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Short communication

Aromatics from 1-tetradecene through conversion over zeolite catalysts

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ABSTRACT

A completely new reaction of conversion of 1-tetradecene to aromatic compounds over HZSM-5 type of zeolites was studied. A full factorial design of experiments (DOE) was used to determine significant reaction conditions (factors) and their interactions. Experiments were conducted in a fixed head bench top batch autoclave reactor. The liquid products were analyzed by GC-FID. Reaction temperature and olefin to catalyst ratio (OCR) were identified as individual factors significantly affecting aromatization. A decrease in the SiO_2:Al_2O_3 ratio of zeolite increased the aromatics selectivity. Formation of C_6 to C_8 aromatic hydrocarbons in one step catalytic conversion process leads to the conclusion that cracking of tetradecene chain is an inevitable first step in the formation of aromatics.

1. Introduction

Current academic as well as industrial research is focused on the production of aromatic compounds from petroleum based light alkanes and alkenes (Krishnamurthy et al., 2010: 370–385; Bhan and Delgass, 2008: 19–151; Choudhary et al., 2002: 243–251). Fatty acids (Fegade et al., 2011a,b) and olefins such as ethylene, propylene, butene, hexene and octene have been aromatized by using zeolite catalysts. 1-Hexene was successfully converted into aromatics in a plug flow reactor by using Ga doped HZSM-5 catalysts by Nash et al. (1996: 285–297) and it was observed that C_8 aromatics are major aromatic products at lower temperatures. Yuning Li and coauthors reported (Li et al., 2009: 8–16; Li et al., 2008: 100–113) the conversion of 1-hexene to aromatic compounds in a continuous fixed bed reactor by using ZSM-5 type zeolites. This conversion of α-olefins to aromatics was achieved between temperature ranges of 350–480 °C.

Aromatization of *n*-octene over nanoscale HZSM-5 catalyst yielded toluene and xylenes were the major aromatics (Long et al., 2009: 18–22). In another study of *n*-octene aromatization over nanoscale HZSM-5 catalysts (Long et al., 2008: 378–382), it was observed that lower temperature reaction produces xylenes, and that selectivity toward benzene and toluene formation increases with an increase in temperature.

Although there is work being done on aromatization of lower olefins and mid chain (C_6, C_8) olefins, there is a lack of work being done on aromatization of α-olefins having more than 10 carbon atoms. 1-Tetradecene is a commercially important α-olefin for the manufacture of detergents, surfactants, linear alkylbenzenes (Lappin and Sauer, 1989; Burdick and Leffler, 2001; Wittcoff et al., 2004; ASTM Committee D-2 on Petroleum Products and Lubricants et al., 1991). Most of the academic and industrial research studies on 1-tetradecene have been presently concentrated on using it as comonomer in copolymerization reactions (Koivumäki, 1996: 7–12; Kotzabasakis et al., 2009: 876–886; Akhmedov and Levshina, 1986: 300–301). 1-Tetradecene is also used in functional drilling fluids, lubricants, automotive additives, and metal working agents. Apart from these, the applications of 1-tetradecene are limited and hence there is a need to explore new applications for this α-olefin. In the present study,

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Table 1 – Factors with their low and high values.

Factors	Low	High
Coded units	−1	+1
(A) Temperature (°C)	300	375
(B) Olefin to catalyst ratio (OCR)	10	20
(C) Time (min)	30	60

the preliminary objective is to study the feasibility of using 1-tetradecene as a source for producing light aromatic compounds.

