Alpha-methylstyrene from Dehydrogenation of Cumene over Fe₂O₃-Cr₂O₃-K₂CO₃ Catalyst

Hiroshi MIURA*, Satoshi TAKAHASHI, Yohji MIZUSHIMA, Kazuo SUGIYAMA,
and Tsuneo MATSUDA

Department of Applied Chemistry, Saitama University,
Shimo-okubo, Urawa-shi 338

(Received July 29, 1988)

The rate of dehydrogenation of cumene over Fe₂O₃-Cr₂O₃-K₂CO₃ catalyst to derive α -methylstyrene has been studied. The reaction rate has been interpreted on the basis of a reaction model taking account of competitive adsorption of cumene, α -methylstyrene, styrene and CO₂. The kinetic parameters were compared with those of dehydrogenation of ethylbenzene. The dehydrogenation of cumene proceeded more rapidly than that of ethylbenzene because the effect of product retardation was less serious.

1. Introduction

While detailed studies have been made on the dehydrogenation of ethylbenzene^{1)–5)}, there have been only few papers on the dehydrogenation of alkylbenzenes other than ethylbenzene.^{5),7),8)}

The decomposition of cumene has frequently been tried in studying the acid-base properties of oxide catalysts, since cumene is decomposed to benzene and propylene over Bronsted acid catalysts⁹⁾, whereas it is dehydrogenated over base catalysts. The product of dehydrogenation, α -methylstyrene (α -MS), is recently being used as a raw material for such specialty plastics as heat resistant ABS resin and modified alkyd or polyester resins. This reaction, however, has not been studied on kinetics using industrial catalysts. We examined this reaction over an industrial Fe₂O₃-Cr₂O₃-K₂CO₃ catalyst, for kinetic analysis, comparing the kinetic parameters with those of dehydrogenation of ethylbenzene.

2. Experimental

Catalyst: A commercial Fe₂O₃-K₂CO₃-Cr₂O₃ catalyst, Nissan Girdler G-64A (1/8" extrude), was used. The extrude was ground and granules in the range of 20 and 60 mesh were submitted for experiments. Since this catalyst is reduced (Fe₂O₃ $\rightarrow$ Fe₃O₄) during the reaction, accompanied with a gradual change in activity, it was prereduced in a flow of H₂/H₂O (1:5 molar ratio) in the reactor at 600 °C for 5 h. After this pretreatment, there was no change in the catalytic activity except the first 1 hour on stream.

Kinetic Measurements: The reaction was carried out using a conventional flow reactor equipped with a stainless steel reactor tube (10 mm diameter)

operated at ambient pressure. Kinetic parameters were obtained by means of differential reactor technique, keeping the cumene conversion less than 10% (in most cases less than 5%). Such experiments were carried out at a temperature of 535 °C, with catalyst weighing 0.5 g, molar ratio of cumene/H₂O=1/12 and contact time of 10–30 g·h/mol. The rate equation thus obtained was verified along with the data obtained using the integral reactor, in which case cumene conversion had changed from 5% to 80%. Such experiments were carried out at temperatures of 535, 620 and 660 °C, with catalyst weighing 0.5–2 g, and contact time of 10–100 g·h/mol.

3. Results and Discussion

Carra and Forni¹⁰⁾ reported that the rate of ethylbenzene dehydrogenation over Fe₂O₃-K₂CO₃-Cr₂O₃ (Shell 105) was interpreted on the basis of a kinetic model taking into account of the competitive adsorption of ethylbenzene and styrene. We also suppose a similar model for cumene dehydrogenation; the Langmuir-Hinshelwood type unimolecular reaction of adsorbed cumene, including competitive adsorption of reactant and products. The rate equation is expressed as eq. (1).

$$r = \frac{k b_{cu} P_{cu}}{1 + \sum b_i P_i} = \frac{k b_{cu} P_{cu}}{1 + b_{cu} P_{cu} + b_{\alpha} P_{\alpha} + b_{st} P_{st} \dots} \quad (1)$$

When cumene conversion is low, the yield of by-products (styrene, toluene, benzene, CO₂, CH₄, CO, C₂H₄) is very small because selectivity to α -methylstyrene is higher than 95%, and their adsorption terms may be neglected (eq. 2).

