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Kinetics inversion of chloro-olefine in the solid acid system

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ABSTRACT

The reaction kinetics of the isomerization 3,4-dichlorobutene-1 to 1,4-dichlorobutene-2 was investigated by using gas-liquid chromatography method in the presence of Fe_2O_3/MgO as solid catalyst in the temperature range 25-55°C. Fe_2O_3/MgO has been prepared by the support saturation method, tested in the isomerization of 3, 4-dichlorobutene-1 into 1, 4-dichlorobutene-2. This catalyst shows a high activity opposite to pure MgO in this reaction. The present investigation focuses on the reactivity of Fe_2O_3/MgO with the 5 wt % Fe_2O_3 on the surface of MgO. At the optimizing conditions, the activation parameters have been evaluated using the Arrhenius and Eyring plots. The structure of catalyst was investigated by using Mossbauer spectroscopy.

Keywords: Isomerization of chloro- olefin, Kinetics, Heterogeneous catalysis, Mossbauer spectroscopy.

1. Introduction

The isomerization of allyles halogen-containing derivatives have an important role in the chemical synthesis. One of the process is the isomerization 3, 4-DCB-1 to 1, 4-DCB-2 which is a useful and efficient step in the synthesis of styrene-butadiene rubber:

$$ClCH_2CHClCH\!\!=\!\!CH_2$$

$$trans\text{-}ClCH_2CH\!\!=\!\!CHCH_2Cl$$

This reaction was investigated by acidic homogeneous catalysts and homogeneous complexes of transition series [1-5]. The positional isomerization 3, 4- DCB-1 to 1, 4- DCB-2 is strongly catalyzed by soluble iron complexes. Kinetic data and other observations point to a mechanism involving π-allyliron intermediate [6]. Recently heterogeneous catalysts, nonmetals and nanocomposites [7-9] have also been employed for this reaction. Heterogeneous catalysts in an insoluble form have many advantages over liquid acid systems, because they cause a lower corrosion rate, ensure safer handling of the catalyst, simple catalyst regeneration, and are easily recyclable. Iron (III) oxide (Fe_2O_3) is used as a catalyst in many chemical reactions, such as dehydration of ethyl benzene, CO hydrogenation, alkylation, and the process where halogen- containing alkenes were used as substrates [10, 11], Therefore,

this compound seems to be an appropriated catalyst for conversion of 3, 4- DCB-1 to 1, 4- DCB-2, because this reaction includes the breaking of the C-Cl bond. The process is structurally sensitive and can be promoted with ultra disperse metals or metal oxides, among which iron oxides are the most efficient. In this article an attempt has been made to investigate the conversion of 3, 4- DCB-1 to 1, 4- DCB-2 by heterogeneous acid catalysis Fe_2O_3 / MgO.

2. Experimental

MgO was used as a support. Its specific surface area, S, determined by the thermal desorption of nitrogen equaled 55 m^2/g. In the preparation of the catalysts by support saturation method the solid supported solution of $FeCl_3$ (III) was heated in the 100°C for at least 6 hours. The properties of this catalyst (5 Fe on the surface of MgO, % mass) was investigated for the isomerization reaction of 3, 4 - DCB-1 to 1,4 - DCB-2 in the temperature range of 25 - 55°C. This reaction was investigated with 0.04 g catalyst (for the 5 wt % Fe_2O_3 on the surface of SiO_2 – 0.000036 mol Fe) in 0.3 ml (0.0028 mol) stirred 3,4-DCB-1. The following procedure was used to obtain catalytic data. An accurately weighed portion 0.04 g (3.6×10^{-5} mole Fe) of the catalyst sample was placed in a glass ampoule and 0.3-mL of freshly distilled 3, 4-dichlorobutene-1 was added into the ampoule. Then, the ampoule was sealed, and the reaction mixture was stirred under thermostatic conditions at temperatures varied from 25 to 55°C. After a certain time, the sample was taken off