2. Experimental

ZSM-5 catalysts (CBV5524G and CBV 2314) were purchased from Zeolyst International. CBV 5524G zeolite has SiO_2/Al_2O_3 mole ratio = 50, Na_2O content = 0.05 wt%, surface area of 425 m^2/g. CBV 2314 zeolite has SiO_2/Al_2O_3 mole ratio = 23, Na_2O content = 0.05 wt%, surface area of 425 m^2/g. 1-Tetradecene (97%) was purchased from Sigma–Aldrich. GC grade standards, benzene, toluene, ethylbenzene, p-xylene, o-xylene and 2-chlorotoluene were also purchased from Sigma–Aldrich. The catalysts were calcined at 550 °C for 5 h in an air circulated oven. A Parr Instrument Company series 4575 fixed head, bench top, high temperature, high pressure reactor was used for the aromatization experiments. A 2 level, 3 factor, full factorial experimental design was used to study the catalytic conversion of 1-tetradecene over HZSM-5, having an SiO_2/Al_2O_3 (Si/Al) ratio of 23. The reaction temperature (°C), OCR, and reaction time (minutes) were chosen as the factors to be studied. The low and high values of the factors are shown in Table 1. All the aromatization experiments were replicated and performed in a random order.

Once the reaction was over, the reactor contents were allowed to cool down to room temperature and then the gaseous products were collected in a gas bag by slowly opening a reactor vent. The entire reactor contents were weighed and then filtered to separate coke/solid particles from organic liquid products (OLP). For aromatization experiments, liquid products were distilled and collected in a liquid sample collector. After each aromatization run, the amount of gases produced were determined by subtracting weight of coke and OLP from weight of tetradecene fed to the reactor. Organic liquid product distillates were further analyzed on HP 5890 series II GC using 2-chlorotoluene (as internal standard) to find the benzene, toluene, ethylbenzene, xylene (BTEX) concentrations in volume percent.

Table 3 – Detailed chemical composition of products formed after catalyzed and un-catalyzed reactions of 1-tetradecene conversion (average of two replicates).

Products	Catalyzed reaction[a] (%)	Un-catalyzed reaction[b] (%)
Alkanes	20	11
Alkenes	1.0	78
Dienes	1.2	3
Alicyclic hydrocarbons	13	2
Aromatics	51	ND
Indanes	5	ND

ND = not detected, i.e., below the limit of detection.

[a] The reaction conditions were 375 °C, olefin to catalyst ratio = 10 and reaction time of 30 min.

[b] Absence of a catalyst.

3. Results and discussion

Table 2 shows the test matrix and the results. It was found that the reaction temperature has a significant effect on BTEX yield shown in the Pareto charts of the effects (Fig. 1a). As the reaction temperature increases from 300 °C to 375 °C, the total BTEX concentration increases (Fig. 1b).

Experiments were conducted in an absence of catalyst to distinguish the effect of catalyst from the effect of temperature alone on aromatization. For such non-catalyzed reaction, even at the higher reaction temperature (375 °C), amount of BTEX was below detection limits (Table 3). It is clear that only catalyst is responsible for cyclization and aromatization. Thermal factors were responsible for cracking of long chain of tetradecene molecule. However, only the effect of temperature is not enough for cyclization and aromatization.

Previous study on propylene aromatization suggests that cracking of olefins is an important step in aromatization reactions (Fegade et al., 2013: 1039–1056). An aromatic compound contains a benzene ring which has 6 carbon atoms. Other aromatics such as toluene, ethylbenzene and xylenes contain 7–8 carbon atoms. However, the feed molecule, 1-tetradecene, is composed of 14 carbon atoms. The formation of significant amounts of BTEX and lesser amounts of C_{10}–C_{14} aromatics

Table 2 – Full factorial experimental design including reaction factors and responses.

Run	Temperature (°C)	OCR	Time (min)	Total BTEX (%)	Coke/solids produced (%)
1	300	10	60	1.6	13
2	375	20	60	8.7	16
3	375	20	30	6.2	3.2
4	300	20	30	0.18	6.7
5	375	10	30	26	9.0
6	300	20	60	3.5	6.8
7	300	20	30	0.19	6.8
8	300	20	60	3.5	6.7
9	375	10	30	26	9
10	300	10	30	0.62	12
11	375	20	30	6.3	3.3
12	375	10	60	15	6.0
13	375	20	60	8.7	16
14	300	10	60	1.7	13
15	375	10	60	17	6
16	300	10	30	0.71	12