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Kinetic studies on the dimerization of isobutene with Ni/Al_2O_3 as a catalyst for reactive distillation process ☆

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ABSTRACT

Isooctane is a promising gasoline additive that could be produced by dimerization of isobutene (IB) with subsequent hydrogenation. In this work, the dimerization of IB has been carried out in a batch reactor over a temperature range of 338–383 K in the presence of laboratory prepared Ni/Al_2O_3 as a catalyst and *n*-pentane as solvent. The influence of various parameters such as temperature, catalyst loading and initial concentration of IB was examined. A Langmuir–Hinshelwood kinetic model of IB dimerization was established and the parameters were estimated on the basis of the measured data. The feasibility of oligomerization of IB based on the reactive distillation was simulated in ASPEN PLUS using the kinetics developed. The simulation results showed that the catalyst of Ni/Al_2O_3 had higher selectivity to diisobutene (DIB) and slightly lower conversion of IB than ion exchange resin in the absence of polar substances.
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1. Introduction

As a commonly used additive of gasoline, methyl *tert*-butyl ether (MTBE) can not only enhance the octane rating of gasoline but also reduce the amount of exhaust emissions. However, due to its involvement with groundwater contamination [1], MTBE has been banned as a gasoline blend in California and other states of the United States. Many enterprises and research institutions began to find substitutes for MTBE, such as *tert*-butyl ethyl ether (ETBE), *tert*-amyl methyl ether (TAME) and isooctane [2]. Meanwhile, the shrinking market of MTBE might cause a significant descent in the consumption of IB from fluid catalytic cracking and steam cracking processes. Thus, it is crucial to develop a new route to take full use of the redundant IB. The new route, of which the product can be used as a gasoline additive directly, will be desirable if it can directly take advantageous of the C4 resources and the current MTBE units such as the reactive distillation (RD) column with minimum modification.

Isooctane, one of the branched paraffin with carbon numbers in the range of 8 to 12, is confirmed as a reasonable replacement of MTBE. It is synthesized either by direct alkylation of isobutene with C4 olefines or by indirect alkylation [3]. The process of indirect alkylation of isobutene is divided into 2 steps: (1) the production of diisobutenes (DIBs) including 2,4,4-trimethyl-1-pentene (TMP-1) and 2,4,4-trimethyl-2-pentene (TMP-2) by dimerization of IB; and (2) the synthesis of isooctane by hydrogenation of DIBs.

As demonstrated in Fig. 1, several byproducts such as triisobutene (TIB) and teraisobutene (TEB) can be produced for the complex series–parallel reaction network of oligomerization of IB. These byproducts are not only unsuitable as gasoline additives but also possible to promote the catalyst deactivation [4]. As a sequence, the selectivity toward DIB is a crucial issue to concern. Dimerization of IB can be carried out in the liquid phase using solid acid catalysts. Hauge *et al.* [5] and Yaocihuatl *et al.* [6] studied the reaction on zeolites, and they reached a high selectivity toward DIB. However, the stability of catalyst was not satisfied. Ion exchange resin is also widely used [7–9]. Different polar components such as methanol, MTBE, water and *tert*-butyl alcohol (TBA) [10–12] are used as selectivity enhancers due to its high activity, which causes special costs for the separation of the added components from final products. Besides applying different catalysts, another approach for improving the selectivity to DIB is to employ multifunctional reactors, such as RD. Ouni *et al.* [13] reported a case study of this reaction by RD with 78 ideal stages, which implied a large investment from an industrial point of view. Kamath *et al.* [14] studied the feasibility of the dimerization of IB in RD by simulation and found that a hybrid RD was capable of carrying out the reaction and simultaneously separating the products efficiently. Talwalkar *et al.* [15] made experiments on the dimerization of IB in RD column and reported that the use of polar components as selectivity enhancers was not necessary by RD technology. The above studies on the feasibility of RD were based on the ion exchange resin such as

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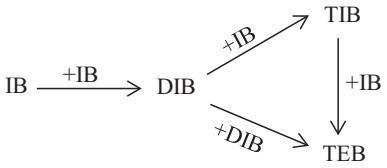

Fig. 1. Reaction network of oligomerization of isobutene.

Amberlyst 15. However, catalytic systems consisting mainly of nickel compounds supported on oxides, zeolites and organometallic nickel complexes have been widely used as dimerization catalysts and their feasibility of IB oligomerizaiton in RD is seldom reported.

The aim of this contribution was to evaluate the feasibility of IB oligomerization by Ni/Al_2O_3 as a catalyst in RD. The influence of the important parameters (*e.g.* temperature, the amount of active component (Ni) loading and initial concentration of IB) on the IB conversion and DIB selectivity was investigated based on the catalyst. A kinetic model was developed for such a system under nonpolar conditions based on the laboratory batch reactor data, which was applied to the simulation of DIB productions by RD.

