Kinetic Study of 1-Butene Isomerization over Hydrotalcite Catalyst

S. Sripinun, K. Suriye, S. Kunjara Na Ayudhyab, P. Praserthdam, S. Assabumrungrat

Abstract—This work studied the isomerization of 1-butene over hydrotalcite catalyst. The experiments were conducted at various gas hourly space velocity (*GHSV*), reaction temperature and feed concentration. No catalyst deactivation was observed over the reaction time of 16 hours. Two major reaction products were *trans*-2-butene and *cis*-2-butene. The reaction temperature played an important role on the reaction selectivity. At high operating temperatures, the selectivity of *trans*-2-butene was higher than the selectivity of *cis*-2-butene while it was opposite at lower reaction temperature. In the range of operating condition, the maximum conversion of 1-butene was found at 74% when $T = 673$ K and *GHSV* $= 4$ m^3/h/kg-cat with *trans*- and *cis*-2-butene selectivities of 54% and 46%, respectively. Finally, the kinetic parameters of the reaction were determined.

Keywords—Hydrotalcite, isomerization, kinetic, 1-butene.

NOMENCLATURE

C_i concentration of species i in the fixed bed reactor (mol/ml)
F_i molar flow rate of species i in the fixed bed reactor (mol/s)
W weight of the catalyst (g)
k_i apparent rate constant for the ith reaction (L/s•g catalyst)
K_e equilibrium constant
E_a apparent activation energy (kJ/mol)
A_0 pre-exponential factor for the ith reaction
r_i rate of species i of the ith reaction

I. INTRODUCTION

1-BUTENE isomerization reaction can occur via the skeletal isomerization to isobutene or the double bond isomerization to *cis*- and *trans*-2-butene. This reaction has been studied over many solid base catalysts while the first study of solid base catalyst included sodium dispersed on alumina in 1950s for double bond isomerization of alkenes [1]. One among efficient base catalysts is hydrotalcite. The studies of hydrotalcite catalyst have become attractive as its number and strength of basic sites can be adjusted accurately to a specific reaction. Moreover, the structure, composition parameters, and calcination temperature, typically at 673-773 K, can affect the basicity of hydrotalcite [2], [3] on various

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extent depending on Mg/Al ratio [4]. According to the literature so far, there has been only a few researches on the isomerization of 1-butene over hydrotalcite catalyst. Beres et al. [5] synthesized hydrotalcite and tested catalytic activities in 1-butene isomerization after calcination at 723 K. It was found that the heat treatment destroyed the hydrotalcite-like structure and created mixed oxides. However, the rate expression of this reaction on hydrotalcite catalyst has never been reported. Thus, the present work examines the isomerization of 1-butene over hydrotalcite catalyst and determines its reaction rate expression.
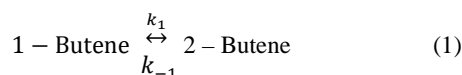
II. MATERIALS AND METHODS

A. Evaluation of Hydrotalcite Catalyst

The commercial hydrotalcite catalyst was grinded and screened to get particles having sizes smaller than 250 microns. A 0.3 gram of hydrotalcite catalyst was packed in a fixed bed reactor having plugs of quartz wool and inert balls on both ends. The catalyst was pretreated at 773 K under N$_2$ (99.99% purity) flow of 50 ml/min for 1 hour. It was cooled to a desired reaction temperature between 623, 673 and 723 K. The gaseous feed of 10% 1-butene in nitrogen was fed downwards through the packed catalyst and co-fed by N$_2$ (99.99% purity). The concentration of 1-butene (2.4 -10 mol% in feed) was controlled by increasing N$_2$ co-feed. Gas hourly space velocity (*GHSV*) was studied in a range of 4 – 16 m^3/h/kg-cat. The reaction was carried out at atmospheric pressure. The outlet gas was analyzed by a gas chromatography equipped with an FID detector. All instruments were set up as shown in Fig. 1.

B. Reaction Rate Expressions

The isomerization of *n*-butene does not only involve *cis/trans* rearrangements, but also simultaneous reversible rearrangement to isobutene. The three possible reactions are illustrated in Fig. 2. For the whole temperature range evaluated, no isobutene was found. Thus the isomerization of *n*-butene in this study considered only reaction <1> shown in Fig. 2.

