- 2) Honma, T., M. Hasegawa and Y. Asaba: *Kagaku Kogaku Ronbunshu*, **6**, 527 (1980).
 3) Honma, T., M. Hasegawa and Y. Kanda: *J. Chem. Eng. Japan*, **15**, 240 (1982).

- 4) Mori, Y. and G. Jinbo: *Kagaku Kōgaku*, **22**, 363 (1958).
 5) Ramanujam, M. and D. Venkateswarlu: *Powder Tech.*, **3**, 92 (1969/70).

ALKYLATION RATE OF TOLUENE BY 1-BUTENE OVER ALUMINA-BORIA CATALYST WITH FOULING

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Introduction

Various reactions including the cracking of hydrocarbon, etc. were carried out in the presence of solid acid catalysts. The industrial importance of such reactions has stimulated many workers' interest⁵⁾ in studying the kinetics. There are, however, questions as to whether their results can accurately express the behavior of such reactions, since they have not always well-considered the rate dependency on catalyst acid-properties, i.e. the amount, strength and type.⁶⁾

This work intends to develop the kinetics of toluene-alkylation with 1-butene over $\text{Al}_2\text{O}_3\text{-B}_2\text{O}_3$ of a solid acid with regard of the reaction characteristics stated above.

1. Derivation of Rate Equations

Reactions of this kind have been considered to proceed via a carbonium ion mechanism,²⁾ so that the alkylation may occur through a scheme shown in Fig. 1.

The following points are assumed: (a) The fraction of the sites covered with either *O* or *P* is small. (b) The equilibria of elementary reactions lay far to the right. (c) Their rates obey Polanyi's law.²⁾ (d) Fouling is slow enough for the alkylation to proceed at steady state. (e) $H_0 = -\log K_A + \beta$. It is derived from the definition for solid acid strength⁶⁾ and the relation of K_A with the activity of a dissociating acid site. (f) $\bar{C}_H$ is constant through measured H_0 .

The alkylation-rate equations were derived for each case where adsorption Eq. (2), surface reaction Eq. (3)

or desorption Eq. (4) controls the reaction rate:

$$-R_{Ta} = k_{Ta}C_0, \quad -R_{Ts} = K_{Ts}C_TC_0, \quad (8)$$

$$-R_{Td} = k_{Td}C_TC_0$$

where *k*'s are represented in such a way that

$$k_{Ta} = \varepsilon_a \int_{H_{0h}}^{H_{0l}} \exp(-\alpha_a H_0 \ln 10) C_H dH_0 \quad (9)$$

If *n*-mer causes coke precursor formation, the fouling rate equation of the sites of H_0 is equal to $k_f \exp(-H_0 \ln 10) C_H C_0^n$. Its integration leads to

$$-R_A = k_A C_0^n = \left[k_f \int_{H_{0h}}^{H_{0l}} \exp(-H_0 \ln 10) C_H dH_0 \right] C_0^n \quad (10)$$

Fouling factor ϕ at $t=t$ is defined as the ratio of the rate at $t=t$ to that at $t=0$ under a temperature and reactant, concentrations identical with those at $t=t$. Consequently, $\phi = k/\bar{k}$.

The mass balance equation of the site of H_0 at $t=t$ is derived from the fouling rate equation, being solved by assuming that the fouling is of pseudo-first order

Fig. 1. Reaction scheme.

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with respect to the sites owing to the excessive presence of O . Thus

$$C_H = \exp[-k_f \exp(-H_0 \ln 10) C_0^{*n} t] \bar{C}_H.$$

From the definition and derived equations,

$$\phi_{at} = \alpha t^{-\alpha} \int_0^t t'^{\alpha-1} \exp(-\delta t') dt' \quad (11)$$

where $\alpha=1$ or $0<\alpha<1$ according as the surface reaction or adsorption and desorption control the reaction rate. The restraints of α arise from the Brönsted relationships for this reaction system, which are derived in a similar manner as that for a homogeneous liquid system.¹⁾ Similarly,

$$\phi_f = [1 - \exp(-\delta t)] / \delta t$$

2. Examination of Rate Equations

At longer t when fouling proceeds slowly, $x_T \ll 1$ and also $C_T \doteq C_0$ under the equimolar feed of reactants.

Thus the mass balance of T at t is approximated to

$$\frac{dx_T}{d\tau} = \rho \bar{k}_T C_0^{*m} \alpha t^{-\alpha} \left[\int_0^t t'^{\alpha-1} \exp(-\delta t') dt' \right] \quad (12)$$

where m has a value of 0 or 1 according as the adsorption or surface reaction and desorption control the reaction rate.

