

## 天然제올라이트 촉매에 의한 톨루엔不均化反應

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## Toluene Disproportionation Reaction with Acid-Treated Natural Zeolite Catalyst

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### 約 要

慶北 九龍浦 地域에서 産出되는 일부 mordenite 成分을 포함한 天然 제올라이트를 酸처리한 觸媒를 使用하여 固定層反應器에서의 톨루엔 不均化 反應에 對한 실험이 行해졌다. 反應溫도와 空間時間이 增加할수록 轉化率은 增加했으며 크실렌의 選擇度는 空間時間의 增加에 對해 뚜렷한 減少를 보였다. 高溫에서의 높은 活性低下는 수소의 공급량을 높임으로써 어느정도 방지할 수 있었으며, 使用한 觸媒의 再生能力에 있어서는 再生回數가 增加할수록 初期活性은 점진적으로 減少했으나 反應時間에 따른 活性低下는 훨씬 적어지는 結果 나타났다.

### Abstract

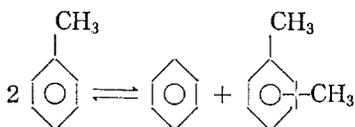
The effects of operating conditions on conversion and selectivity for toluene disproportionation reaction in a packed-bed reactor were investigated with the catalyst which is prepared by treating natural zeolite mined in Kuryongpo, Kyung-sang-bukdo with hydrochloric acid solutions. The experimental results showed that toluene conversion increased with an increase in the reaction temperature or space time. Xylene selectivity decreased with an increase in space time. Deactivation by coke deposition decreased with an increase in hydrogen to toluene mole ratio. Regeneration of spent catalysts resulted in a slight decrease in the initial activity and a marked improvement in deactivation characteristics.

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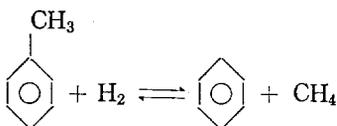
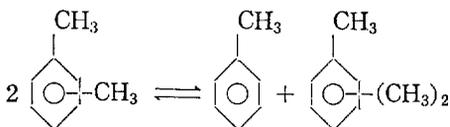
## Introduction

Toluene is usually converted to produce various derivatives of industrial importance because of its low economic value and restricted uses. Dealkylation and disproportionation of toluene are two major industrial processes for the production of benzene, the latter having preeminence.

Disproportionation reaction is a kind of isomerization reaction by alkyl transfer. The main reaction of disproportionation reaction is as follows:



Side reactions may occur;



Disproportionation process is more advantageous than dealkylation process because it involves milder operating conditions and xylene is produced instead of less valuable methane<sup>1)</sup>.

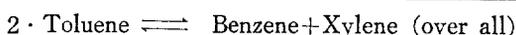
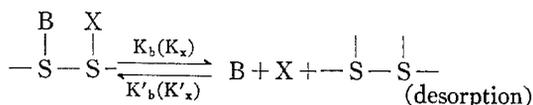
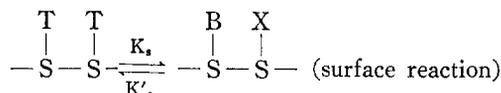
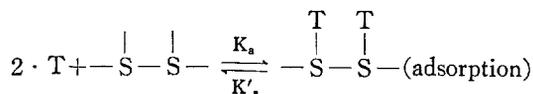
A number of disproportionation processes have been developed using acid-site catalysts such as silica-alumina, and synthetic or natural zeolites<sup>2-6)</sup>. Mordenite is one of the suitable catalysts for the reaction because of its high thermal stability and catalytic activity<sup>7)</sup>. Natural zeolite of partial mordenite structure mined in Kuryongpo, Kyung-sang-bukdo was used as catalyst in

the present study.

The product conversion and xylene selectivity in a fixed-bed reactor packed with acid treated natural zeolite were observed at various operating conditions. The reaction kinetics of the reaction was studied by integral analysis of packed-bed reaction data.

## Theory

The reaction mechanism of toluene disproportionation may be written as follows:



where B, T, X, and S represent benzene, toluene, xylene, and vacant active sites on the surface of a catalyst, respectively.