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from the thermostat and cooled. Five to eight ampoules were used to obtain one catalytic curve. The analysis of product was carried out by gas- liquid chromatography on a Tsvet-100 chromatograph with a flame ionization detector, equipped with a glass column (180 × 0.25 cm) packed with a 5% SE-30 stationary phase applied on Chromaton N-AW-DMCS. The column was stabilized at 70°C. The major product of reaction is trans-1,4 - DCB-2, and cis- 1, 4 - DCB-2 produced less than 2%. Other products in the isomerization reaction was not observed. A typical chromatogram at 55°C after 30 min is presented in Fig. 1. To complete research work we also examined the structure of active phase from Mossbauer spectroscopy [12,13]. The features of a Mossbauer spectrum depend essentially on the character of the magnetic state of the sample: paramagnetic, ferromagnetic or antiferromagnetic. This dependence is strictly connected with the electron spin lattice relaxation times of the material or the time between transitions from one orientation of the net electron spin to another. Mossbauer measurements are generally performed to analyze the samples containing iron [14-17]. Mossbauer spectra was recorded on a conventional gamma-resonance spectrometer with 57 CO (Rh) as a source.

3. Results and Discussion

The effect of temperature on the rate of isomerization reaction 3, 4- DCB-1 to 1, 4- DCB-2 is shown in Fig. 2. This figure shows the amount of product in various temperatures. The rate of isomerization reaction is increases with increasing temperature. This means that the reaction is faster at highest temperatures.

3.1. The catalytic activity of catalyst

The catalytic activity of catalyst can be determined by kinetic curves of isomerization reaction using the following equation:

$$A = \frac{C_{1,4-DCB}}{n_{Fe} \times t}$$

Where $C_{1,\ 4-DCB-2}$ and n_{Fe}, are defined the mole fraction of product and the number of Fe moles on the surface of support in t time (hour). The experimental results illustrated in Table 1. According to results, the catalytic activity is decreased with decreasing temperature. This means that the catalyst is more active at higher temperatures.

3.2. The kinetics of isomerization 3, 4- DCB- 1 to 1, 4- DCB-2

The reaction exhibits the reversible first order behavior with the following rate law

$$\ln\left[\frac{C_\infty - C_t}{C_\infty - C_0}\right] = -(k_1 + k_{-1}) \cdot t = -k_{ef} \cdot t$$

Where C_t, C_o and C_∞ are the concentration product at t time, initial time (t=0) and equilibrium state reaction. k_1, k_{-1} and k_{ef} are the direct, indirect and effective rate constants of reaction. By knowing that C_t (experimental) and thermodynamically equilibrium constants at different temperatures [18,19] were determined k_1, k_{-1} and k_{ef}.

It is clear that the plots of $\ln\left[\frac{c_\infty - c_t}{c_\infty - c_0}\right]$ vs. t (s) should be linear. For example in Fig. 3. is presented the plot of $\ln\left[\frac{C_\infty - C_t}{C_\infty - C_0}\right] = \ln[Y]$ vs. t (s) at 55°C.

Similarly, the direct, indirect and effective rate constants at different temperatures are obtained. The values being reported in Table 2. Using the obtained data on the rate constantans and applying Arrhenius equation, that is, $\ln k = \ln A - \frac{E_a}{RT}$ the direct (Ea_1), indirect (Ea_{-1}) and effective activation energy (Ea_{ef}) can be determined.
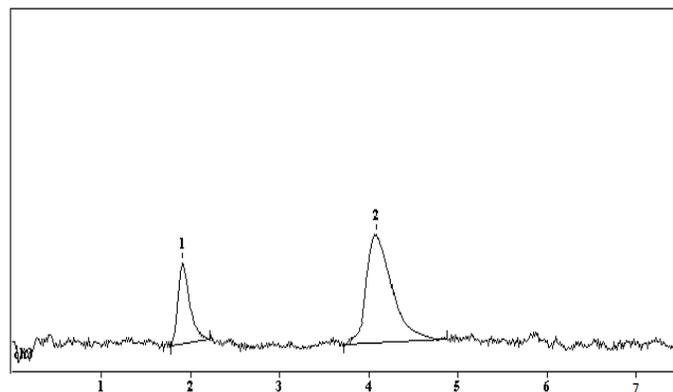

