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STUDY ON THE ALKYLATON MECHANISM OF ISOBUTANE WITH 1-BUTENE USING ENVIRONMENTAL FRIENDLY CATALYSTS

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Abstract

The alkylation of light hydrocarbons leads to produce the high octane number gasoline blending components. The homogeneous catalytic alkylation reaction is usually carried out at low temperature in the presence of H_2SO_4 and HF. The use of heterogeneous catalysis for this reaction is a promising solution for the replacement of hazardous acids to environmentally friendly zeolite catalyst. The alkylation reaction of isobutane with 1-butene was studied on selected zeolite catalysts. The objective of the research was to study the mechanism of the alkylation reaction with taking the rate determining step and irreversible step into consideration.

Keywords: alkylation, catalysis, mechanism, rate determining step

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1. Introduction

Due to the continuously increasing demand for high quality fuels the alkylation reaction is very important to provide high octane number blending components for the gasoline pool (Olah, 1964). Several industrial technologies are available to produce C_8 hydrocarbons from light saturated and unsaturated hydrocarbons. Usually, isobutane is reacted with propylene, 1-butene and 2-butene in the presence of sulfuric acid or hydrofluoric acid (Dixon and Allen, 1960; Shengwei et al., 2009). $AlCl_3$, BF_3 catalysts can also be used, but hydrofluoric acid and sulfuric acid are widely used in refineries. The typical reaction parameters are as follows: low reaction temperature up to 50°C, isobutane-olefin molar ratio of 3-12 and moderate pressure to keep the reactants in liquid state and to carefully control the rate of evaporation of the reactants (Hatch and Matar, 1981). The alkylate can be characterized with high octane number (over 90).

The strong acids exhibit significant dangers both to environment and human beings therefore extremely strict technological procedures are in effect and those should be fully observed. Even high level contingency plans should be elaborated for refineries using alkylation technologies with strong acids and the preparedness must be provided in full extent. In order to substitute the strong acids with environmentally more friendly catalysts, such zeolites, the use of acidic ion exchange resins were studied in the alkylation reaction. The natural

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zeolites, the modified zeolites as well as the synthetic zeolites have been widely used in various industrial applications based on their properties to act as catalysts, adsorbents, carriers etc. (Apostol and Gavrilescu, 2009; Apreutesei et al., 2008; Catrinescu et al., 2002, Tudorache Fertu and Gavrilescu, 2012).

The study on alkylation reaction of isobutane with light olefins with using ion-exchanged zeolites (Sievers et al., 2007) is important since the replacement of the hydrofluoric acid or sulfuric acid catalysts could possibly be realized in this technology therefore this objective was aimed at in the paper. The kinetics and mechanism of the alkylation reaction was also studied.

2. Experimental

FAU,Y-type zeolite was used after ion-exchange procedure and pretreatment. The zeolite was ion-exchanged with NH_4Cl and rare earth element (La). The ion-exchanged zeolites were pretreated according to the standard procedure (Rédey, 1982) and were used for the experiments after treatment in the temperature range of 300-550°C. The following abbreviations are used: La-FAU,Y (lanthanum ion-exchanged faujasite Y type zeolite); H/NH_4/-FAU,Y (ammonium ion-exchanged Y zeolite); H/NH_4/,RE-FAU, (ammonium and rare earth element ion-exchanged Y zeolite). The experiments were carried out in a batch reactor and in continuous tube reactor.

The kinetic measurements were carried out in the temperature range of 40-160°C, isobutane-1-butene molar ratio of 8:1 and liquid load of 0.2-0.4 cm^3/cm^3h. The pressure was set to 5 bar during the kinetic measurements. The main goal of this work was to understand the mechanism of the alkylation reaction rather than the study on the effect of the technological parameters (temperature, molar ratio of isobutane to 1-butene, residence time) on the alkylate yield and composition.

3. Results and discussions

3.1. Ion-exchange procedure of Y type zeolite

The NH_4^+ (NH_4Cl) ion-exchange is more favorable for zeolites, followed by the thermal removal of NH_3, leaving behind Brönsted acid centers (Ward, 1967; Ward, 1969). The H-form obtained in this way contains very loosely bound, easily removable protons, Brönsted sites (Fig. 1). At temperatures higher than 550°C dehydroxylation (loss of water) occurs and the Brönsted acid sites formed are converted by the loss of water into the Lewis acid sites (Ward, 1968). Therefore the proper selection of the pretreatment is very important in balancing the acid site distribution.

The H/NH_4/-FAU,Y zeolite was further ion-exchanged with rare earth element (RE) to produce H/NH_4/,RE-FAU,Y zeolite. The exchange procedure can be followed in Fig. 2. Lanthanum was the selected rare earth element for the ion-exchange.

