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Kinetics modeling of disproportionation and ethylation of ethylbenzene over HZSM-5: Effects of SiO_2/Al_2O_3 ratio

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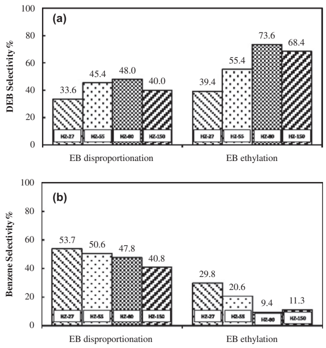
HIGHLIGHTS

- Effects of SiO_2/Al_2O_3 ratio of HZSM-5 in disproportionation/ethylation EB are studied.
- Main product is DEB and benzene.
- At low temperature ethylation is favorable than disproportionation to produce DEB.
- HZSM-5 with Si/Al = 80 gives highest EB conversion and selectivity of DEB.
- Activation energy for DEB formation on Si/Al = 80 is smaller than other HZSM-5 samples.

GRAPHICAL ABSTRACT



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ABSTRACT

This article deals with the effects of SiO_2/Al_2O_3 ratio of HZSM-5 catalysts in disproportionation and ethylation of ethylbenzene to produce para-diethylbenzene (p-DEB). The physicochemical characterization of the catalyst samples shows that the variation of SiO_2/Al_2O_3 has minimal impact on the crystallinity of HZSM-5 samples. On the other hand, the acidity of the materials decreased while specific surface area increased with increasing the SiO_2/Al_2O_3 ratios. The catalytic experiment in the CREC Riser Simulator shows that low temperature favors the EB ethylation reaction while higher temperature is favorable for disproportionation. The DEB selectivity is found to be significantly higher in ethylation of EB with ethanol than disproportionation. Among the five HZSM-5 catalysts, the sample with $SiO_2/Al_2O_3 = 80$ gives highest EB conversion and is more selective to DEB although the p-DEB/m-DEB for the catalysts are comparable with other samples. The value of the activation energy for EB cracking is comparable to the activation energy of EB disproportionation which is consistent to the high benzene selectivity in this route. During the EB ethylation with ethanol, a small amount of benzene was formed via the cracking of EB, which is reflected by higher activation energy of the EB cracking reaction. The kinetics analysis also confirms that during EB ethylation, the disproportionation and cracking of EB is negligible. In EB ethylation, the HZSM-5 catalyst with $SiO_2/Al_2O_3 = 80$ requires lowest amount of activation energy to form DEB which is reflected in higher DEB selectivity of the catalyst.

1. Introduction

p-Diethylbenzene (p-DEB), the most desirable among the three DEB isomers, have found wide range of applications in the chemical and petrochemical industries. It is commonly utilized as monomer for the production of ion exchange resin and viscosity modifiers for lubricating oil [1]. A significant amount of the produced p-DEB goes in producing divinylbenzene (DVB), an intermediate used as a cross-linking agent in the manufacture of certain plastics [2]. p-DEB is employed as a desorbent in UOP para-ex and IFP-eluxyl desorption processes [1,3]. It also works as an

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Nomenclature

C_i	concentration of specie i in the riser simulator (mol/m^3)
CL	confidence limit
E_i	apparent activation energy of the ith reaction (kJ/mol)
k_i	apparent rate constant for the ith reaction (m^3/kg of catalysts)
k_{oi}	pre-exponential factor for the ith reaction after re-parameterization (m^3/kg of catalysts)
MW_i	molecular weight of specie i
r_i	rate of reaction for species i
R	universal gas constant (kJ/kmol K)
t	reaction time (s)
T	reaction temperature (K)
T_o	average temperature of the experiment
V	volume of the riser (45 cm^3)
W_c	mass of the catalyst (0.81 g)
W_{hc}	total mass of the hydrocarbon injected the riser (0.162 g)
y_i	mass fraction of ith component