Values of the parameters, $\bar{k}_T C_0^{*m}$, α and δ , are estimated with a curve-fitting technique³⁾ using experimental data in the slow fouling region. Both the values of m evaluated from the estimated $\bar{k}_T C_0^{*m}$ values and estimated values of α allow the determination of a controlling step: when $m=0$ and $0<\alpha<1$, $m=1$ and $\alpha=1$ or $m=1$ and $0<\alpha<1$, the adsorption, surface reaction or desorption control the reaction rate, respectively. The dependence of estimated values of δ on C_0^* brings fouling order n . These results are applied to strict mass balance equations of the reactants. Optimum values of $\bar{k}_A$ in the equations are estimated in a similar manner to that for $\bar{k}_T C_0^{*m}$ etc. from the whole experimental data.

3. Experiments

Al_2O_3 -mounted B_2O_3 was used as a catalyst. The plot of $\bar{C}_H$ vs. H_0 was constant. Most of the sites were of Brönsted type.⁴⁾ Reaction conditions were selected so that internal and external mass transfer resistances might have no influence on reaction behavior. The reaction was carried out at 180°C, atmospheric pressure and equimolar feed of the reactants. The other conditions were the same as those described in a previous paper.⁴⁾

4. Results and Discussion

Figure 2 shows experimental results. From them the

Fig. 2. Toluene conversion (x_T) vs. time on stream (t).

Fig. 3. Dependence of rate parameter values on C_0^* .

fouling is found to become considerably slower in about 30 min. Thus 37.5 min or above was adopted as the longer t specified in the derivation of Eq. (12). Over such t 's curve fitting was made for changes in $\bar{x}_T$ with t at different values of constant C_0^* . Figure 3 shows the parameter-estimation results. It indicates that the values of α and $\bar{k}_T C_0^{*m}$ are independent of C_0^* to be 0.21- and 1.92 $cm^3 g^{-1} min^{-1}$ and that the slope for δ is close to 2. These results indicate that the controlling steps were adsorption for the alkylation and dimerization for the fouling. The above findings were applied to the strict mass balance equations, and optimum values of $\bar{k}_A$ in the equations were estimated using the whole experimental data. The values are shown in Fig. 3. It is likely that they are independent of C_0^* . For comparison with experimental reaction courses, calculated ones are given in Fig. 2. They were simulated using optimum values of the parameters, and are in good agreement with each other.

Nomenclature

A^-H^+, H_0, O, P, T	= acid site, Hammett activity function, 1-butene, aromatic product and toluene
C	= concentration [$mol \cdot g^{-1}$ or $mol \cdot cm^{-3}$]
K	= equilibrium constant [$cm^3 \cdot mol^{-1}$], etc.
R	= reaction rate [$mol \cdot g^{-1} \cdot min^{-1}$]
k	= rate constant [$cm^3 \cdot mol^{-1} \cdot min^{-1}$], etc.
m, n	= reaction order or integer [—]
t, t'	= time on stream and its dummy [min]
x	= fractional conversion [—]
α, β	= positive fractional constant relating to Polanyi's law and constant referring to the relation between H_0 and K_A [—]
δ	= $k_f \exp(-H_{0f} \ln 10) C_0^{*n}$ [min^{-1}]

ε	= positive constant	$[\text{cm}^3 \cdot \text{mol}^{-1} \cdot \text{min}^{-1}]$, etc.
ϕ	= fouling factor	$[-]$
ρ	= molar density	$[\text{mol} \cdot \text{cm}^{-3}]$
τ	= contact time	$[\text{g} \cdot \text{mol}^{-1} \cdot \text{min}]$

<Subscripts and Superscripts>

A, H, K, O, T	= acid site, H_0 , K_A , 1-butene and toluene
a, d, s	= adsorption- desorption- and surface reaction- controlling
$al, f, h, l, +, *, =, \sim$	= alkylation, fouling, highest, lowest, carbonium ion, feed concentration, nonfouling and experimental

Literature Cited

- 1) Boudart, M.: "Kinetics of Chemical Process" (translated into Japanese by E. Ohshima), p. 140, Maruzen, Tokyo (1970).
- 2) Makishima, S., Y. Yoneda, Y. Saito, T. Uchiyama, K. Hiraki, T. Hirano, E. Hirai, K. Morikawa and T. Shirasaki: "Kindai Kogyo Kagaku 8," pp. 71, 230, Asakura Shoten, Tokyo (1971).
- 3) Marquardt, D. W.: *J. Soc. Ind. Appl. Math.*, **11**, 431 (1963).
- 4) Morita, M., S. Sato, T. Mizukami, M. Shiino and R. Suzuki: *Nippon Kagaku Kaishi*, 312 (1974).
- 5) Otake, T. and E. Kunugita: *Kagaku Kōgaku*, **30**, 87 (1966).
- 6) Tanabe, K.: "Solid Acids and Bases," p. 1, Kodansha, Tokyo (1970).