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Methanol Conversion to Aromatic Hydrocarbons by Using Gamma Alumina and H-Beta Zeolite

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Abstract

In the present work, the obtained results are presented for aromatic hydrocarbons producing by gamma alumina and H-Beta zeolite as catalysts. Gamma alumina is placed at the entrance zone of a Vertical fixed bed reactor with up to down flow stream in order to convert methanol to dimethyl ether, and H-beta zeolite is loaded at follows for converting dimethyl ether to aromatic hydrocarbons. Both catalysts have sizes between 1 and 2 millimeter and the same weight ratio. The weight of each catalysts in the reactor is 2 grams. Silica to alumina ratio and specific surface area of H-beta are 7.9 and 500 m^2/g respectively. Also, the specific surface area of the used gamma alumina is 192 m^2/g. Experiments were done at 250 up to 370°C. The desired space velocity (WHSV) for H-Beta at 370°C was 7.11h^{-1}. According to Gc-Mass analysis on the reactor products, the main component at the above mentioned conditions was Hexa-methyl Benzene. Formation of this component was satisfied by IR-spectroscopy and C-NMR and H-NMR analysis. Addition to hexa-methyl benzene, the analysis confirmed that some other components such as tri ethyl benzene, ethyl penta-methyl benzene and dimethy ethyl benzene were formed by the reaction.

Keywords: Methanol Conversion, Zeolite, Dimethyl Ether, Hydrocarbon, Gamma Alumina.

Introduction

Methanol conversion to different hydrocarbons can be regarded as an important step in gas conversion processes. In this regard, some processes can be mentioned such as conversion of methanol to olefins (MTO), methanol to propane (MTP), methanol to gasoline (MTG) and methanol to aromatics (MTA) [1]. Also, there are different references about the mechanisms of methanol to hydrocarbon conversion in the literature [2-5].

For all of these processes, different types of zeolites can be used as chemical catalysts. Selection of the appropriate zeolite depends on the chemical reaction conditions, kind of hydrocarbons, selectivity, reaction yields, and so on.

In this the ability of gamma alumina and H-Beta zeolite as commercial catalysts are investigated for converting methanol to aromatics.

Experimental Procedure

Chemicals and Apparatus

Methanol was prepared from the Iran Petro-Chemical Company with 99.99% purity. Gamma alumina (Kat. D-10-10 S4) and H-Beta zeolite (H-Beta 25) were prepared from BASF and Sud-Chemie Companies, respectively. Silica to alumina ratio and specific surface area of H-Beta are 7.9 and 500 m^2/g, respectively. Also, the specific surface area of the used gamma alumina is 192 m^2/g. The reactions were performed in a catalyst tester with a fixed bed reactor at isothermal and isobaric conditions. The products were analyzed by GC-MS (CP3880 and Saturn 2200, Varian, Holland), NMR (500 MHz, Bruker, Germany), FT-IR (Tensor 27, Bruker, Germany) spectrometers and the melting point was measured by model 510 Büchi (Switzerland) apparatus.

Experimental Method

In each experiment, 2 g of gamma alumina and 2 g H-Beta were loaded in the reactor, separately. So, gamma alumina was placed in the first zone of the reactor following by the H-Beta in the second zone. Methanol was heated and super-heated before entering to the reactor. The reactions were carried out at a fixed temperature by adjusting and controlling the reactor temperature. The exit gases from the reactor were cooled to ambient temperature and separated into liquid and gas phases. Analyzing of the products was done on gas and liquid phases. Also, It was observed that a white solid product as needle crystals was formed on the thermo-well tube (Figure 1) which was analyzed.

Figure 1. Needle solid crystalline which was formed around the reactor thermo-well.

Discussion and Results

The reaction temperature was changed from 250 up to 370 °C. Two main reactions were occurred in these conditions in the reactor. At first, dimethyl ether (DME) was formed by dehydration of methanol on gamma alumina at temperatures more than 220 °C. In follows, DME was converted to different products on H-Beta catalyst. The desired space velocity (WHSV) for H-Beta at 370°C was 7.11 h^{-1}. At 300°C a needle solid crystalline phase product was formed. Elemental CHNS

analysis of this product showed that it was a hydrocarbon containing 81.4872 wt% carbon and 10.3981 wt% hydrogen with general formula of $(C_2H_3)n$. The obtained results of the other analyzing methods showed that the product was hexamethylbenzene. Formation of this component was satisfied by FT-IR, 1H-NMR and 13C-NMR spectroscopies. Addition to hexamethylbenzene, the analysis of the products confirmed that some other components such as triethylbenzene, ethyl penta-methylbenzene and dimethyl ethylbenzene were formed by the reaction. The main components which were detected by GC-MS analysis are reported in Table 1.

Conclusion

The conversion of methanol to aromatic hydrocarbons through dimethylether intermediate was performed in a fixed-bed reactor by using a two-step γ-alumina and H-beta zeolite catalysts. At temperatures above 300°C, especially at 370°C, a needle solid crystalline product was mostly formed which identified by using different analytical and spectroscopic methods as hexamethyl-benzene. The desired space velocity for H-Beta at 370°C was 7.11 h^{-1}. The GC-MS analysis of the outlet products from the reactor showed that some other components such as triethylbenzene, ethyl penta-methylbenzene and dimethyl ethylbenzene were formed by the reaction.

Table 1. The main components detected by GC-MS in organic phase of the products.

No.	Component	Percent (%)	Chemical Formula
1	o-xylene	0.131	C_8H_{10}
2	p-xylene	0.122	C_8H_{10}
3	pentamethylbenzene	0.125	$C_{11}H_{16}$
4	1,3,5-triethylbenzene	4.474	$C_{12}H_{18}$
5	Dimethyl diethyl benzene derivations	1.359	$C_{12}H_{18}$
6	Hexamethylbenzene	84.98	$C_{12}H_{18}$
7	Ethyl pentamethyl benzene	3.138	$C_{13}H_{20}$
8	1,4-dimethyl-2,5-bis (2- propyl) benzene	3.003	$C_{14}H_{22}$

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