* To whom correspondence should be addressed.

$$r = \frac{k b_{cu} P_{cu}}{1 + b_{cu} P_{cu} + b_{\alpha} P_{\alpha}} \quad (2)$$

To simplify this equation further, the effect of cumene pressure on the reaction rate was examined, changing H₂O/cumene ratio in the feed. It was found that the rate was independent of the cumene pressure in the range of 40–120 Torr. Equation (2), therefore, is further simplified (eq. 3).

$$r = \frac{k b_{cu} P_{cu}}{1 + b_{cu} P_{cu} + b_{\alpha} P_{\alpha}} \doteq \frac{k b_{cu} P_{cu}}{b_{cu} P_{cu} + b_{\alpha} P_{\alpha}} \quad (3)$$

$$= \frac{k P_{cu}}{P_{cu} + z_{\alpha} P_{\alpha}} \quad (z_{\alpha} = b_{\alpha} / b_{cu})$$

3.1 Effect of α -Methylstyrene

Equation (3) shows that the rate is controlled by the value of z_{α} , which indicates the relative strength of α -MS adsorption with respect to cumene. The effect of adding α -MS to the feed mixture was examined. **Figure 1** shows that the reaction rate decreased significantly by the addition of α -MS. Then, determination of the z_{α} value following the method of Carra and Forni¹⁰⁾ was tried.

Let X indicate the conversion of cumene to α -MS, eq. (3) becomes eq. (4) and k is obtained from eq. (5). When X is sufficiently small, eq. (5) is simplified as eq. (6), using the approximation, $-\ln(1-X) \doteq X$.

$$r = dX/dt = k(1-X)/[(1-X) + z_{\alpha}X] \quad (4)$$

$$k = 1/t[X(1-X) + z_{\alpha}\ln(1/1-X)] \quad (5)$$

$$\doteq X/t \quad (6)$$

When α -MS is added to the feed, and let M indi-

cate the mol percentage of cumene in the feed mixture, eq. (3) becomes eq. (7), on the assumption that the amount of α -MS formed by the reaction is much smaller than that added in the feed. The equation is rearranged (eq. 8), which indicates that plotting k/r against $1/M$, a straight line should be obtained, both the slope and the intercept giving z_{α} value.

$$r = kM/[M + z_{\alpha}(1-M)] \quad (7)$$

$$k/r = (1 - z_{\alpha}) + z_{\alpha}/M \quad (8)$$

First calculating the approximate value of k using eq. (6), a temporary z_{α} value was obtained by eq. (8). This temporary value was used for eq. (5) to get more accurate value of k , which was again used in the calculation of z_{α} from eq. (8). The experimental data are shown in **Fig. 2**. The z_{α} value obtained from the slope was in agreement with that from the intercept, and the value was decided to be 4.28.

3.2 Effect of the By-Products

When cumene conversion is high, considerable amounts of by-products are formed and the effect of their adsorption should be included in the rate equation. We found the following by-products: CO, CH₄, CO₂, C₂H₄, benzene, toluene, styrene.

Because the formation of CO and C₂H₄ was very small, the effect of their adsorption seems negligible. The adsorption of methane seems very weak at such high temperatures. When benzene or toluene was added to the feed, the rate of reaction changed only slightly. Thus, only the z values of styrene (z_{st}) and CO₂ (z_{co2}) were obtained, adding them to the feed mixture. Analysis was made in the same manner as the case of z_{α} , and the results are shown in **Table 1**. Finally, eq. (9) was obtained as

Fig. 1 Effect of α -MS or Styrene Added to the Feed Mixture on the Rate of Cumene Dehydrogenation

● no addition, ○ α -MS addition, ● styrene addition. Reaction temperature: 535 °C

Fig. 2 Relation of k/r to $1/M$ in Eq. 8 for Dehydrogenation of Cumene

Relative adsorption coefficients, z_{α} and z_{st} , were calculated from the slope and intercept of the straight lines. ○ α -MS addition, ● styrene addition.

