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ISOMERIZATION AND DIFFUSION OF XYLENES OVER THE H-FORM OF ZEOLITE Y

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An extensive amount of patent literature is devoted to the isomerization of xylenes and to the disproportionation of alkylaromatic hydrocarbons as well [1-3]. Zeolite catalysts have recently been used for these reactions [4-6]. In analyzing the results obtained in catalysis on zeolites, it is necessary to evaluate the role of reactant molecule diffusion within the intracrystalline zeolite channels. It is now possible to settle this question by calculation, by determining the catalyst efficiency [7].

In this research, we studied isomerization and explored the diffusion of xylenes in zeolite HY by a thermal desorption method [8, 9], with the aim of determining the regions in which isomerization takes place.

EXPERIMENTAL

A thermal desorption apparatus [10] was used to study the isomerization of xylenes and the diffusion of these hydrocarbons in zeolite HY. The carrier gas was He (25 ml/min), purified from traces of moisture by passage through a zeolite column at -196°C. In the xylene desorption study, the xylenes were adsorbed at ~ 20 °C or higher by adding different amounts of the hydrocarbon to a current of the carrier gas with a microsyringe. The procedure for analyzing the thermal desorption peaks to calculate diffusion coefficients has been described in [8, 9].

To study xylene isomerization, the reactor in the thermal desorption apparatus operated in a pulsed mode. The reaction was studied between 250 and 500°C. At each test temperature, four to five pulses of material were supplied to the reactor. The volume of one pulse was 10 μ 1.

The catalyst used was the H-form of zeolite Y $(SiO_2/Al_2O_3 = 4.3)$, which was produced by ion exchange with an NH₄Cl solution. The zeolite was calcined at 500°C between ion-exchange operations. The degree of ion exchange, determined with respect to sodium in the mother liquor by flame photometry, was 98% (equiv.) A fresh sample of catalyst was used for each test (20 mg).

The reaction products were collected in a cooled trap with n-pentane and analyzed by gasliquid chromatography (GLC) in a 2 m \times 3 mm column with a petrolatum-bentonite mixture on Chromosorb P at 75°C, with a carrier gas at 30 ml/min. All the isomeric xylenes were completely separated under these conditions.

In order to determine the amount of original hydrocarbon produced as coke or highmolecular-weight condensed products, benzene was added as an internal standard to the trap with the n-pentane and the reaction product before the GLC analysis. Thus, for example, on isomerization of m-xylene at 500°C, the original hydrocarbon losses amounted to 40%. The large amount of hydrocarbon which went into coke formation is apparently typical of zeolites under pulsed microreactor conditions [10, 11].

N. D. Zelinskii Institute of Organic Chemistry of the Academy of Sciences of the USSR, Moscow. Translated from Izvestiya Akademii Nauk SSSR, Seriya Khimicheskaya, No. 7, pp. 1474-1478, July, 1981. Original article submitted October 16, 1980. The isomerization rate constant for xylenes was calculated by an equation for a pulsed microreactor [12, 13]. The apparent activation energy was found from the temperature dependence of the reaction rate constant at four points. The error in the activation energy determination was not greater than ±3 kcal/mole.

DISCUSSION OF RESULTS

Figure 1 shows that when m-xylene is isomerized at 350°C, the o- and p-xylene yields are practically independent of the number of pulses. The toluene yield drops somewhat and, as a result, the conversion of the original hydrocarbon is reduced significantly (m-xylene concentration increases).

Similar tendencies are found at other temperatures as well for the different xylene isomers. Along with the products mentioned, isomerization of p-xylene at certain temperatures resulted in the formation of trimethylbenzenes, but in smaller amounts than toluene. Apparently, this indicates that toluene appears mainly as a result of xylene demethylation and not as a result of xylene disproportionation.

If we calculate the relative content of the xylene isomers without including the toluene and the trimethylbenzenes in the isomerization products of the different xylenes when they are formed, we can plot a triangular diagram (Fig. 2) which shows how this three-component mixture approaches equilibrium, starting from one particular isomer. Figure 2 indicates that when m-xylene is isomerized, o- and p-xylene are formed with equal probability, since the line of approach to equilibrium divides the triangle into two practically equal halves. However, mxylene is formed preferentially from the o-isomer or the p-isomer, evidence that xylene isomerization proceeds as a result of 1-2 methyl-group shift. A similar conclusion was reached in [13] in a study of xylene isomerization on a Ni/SiO₂·Al₂O₃ catalyst in which an atomtracer technique was employed.

