Steam Dealkylation of Methylquinolines over Several Supported Metal Catalysts

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The steam dealkylation of various methylquinolines was investigated over several supported metal (Ni, Pd, and Rh) catalysts in the temperature range of 300—400°C. An alumina-supported palladium catalyst exhibited the highest selectivity for quinoline. Indole and methylindoles were also formed during the dealkylation of methylquinolines.

1. Introduction

Alkylquinolines such as methylquinolines are contained in coal-tar or in heavy oil. However, their utilization is very limited because it is difficult to separate individual alkylquinolines from a mixture of alkylquinolines. On the other hand, quinoline is widely used as a raw material for chemical products such as nicotinic acid, dyes, and agricultural chemicals. Therefore, dealkylation of alkylquinolines for producing quinoline is industrially important. However, there has so far been no report on the synthesis of quinoline by dealkylation of alkylquinolines. Since steam dealkylation of alkylpyridines or of alkylbenzenes has been widely investigated for producing pyridine or benzene\(^1\),\(^2\), steam dealkylation of various methylquinolines was investigated over several supported metal catalysts in the present study.

2. Experimental

The catalysts used in the present study were a zirconia-supported nickel (Ni/ZrO\(_2\)), a silica-alumina-supported rhodium (Rh/SiO\(_2\)-Al\(_2\)O\(_3\)), and an alumina-supported palladium (Pd/Al\(_2\)O\(_3\)). Preliminary experiments showed the catalyst supports for Ni, Rh and Pd that gave high selectivity for quinoline were zirconia, silica-alumina, and alumina, respectively. The catalysts were prepared by impregnating a catalyst support in an aqueous solution of metal nitrate or chloride, then drying it at 100°C, and finally calcining it at 400°C for 3 h. The metal loadings of Ni/ZrO\(_2\), Rh/SiO\(_2\)-Al\(_2\)O\(_3\), and Pd/Al\(_2\)O\(_3\) were 20%, 5%, and 5% by weight, respectively. The metal catalysts were reduced in a flow of hydrogen at 400°C for 2 h before use.

Dealkylation experiments were carried out in the temperature range of 300—400°C using a fixed bed flow reactor. The reaction products were analyzed by gas-chromatography.

3. Results and Discussion

The reaction products contained quinoline (QN), aniline (AN), methylanilines (MAN), picoline (PI), benzene, gas (CO, CO\(_2\), CH\(_4\), H\(_2\)), indole (IND), methylindoles (MIND), dimethylquinolines, and other unknown compounds.

Activities and selectivities of Ni, Rh, and Pd catalysts for dealkylation of methylquinolines are shown in the Table 1. The palladium catalyst exhibiting the lowest activity, but the highest selectivity for quinoline, was not greatly dependent on the position of the methyl group substituted. The nickel catalyst produced quinoline more selectively in the dealkylation of 2- and 8-methylquinolines than in the dealkylation of the other methylquinolines, indicating that the methyl groups substituted at the position near N atom can be eliminated more easily than those far from N atom. The rhodium catalyst was found to have an intermediate characteristic between nickel and palladium catalysts with regard to the selectivity for quinoline.

The selectivity for indole on the palladium
catalysts was higher in the reaction at 400°C than at 350°C. This suggests that indole is formed via the quinoline resulted from the dealkylation of methylquinolines. Methylindoles were found in the dealkylation of 6-methylquinoline and also in the dealkylation of 5-, and 7-methylquinolines mixtures, but not found in the dealkylation of 2-, 3-, or 4-methylquinolines. The possible reaction network can be shown in Fig. 1 on the basis of the results described above.

Table 2 shows the results of the dealkylation of a mixture of methylquinolines (MQMIX) over metal catalysts.

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>React. temp. [°C]</th>
<th>Total conv. [%]</th>
<th>Product selectivity [%]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pd</td>
<td>350</td>
<td>29.5</td>
<td>QN: 85.4, IND: 2.0, MIND: 3.0, Gas: 4.0</td>
</tr>
<tr>
<td>Rh</td>
<td>350</td>
<td>29.4</td>
<td>QN: 79.1, IND: 9.1, MIND: 1.3, Gas: 2.8</td>
</tr>
<tr>
<td>Ni</td>
<td>350</td>
<td>25.0</td>
<td>QN: 25.4, IND: 1.8, MIND: 5.5, Gas: 14.8</td>
</tr>
</tbody>
</table>

a) Reaction conditions: pressure=3 kg/cm², MQMIX:H₂O:He=1:30:31, feed rate of MQMIX=1.4×10⁻⁴ mol/min.

Weight of catalyst=4.0 g (Pd), 3.0 g (Rh), 4.0 g (Ni).

Composition of MQMIX (wt%): 2MQ 23.7%, 3MQ 8.5%, 4MQ 12.8%, 5MQ 3.0%, 6MQ 9.7%, 7MQ 13.4%, 8MQ 9.9%.

The possible reaction network can be shown in Fig. 1 on the basis of the results described above.

Reference
要 旨

数種の担持金属触媒上でのメチルキノリン類の水蒸気脱アルキル

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アルキルキノリン類はコールタールあるいは重質油中に含まれているが、各アルキルキノリンの単離が困難であるためそれらはほとんど利用されていない。一方、キノリンは化学薬品、農薬などの原料として利用されている。そこで著者らは、アルキルキノリンの脱アルキルによるキノリンの製造に着目して、数種の担持金属触媒上での数々のメチルキノリンの水蒸気脱アルキルを検討した。触媒としては、Ni(20)/ZrO₂, Rh(5)/SiO₂・Al₂O₃, Pd(5)/Al₂O₃を使用した。メチルキノリンの水蒸気脱アルキル反応は固定床連続反応装置を用いて行い、生成物の分析はガスクロマトグラフを用いて行った。メチルキノリンの水蒸気脱アルキルにおける生成物はキノリン、インドール、メチルインドール、アゾリン、分解ガス（CO, CO₂, CH₄, H₂）等であった。3 種の触媒を用いて反応を行ったところ、Pd 鋼媒が最も高いキノリン選択性を示し、メチル基の置換位置やより依存しないことがわかった。インドールはキノリンを経由して生成するものと考えられる。また、インドールは 5-, 6-, 7-メチルキノリンから生成するが、2-, 3-, 4-メチルキノリンから生成しないことがわかった。

つぎに、コールタールの 230〜280℃留分中のメチルキノリン組成と同様の組成のメチルキノリン混合物の水蒸気脱アルキルを行ったところ、Pd 鋼媒が最も高いキノリン選択性を示すことがわかった。

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Keywords

Supported metal catalyst, Steam dealkylation, Methylquinoline