Fig. 1. The chromatogram of reaction at 55°C after 30 min.
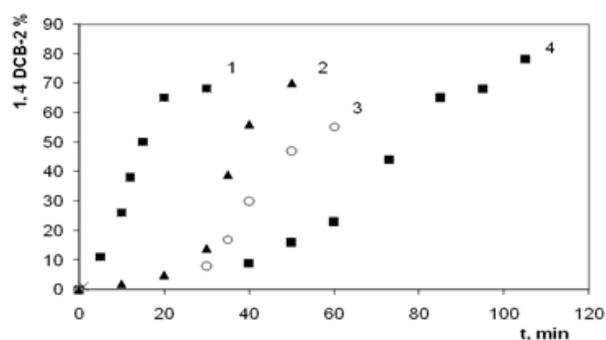1) 3, 4- DCB-1, 2) 1, 4- DCB-2

Fig. 2. The plot of product percentage 1, 4- DCB-2 *vs.* t (min) at 25-55°C.
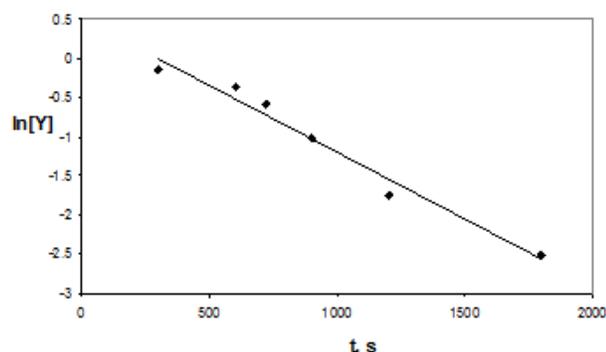

Fig. 3. Dependence of $\ln\left[\dfrac{C_\infty - C_t}{C_\infty - C_0}\right] = \ln[Y]$ *vs.* *t*(s) at 55°C.

The calculated values are presented in Table 3. Fig. 4. Shows the Arrhenius plot (ln k_{ef} vs. 1/T) of the present system. From the slope of this plot the activation energy for isomerization 3, 4- DCB- 1 to 1, 4- DCB-2 over Fe$_2$O$_3$/MgO is computed and is 30.33 kJ.mol^{-1}. The Eyring equation may be suitably applied in the flowing form:

$$k = \frac{RT}{Nh} \exp\ (T\Delta S^* - \Delta H^*)/RT$$

The equation leads to:

$$\ln(\frac{k}{T}) = \ln(\frac{R}{Nh}) + (-\frac{\Delta H^*}{RT}) + (\frac{\Delta S^*}{R})$$
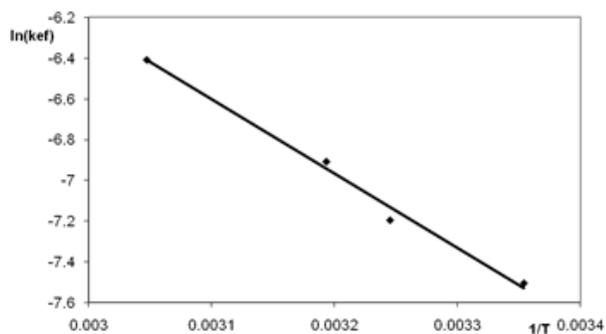

Fig. 4. Plot of Arrhenius ln (k_{ef}/T) *vs.* 1/T.