The data we obtained at different temperatures on zeolite HY and the data on xylene isomerization at 400°C on a Ni/SiO₂·Al₂O₃ catalyst [13], fit the same curve (see Fig. 2). The trajectory of the approach to equilibrium in this system is identical for the different catalysts, the catalysts differing only in their rate of approach.

Figure 3 shows that the region in which thermal desorption of m-xylene takes place on HY and the temperature interval over which the reaction occurs partly intersect. The yield of isomerization products increases with temperature between 250 and 350°C and is practically constant above that temperature as the system approaches equilibrium.

The energy of activation of these reactions



(1)

was calculated from values of the isomerization rate constants for the different xylene isomers between 250 and 350°C (Table 1) (the numbers on the arrows denote the activation energy in kcal/mole).

Let us designate as K_1 the equilibrium constant of the transition of the o-isomer to the p-isomer through the m-isomer



Fig. 1. Change in composition of the gaseous reaction products in the conversion of m-xylene at 350°C vs the number of pulses n: 1) m-xylene; 2) toluene; 3) p-xylene; 4) o-xylene.



Fig. 2. Change in xylene composition on approach to equilibrium (open points represent data from [13]).



Fig. 3. Thermal desorption peak of m-xylene (a = 0.08 mmole/g) and the yield of different reaction products vs. temperature of m-xylene conversion: 1) total isomerization product yield (oand p-xylene); 2) sum of o- and p-xylene and toluene produced.

TABLE 1. Isomerization Rate Constants for Xylenes (k, sec⁻¹)

т., ℃	^k o→m	$k_{m \to 0}$	$k_{m \to p}$	$k_{p \rightarrow m}$	$k_{p \rightarrow 0}$	k _{o→} p
250	1,87	0,64 $1,23$	0,16	1,05	0,16	0,10
350	3,05		1,60	3,07	0,70	0,86

$$K_1 = \frac{k_{0 \to m}}{k_{m \to 0}} \cdot \frac{k_{m \to p}}{k_{p \to m}} \cdot$$
(2)

At the same time, the equilibrium constant between the o- and p-isomers can also be evaluated from the equation

$$K_2 = \frac{k_{o \to p}}{k_{p \to o}}$$
 (3)

By definition, $K_1 = K_2$. The data in Table 1 indicate that K_1 and K_2 are, respectively, 0.44 and 0.62 at 250°C and 1.28 and 1.23 at 350°C. Consequently, the xylene isomerization rate constants found from the test agree satisfactorily enough. From Eqs. (2) and (3) and also for independent reasons, it can be shown that the sum of the activation energies clockwise around the circumference of triangular diagram (1) ($\Sigma E(Q)$) should be equal to the counterclockwise sum ($\Sigma E(Q)$). In fact, if we start with o-xylene, for example, we obtain from diagram (1) $\Sigma E(Q) = 35$ and $\Sigma E(Q) = 36$, i.e., the activation energies obtained also agree well with each other.

Original hy- drocarbon	D _e • 10 ¹² , em ² /sec at 250°C	Reaction	Thiele mo- dulus; * φ_1/φ_2	Efficiency* η_1/η_2
o-Xylene	1,5	$o \to m$ $o \to p$	$ \begin{array}{r} \underline{113,0} \\ \underline{56,3} \\ \underline{25.9} \\ \underline{24,0} \\ \end{array} $	$ \begin{array}{r} 0.1 \\ 0.1 \\ 0.1 \\ 0.1 \end{array} $
<i>m</i> -Xylene	5,9	$m \rightarrow p$ $m \rightarrow o$	$ \begin{array}{r} 16.3 \\ 30,4 \\ 32.9 \\ \overline{66,0} \end{array} $	$\begin{array}{r} 0.2 \\ 0.1 \\ 0.1 \\ 0.1 \end{array}$
p-Xylene	1,7	$p \rightarrow m$ $p \rightarrow o$	78.4 42,1 30,4 32,8	$\begin{array}{r} 0.1 \\ 0.1 \\ 0.1 \\ 0.1 \end{array}$

TABLE 2. Xylene Diffusion Coefficients and Catalyst Efficiencies

 $*\varphi_1$ and η_1 were calculated on the original hydrocarbon; φ_2 and η_2 on the reaction product.

