Chloroaluminate ionic liquid catalyzed isomerization of n-pentane in the presence of product distribution improver

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Abstract: The ionic liquid $\text{Et}_3\text{NHCl-2AlCl}_3$ can catalyze the isomerization of n-pentane. This paper investigates the ionic liquid catalyzed isomerization performance of n-pentane with several product distribution improvers in an autoclave. The product distribution of n-pentane isomerization could be improved by such improvers as benzene, cyclohexane, and methyl cyclohexane at the expense of conversion of n-pentane. The optimal product distribution improver was determined to be cyclohexane. The yield of isomerate and the selectivity of liquid isoalkanes increased, whereas the conversion of n-pentane decreased, with increasing cyclohexane amount. At the same conversion of n-pentane, the research octane number (RON) of liquid product, with cyclohexane amount of 0.5 wt%, was about 1.3 higher than that without cyclohexane. At the same reaction conditions, the presence of cyclohexane enhanced the yield of isomerate, the selectivity of liquid isoalkanes, and the RON of the liquid product, but reduced the conversion of n-pentane.

Key words: Isomerization, ionic liquid, improver, pentane, cyclohexane

1 Introduction

The isomerization of normal alkanes into their corresponding branched isomers, which have high octane number, low sensitivity (the difference between research octane number (RON) and motor octane number (MON)), and low sulfur content, is an important petroleum refining process. Isomerate can burn easily and cleanly, and is a good blending component for clean motor gasoline (Hancsók et al. 2007).

Friedel-Crafts catalysts are early industrial catalysts used for many isomerization processes. These catalysts usually operate at low temperatures, but they show poor selectivity, strong corrosion and are difficult to treat (Ono, 2003). The current industrial isomerization catalysts are bifunctional catalysts that have good selectivity. However, they still have some disadvantages, such as high cost due to the utilization of noble metals, large investment and operating cost because of the use of hydrogen, high reaction temperature for zeolite-supported Pt catalysts, and environmental concerns for chlorinated-alumina-supported Pt catalysts.

There is a great incentive to develop novel isomerization catalysts, which include Pt- or Ni- supported on zeolite (Yoshioka et al, 2005; Zakarina et al, 2005; Jordao et al,

2007; Wei et al, 2007), sulfated zirconia and metal-supported sulfated zirconia (Essayem et al, 2003; Vijay and Wolf, 2004; Loften and Blekkan, 2006; Volkova et al, 2007), tungsten oxide supported on zirconia (Lukinskas et al, 2007), heteropoly acids (Essayem et al, 2003), and so on. However, the desired isomerization catalysts must be environmentally friendly and should operate at low temperature.

Ionic liquids have been widely investigated as a new reaction medium or as catalysts (Gordon, 2001; Zhao et al, 2002; Welton, 2004). Some acidic ionic liquids are reported to catalyze the alkylation of isobutane with butene (Yoo et al, 2004; Zhang et al, 2007; Thi et al, 2009) and the oligomerization of butene (Magna et al, 2009; Yang et al, 2009). Acidic ionic liquids can also be used as isomerization catalysts. The isomerization of $\text{C}_5\text{-C}_8$ alkanes can be catalyzed by ionic liquids comprising an N-containing heterocyclic or aliphatic organic cation and an anion derived from metal halides (Vasina et al, 2003). The ionic liquid, when combined with a metal salt additive, is favorable to the formation of multi-branched paraffins (Herbst et al, 2003a; 2003b). Compared with industrial bifunctional catalysts, ionic liquid catalysts exhibit many advantages, such as low reaction temperature, the absence of coke formation, and low investment and operating cost because the lack of hydrogen requirement.

The isomerization of n-pentane can be effectively catalyzed by the ionic liquid $\text{Et}_3\text{NHCl-2AlCl}_3$, and the

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Received November 6, 2010

reaction performance has been reported (Zhang et al, 2008). It is reported that the selectivity for multi-branched isoalkanes can be enhanced by using a cyclic hydrocarbon containing a tertiary carbon atom (Houzvicka et al, 2004). This paper aims to further investigate the isomerization performance of n-pentane catalyzed by the ionic liquid Et_3NHCl - 2AlCl_3 in the presence of product distribution improvers.

2. Experimental

2.1 Preparation of ionic liquid

The cation and anion of the ionic liquid are provided by triethylamine hydrochloride (Et_3NHCl) and anhydrous AlCl_3 , respectively. The ionic liquid was prepared under the protection of dry nitrogen. Et_3NHCl was added to a three-necked flask and then stirred. Anhydrous AlCl_3 , equal to double the amount of Et_3NHCl in mole fraction, was added to the flask little by little. The mixture was stirred at room temperature for 30 min and then heated to 80 °C. Ionic liquid was obtained within 3-4 h. The ionic liquid was marked as Et_3NHCl - 2AlCl_3 .

