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Up-Grading of FCC Gasoline by Olefin Hydration over Hβ Zeolite

WANG Hua, HUANG Tao, DU Juan, LIU Zhongmin

(Natural Gas Utilization and Applied Catalysis Laboratory, Dalian Institute of Chemical Physics, The Chinese Academy of Sciences, Dalian 116023, Liaoning, China)

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The large increase in automobiles and the greatly increased consumption of fuel has caused very serious air pollution from the emission of tail gas[1]. Governments all over the world have regulated new standards for the components of gasoline. Decreasing the olefins, limiting the aromatics, and increasing the oxygenates in gasoline are the general requirements. Approximately 80 % of the gasoline used in our country comes from fluidized catalytic cracking (FCC). The gasoline produced by a conventional FCC process contains more than 45 % olefins, which is greatly in excess of the standard that will become effective (the permitted content of olefins in the new standard is 35 %[2]). To meet the requirements of the new standard, several technologies have been developed, such as the optimization of the FCC process by using new FCC catalysts[3], hydrogenation[3], isomerization and aromatization[4～6]. These methods focus on decreasing the olefins. The hydration of the light fraction of FCC gasoline can provide a way to increase oxygenate content and reduce olefin content at the same time. Moreover, the process of olefin hydration possesses a high atom economy. The aim of this work is to upgrade FCC gasoline by hydration of olefins over Hβ zeolite.

The composition of the light FCC gasoline (≤80 °C) is listed in Table 1. β zeolite with $n(Si)/n(Al)$ = 46.2 was obtained from Fushun Petrochemical Company. The zeolite was first ion-exchanged to the ammonium form by treatment with 0.1 mol/L NH_4NO_3 solution and then calcined at 550 °C for 3 h to obtain Hβ zeolite. The catalyst (20～40 mesh, 6 g) was charged into a stainless steel reactor with 12 mm inner diameter, and the hydration reaction was performed under 5.0 MPa, WHSV = 1 h^{-1} and 100～170 °C conditions for 10 h. The effluent was collected in a chilled flask containing 5 g acetone to dissolve both the aqueous and organic phase products, and the mixtures were analyzed by a Varian CP-3800 gas chromatograph equipped with an FFAP capillary column (25 m) and an FID detector. Benzene, which is inert in the hydration reaction, was used as the internal standard. To simplify the calculation, the response factor of *tert*-pentyl alcohol, the major hydration product, was taken as the response factor of all the oxygenate products. The conversion was calculated based on the olefins in the gasoline.

Table 1 Composition of light FCC gasoline (≤80 °C)

Composition	*w*/ %	*φ*/ %	*x*/ %
Olefin	43.6	43.4	45.4
Aromatics	1.3	1.0	1.3
Cycloparaffin	42.1	43.1	40.8
n-Paraffin	5.7	5.1	5.3
i-Paraffin	4.8	4.9	4.8
Others	2.5	2.5	2.4

The gasoline was analyzed with DHA software on a Varian CP-3800 gas chromatograph equipped with a PONA capillary column (100 m ×0.25 mm).

Fig 1 shows the effect of the water/oil ratio on olefin hydration over Hβ zeolite. It can be seen that Hβ is an effective catalyst for hydration of olefin in FCC gasoline and gave a dramatic decrease of the olefins. In all the cases investigated, the concentration of polymerization products in the bulk liquid reaction medium was below the detection limit. Thus the small amount of oligomers that might have formed could hardly affect the conversion and carbon balance, and the selectivity for hydration was taken as 100 %.

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Corresponding author: LIU Zhongmin. Tel: (0411)84685510; E-mail: liuzm@dicp.ac.cn.

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Increasing the ratio of water/oil gave a sharp increase of olefin conversion that went through a maximum at $V(H_2O)/V(oil) = 0.6$ and then decreased.

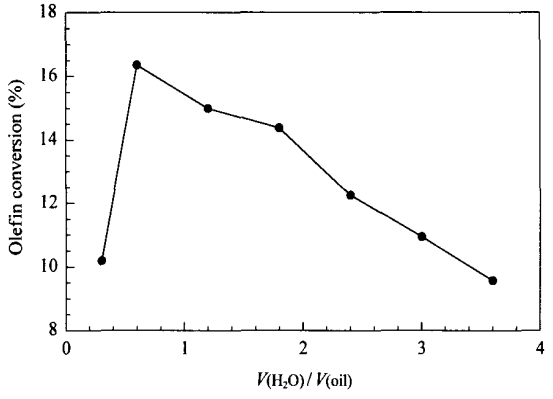

Fig 1 Effect of water/oil ratio on olefin hydration over Hβ zeolite

The reaction temperature is an important parameter in the hydration process as it both influences the reaction rate and has a major impact on the distribution of the alcohols in the organic and aqueous phases, which affects the balance of the forward reaction (hydration of olefins) and the reverse reaction (dehydration of alcohols). The effect of the reaction temperature on hydration of olefin is shown in Fig 2. The conversion of olefins increased with the reaction temperature and reached 16.7% at 140 ℃, and it remained unchanged at 140～170 ℃, which indicated that the forward and reverse reactions were balanced in this temperature range. The content of oxygenated products was about 9.5% at the highest olefin conversion. GC-MS results showed that besides the major hydration product (*tert*-pentyl alcohol), there were several oxygenates in the effluent such as *tert*-butyl alcohol, 2-butanol, 2-pentanol, 2-hexanol, 3-hexanol, 2-methyl-2-butanol, 3-methyl-2-butanol, 2,3-dimethyl-2-butanol and 4,4-dimethyl-3-pentanol.

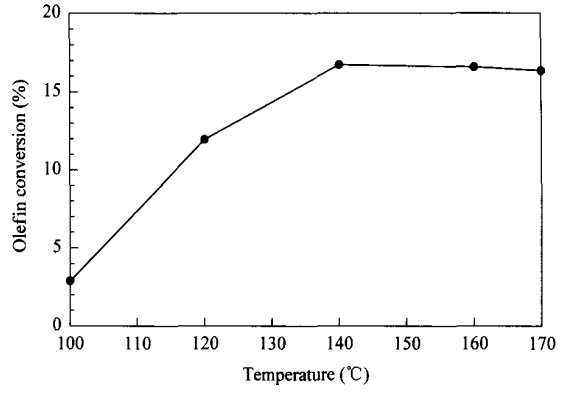

Fig 2 Effect of reaction temperature on olefin hydration over Hβ zeolite at V(H2O)/V(oil) = 0.6

In conclusion, the hydration of olefins over Hβ zeolite is a promising way for reducing olefins and increasing oxygenates in FCC gasoline. An olefin conversion of 16.7% and 9.5% oxygenates can be obtained under the given conditions.

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通过 Hβ 分子筛上的烯烃水合反应提高 FCC 汽油品质

王 华, 黄 韬, 杜 娟, 刘中民*
(中国科学院大连化学物理研究所天然气化工与应用催化研究室, 辽宁大连 116023)

摘要: 以 Hβ 分子筛为催化剂,通过烯烃水合反应可以降低 FCC 轻汽油(≤80 ℃)中烯烃含量并提高含氧化合物含量,从而提高汽油的品质. 在 $V(H_2O)/V(oil) = 0.6$, WHSV = 1 h^{-1}, p = 5.0 MPa, θ = 140 ℃和 t = 10 h 的条件下, FCC 轻汽油中烯烃的转化率为 16.7%,产物中含氧化合物的含量为 9.5%.

关键词: 烯烃, 水合, FCC 汽油, 改质, Hβ 分子筛

(Ed YHM)