2. Experimental

2.1. Materials

IB (>99.0%, by mass) was obtained from Foshan Shike Air Chemical Ltd. and *n*-pentane (AR, >98.5%) was supplied by Shanghai Linfeng Chemical Reagents Ltd., both were used as received. $NiSO_4 \cdot 6H_2O$ (AR, >98.5%) and N_2 (>99.999%) were purchased from Guoyao Chemical Reagents Ltd. The catalyst support Al_2O_3 was supplied by Jiangxi Xinquan Packing Ltd. Its physical–chemical properties are given in Table 1.

2.2. Catalyst preparation and characterization

Ni/Al_2O_3 catalyst was prepared by the incipient impregnation method. The Al_2O_3 support was immersed in the solutions that contained a specific amount of Ni for 4 h at 333 K. The solid was dried for 12 h at 393 K and then calcined for 8 h at 773 K. After the above described treatment, the amount of Ni loading was detected by inductively coupled plasma-atomic emission spectroscopy (ICP-AES) (IRIS 1000 Thermo Elemental Co. Ltd. USA). X-ray powder diffraction (XRD) measurements were performed on a Rigaku D/MAX 2550 VB/PC instrument with scan speed of $2(°)\cdot min^{-1}$, scan range of 10°–80° at 40 kV and 100 mA. The Thermo Gravimetric Analysis (TGA) pattern was detected by thermos-gravimetric analyzer (SDT Q600 TA Co. USA). The sample was heated from 298 K to 1073 K at a heating rate of $10\ K\cdot min^{-1}$ with air atmosphere in flow of $100\ ml\cdot min^{-1}$.

2.3. Apparatus and procedure

A 500 ml stainless steel autoclave (Berghof Ltd., Germany), equipped with speed and temperature monitoring facilities and an automatic cooling system, was used for all batch reactions. Two calibrated feed containers (150 ml and 75 ml) were used to precisely adjust feed concentration that was pressed into the batch reactor by pressured N_2. At the beginning, the specific quantities of the catalyst were charged into the reactor and N_2 was fed into to exclude air. Then, the solvent *n*-pentane in the feed container (150 ml) was charged into the reactor. As the mixture was heated to given temperatures, the IB in the feed container (75 ml) was fed into the reactor and the agitation was activated. Meanwhile, the pressure of the reactor was adjusted to a desired value by N_2 and the corresponding time was regarded as the zero reaction time. Samples were withdrawn at the different time intervals by a self-made micro sampler. All the samples were frozen by ice to avoid the volatilization.

2.4. Sample analysis

All reactants and products were analyzed by a gas chromatograph (Agilent 7890A) using DB-1 column (connected to FID). The column temperature was maintained at 318 K for the first 2 min and then was raised at a rate of $15\ K\cdot min^{-1}$ to 523 K for 5 min. The correction factors of all components were close to 1.0, so the area of peak normalization method was applied to calculate the mass fraction of reactants and products.

2.5. Conversion and selectivity

The conversion of IB (X_{IB}) and selectivity (S_i) to DIB, TIB and TEB were calculated on the basis of various products formed:

$$X_{IB} = 100 - \frac{m_{IB}}{m_{IB} + m_{DIB} + m_{TIB} + m_{TEB}} \times 100 \quad (1)$$

$$S_{DIB} = \frac{m_{DIB}}{m_{DIB} + m_{TIB} + m_{TEB}} \times 100 \quad (2)$$

$$S_{TIB} = \frac{m_{TIB}}{m_{DIB} + m_{TIB}} \times 100 \quad (3)$$

$$S_{TEB} = \frac{m_{TEB}}{m_{DIB} + m_{TEB}} \times 100. \quad (4)$$

3. Results and Discussion

3.1. General course of the reaction

The oligomerization of IB is effected by various factors such as active component (Ni) loading, catalyst loading, temperature and initial IB concentration. With the increase of Ni loading, the conversion of IB is dramatically enhanced, while the selectivity to DIB is dropped. The temperature also plays an important role in the oligomerization of IB. As a strong exothermic reaction ($\Delta H_r = -346.9\ kJ\cdot mol^{-1}$) [16], high temperatures facilitate the desired dimerization of IB as well as the undesirable trimerization and oligomerization.

In this work, the effect of three major reaction conditions (temperature, catalyst loading and initial IB concentration) was examined with a suitable Ni loading decided by experiments. Moreover, properties of catalyst were analyzed through XRD and differential scanning calorimetry-thermogravimetric analysis (DSC-TG).

3.2. Mass transfer effect

Stirrer speeds of 200, 350 and $500\ r\cdot min^{-1}$ were tested during a preliminary experiment to ensure that external mass-transfer limitations were not present in the experiments. As shown in Fig. 2, the mass

Table 1
Physical-chemical properties of catalyst support

	Configuration/mm	Pore diameter/nm	Porosity	Specific surface area/$m^2\cdot g^{-1}$	Pore volume/$ml\cdot g^{-1}$	Bulk specific mass/$kg\cdot L^{-1}$	Radial crushing strength/$N\cdot mm^{-2}$
Specifications	OD φ3.5 × ID φ1.2 × H 3.8	5–7	≥55%	≥150	0.5–0.7	0.55–0.7	≥20

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