The Brönsted acidity of the modified zeolites was investigated with infrared spectroscopic method in the wavenumber range of 3200-4000cm^{-1}. The wavenumber of 3640cm^{-1} was attributed to Brönsted acidic sites formed on the surface of the catalyst. This band has high intensity for rare earth (La) ion-exchanged zeolite treated between 450 and 550°C. Under 450°C pretreatment temperature range the Brönsted active sites are covered by molecular absorbed water in the bulk of the samples. Temperatures above 550°C significantly decrease the OH–groups on surface of the sample, which means dehydroxilation.

3.2. Catalytic test

The alkylation catalytic tests were carried out on the H/NH_4/,La-FAU,Y- and H/NH_4/,RE,FAU,Y-zeolite samples. The highest yield of the valuable C_8 compounds was achieved on rare earth (La) ion-exchanged zeolite at 80°C reaction temperature.

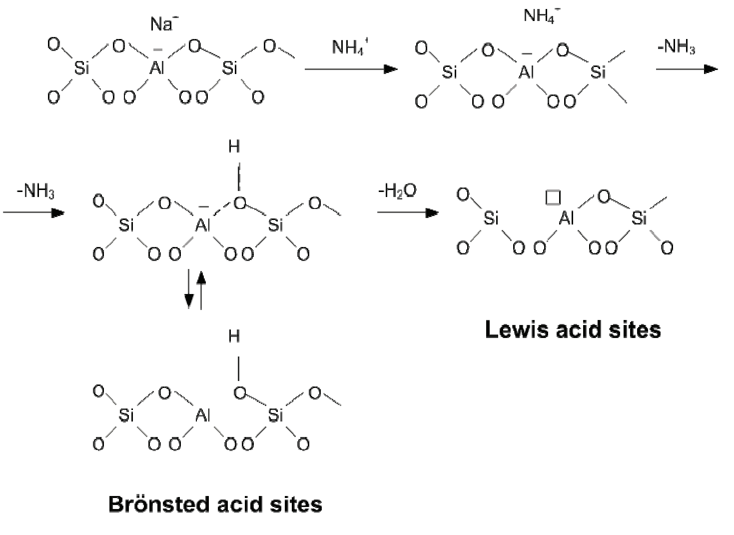

Fig. 1. Formation of acid sites on zeolites

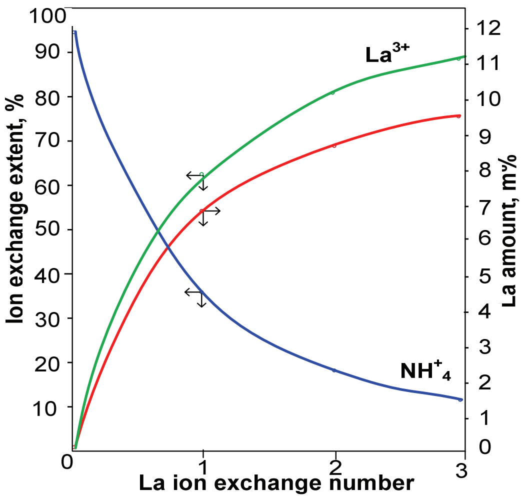

Fig. 2. The extent of the ion-exchange in the function of number of ion-exchanges

The initial reaction mixture isobutane : 1-butene molar ratio was 8:1 respectively. The C_8 content of the alkylate was 40% and the trimethyl-pentane (TMP) content of the alkylate was about 32%. The alkylation reaction can be given as follows:

$$n-C_4H_8+i-C_4H_{10}\rightarrow i-C_6H_{18}$$

gas gas liquid

A + B → C

The catalyst activity decreased vs. time so that, after five hours on stream, the alkylation yield declined and C_8 olefin content increased. This indicated that the parallel reaction, specifically the polymerization of the 1-butene became the determining reaction. The temperature range of 60-70°C and the pressure of 30 bar are the most appropriate values of parameters for alkylation. The trimethyl-pentane yield has the maximum in the temperature range of 50-70°C. At higher temperatures (80-100°C) the formation of dimethyl-hexanes is favored. The distribution of the trimethyl-pentanes in the function of temperature is given in Fig.3.