Under the assumption of surface phenomenon control, the net rate depends on three processes, namely adsorption, surface reaction and desorption.

The rates of individual processes are:

$$\text{Adsorption} \quad : \quad r_a = k_a p_t C_v - k'_a C_t \quad (1)$$

$$\text{Surface reaction} : \quad r_s = (k'_s C_t - k_s C_b C_x) / C_s \quad (2)$$

$$\text{Desorption} \quad : \quad r_d = k_b C_b - k'_b p_b C_v \quad (3)$$

$$r_d = k_x C_x - k'_x p_x C_v \quad (4)$$

If the surface reaction is the controlling step, and hydrogen adsorption effect is considered, the overall reaction rate becomes:

$$r_s = \frac{k_s C_s (K_a^2 p_t^2 - K_b K_x p_b p_x / K_s)}{(1 + K_a p_t + K_b p_b + K_x p_x + K_h p_h)^2} \quad (5)$$

Assuming that the reaction is irreversible and only the adsorption equilibrium constant  $K_a$ , is considered significant being.

$$r_s = \frac{k K_a^2 p_t^2}{(1 + K_a p_t)^2} \quad (6)$$

where  $k = k_s C_s$ .

Under the plug flow assumption, the reaction rate for an isothermal fixed-bed reactor can be written as follows:

$$r = F \frac{dx}{dW} \quad (7)$$

or

$$\frac{W}{F} = \int_0^x \frac{dx}{r} \quad (8)$$

Substitution of equation (6) to equation (8) gives:

$$\frac{W}{F} = \int_0^x \frac{(1 + K_a p_t)^2}{k K_a^2 p_t^2} dx \quad (9)$$

where

$$p_t = p_{t0}(1 - X) \quad (10)$$

Combining equation (9) and (10), and an integration results as,

$$\frac{W p_{t0}^2}{F} k = \frac{1}{K_a^2} \frac{X}{1 - X} - \frac{2 p_{t0}}{K_a} \ln(1 - X) + p_{t0}^2 X \quad (11)$$

