KINETICS OF BENZENE HYDROGENATION ON SUPPORTED PLATINUM, PALLADIUM, RHODIUM AND RUTHENIUM CATALYSTS

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Although benzene hydrogenation has been widely utilized as a test reaction for the investigation of catalytic activity, the reaction mechanism has not been well elucidated.

As to the Langmuir-Hinshelwood rate equations, there have been many reports for the reaction on nickel catalysts[4-6], but few papers have been published on platinum metal catalysts[1], especially on rhodium and ruthenium catalysts.

In this communication, reaction rates were measured for benzene hydrogenation over commercially available Pt-, Pd-, Rh- and Ru-Al₂O₃ catalysts and the rate equation was derived. The thermodynamic consistency of the rate equation was then tested in the light of the rules established by Boudart et al.[2] and Vannice et al.[10].

1. Experimental

The catalysts used in this work were 0.5wt.%Pt-, Pd-, Rh- and Ru-Al₂O₃ (ca. 3.3 mmφ x 3.3 mm cylindrical pellets) supplied by Nippon Engelhard Co. Ltd.

The reaction rate measurements were performed using a conventional fixed-bed differential reactor at atmospheric pressure. The reaction temperatures ranged from 130 to 170°C (for Pd-Al₂O₃), from 90 to 110°C (Rh-Al₂O₃), from 90 to 150°C (Ru-Al₂O₃) and from 110 to 150°C (Pt-Al₂O₃). The hydrogen partial pressures ranged from 0.35 to 0.88 atm, and the benzene partial pressures from 0.06 to 0.25 atm.

All the reaction rate data were obtained under reaction control. Catalyst deactivation was observed in all systems except the palladium-alumina catalyst, so that the rates were corrected by using the "bracketing method" recommended by Siñeuf et al.[11].

2. Results and Discussion

In the previous paper[7], the amount of benzene adsorbed on Pd-Al₂O₃ was measured in a stream of helium or hydrogen as a carrier gas. Under a hydrogen atmosphere, it was found that benzene adsorbed on the metal atoms was negligibly small compared with the amount of physisorbed benzene on the support. Then, the hydrogenation rate was proportional to the number of surface metal atoms, from which it was deduced that benzene adsorbed on the support migrates to the metal active sites situated near the metal-support boundary, and reacts with hydrogen. On the other hand, from the measurements of the amount of hydrogen adsorption and the rate of benzene hydrogenation on Pd-Al₂O₃ diluted with several types of alumina or tungsten trioxide particles, we found that hydrogen atoms dissociated on the metal atoms spill over onto the surface of the support and the diluents[9] and these mobile hydrogen atoms affect the reaction rate[8]. From these facts, it is considered that mobile hydrogen atoms are accessible to benzene molecules bound to the active sites and react successively with benzene molecules to produce cyclohexane. Some papers[4,5] published recently suggest that the hydrogenation of benzene may proceed as a sequence of hydrogen addition steps. This mechanism may be accepted for the systems of platinum metal catalysts used in this work because a trace amount of cyclohexene, which is one of the intermediate products in the successive hydrogenation of benzene to cyclohexane, was produced under extreme conditions. The hydrogenation rates for cyclohexadiene and cyclohexene are known to exceed greatly the corresponding rate for benzene hydrogenation[9]. Further, the reaction orders with respect to the hydrogen partial pressures were found to be 0.7 to 2.8 in the range of the reaction temperatures. From these facts, we supposed that the rate-determining step of benzene hydrogenation is the sixth step of hydrogen addition to the partially hydrogenated benzene molecule and that the other steps are equilibria up to the rate-determining step.

In conclusion, the reaction pathways are described as follows:
The surface coverages of the reactive components on the active sites expressed by $\theta_{B} = K_{B} C_{H} \theta_{H} = K_{B} C_{H} \theta_{H} = K_{B} C_{H} \theta_{H} = K_{B} C_{H} \theta_{H} = K_{B} C_{H} \theta_{H} = K_{B} C_{H} \theta_{H} = K_{B} C_{H} \theta_{H}$.

