Advances in Engineering Research, volume 115
2nd Annual International Conference on Energy, Environmental & Sustainable Ecosystem Development (EESED 2016)

Research on the preparation of metallocene/Hβ catalyst for n-hexane isomerization

Jin-She Chen[a], Zhao-Yang Song[b], Zun-Bin Duan[c],
Li-Jun Zhu[d] and Dao-Hong Xia[e, †]

State Key Laboratory of Heavy Oil Processing,
China University of Petroleum,
Qingdao 266580, People's Republic of China
[a]E-mail: chenjins2010@163.com, [b]E-mail: szyfir@163.com,
[c]E-mail:duan_zunbin@163.com, [d]E-mail:zhulj2002@163.com,
[†, e]E-mail: xiadh@upc.edu.cn

The research on isomerization technology of n-alkanes is necessary, and there is few study on metallocene catalysts for isomerization of n-alkanes. In this study, novel ferrocene/Hβ, acetylferrocene/Hβand titanocene dichloride/Hβ catalysts for isomerization of n-hexane was prepared, and the isomerization activity of them was investigated. Moreover, the optimum reaction conditions for catalysts were investigated, respectively. The results showed that the optimal loading of active components were 0.2%, 0.2% and 2.0%, and the optimal reaction temperature of them was 300 and 310 °C, respectively. The study of this kind of catalysts has importantly theoretical and practical significance.

Keywords: N-hexane Isomerization; Metallocene Catalysts; Reaction Conditions.

1. Introduction

With the rapid development of automobile industry, the octane number of gasoline becomes increasingly strict. In recent years, the gasoline of lead-free, low aromatics, low vapor pressure and high octane number needs to be produced more and more because of the strict environmental protection requirement [1-3]. Meanwhile, there is rich naphtha in our country, which can be processed as raw materialforhigh-octane gasoline. Therefore, the research on isomerization technology of n-alkanes is necessary, which can be used to produce good additive of gasoline with high octane number. In general, noble metals such as platinum are used as active components for isomerization catalysts of n-alkanesat home and abroad, however, they have disadvantage of high costs [4]. Therefore, non-noble metal catalysts which can be used instead of noble metalsneed to be further studied. As we all know, metallocene catalysts play an important role indifferent reaction, but there is few study on metallocene catalysts for isomerization of n-alkanes, so the study of this kind of catalystshas theoretical and practical significance [5].

2. Experiment Methods

2.1. *Ferrocene/Hβcatalyst*

A certain amount of Hβ and Al_2O_3 was mixed well, and then appropriate amount of distilled water was added into them. After extrusion, the mixtures were dried at 100 °C for 2 h, and then calcined at 500 °C for 4 h. After being cooled to room temperature, they were smashed into particles whose diameter ranges from 0.2 mm to 0.6 mm, and then supporters were prepared. Different quantities of ferocene were dissolved in petroleum ether and above supporters were impregnated in them for 24 h. Finally catalysts were dried at 50 °C for 2 h and kept under seal.

2.2. *Acetylferrocene /Hβcatalyst.*

Synthesis of acetylferrocene:

1.86g ferrocene and 10 ml acetic anhydride were added into 100 ml round bottomed flask, and 2 ml 85% phosphoric acid were added slowly under stirring condition. The reaction was carried out under the water bath condition at 70 °C for about 20 minutes. And then the products were added into the beaker which contained 20 g crushed ice. 25 g sodium bicarbonate was added into the beaker in batches and the process was kept under stirring condition until bubbles disappear (pH≈7). After being filtered and washed by distilled water, the raw products were obtained. Raw products were dissolved in petroleum ether at 70 °C and impurities in the products were removed by filtration in order to get the pure products.

The preparation methods of supporters were as before. Different quantities of acetylferrocene were dissolved in petroleum ether, and supporters were impregnated in them for 24 h. Finally catalysts were dried at 50 °C for 2 h and kept under seal.

2.3. *Titanocene dichloride/Hβcatalyst.*

The preparation methods of supporters were also followed by section 2.1. Different quantities of titanocene dichloride were dissolved in trichloromethane, and then supporters were impregnated in them for 24 h. Finally catalysts were dried at 120 °C for 2 h and kept under seal.

2.4. *Evaluation of catalysts.*

The isomerization of n-hexane was performed under hydrogen atmosphere in a micro catalytic reactor at different temperature. 4 g catalysts were used every time and the products were analyzed by a 6820 Agilent Gas Chromatograph equipped with a FID and a Al_2O_3 capillary column. The relative retention was used as qualitative analysis and the area normalization method was used as the quantitative analysis.