Equation (11) was used to obtain values of  $k$

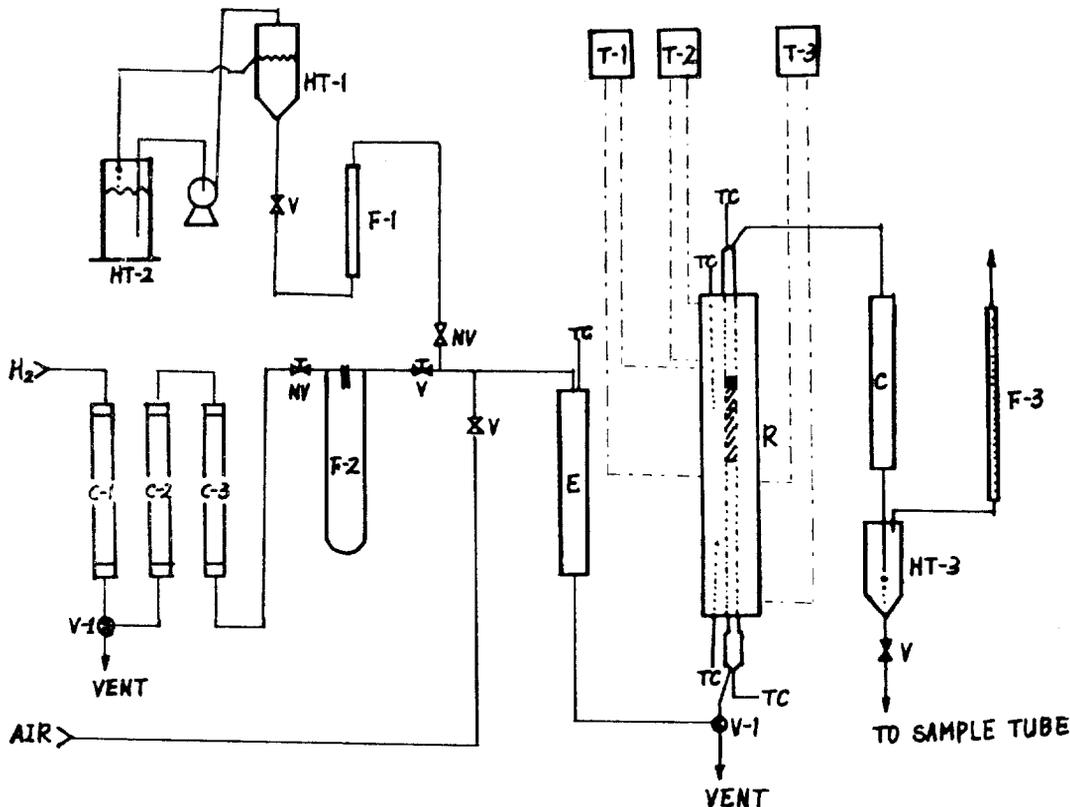


Fig. 1. Flow diagram of the packed-bed reaction system.

C: Condenser, C-1: O<sub>2</sub> Eliminator, C-2, 3: Drier, E: Evaporator F-1: Rotameter, F-2: Capillary flow meter, F-3: Bubble flow meter, HT-1: Constant head tank, HT-2: Toluene storage tank HT-3: Gas and liquid separator, NV: Needle valve, R: Reactor and furnace, T-1, 2: Proportional temperature controller, T-3: Transformer, TC: Thermocouple, V: On-off valve, V-1: Three way valve.

and  $K_a$  by a least-squares technique.

The rate constant  $k$  should vary with temperature according to Arrhenius equation:

$$\frac{d \ln k}{d(1/T)} = \frac{-\Delta E}{R} \quad (12)$$

The adsorption equilibrium constant  $K_a$  should follow the analogous form:

$$\frac{d \ln K_a}{d(1/T)} = \frac{\Delta H}{R} \quad (13)$$

## Experimental

The schematic flow diagram of the packed-bed reaction system is shown in Fig 1. The detailed reactor geometry is described in Fig 2. The reactor was fabricated with a stainless steel pipe, 1.1cm in I. D. and 80cm in height. A thermocouple well of 3mm O. D. was inserted to the center of the reactor for temperature measurement at various axial positions.

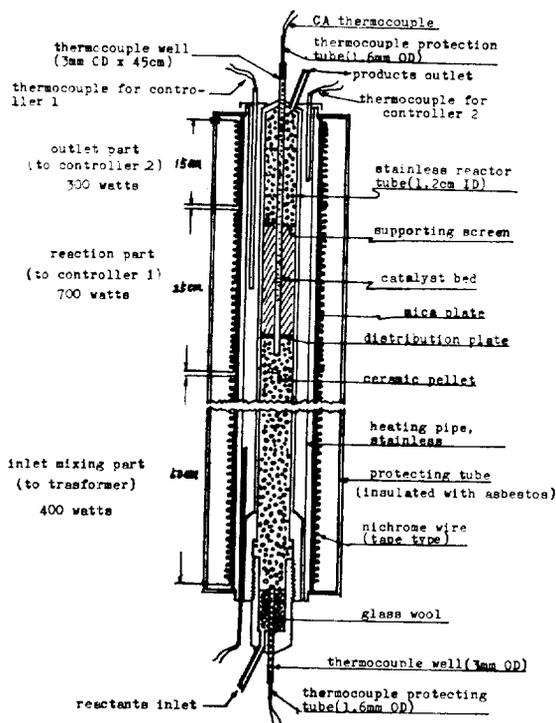


Fig. 2. Details of reactor and heater.

The reactor was heated by an electric heater which was made for isothermal operations. The temperatures at reaction and outlet parts were controlled by proportional controllers. All feed lines were  $\frac{1}{4}$ -inch copper tubings and preheating and reactor exit lines were  $\frac{1}{4}$ -inch stainless steel pipe. The reactor was packed with 5 to 10 grams of cylindrical catalyst pellets.

The feed hydrogen was purified by an oxygen eliminator (C-1) packed with  $\text{Cu}_2\text{O}$ , and two drying units, one (C-2) packed with  $\text{CaCl}_2$  and the other with Zeolite 5A. Toluene was dried with Zeolite 5A for one day prior to use.