However, in this study, both *cis*- and *trans*- isomer are not considered separately but combined as 2-butene. The reaction is written as (1).

$$1-\text{Butene} \underset{k_{-1}}{\overset{k_1}{\leftrightarrow}} 2-\text{Butene} \qquad (1)$$

In the system of heterogeneous catalyst, rate of the reaction of component A is defined as mol A/s-g catalyst and the

design equation for a packed-bed catalytic reactor can be written as (2). Assuming power rate law model and elementary reaction, then the rate expression of 1-butene can be written in forms of (3) – (4).

$$\frac{dF_A}{dW} = \dot{r}_A \tag{2}$$

$$-\dot{r}_A = k_1(C_A - \frac{C_B}{K_e}) \tag{3}$$

$$\dot{r}_B = k_1(C_A - \frac{C_B}{K_e}) \tag{4}$$

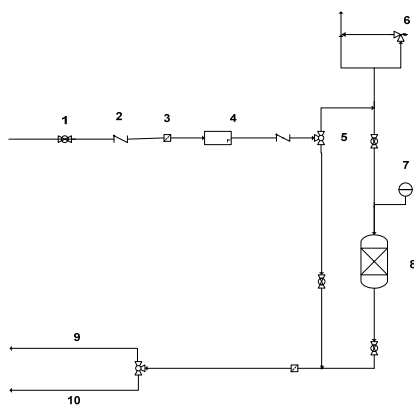where A and B represent 1-butene and 2-butene, respectively.

Fig. 1 Schematic diagram of 1-butene isomerization system; 1 = on-off valve, 2 = check valve, 3 = filter, 4 = mass flow controller, 5 = 3-ways valve, 6 = relief valve, 7 = pressure gauge, 8 = reactor, 9 = gas chromatography, 10 = open vent
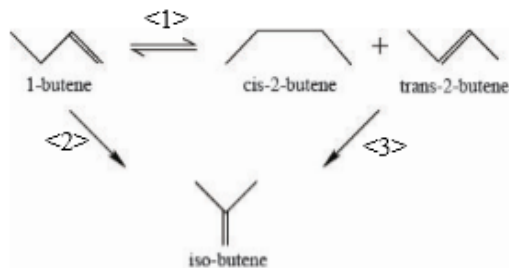

Fig. 2 Isomerization of butene [6]

The thermodynamic equilibrium was simulated between 1-butene, *cis*-2-butene and *trans*-2-butene by using Aspen Plus Software in a REquil reactor with NRTL (Non Random To Liquid) method. The equilibrium constants (K_e) at temperature 623 K, 673 K, and 723 K and pressure 1 bar. are 3.591, 3.118, and 2.757, respectively. This shows that the maximum conversion of 1-butene at 623 K, 673 K, and 723 K are 78%, 76% ,and 73%, respectively.

C. Numerical Analysis

To solve multiple ordinary differential (3) and (4) in order to obtain all reaction rate constants, *k*, 4th order Rung-Kutta method was selected.

III. RESULTS AND DISCUSSION

A. Effect of Reaction Parameters on Hydrotalcite Catalytic Performance

To investigate the effect of temperature on the activity of catalyst, the temperature of isomerization of 1-butene was varied between 623 and 723 K. From Fig. 3, generally for every *GHSV* range the highest conversion of 1-butene was obtained at the highest temperature (723 K) and followed by 673 and 623 K, sequentially. This is agreed to Arrhenius equation that the reaction rate significantly increased at elevated temperature. It can be noticed that the gap increase of the activity when the temperature changes from 623 to 673 K was quite large compared to that when the temperature was changed from 673 to 723 K.
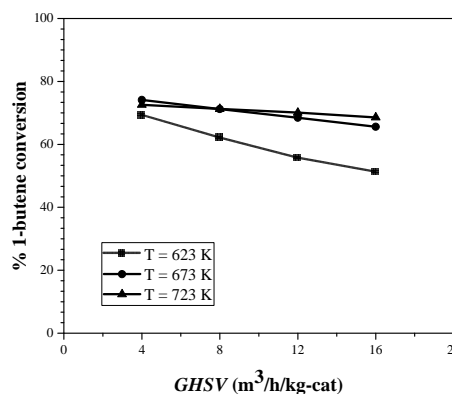

Fig. 3 Effect of *GHSV* and reaction temperature on conversion of 1-butene: Reaction condition *P* = 1 bar, 0.3 g of catalyst, 5%mol 1-butene in feed

Another parameter which involves in the performance of catalyst is *GHSV*. From Fig. 3, at the temperature of 623 K, the amount of 1-butene converted was greatly affected by changing *GSHV*. By increasing *GHSV* from 4 to 16 m^3/h/kg-cat, 1-butene conversion decreased from about 69.3% to 51.1 %. This is because of the lower contact time of the reactant in the catalyst bed at the high *GHSV* [7]. When the operating temperature was higher, the effect of *GHSV* on 1-butene conversion became less observable. This is due to the predominant effect of the reaction rate at the high temperatures. It can be concluded that *GHSV* effect is dominant especially at low reaction temperature.