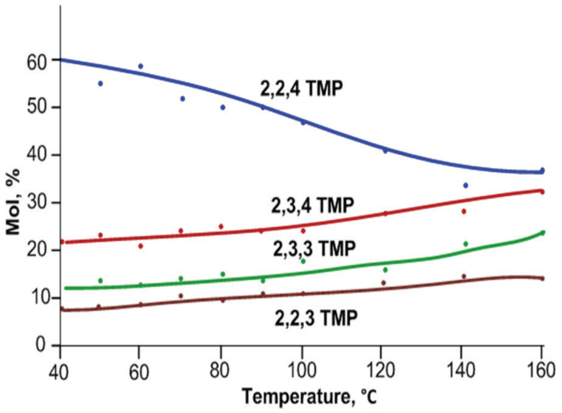

Fig. 3. Distribution of TMP-isomers with temperature

3.3. Kinetics and mechanism of alkylation reaction

Kinetics of the heterogeneous catalytic conversion in case of alkylation reaction, namely the A+B→C type reaction was studied. In order to clarify the reaction mechanism and kinetics, the alkylation reaction was studied in vapor phase. The elementary reactions steps were taken into consideration. The following steps were considered: adsorption, chemical reaction on surface and desorption. Our goal was to develop a generally valid kinetic formula on the basis of assumption of the rate determining and irreversible steps.

The reaction rate can be expressed in terms of rate constants, partial pressure and surface coverage (Rédey, 1981; Szabó and Kalló, 1976). The elementary steps of the alkylation reaction (A+B→C) can be given as follows:

1. Adsorption of component A (1-butene):

$$A+l\Leftrightarrow Al=A_a$$
$$r_A=k_Ap_A\Theta_0-k_{-A}\Theta_A$$

2. Adsorption of component B (isobutane):

$$B+l\Leftrightarrow Bl=B_a$$
$$r_B=k_Bp_B\Theta_0-k_{-B}\Theta_B$$

3. Surface reaction of components A and B:

$$A_a+B_a\leftrightarrow C_a+l$$
$$r_f=k_{AB,C}\Theta_A\Theta_B-k_{-AB,C}\Theta_C\Theta_0$$

4. Desorption of component C (trimethyl-pentane):

$$C_a\Leftrightarrow C+l$$
$$r_{-c}k_{-C}\Theta_C-k_Cp_C\Theta_0$$
$$\Theta_0^*+\Theta_A^*+\Theta_B^*+\Theta_C^*=1$$

where: *l* - represents the active site of the catalyst; A_a, B_a, C_a - represent species *A, B, C* in adsorbed phase; r_A, r_B, r_f, r_{-C} - reaction rates of the elementary steps; θ_0 - uncovered surface active sites; θ_A, θ_B, θ_C - surface active sites covered by components *A, B, C.*

The surface chemical reaction can be depicted according to the following steps:

$$i-C_4H_{10}+n-C_4H_8\Leftrightarrow i-C_8H_{18}$$

$$1.\ n-C_4H_8+H^+\Leftrightarrow s-C_4H_9^+$$
$$2.\ s-C_4H_9^++i-C_4H_{10}\Leftrightarrow n-C_4H_{10}+(CH_3)_3C^+$$
$$3.\ (CH_3)_3C^+\Leftrightarrow i-C_4H_8+H^+$$
$$4.\ (CH_3)_3C^++n-C_4H_8\Leftrightarrow i-C_8H_{17}^+$$

$$5.\ i-C_8H_{17}^{+}+i-C_4H_{10}\Leftrightarrow i-C_8H_{18}+(CH_3)_3C^{+}$$

where:

Step 1. The Brönsted acid centre of the zeolites can protonate the 1-butene and this results in s-butyl carbenium ion;

Step 2. The s-butyl-carbenium ion reacts with isobutane producing t-butyl-carbenium ion;

Step 3. The t-butyl-carbenium ion can be transformed into isobutene and proton;

Step 4. The t-butyl-carbenium ion reacts with 1-butene resulting in isooctyl-carbenium ion;

Step 5. Hydride ion abstraction from an isobutane by isooctyl-carbenium ion results in trimethyl-pentane and t-butyl-carbenium ion.

The t-butyl-carbenium ion formed in step 5 can be considered as the active surface site and maintains the reaction loop with starting in step 4. Taking into consideration that the first three reaction steps can be considered as an initialization, the step 4 and step 5 are considered only in following:

Step. 4: Formation of isooctyl-carbenium ion and

Step. 5: Formation of product trimethyl-pentane

$$4.\ (CH_3)_3C^{+}+n-C_4H_8\Leftrightarrow i-C_8H_{17}^{+}$$

$$5.\ i-C_8H_{17}^{+}+i-C_4H_{10}\Leftrightarrow i-C_8H_{18}+(CH_3)_3C^{+}$$

Step 4. $Z+A\Leftrightarrow ZA$ coverages: $(CH_3)_3C^{+}=\Theta_Z$

Step 5. $ZA+B\Leftrightarrow C+Z$ $\quad i-C_8H_{17}^{+}=\Theta_A$

where: *Z* - represents the active site of the zeolite, i.e.: the t-butyl-carbenium ion adsorbed on the Brönsted acid centre of the zeolite.