Initially, the packed catalyst was calcinated with air which was fed to the reactor at  $550^\circ\text{C}$  at the flow rate of 100 cc/min for two hours. Hydrogen was passed through the reactor 30 minutes to drive out water and other impurities in catalyst.

After all temperatures reached steady states, the three-way valve positioned below the reactor was turned to vent position. Toluene was then passed from the constant head tank and hydrogen from the gas cylinder. The ranges of flow rates of toluene and hydrogen were 3-7ml/hr and 30-200ml/min respectively. After the feed rates reached steady states, the three-way valve was turned to reactor position and the reaction was started.

The product was condensed and liquid samples were drawn from the gas-liquid separator for composition analysis by Varian gas chromatograph, Moduline, with OV-1 column and TC detector.

## Results and Discussion

The Natural Zeolite catalyst for disproportionation reaction was subject to rapid deactivation with process time as shown in Fig 3. Both conversion and deactivation tendency showed

maximum values when HCl concentration was 2N. The experimental runs were made using natural zeolite treated with 2N or 3N acid solutions as catalysts.

Fig. 4 shows the dependence of conversion and selectivity on space time. As space time increased, conversion approached the thermodynamic

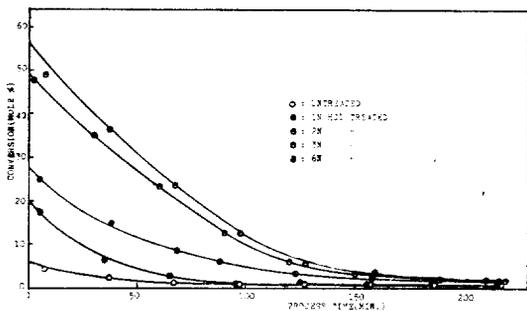


Fig. 3. Conversion of toluene vs. process time.

Catalyst, original and HCl treated, Reaction temp., 500°C; W/F, 32; Hydrogen to toluene mole ratio, 6. 8.

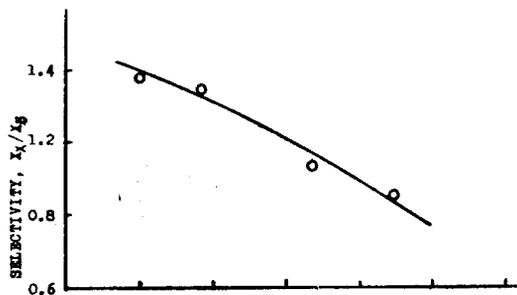


Fig. 4. Effect of catalyst-feed rate ratio.

Catalyst, 3N acid-treated; Reaction temp, 460°C

equilibrium value.<sup>8)</sup> The xylene selectivity decreased with an increase in space time, indicating that the contact time of reactant to catalyst was long enough to induce further reaction of already reacted products at a higher space time.

Fig. 5 shows that conversion increased with an increase in the reaction temperature. However, catalyst deactivation was severe at higher temperatures, possibly because of catalyst deactivation and coke deposition. At temperatures lower than 400°C, deactivation phenomenon was not observed under the reaction conditions adopted in the present study. Xylene selectivity was unaffected by temperature within the temperature range adopted for experiments.

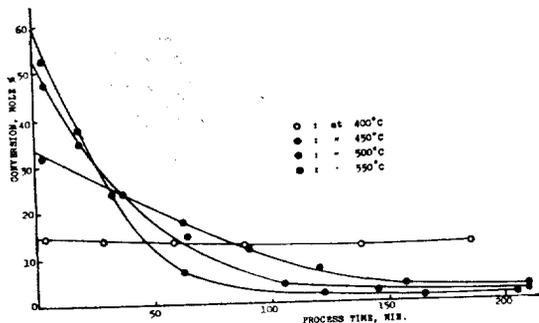


Fig. 5. Effect of temperature.

Catalyst, 2N Acid-treated; W/F, 22; Hydrogen to toluene mole ratio, 7. 0.