On the other hand, *GHSV* showed only a minor effect on *cis*- and *trans*-2-butene selectivity as illustrated in Figs. 4 and 5 in every temperature. It was observed that the selectivity of *cis*- and *trans*-2-butene did not remarkably change in the *GHSV* range of 4 to 16 m^3/h/kg-cat. For the whole temperature range evaluated, no skeletal isomerization of 1-butene to isobutene was found over hydrotalcite catalyst. The major selectivity was towards *trans*-2-butene, followed by *cis*-2-butene for the 673 and 723 K cases. In contrast, at the temperature 623 K, the selectivity of *cis*-2-butene was the major one. This is because the reaction rate at 623 K was the slowest of all temperatures and the activity of catalyst was

away from the equilibrium. Moreover, the selectivity of *cis*-2-butene was increased differing from *trans*-2-butene when *GHSV* was risen. It is reasonable to summarize that 1-butene was isomerized to *cis*-2-butene first and then geometrically isomerized to *trans*-2-butene. This is agreeable with the literatures [8] which studied the base-catalyzed isomerization of 1-butene. The characteristic selectivity of the product isomers in base catalyst depends on the relative stability of two allylic carbanions which is the intermediates form [9]. Since allylic carbanion in *cis* form is more stable than *trans* form on the surface of solid base catalyst,, the concentration of allylic carbanion in *cis* form is higher than *trans* form. Thus, in the initial stage of 1-butene isomerization *cis*-2-butene is predominantly formed over *trans*-2-butene [5].
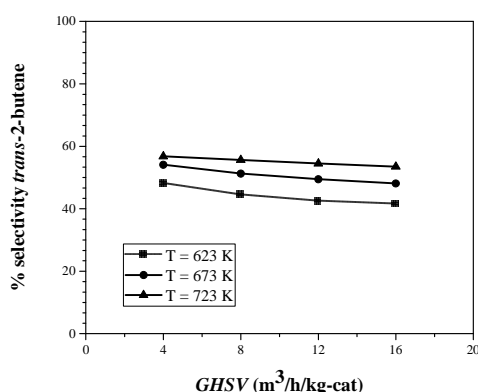

Fig. 4 Effect of *GHSV* and reaction temperature on the selectivity of *cis*-2-butene: Reaction condition P = 1 bar, 0.3 g of catalyst, 5% mol 1-butene in feed
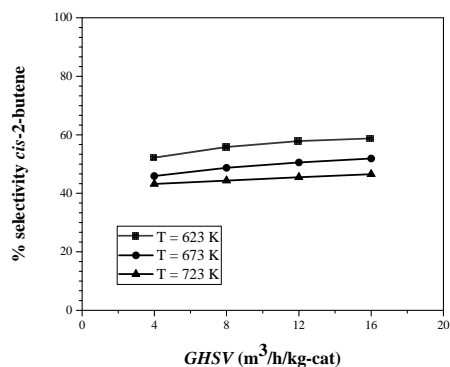

Fig. 5 Effect of *GHSV* and reaction temperature on the selectivity of *trans*-2-butene: Reaction condition P = 1 bar, 0.3 g of catalyst, 5% mol 1-butene in feed

In order to investigate the effect of concentration of 1-butene feed on the activity of catalyst, the experiments were set up by varying the concentration of 1-butene feed between 2.4 to 10 mol%. It was found that the conversion was slightly changed when changing feed concentration. In the kinetic study of reactions, the concentration of reactant was directly involved in the rate of the reactions. In spite of the same equilibrium conversion, it did not mean that the reactions were not affected by concentration of 1-butene feed. In this study,

the concentration has just a minor effect on the activity of catalyst because of the narrow range of varied concentration of feed.
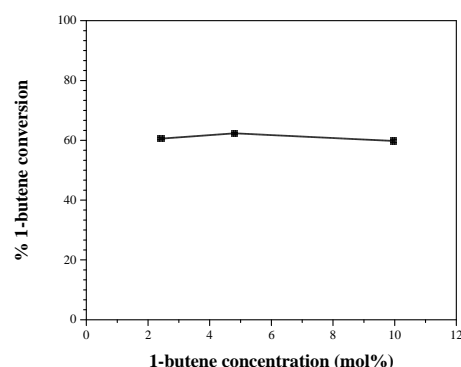