Analyzing the thermal desorption peaks by the procedure described earlier [8, 9], we calculated xylene diffusion coefficients in zeolite HY and then, taking the reaction rate constants into account (see Table 1), we estimated Thiele moduli (φ) and catalyst efficiencies (n) by the two techniques (Table 2). In the former case, the diffusion coefficient of the original hydrocarbon was taken and in the latter case, that of the reaction product. In both cases, values of n were obtained which coincided and did not exceed 0.1. The low value of n indicates that the reaction occurs in the diffusion region. The rather low value of the isomerization activation energy listed above is also indirect evidence of this fact.

Apparently, the relationship between the thermal desorption and reaction temperature intervals can also serve as a qualitative criterion of the region in which the catalytic reaction occurs on zeolites. If these intervals intersect to a significant extent, as in Fig. 3, for example, the reaction is limited by diffusion of the reactant molecules through the zeolite channels. At the same time, it can be assumed that if thermal desorption occurs at much lower temperatures than the reaction, the process takes place in the kinetic region, since the diffusion coefficient found at low temperatures and extrapolated to the reaction temperature will be quite large. This indirectly confirms the fact that the temperature of the thermal desorption peak maximum decreases significantly on going from the univalent to the divalent to the trivalent cationic forms of zeolite Y (for example, to the Nd-form) [9]. We also known from [5] that the La-form of zeolite Y has an activity energy of 30 kcal/mole for the isomerization of m-xylene, evidence that the reaction takes place in the kinetic region.

CONCLUSIONS

1. The thermal desorption and isomerization of different xylene isomers on the H-form of zeolite Y was studied and the diffusion coefficients and reaction rate constants were determined.

2. The catalyst efficiencies were not greater than 0.1 to 0.2, i.e., the reaction takes place in the diffusion region.

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OXIDATIVE ACETOXYLATION OF PROPYLENE IN THE PRESENCE OF PALLADIUM

CATALYSTS.

I.* CATALYTIC COMPOSITION

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By the catalytic oxidative acetoxylation of olefins and aromatic compounds in the presence of Pd catalysts, such important products as the vinyl, alkylphenyl, benzyl, and allyl esters of acetic acid can be prepared in a single stage from the available raw material; for example, allyl acetate (AA) [2] can be obtained by the reaction

$$CH_{2} = CHCH_{3} + AcOH + 0.5O_{2} \rightarrow CH_{2} = CHCH_{2}OAc + H_{2}O.$$
(1)

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The most promising processes are the gas-phase oxyacetoxylation of olefins [3], with the majority of investigations in recent years being concentrated on their development. The gasphase oxyacetoxylation of ethylene is the basis of an industrial method of obtaining vinyl acetate [4]; the development and successful experimental-industrial testing of a process for AA synthesis by the joint oxidation of propylene and AcOH in the gas phase on a Pd catalyst has been reported [5].

The mechanism of the oxidative acetoxylation of propylene and other olefins has been little studied. The few publications are mainly concerned with the kinetics of ethylene acetoxylation and the kinetic equations introduced differ substantially [6, 7].

Our present work has been carried out on propylene, which contains both vinyl and allyl H atoms, and our aim has been to study the general principles of the oxidative acetoxylation of olefins, to clarify the nature of active centers, and to establish the most probable mechanism for the process. We have also investigated the effect of the catalytic composition and the support structure on the main parameters of this process.

EXPERIMENTAL

The kinetic studies were carried out on an apparatus which in essence was an improved version of the nongradient stainless-steel reaction vessel as described by Korneichuk [8]. The assembly of this vessel is shown in Fig. 1. Heat transfers in the reaction vessel between the catalyst layer and the circulating liquid coolant occurred directly across the metal wall. The original propylene, O₂, and inert gas (mainly N₂) mixture was prepared in a cylinder

*For preliminary article, see [1].

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