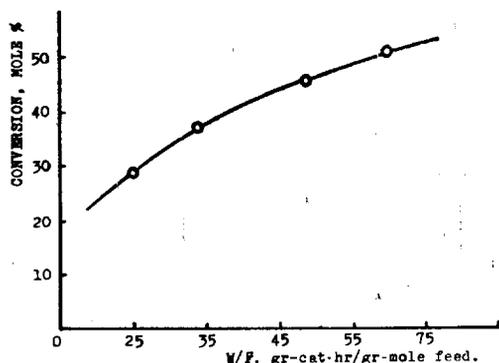


Fig. 6. Effect of temperature.

Catalyst, 2N acid; W/F, 22; Hydrogen to toluene mole ratio, 7. 0.

Hydrogen was fed as an inert gas to minimize coke deposition on catalyst surfaces<sup>9</sup>. Fig. 7 shows the effect of hydrogen to toluene mole ratio on catalytic activity at a fixed toluene feed rate. Higher hydrogen to toluene feed ratio resulted in lower conversions during the initial stages of reaction but lower deactivation rates with process time. The results confirmed that hydrogen had an anticoking ability. Since the catalytic properties were changed with process time for different hydrogen to toluene feed ratios, initial reaction rates were used for kinetic study.

To investigate the regeneration characteristics, used catalysts were burnt with air for one hour at 550°C and 100ml/min. Fig. 8 shows that the deactivation tendency decreased with the number of regenerations. The initial conversion decreased only by 8 percent after third regeneration, showing that regeneration improved the catalyst quality. These results imply that catalyst deactivation was caused largely by mechanical covering, or coke deposition, rather than chemical poisoning, and strong acid sites gradually disappeared as the number of regenerations increased, leaving only mild and weak acid sites for reaction.

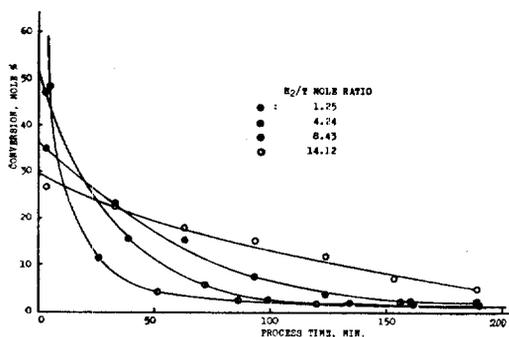


Fig. 7. Effect of hydrogen on catalytic activity. Catalyst, 3N acid-treated; Reaction temp., 460°C; WHSV, 0.5.

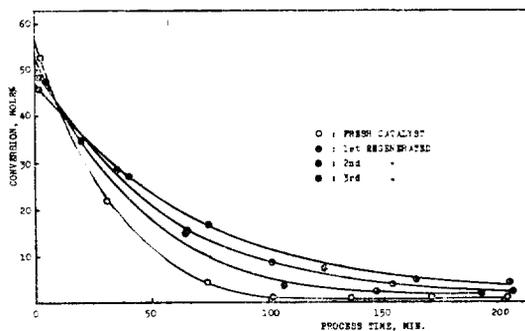


Fig. 8. Regeneration characteristics of spent catalysts. Catalyst, 2N acid-treated; Reaction temp., 550°C; W/F, 22; Hydrogen to toluene mole ratio, 7.9.

The reaction rate was studied by the integral method<sup>10</sup> with the packed-bed conversion data under isothermal condition. The plug flow assumption was readily satisfied by utilizing long enough tube. The deviation of conversion at different particle sizes was within the range of experimental error, indicating the absence of pore diffusion.