Fig. 6 Effect of 1-butene concentration on the conversion of 1-butene: Reaction conditions P = 1 bar, T = 623 K, total feed flow rate (1-butene + N_2) = 45 ml/min

B. Parameter Estimation and Kinetic Evaluation

Based on experimental data at different temperatures, the kinetic parameters in (1) can be evaluated and summarized in Table I.

TABLE I
ESTIMATED RATE CONSTANTS OF ALL 1-BUTENE ISOMERIZATION REACTIONS

	Reaction rate constants (L/s· g catalyst)		
	623 K	673 K	723 K
k_1	0.008065	0.014207	0.023143
k_{-1}	0.002246	0.004559	0.008394

$$k = A_0 \, exp \, (-E_a/RT) \qquad (5)$$

According to Arrhenius (5), the rate constants which depend on temperature are represented in Fig. 7. The parameters of the Arrhenius equation which display the plot of ln$k$ versus 1000/T are estimated and represented in Table II and Fig. 7. The straight line with negative slopes of the Arrhenius plot of the rate constants confirms the thermodynamic consistency of the present Power Law model.

TABLE II
ARRHENIUS EQUATION PARAMETERS

Reaction rate constant	A_0	E_a (kJ mol^{-1})
k_1	16.50	39.50
k_{-1}	31.06	49.40

Fig. 8 shows the comparison between the experimental data and model predictions for the reaction scheme. It is clear that the values predicted and the values measured experimentally are in good agreement for the reactions at 623, 673, and 723 K.
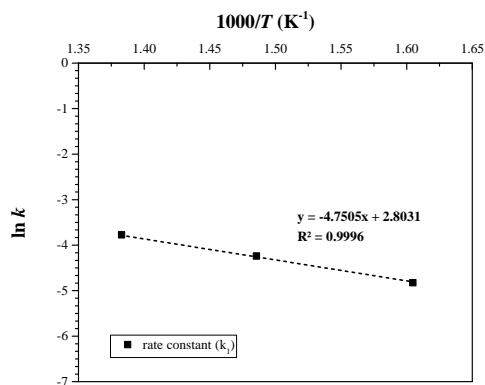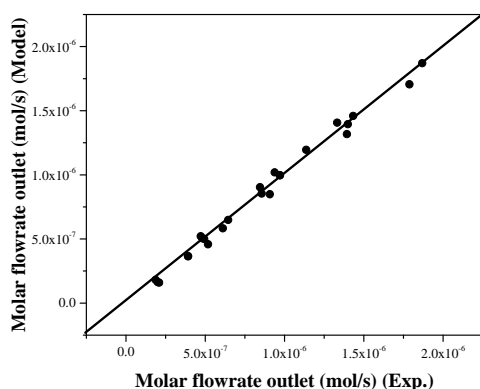
Fig. 7 Arrhenius plots of isomerization pathways

Fig. 8 Comparison between experimental results and model predictions for 1-butene and 2-butene at the reaction temperature at 623, 673, and 723 K

IV. Conclusion

The present investigation is to estimate kinetic parameters and to study the effect of reaction parameters on 1-butene isomerization reaction over hydrotalcite catalyst which leads to the following conclusions. The experiments were performed at various temperature and gas hourly space velocity (*GHSV*); therefore, the rate constant of the reaction can be determined. The rate constant (*k*) at temperature 623, 673, and 723 K. are 0.008065, 0.014207, and 0.023143 respectively. The reaction rate was increased at elevated temperature. This is the reason why the activity of 1-butene isomerization over hydrotalcite catalyst exhibits high 1-butene conversion at high temperature and low *GHSV*. The product selectivity is significantly influenced by the reaction temperature, but slightly affected by gas hourly space velocity (*GHSV*) and feed concentration. The kinetics investigation shows that the activation energy of 1-butene and 2-butene isomerization were 39.50 and 49.40 kJ/mol, respectively.

Acknowledgment

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