In case of stationary conditions there is no material accumulation on the catalyst surface, that is surface coverages do not change with time and the sum of the surface coverages is equal to 1:

$$\frac{d\Theta_i}{d\tau}=0 \qquad \sum\Theta_i=1$$

On the basis of the above mentioned assumptions a generally valid kinetic equation (Table 1) can be devised for the alkylation reaction, namely for reaction steps 4 and 5 with considering the adsorbed t-butyl-carbenium ion to be the active site (*Z*) on the catalyst surface. With using the assumptions for the rate determining step and for the irreversible step the kinetic equations can be determined for the different theoretical cases as given in Table 1.

Table 1. Kinetic equations for the alkylation reaction of isobutane and 1-butene

<table>
<tr><td colspan="3" rowspan="5">Kinetic equations for the catalytic reaction:
1. Z + A ⇔ (A)a
2. (A)a +B ⇔ C +Z</td><th colspan="2">Kinetic equations</th></tr>
<tr><td colspan="2">$r=\frac{k_1k_2p_Ap_B-k_{-1}k_{-2}p_C}{k_1p_A+k_{-1}+k_2p_B+k_{-2}p_C}$</td></tr>
<tr><th colspan="2">Irreversible step</th></tr>
<tr><td>1. $k_{-1}\approx 0$</td><td>2. $k_{-2}\approx 0$</td></tr>
<tr><td>$r=\frac{k_1k_2p_Ap_B}{k_1p_A+k_2p_B+k_{-2}p_C}$</td><td>$\bar{r}=\frac{k_1k_2p_Ap_B}{k_1p_A+k_{-1}+k_{-2}p_C}$</td></tr>
<tr><th rowspan="2">Rate determining steps</th><td>1.</td><td>$r=\frac{k_1p_A}{k_2p_B+k_{-2}p_C}$
$r=\frac{k_1k_2p_Ap_B}{k_2p_B+k_{-2}p_C}$</td><td>$k_1^{*}<<k_2^{*},k_{-2}^{*}$
$r=\frac{k_1p_A}{k_2p_B+k_{-2}p_C}$
$r=\frac{k_1k_2p_Ap_B}{k_2p_B+k_{-2}p_C}$
2/1-1</td><td>$k_1^{*},k_{-1}^{*}<<k_2^{*}$
$r=\frac{k_1p_A}{k_2p_B+k_{-2}p_C}$
$r=k_1p_A$
2/1-2</td></tr>
<tr><td>2.</td><td>$r=\frac{k_2p_B}{k_1p_A+k_{-1}}$
$r=\frac{k_1k_2p_Ap_B}{k_1p_A+k_{-1}}$</td><td>$k_2^{*},k_{-2}^{*}<<k_1^{*}$
$r=\frac{k_2p_B}{k_1p_A+k_{-1}}$
$r=\frac{k_2p_B}{k_1p_A+k_{-1}}$
2/2-1</td><td>$k_2^{*}<<k_1^{*},k_{-1}^{*}$
$r=\frac{k_2p_B}{k_1p_A+k_{-1}}$
$r=\frac{k_1k_2p_Ap_B}{k_1p_A+k_{-1}}$
2/2-2</td></tr>
</table>

On the basis of the evaluation of the kinetic measurements the reaction step 4, the addition reaction of 1-butene addition onto the adsorbed t-butil-carbenium ion is the rate determining and irreversible steps (Table 1. 2/1-1).

The mechanism of the alkylation of isobutane with 1-butene was studied in order to determine the rate determining and irreversible steps. Different reaction mechanisms and paths were taken into consideration. Brönsted acid sites of the zeolite catalyst are active in the alkylation (Feller et al., 2004). The Brönsted acidity of the zeolites can protonate the 1-butene and this results in a s-butyl-carbenium ion. This carbenium ion reacts with isobutane producing a t-butyl-carbenium ion. The t-butyl-carbenium ion reacts with 1-butene resulting in t-octyl-carbenium ion. The hydride ion abstraction from an isobutane with t-octyl-carbenium ion results in trimethyl-pentane and t-butil-carbenium ion.

4. Conclusions

The kinetic results support the notion that the addition reaction of $(CH_3)_3C^+$ ion with n-C_4H_8 is the slowest reaction step in the studied heterogeneous catalytic process; therefore Step 4, from the five elemental steps is the rate determining step.

The highest catalytic activity regarding the alkylate yield (40%) was observed in case of rare earth ion-exchanged H/NH_4/,RE-FAU,Y-zeolite. Therefore this type of catalyst can be considered for further studies for the alkylation of isobutane with light olefins instead of classical H_2SO_4 and HF catalysts.

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