2.2 Isomerization apparatus and process

The apparatus for n-pentane isomerization is shown in Fig. 1. First, ionic liquid was placed inside the autoclave, and n-pentane and the additive were kept in the feed tank. The autoclave and feed tank were separately heated to desired reaction temperatures. Then, the stirrer was started at 1,200 r/min. The valve for high-pressure nitrogen was opened to

force the feed and additive into the autoclave, and the timer was started. The pressure of the autoclave was kept at 0.7 MPa to ensure the feedstock and products in the liquid state. At last, the autoclave was cooled and the gas product sample was collected by the drainage method. The liquid sample, which did not dissolve in the ionic liquid, was collected by decantation. Experiments were conducted in batch mode, with reaction temperature, reaction time, and catalyst-to-oil volume ratio (C/O ratio) of 30-60 °C, 0.25-8 h, and 1:1, respectively.

2.3 Methods for analyzing isomerization products

The gas sample was analyzed by using an Agilent 6890 gas chromatograph equipped with a hydrogen flame ionization detector, a thermal conductivity detector, and ChemStation software to determine the volume percentage of the components. Data were converted to mass percentages with the ideal gas equation of state. The liquid sample was analyzed using an Agilent 6890 gas chromatograph equipped with a flame ionization detector. Qualitative analysis was performed according to the holding time of the peak, and quantitative analysis was conducted by the area normalization method.

The purpose of isomerization was to produce liquid isoalkanes with high RON. However, some side reactions, such as disproportionating and cracking reactions, also occurred, forming isobutane that will be gaseous state at room temperature and atmospheric pressure. Four evaluation indicators were used to describe the reaction performance, namely the conversion of n-pentane (x , wt%), the yield of isomerate (y_i , wt%), the selectivity of liquid isoalkanes (s_{ia} , %), and the RON of the liquid product, as shown in Equations (1) to (4). Here, isomerate refers to hydrocarbons with carbon number above 4 after reaction including the unreacted n-pentane, whereas the liquid product refers to hydrocarbons with carbon number above 4 after reaction excluding the unreacted n-pentane.

$$x = \left(1 - \frac{w_{np}}{w_f} \right) \times 100\% \quad (1)$$

$$s_{ia} = \frac{w_{ia}}{w_f - w_{np}} \times 100\% \quad (2)$$

$$y_i = \frac{w_i}{w_f} \times 100\% \quad (3)$$

$$\text{RON} = \sum_{i=1}^n C_i \cdot \text{RON}_i \quad (4)$$

In Equations (1) to (4), w_f is the mass of n-pentane before reaction, g; w_{np} is the mass of n-pentane after reaction, g; w_{ia} is the mass of liquid isoalkanes after reaction, g; w_i is the mass of isomerate, g; C_i is the mole percentage of component i , %; and RON_i is the RON of component i .

Fig. 1 Apparatus for the isomerization of n-pentane (1-constant pressure nitrogen, 2-feed tank, 3-counterbalance valve, 4-stirrer, 5-autoclave, 6-feedstock and product, 7-ionic liquid, 8-constant temperature water)

3 Results and discussion

3.1 Investigation of product distribution improvers

Cyclic hydrocarbons such as aromatics and cycloalkanes have an inhibition function to disproportionating reactions. The effect of improvers, such as benzene, cyclohexane, and methyl cyclohexane, on the isomerization of n-pentane was investigated, with the reaction temperature, reaction time, C/O ratio, and improver amount of 30 °C, 3 h, 1:1, and 0.5 wt%, respectively. The results are shown in Table 1 and Fig. 2.

Table 1 Components content in product after reaction with and without improvers

Components after reaction, wt%	Improvers			
	None	Benzene	Cyclohexane	Methyl cyclohexane
i-Butane	3.93	0	1.50	0.48
i-Pentane	32.34	1.59	24.18	13.54
n-Pentane	55.39	98.23	72.10	84.82
i-Hexane	5.73	0.18	1.69	1.05
n-Hexane	0.30	0	0.09	0.03
i-Heptane	2.03	0	0.44	0.08
C ₈₊	0.28	0	0	0

Fig. 2 Conversion of n-pentane, yield of isomerate, and selectivity of liquid isoalkanes with and without improvers

It can be seen from Table 1 and Fig. 2 that the presence of these improvers reduced the yields of i-pentane, i-butane, i-hexane, and i-heptane. Benzene showed a strong inhibition effect and it greatly inhibited both disproportionating and isomerization reactions. Compared with the product distribution without any improver, the yield of i-butane, with cyclohexane and methyl cyclohexane as improvers, was much lower; the yield of isomerate was increased by about 2 wt%, and the selectivity of liquid isoalkanes was enhanced by about 5%. The conversion of n-pentane with cyclohexane as the improver was higher than that with methyl cyclohexane as the improver, while the yield of isomerate and the selectivity

of liquid isoalkanes with cyclohexane as the improver were similar to those with methyl cyclohexane as the improver. The optimal improver was cyclohexane.