Greek letters

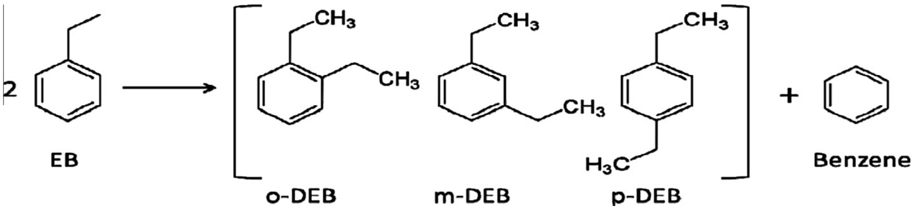
α	apparent deactivation function
λ	catalyst deactivation constant (RC model)

Abbreviations

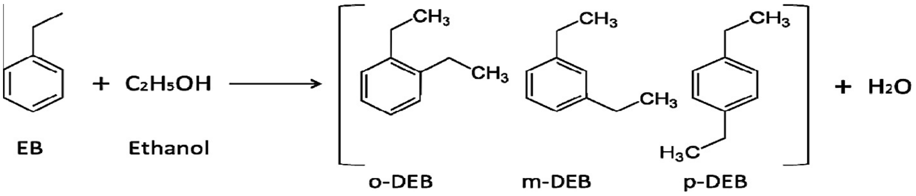
BZ	benzene
EB	ethylbenzene
DEB	diethylbenzene
p-DEB	para-diethylbenzene
m-DEB	meta-diethylbenzene
o-DEB	ortho-diethylbenzene

additive in industrial heat transfer fluids. Accounting for all the after mentioned applications, current worldwide demand for p-DEB is estimated to 12,000 tons per years, which is expected to grow further [2]. With the present market prices of $4000/per metric ton, the annual sales volume is approximately around US$ 48 million dollars [2]. Considering the attractive price and increasing demand, in recent years there are significant initiatives to increase the p-DEB productions. Conventionally, p-DEB is produced by reduction of diacetophenone. The other alternative routes are, disproportionation of ethylbenzene (EB) and/or alkylation of EB with ethanol, ethylene, or ethyl chloride [1,3–5] according to the following reactions:

- Disproportionation of ethylbenzene:



- Alkylation of ethylbenzene with ethanol:



One can see from the above alternative routes; alkylation of each mole of EB gives one mole of DEB while the disproportionation of EB requires two moles of EB to produce one mole of DEB. Also, disproportionation gives one mole of benzene per mole of DEB produced. Therefore, the alkylation with an appropriate agent appears to be more preferable. Among the after mentioned alkylation agents, ethanol is considered to be the most economical due to its ample availability and relatively cheaper prices. From the technical view point, ethanol is also desirable given that the water produced during alkylation with ethanol helps suppressing the coke formation, resulting sustained catalyst activity for longer period of time. To apprehend the advantages of EB alkylation with ethanol there are significant research initiatives that have been under taken around the world to develop industrial scale EB alkylation technology.

The majority of those literature articles are focused on the catalyst development and establishing the possible reaction mechanisms. Most of the previous studied catalysts are based on various types of zeolites, such as mordenite, USY, Beta, MCM-22 and ZSM-5 [4,6]. These catalysts show good catalytic activity and stability in EB disproportionation/alkylation using different types of reactor and reaction conditions. The main limitations of these catalysts is the low selectivity of p-DEB due to the thermodynamic equilibrium with other DEB isomers (para:meta:ortho = 30:54:16) [1,6]. Cracking of EB on the acidic sites is the other important issue related to the zeolite base catalysts. It not only consumes the EB feed to produce undesired products (mainly benzene) but also responsible for catalyst deactivation by coke formation. Modification of the catalyst is one of the most widely accepted ways to increase the selectivity of p-DEB. There are two possible alternatives of modifying the zeolite based catalysts: (i) passivation of the external acidic sites, minimizing the secondary isomerization of p-DEB (to form the m- or o-DEB) and cracking reaction and (ii) modifying the structure of the zeolite to facilitate the