The conversion of n-hexane (X) was calculated by Eq. (1)

$$X=\frac{\sum A-\sum An}{\sum A} \tag{1}$$

Where$\sum$A is the corrected total peak area for all compounds and $\sum$Anis the corrected peak area of n-hexane.

The yield of is o-alkanes (Y) was determined by Eq. (2)

$$Y=\frac{\sum Aiso-hexane}{\sum A} \tag{2}$$

Where $\sum$Aiso-hexane is the corrected peak area for iso-alkanes.

The selectivity to iso-alkanes (S) was calculated according to Eq. (3)

$$S=\frac{Y}{X} \tag{3}$$

3. Results and Discussion

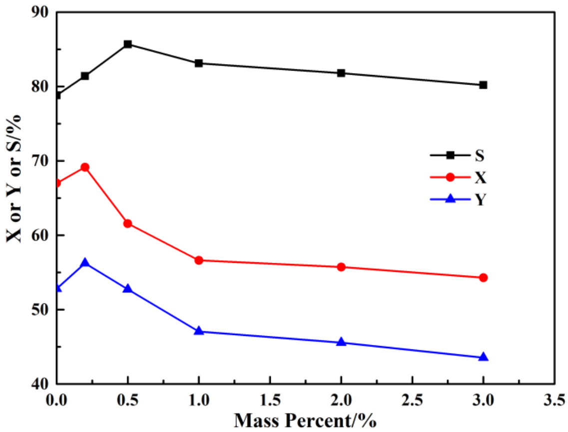

Fig. 1. Effect of ferrocene loading on the performance of ferrocene/Hβcatalyst.

Figure 1 shows the effect of ferrocene loading on the performance of ferrocene/Hβ catalyst. As can be seen from Figure 1, the conversion of n-hexane, the yield of iso-alkanes and the selectivity to iso-alkanesall increase firstly and then decrease with the increase of ferrocene loading, which follow the same trends. Moreover, the highest yield of iso-alkanes can be obtained when the ferrocene loading was 0.2% and the yield of iso-alkanes could reach 56.25%.

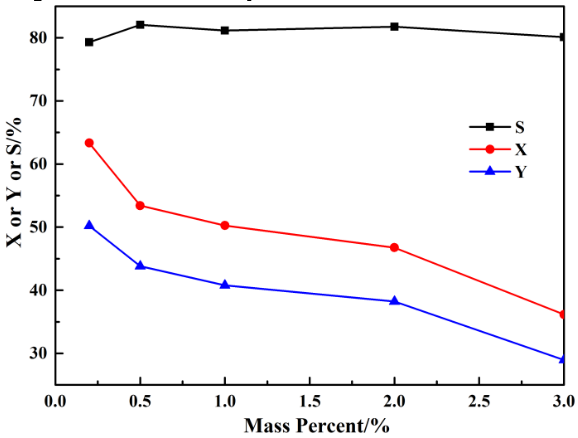

Fig. 2. Effect of acetylferrocene loading on the performance of acetylferrocene /Hβcatalyst.

It is shown in Figure 2 that the effect of acetyl ferrocene loading on the performance of acetylferrocene/Hβcatalyst. It is obvious that the selectivity to iso-alkanesincreases at first, then decreases and the best selectivity to iso-alkanes can be obtained when the acetylferrocene loading was 0.5%. Meanwhile, the conversion of n-hexane and the yield of iso-alkanes showed the same tend, which decrease gradually with the increase of acetylferrocene loading, and the highest yield of iso-alkanes was showed for the sample with 0.2% acetylferrocene.

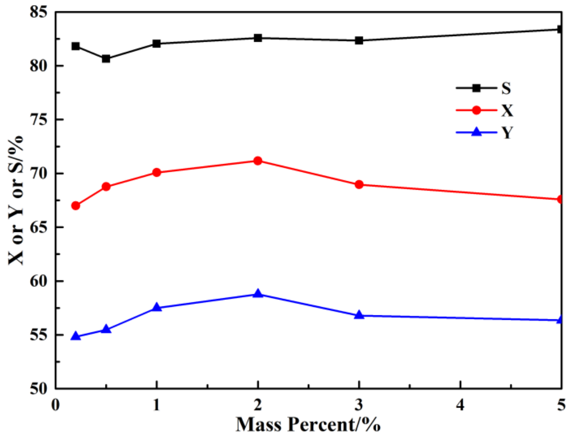

Fig. 3. Effect of titanocene dichloride loading on the performance of titanocene dichloride/Hβcatalyst.