3.2 Effect of cyclohexane amount on n-pentane isomerization

The effect of cyclohexane amount on n-pentane isomerization was investigated, under the conditions of the reaction temperature, reaction time, and C/O ratio constant of 30 °C, 3 h, and 1:1, respectively. The results are shown in Table 2 and Fig. 3.

Table 2 Components content in product after reaction as a function of cyclohexane amount

Components after reaction, wt%	Cyclohexane amount, wt%				
	0.1	0.5	1	2	3
i-Butane	3.02	1.50	0.56	0.28	0.18
i-Pentane	31.23	24.18	18.30	13.38	10.27
n-Pentane	60.59	72.10	80.16	85.48	88.81
i-Hexane	3.64	1.69	0.72	0.46	0.30
n-Hexane	0.17	0.09	0.05	0.04	0
i-Heptane	1.35	0.44	0.21	0.32	0.33
n-Heptane	0	0	0	0.04	0.11

Fig. 3 Conversion of n-pentane, yield of isomerate, and selectivity of liquid isoalkanes as a function of cyclohexane amount

From Table 2 and Fig. 3, it can be seen that with increasing cyclohexane amount, the conversion of n-pentane decreased, the yields of i-pentane, i-butane, i-hexane and i-heptane decreased, while the yield of isomerate and the selectivity of liquid isoalkanes increased. As the amount of cyclohexane increased from 0.1 to 1 wt%, the conversion of n-pentane decreased from 39.41 to 19.84 wt%, while the yield of isomerate and the selectivity of liquid isoalkanes only increased by 2.95 wt% and 4.69%, respectively. When the cyclohexane amount increased from 1 to 3 wt%, the n-pentane conversion decreased slowly, and the yield of isomerate and the selectivity of liquid isoalkanes changed little.

3.3 Product distribution with and without improver

The addition of cyclohexane aimed to enhance the yield of isomerate and the selectivity of liquid isoalkanes. This result could also be achieved by reducing the reaction time without any improver (Zhang et al, 2008). The product distribution with and without the improver as a function of n-pentane conversion is shown in Fig. 4.

Fig. 4 Yield of isomerate and selectivity of liquid isoalkanes with and without cyclohexane as a function of the conversion of n-pentane

The yield of isomerate showed decreasing trends whether the improver was used or not. The selectivity of liquid isoalkanes without improver remained almost constant at about 90.7% when n-pentane conversion was below 40 wt%, and then decreased with increasing conversion. The selectivity of liquid isoalkanes with the improver decreased with increasing conversion. At the same conversion, the yield of isomerate and the selectivity of liquid isoalkanes with cyclohexane as the improver were higher than those without improver. The gap between the yields of isomerate with and without cyclohexane as the improver varied slightly with increasing conversion. The gap between the selectivities of liquid isoalkanes with and without cyclohexane as the improver became small. The presence of cyclohexane effectively improved the product distribution when the conversion of n-pentane was below 40 wt%.

3.4 RON of liquid product with and without improver

The RON of the liquid product with and without cyclohexane as a function of n-pentane conversion is shown in Fig. 5. The RON of the liquid product varied slightly at low conversion, and then decreased with increasing conversion. The RON of the liquid product with cyclohexane as the improver was about 1.3 higher than that without cyclohexane.

Table 3 lists the result of n-pentane isomerization with and without improver. Compared with the isomerization at a reaction temperature of 30 °C, a reaction time of 3 h and a C/O ratio of 1:1 without cyclohexane, the presence of cyclohexane with 0.5 wt% at the same reaction conditions decreased the conversion of n-pentane by 16.71 wt%,

increased the yield of isomerate by 2.37 wt%, increased the selectivity of liquid isoalkanes by 3.56%, and increased the RON of the liquid product by 2.68.

Fig. 5 RON of the liquid product with and without cyclohexane as the improver as a function of the conversion of n-pentane

Table 3 Isomerization performance of n-pentane with and without cyclohexane (reaction temperature: 30 °C, reaction time: 3 h, and C/O ratio: 1:1)

Item	Without cyclohexane	With cyclohexane, 0.5 wt%
Conversion of n-pentane, wt%	44.61	27.90
Yield of isomerate, wt%	96.07	98.44
Selectivity of liquid isoalkanes, %	90.52	94.08
RON of the liquid product	89.21	91.89

4 Conclusions

(1) Cyclohexane can modify the product distribution for n-pentane isomerization catalyzed by the ionic liquid $\text{Et}_3\text{NHCl}-2\text{AlCl}_3$.

(2) The yield of isomerate and the selectivity of liquid isoalkanes increased with increasing amount of cyclohexane, while n-pentane conversion decreased.

(3) At the same reaction conditions, the presence of cyclohexane enhanced the yield of isomerate, the selectivity of liquid isoalkanes, and the RON of the liquid product, but reduced the conversion of n-pentane.

Acknowledgements

Financial support was provided by the National Science Foundation of China (Grant Nos. 20806091, 20976194, and 21036008).

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(Edited by Zhu Xiuqin)