Table 1 shows experimental runs for 2N acid-treated catalyst. The reaction rate constant

Table 1. Experimental run data for 2N acid-treated catalyst

Temp (°C)	Run number	W (gr)	F (mole/hr)	Pto (atm)	X
400	24	14.0	0.032	0.205	0.22
	26	10.0	0.034	0.249	0.16
	27	13.0	0.034	0.122	0.15
	32	11.5	0.031	0.252	0.20
	33	8.5	0.034	0.161	0.11
450	14	6.5	0.033	0.098	0.32
	15	6.0	0.040	0.121	0.28
	16	10.0	0.075	0.191	0.34
	17	10.0	0.032	0.119	0.51
	23	5.8	0.028	0.100	0.33
500	4	9.0	0.038	0.083	0.50
	9	4.5	0.037	0.126	0.45
	10	5.0	0.038	0.103	0.41
	12	8.3	0.058	0.130	0.52

Table 2. Reaction rate constant and adsorption equilibrium constant

Temperature (°C)	400	450	500
K (molek/hr-grcat)	0.00080	0.0051	0.019
K <sub>a</sub> (atm <sup>-1</sup> )	20.8	15.3	8.6

$k$  and the adsorption equilibrium constant  $K_a$  were obtained from the equation (11) by use of a least-squares method and were shown in Table 2.

The activation energy and the heat of adsorption were calculated from the slopes of Arrhenius plots (Fig 9). The calculated values of the activation energy and the heat of adotrpsion were 31.7 and 6.9Kcal/mole respectively.

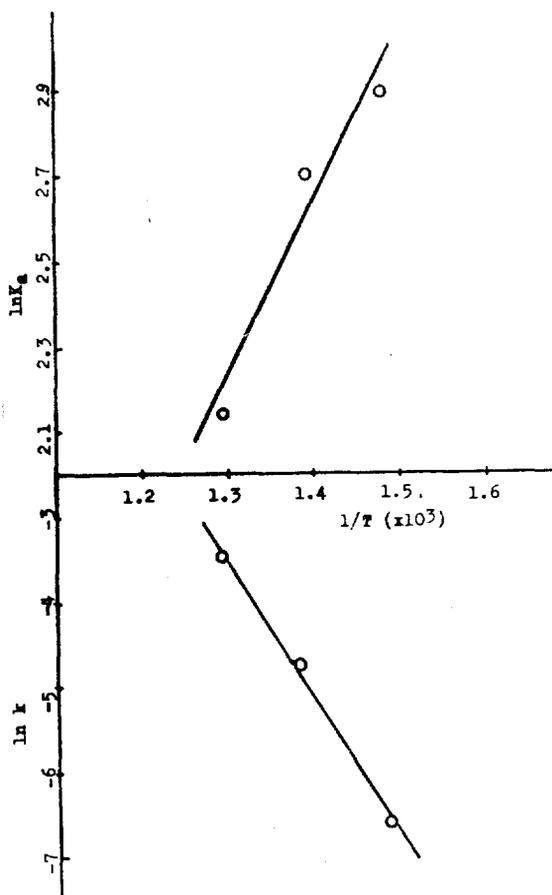


Fig. 9. Temperature dependence of K and K<sub>a</sub>.

## Conclusions

1. Toluene conversion increased with an increase in the reaction temperature or space time. Xylene selectivity decreased with space time and was unaffected by temperature.
2. Higher hydrogen to toluene feed ratio with the toluene feed rate fixed resulted in lower conversions during the initial stages of reaction but lower deactivation rates with process time.
3. Regeneration of used catalysts resulted in a slight decrease in the initial activity but a marked improvement in deactivation characteristics.
4. The values of the activation energy and heat of adsorption were 31.7 and 6.9Kcal/mole, respectively.

## Nomenclatures

- $C$  Surface concentration of adsorbed molecules, molecules/cm<sup>2</sup>  
 $\Delta E$  Activation energy, Kcal/gr-mole  
 $F$  Flow rate, gr-mole/hr  
 $\Delta H$  Heat of adsorption, Kcal/gr-mole  
 $k$  Reaction rate constant, gr-mole/hr gr-catalyst  
 $K$  Equilibrium constant,  $k/k'$ , dimensionless  
 $p$  Partial pressure of reactants and products and products, atm  
 $r$  Reaction rate, gr-mole/hr gr-catalyst  
 $R$  Gas constant, 1.987 cal/gr-mole °K  
 $T$  Absolute temperature, °K  
 $W$  Catalyst mass in the reactor, gr  
 $X$  Toluene conversion, dimensionless

## Subscripts

- $b$  Benzene  
 $o$  Reactor inlet

*t* Toluene  
*x* Xylene

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