Table 1 Kinetic Parameters for Dehydrogenation of Cumene and Ethylbenzene

	Cumene	Ethylbenzene
Rate constant (mol/g·min)	6.54×10^{-4}	3.86×10^{-4}
Activation energy (kcal/mol)	43.3	47.1
Relative adsorption coefficients		
α -MS(z_α)	4.28	
styrene(z_{st} , z'_{st})	1.35	21.0
CO ₂ (z_{co2} , z'_{co2})	2.39	37.0

Fig. 3 Correspondence of Experimental Results with Calculated Values Using Eq. 9
Solid lines: calculated, using eq. 9
Plots: experimental results. □: 660 °C, △: 620 °C, ○: 535 °C.

the rate equation of cumene dehydrogenation over Fe₂O₃-K₂CO₃-Cr₂O₃ catalyst.

$$r = kP_{cu}/(P_{cu} + z_\alpha P_\alpha + z_{st} P_{st} + z_{co2} P_{co2}) \quad (9)$$
$$z_\alpha = 4.28, z_{st} = 1.35, z_{co2} = 2.39.$$

Equation (9) was compared with experimental results using an integral reactor, in the conversion range of 5-80%. As shown in Fig. 3, a good agreement between the experimental results and the rate equation was found.

In eq. (9) we supposed that the effect of CO₂ was limited to competitive adsorption with the reactant, cumene. Hirano²⁰ reported, however, that the presence of CO₂ in the gas phase resulted in the decomposition of KFeO₂, which was regared as the active phase in the catalyst system. We tried to estimate the extent of K₂CO₃ decomposition, which is contained in the fresh catalyst, at high temperature by measuring the amount of CO₂ evolved. The catalyst in the amount of 1.0 g was packed in a quartz U-tube, and the temperature elevated gradually while 50 Torr of air was recirculated. When the recirculating gas was passed through a liquid nitrogen trap, more than 98% of K₂CO₃ was decomposed by heating at

Fig. 4 Relationship of Conversion and Reaction Temperature: Comparison of Dehydrogenation of Cumene with That of Ethylbenzene
□: cumene dehydrogenation, ○: ethylbenzene dehydrogenation.

750 °C for 5 hr. In the absence of the trap, however, the evolution of CO₂ was very slow at temperatures of 600–650 °C and only 20% of K₂CO₃ was decomposed after 1 hr at 650 °C. The uptake of CO₂ on the catalyst in which 98% of K₂CO₃ was decomposed was also examined, and it was found that the absorption process was slow; only 30% of K₂CO₃ was restored after 3 hr in contact with CO₂ at 650 °C. Thus, it was found that the evolution-absorption of CO₂ was a very slow process compared with the rapid change in the catalytic activity following the concentration of CO₂ in the feed mixture. In such brief experiments, the effect of CO₂ seemed to be ascribed mainly to its adsorption, as supposed in eq. (9).

3.3 Comparison with Dehydrogenation of Ethylbenzene

Reaction rates in dehydrogenation of cumene and ethylbenzene were compared at the same reaction conditions. Figure 4 shows that dehydrogenation of cumene proceeded more rapidly than that of ethylbenzene. The former is thermodynamically more favorable than the latter¹¹, but in this case, conversion was kept low and the difference seemed to be due to kinetic reasons. An attempt was made to obtain the rate equation for ethylbenzene dehydrogenation, adding styrene to the feed mixture to determine z' ($=b_{st}/b_{eb}$). As shown in Table 1, z'_{st} for ethylbenzene dehydrogenation was larger than z_α for cumene, suggesting that the product retardation was more serious for ethylbenzene than for cumene. The rate constant, k_{eb} , at 620 °C was smaller than k_{cu} , whereas the activation energy E_{eb} was larger than E_{cu} .

Such differences in kinetic parameters are understood by the relative stability of the reaction

Fig. 5 Effect of Styrene Added to the Feed Mixture of Ethylbenzene Dehydrogenation
Reaction temperature; 575 °C

intermediates. From the z values of Table 1, the relative strength of adsorption of the reactants and products are calculated as follows;

$$b_{cu}/b_{eb} = 15.6, \quad b_{\alpha}/b_{st} = 3.2.$$

It is clear that the effect of increase in the adsorption strength of reactants ($b_{cu} > b_{eb}$) is more significant than the increase in the effect of product retardation ($b_{\alpha} > b_{st}$), resulting in smaller value of z_{α} than that of z'_{st} .