Table 1. The catalytic activity (A) of Fe$_2$O$_3$/MgO catalyst at 25-55°C.

t, °C	A
55	260±13
40	132±6
35	98±4.5
25	74±3.5

Table 2. The direct, indirect and effective rate constants of isomerization reaction 3, 4- DCB- 1 to 1, 4- DCB-2 at various temperature with 5% Fe$_2$O$_3$/MgO as catalyst.

t, °C	k_{ef} (s^{-1})×10^{5a}	k_1 (s^{-1}) ×10^{5b}	k_{-1} (s^{-1}) ×10^{5c}
55	165±8	142±7	19±1
40	100±5	90±4.5	8.5±0.45
35	75±3.5	66±3	5±0.25
25	55±2.5	51±2.5	1.5±0.07

[a] The effective rate constants at 25 - 55°C.
[b] The direct rate constans at 25 - 55°C.
[c] The indirect rate constans at 25 - 55°C.

Thus a plot of $\ln(k/T)$ vs. 1/T should give a straight line, the slope and intercept of which may be used to compute enthalpy of activation, ΔH^* and entropy of activation ΔS^* values, respectively. Dependence of $\ln(k_{ef}/T)$ *vs.* 1/T displayed graphically in Fig. 5. The calculated values are presented in Table 4.

Mossbauer spectrum of 5% Fe on the surface of MgO catalyst is presented in Fig. 6. This spectrum is satisfactorily approximated with a doublet model with relative area of 69 and 31%; the spectral parameters are reported In Table 5. These parameters are represented the octahedral structure of $\gamma - Fe_2O_3$ with superconducting magnets which formed in the process synthesis of catalysts. The doublet with the smaller value of quadrupole splitting corresponds to the iron atoms inside the Fe$_2$O$_3$ particle, while the doublet with the higher value represents the iron atoms situated on the particle surface [20].

Table 3. The direct, indirect and effective activation energy of isomerization reaction 3, 4- DCB-1 to 1, 4- DCB-2.

E_{ef} [a] (kJ/mol)	Ea_1 [b] (kJ/mol)	Ea_{-1} [c] (kJ/mol)
30.33	28.25	45.55

[a] The effective activation energy at 25 - 55°C.
[b] The direct activation energy at 25 - 55°C.
[c] The indirect activation energy at 25 - 55°C.

Table 4. Effective activation enthalpy and entropy for isomerization of 3,4-dichlorobutene-1 to 1, 4-dichlorobutene-2.

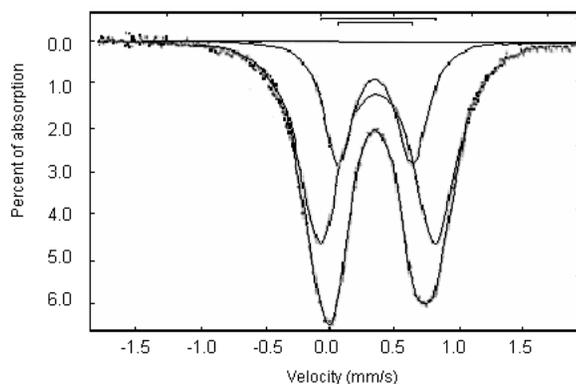| ΔH_{ef}^* (kJ/mol)	ΔS_{ef}^* $(kJ/mol.K)$
-27.73	-0.017

Fig. 6. Mossbauer spectrum of 5% Fe on MgO surface.

Table 5. The parameters of Mossbauer spectroscopy.

δ, mm/s (chemical shift)	Δ, mm/s (quadrupole effects)	area %
0.38±0.1	0.90±0.1	69
0.36±0.1	0.58±0.01	31

4. Conclusions

In this article Fe_2O_3/MgO is prepared using simple procedure under mild conditions. This catalyst is an inexpensive, easily available, noncorrosive environmentally benign compound. In this work, we have reported a convenient and efficient procedure for the preparation of 1, 4- DCB-2 in good yield and short reactions times. This catalyst is indicated high activity even in the room temperature. The results were indicated its catalytic activity in the studied reaction was comparable to or higher than that for the catalysts obtained by the conventional procedure. The notable advantages of this methodology are operational simplicity, generality, availability of reactants and easy work-up.

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