Figure 3 shows the effect of titanocene dichloride loading on the performance of titanocene dichloride/Hβcatalyst, from which it could be seen that the catalyst with 2.0% titanocene dichloride has the highest conversion of n-hexane and the optimum yield of iso-alkanes, which can reach 71.17% and 58.77%, respectively. Meanwhile, the selectivity to iso-alkanes decreases firstly, and then increases.

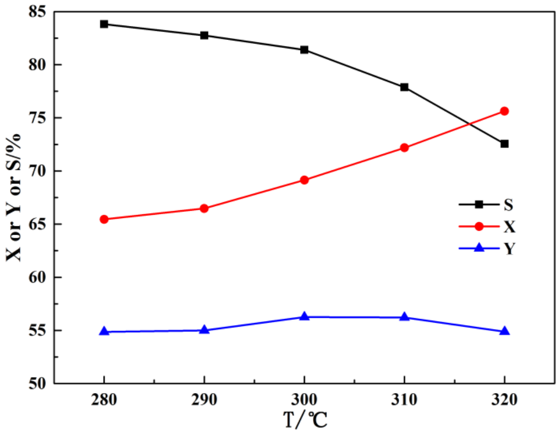

Fig. 4. Effect of reaction temperature on the performance of ferrocene /Hβ catalyst.

As shown in Figure 4, the effect of reaction temperature on the performance of ferrocene/Hβ catalyst was investigated. The conversion of n-hexane increases gradually whiles the selectivity to iso-alkanes decreases gradually with increasing reaction temperature. And the optimal yield of iso-alkanes can be obtained when the reaction temperature was 300 °C.

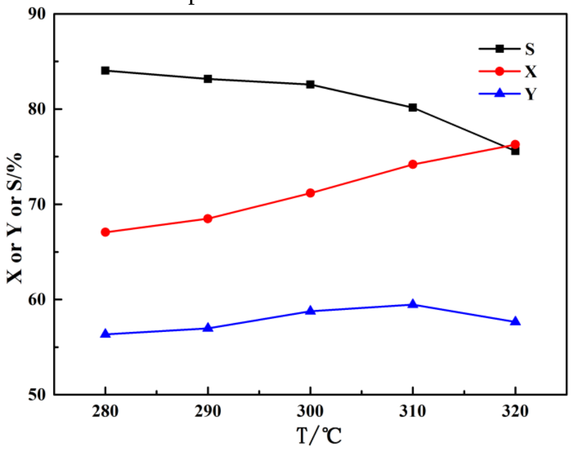

Fig. 5. Effect of reaction temperature on the performance of titanocene dichloride/Hβ catalyst.

Figure 5 shows the effect of reaction temperature on the performance of titanocene dichloride/Hβ catalyst. The conversion of n-hexane and the selectivity to iso-alkanes showed a contrary tendency with the increase of reaction temperature. Moreover, it could be seen that the optimal reaction temperature was 310 °C, at which the highest yield of iso-alkanes can reach 59.46%.

4. Conclusions

The ferrocene/Hβ catalyst, acetylferrocene/Hβ catalyst and titanocene dichloride/Hβ catalyst were prepared and the results showed that the optimal loading of active components for ferrocene/Hβ, acetylferrocene/Hβ and titanocene dichloride/Hβ were 0.2%, 0.2% and 2.0%, respectively. And then the effect of reaction temperature on the performance offerrocene/Hβ catalyst and titanocene dichloride/Hβ catalyst was studied further and the optimal reaction temperature of them was 300 and 310 °C, respectively.

References

1. J. G. Santiesteban, D.C. Calabro, C.D. Chang, J.C. Vartulli, T.J. Fiebig, R.D. Bastian, *J. Catal.* **25**,202 (2001).
2. M. Busto, V. M. Benitez, C.R. Vera, J. M. Grau, J.C. Yori, *Appl. Catal. A: Gen.* **117**, 347(2008).
3. H. D. Setiabudi, A. A. Jalil, S. Triwahyono, *J. Catal.* **128,** 294 (2012).
4. Sha sha Tian, Jixiang Chen. *Fuel Processing Technology*. **120**, 122 (2014).
5. W. Kaminsky, A. Laban. *Appl. Catal. A: Gen*. **47**, 222 (2001).