From the values of relative adsorption coefficients, the following order of adsorption strength was found:

4. Conclusions

1. The rate of dehydrogenation of cumene was interpreted on the basis of a Langmuir-Hinshelwood type kinetic model including the competitive adsorption of cumene, α -MS, styrene and CO_2 .
2. Dehydrogenation of cumene proceeds more easily than that of ethylbenzene, because the

relative adsorption coefficient of product, z_{α} , is smaller than z'_{st} and, accordingly, effect of product retardation is less serious for cumene.

3. The relative strength of adsorption was decided to be as follows: $\alpha\text{-MS} > \text{CO}_2 > \text{styrene} > \text{cumene} > \text{ethylbenzene}$.

Nomenclature

- b_x : adsorption coefficient of compound x
 z_x : relative adsorption coefficient for cumene dehydrogenation, b_x/b_{cu}
 z'_x : relative adsorption coefficient for ethylbenzene dehydrogenation, b_x/b_{eb}
 P_x : partial pressure of compound x
 r : reaction rate, mol/g·min
 k : reaction rate constant, mol/g·min
 X : conversion of cumene
 $t=W/F$: contact time, g·min/mol
 M : mol percent of cumene in the feed mixture
 E_{cu}, E_{eb} : activation energy of dehydrogenation
 cu : cumene
 α : α -MS: α -methylstyrene
 eb : ethylbenzene
 st : styrene

References

- 1) Hirano, T., *Shokubai (Catalyst)*, **29**, 641 (1987).
- 2) Hirano, T., *Applied Catal.*, **26**, 65 (1986).
- 3) Hirano, T., *Applied Catal.*, **26**, 81 (1986).
- 4) Hirano, T., *Applied Catal.*, **28**, 119 (1986).
- 5) Miyata, K., Ozawa, S., Yamazawa, Y., Ogino, Y., *Sekiyu Gakkaishi*, **31**, 210 (1988).
- 6) Lee, E. H., *Catal. Rev. Sci. Eng.*, **8**, 285 (1973).
- 7) Forni, L., Valerio, A., *Ind. Eng. Chem. Process Des. Develop.*, **10**, 552 (1971).
- 8) Tanaka, K., Fujiwara, H., Akaho, M., *Sekiyu Gakkaishi*, **29**, 384 (1986); *ibid.*, **29**, 391 (1986).
- 9) Tanabe, K., "Solid Acids and Bases" p. 127 (1970), Kodansha, Tokyo.
- 10) Carra, S., Forni, L., *Ind. Eng. Chem. Process Des. Develop.*, **4**, 281 (1965).
- 11) Ohta, N. ed., "Shokubai Kogaku Koza" vol. 7, p. 202 (1969), Chijin Shokan, Tokyo.

要 旨

Fe₂O₃-Cr₂O₃-K₂CO₃ 触媒によるクメンの α -メチルスチレンへの脱水素反応

三浦 弘, 高橋 聡, 水嶋 洋三, 杉山 和夫, 松田 常雄

埼玉大学工学部応用化学科, 338 浦和市下大久保 255

Fe₂O₃-Cr₂O₃-K₂CO₃ 触媒を用いたクメンの α -メチルスチレンへの脱水素反応の速度論的研究を行った。反応速度は、クメン、 α -メチルスチレン、スチレン、CO₂ の競争吸着を仮定した Langmuir-Hinshelwood 型の速度式(9)で整理できた。さらに、原料中に α -メチルスチレン、スチレン、

$$r = kP_{cu} / (P_{cu} + z_{\alpha}P_{\alpha} + z_{st}P_{st} + z_{CO_2}P_{CO_2}) \quad (9)$$

CO₂ を加えたときの反応速度の変化から、相対吸着係数 z_{α} , z_{st} , z_{CO_2} を測定し、おのおの 4.28, 1.35, 2.39 であることがわかった。エチルベンゼンの脱水素に比べてクメンの脱水素は容易に進行する。相対吸着係数の比較から、エチルベンゼンの脱水素の方が生成物阻害の影響が強く現れるためであることがわかった。

Keywords

Cumene, Dehydrogenation, Iron oxide catalyst, Kinetics, 2-Propenylbenzene