The reaction rate equation is given by

$$r = k C_{H} \theta_{H} = k K' C_{H} \theta_{H}$$

In the partial pressure range of this work, the reaction rate was independent of benzene partial pressure, and thus $K' C_{H} \theta_{H} \approx 1$. Then the rate equation reduces to

$$r = k' K' C_{H} \theta_{H}$$

The linearized form of Eq. (2) is written by

$$\log (r/r_0) = \log (k' K' C_{H} \theta_{H})$$

The effects of hydrogen partial pressure on reaction rate can be described by Eq. (3) for Pd-, Rh- and Ru-Al$_2$O$_3$ catalysts as shown in Figs. 1-3. For Pt-Al$_2$O$_3$ catalyst, data also fitted well to Eq. (3). The slope and the intercept of the linear lines in the figures gave the adsorption equilibrium constant $K_{H}$ and the rate constant $k'$. The temperature dependences of $K_{H}$ values were described by the equation

$$K_{H} = \exp (\Delta S_{H}/R - \Delta H_{H}/RT)$$

where $\Delta S_{H} = S_{H}(ads) - S_{H}(gas)$ is the standard entropy change of adsorption and $\Delta H_{H}$ is the standard enthalpy change of adsorption for hydrogen. The values of $-\Delta S_{H}$ and $-\Delta H_{H}$ are listed in Table 1.
The thermodynamic consistency of the rate equation was tested using the rule (guideline) presented by Boudart et al.\textsuperscript{2).} Recently, Vannice et al.\textsuperscript{10}) proposed that the rule can also be applied to the reaction where the dissociation of a diatomic molecule occurs. The rule is given as follows:

\[ 10 \leq -\Delta S_H \leq 12.2 - 0.0014\Delta H_H \]

The calculated values of \(12.2 - 0.0014\Delta H_H\) are shown in Table 1, and all the results were found to obey the rule. The activation energies of reaction obtained from \(k'\) values ranged from 17.3 to 18.0 kcal/mol for Rd-, Rh- and Ru-Al\(_2\)O\(_3\) catalysts. For Pt-Al\(_2\)O\(_3\), a value of 21.6 kcal/mol was obtained.

### Nomenclature

- \(C_j\) = surface concentration of j-component [mol/g-cat]
- \(\Delta H_j\) = standard enthalpy change of adsorption of j-component [cal/mol]
- \(K_i, K'_i\) = equilibrium constants of the i-th step reaction [g-cat/mol]
- \(K_3, K'_3\) = adsorption equilibrium constants of j-component [1/atm]
- \(k, k'\) = reaction rate constants [mol/g-cat*s]
- \(n\) = constant of Freundlich isotherm equation [—]
- \(p_i\) = partial pressure of j-component [atm]
- \(R\) = gas constant [cal/mol*K]
- \(r\) = reaction rate [mol/g-cat*s]
- \(\Delta S_j\) = standard entropy change of adsorption of j-component [cal/mol*K]
- \(T\) = temperature [K]
- \(\alpha\) = constant [mol/g-cat]
- \(\beta\) = constant [mol/g-cat*atm\(^{1/2}\)]
- \(\theta_B, \theta_H\) = fractions of surface coverages of benzene and of Bj-component, respectively, on the active sites [—]
- \(\theta_v\) = fraction of vacant active sites [—]

### Table 1

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>(-\Delta S_H) [cal·mol(^{-1})·K(^{-1})]</th>
<th>(-\Delta H_H) [cal·mol(^{-1})]</th>
<th>12.2 - 0.0014(\Delta H_H)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pd-Al(_2)O(_3)</td>
<td>14.9</td>
<td>8130</td>
<td>24</td>
</tr>
<tr>
<td>Rh-Al(_2)O(_3)</td>
<td>20.9</td>
<td>8990</td>
<td>25</td>
</tr>
<tr>
<td>Ru-Al(_2)O(_3)</td>
<td>24.7</td>
<td>8920</td>
<td>25</td>
</tr>
<tr>
<td>Pt-Al(_2)O(_3)</td>
<td>18.3</td>
<td>9110</td>
<td>25</td>
</tr>
</tbody>
</table>

Note: \(K_H = \exp (\Delta S_H/R - \Delta H_H/RT)\); Standard state: 1 atm.

### Literature Cited


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