed by adding distilled water (0.45 g per gram powder) to produce wet extrudes with an outer diameter (OD) of 1 mm and length of 1 mm. The extrudes were dried at 110 °C for 12 h, followed by calcination in a LT 9/11/P330 Muffle Furnace (Nabertherm, Germany) at 550 °C for 5 h at a heating rate of 5 °C min^{-1}. The final catalysts with particle sizes of 1–2 mm were obtained after a calcination for 8 h.

2.3. Catalytic pyrolysis of glycerol

2.3.1. Catalyst screening in a batch micro-reactor (with glycerol loading of 1 mg)

A Rx-3050TR Tandem micro-Reactor (TMR, Frontier Lab, Japan) was employed to rapidly screen the effect of the ZSM-5 to bentonite ratio on catalyst performance. Pure glycerol (1 mg) was charged to the pyrolysis reactor, catalysts (70 mg, 212–425 µm) were charged to the fixed bed reactor. The catalysts were preheated at 550 °C for 30 min under a He flow (54 ml min^{-1}) and maintained at 550 °C during reaction. The pyrolysis of glycerol was performed at 500 °C. The products were analyzed using an on-line HP5890/HP5972 GC–MS (Agilent, USA) equipped with Rx1-5Sil column (30m × 0.25 mm × 10 µm, Restek, USA). The BTX yield was calculated using a single point external calibration.

2.3.2. Experiments in a batch gram scale reactor

A tandem fixed bed reactor heated in a fluidized sand bath (T_{set} = 550 °C) was used to determine the mass and carbon balances during the *ex-situ* catalytic pyrolysis of crude glycerol. The upper bed is used for the thermal pyrolysis of crude glycerol (1 g) under a flow of N_2 gas (11 mL/min), whereas the lower one is for the catalytic aromatization of the pyrolysis vapor over 3 g catalysts. The reactor configuration was designed in such a way to enable stepwise submersion of both beds in the fluidized sand bath. The lower catalyst bed was first submerged to preheat the catalyst until the temperature of the upper bed reached 85 °C. Then, the upper bed was submerged into the sand bath and was kept for 15 min to fulfill the *ex-situ* catalytic pyrolysis of crude glycerol. All the products were transferred to a stainless vessel, which was immersed into a cold trap at −40 to −50 °C, to condense, separate and collect the liquid products. The non-condensable gaseous products were all collected in a gas bag. When the *ex-situ* catalytic pyrolysis was finished, the whole reactor was lifted from the sand bath. The stainless steel collection vessel was then washed with small