The effect of Rh/BAC catalyst preparation and pretreatment methods on benzene hydrogenation

Introduction

Hydrogenation of benzene to cyclohexane is an essential process for the petroleum industry and environmental protection. Although it has been around for more than 200 years, the hydrogenation of aromatic compounds is still important today. For example, incomplete combustion of benzene in petrol produces the carcinogenic compound benzo[α]pyrene in exhaust gases. Thus, according to European standards, the volume of benzene in gasoline should not exceed 1%, and during reforming, 1/3 of the volume is released as aromatic compounds [1–4]. Catalysts are therefore needed to ensure the selective hydrogenation of benzene. Secondly, benzene is needed to store hydrogen: one benzene molecule holds three hydrogen molecules. Other chemical syntheses require new catalysts to store active energy for the hydroge

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porous structure. Because of their adjustable pores, these materials can be used in a variety of processes to form the desired products more selectively.

Due to the toxicity of benzene, much attention has been paid to the hydrogenation of benzene to cyclohexane. Nanoparticles of various metals, including platinum, ruthenium and rhodium, have been used in the benzene hydrogenation process. Since metal nanoparticles tend to aggregate into large particles, a variety of support materials such as carbon nanotubes, titanium dioxide, and silicon dioxide were used to stabilise the metal nanoparticles and improve their function. For example, in benzene hydrogenation, Rh/SiO₂, Ru/SiO₂, Ru/zeolite, Ru/SBA-15, and Pt(0) nanoparticles are highly active catalysts [8].

Despite the large number of published works, it is necessary to find an optimal combination of metal and support to obtain efficient benzene hydrogenation catalysts. Cerium is believed to enhance the nanoparticle activity and stability of metals due to strong metal-support interactions. The high catalytic activity of the cerium oxide-based catalyst is closely related to the exchange of Ce⁴⁺ and Ce³⁺ in cerium oxide during catalytic reactions. The valence and defect structure of CeO₂ can be spontaneously altered by doping with other ions. An example of this is the catalytic use of rhodium nanoparticles deposited on cerium oxide (Rh NPs/CeO₂) in the hydrogenation of benzene [15].

The result of hydrogenation in ethanol and the effect of hydrogen pressure were compared using a rhodium and gold catalyst calcined on an amorphous synthetic aluminosilicate (ASA, Siral-40) substrate with a high specific surface area for benzene and toluene. The catalyst was prepared by two different methods, specifically absorption by moisture capacity and the colloidal method [16]. The impregnation method was also used to prepare the catalyst in two different ways: sequentially impregnating first one metal salt, then the other, and simultaneously impregnating gold and rhodium salts. It was discovered that hydrogenation is most successful for selectively hydrogenating benzene in terms of moisture capacity in catalysts made by impregnation. Catalyst activation depends on the amount of rhodium required to activate benzene and toluene on the catalyst surface. The amount of rhodium on the surface is close to that theoretically possible as it remains on the surface of catalysts prepared by the colloidal method [17].

By analysing recent literature data and experimental studies, it was clearly established that rhodium is highly active in hydrogenation reactions. We supported rhodium on AAC (apricot kernel) and BAC supported subunits and converted benzene to cyclohexane by complete hydrogenation. Rhodium catalysts seeded on AAC supported and modified catalysts showed high selectivity in the hydrogenation of benzene. Hydrogenation of benzene and toluene in the presence of rhodium catalyst supported on rice husk activated carbon (RHAC) and apricot kernel activated carbon (AAC). Since AAC is strong, whereas RHAC is light and volatile and difficult to isolate from the reaction mass, it was shown that birch wood activated carbon could be an effective support. The Rh/RAC catalyst was found to be five times lower than Rh/AAC, which is equivalent to catalysts based on activated Siberian charcoal and rhodium planted on AAC [18].

As can be seen from this work, rhodium was the most active metal in the benzene hydrogenation reaction. In the present study, we present the results on the catalytic activity of Rh/BAC catalysts prepared by different methods in the benzene hydrogenation reaction. The prepared catalysts were characterised by the BET method and scanning electron microscopy (SEM). The effects of catalyst types on benzene hydrogenation and catalytic performance were discussed.

**Experimental**

**Materials**

RhCl₃·3H₂O was purchased from Sigma-Aldrich (Germany). BAC (activated carbon from birch wood, Sorbis Group, Russia) was used as support. Ethanol was used as a solvent in the hydrogenation of benzene.

**Hydrogenation method**

Hydrogenation of benzene was carried out in a high-pressure kinetic system capable of maintaining a constant temperature and pressure of hydrogen. The autoclave part of the unit is equipped with an ultra thermostatic layer and turbulent stirrer. The amount of hydrogen that is absorbed from the burette is controlled as part of the research experiment, which is conducted by simultaneously adding the necessary amount of catalysts and reagents to the autoclave and heating it to the necessary pressure and temperature. Calculation of the reaction rate is thoroughly described in detail in the following literature [19–21].

**Preparation of the catalyst**

The catalysts were prepared by the methods of moisture absorption and adsorption. In the moisture absorption method, the required amount of a sample of the BAC studied was heated in a muffle furnace at a
temperature of 400 °C for 4 hours. On the second day, the mass was measured and the moisture content was determined. To determine the moisture content, water was dripped from a burette up to a certain volume and stirred until a paste was formed. We determined that one volume of support was equal to the moisture content of water. A sample of the required quantity of RhCl₃·3H₂O salt was taken from the glass bottle, dissolved in water with the required amount of moisture content, dried with careful mixing and left for the second day. After repeated stirring in the drying oven at 120 °C, we left it overnight and the next day for 4 hours in a furnace. It was then reduced with hydrogen at a temperature of 350–400 °C. The desired mass was measured and used for the hydrogenation reaction. Adsorption method: RhCl₃·3H₂O salt required for the support was dissolved in a large volume of water, a support was added to it and kept for 30 minutes, heated with a stirrer up to 60–80 °C. When rhodium ions were adsorbed on the surface of the support, the solution became colourless and transparent. At this point, we assume that all the rhodium ions have been adsorbed. The catalyst was filtered by the vacuum filtration on the Buchner funnel, then it was heated in a drying oven at about 120 °C for 4-6 hours and it was left for the next day.

Characterisation of the catalyst

The following physical methods were used to characterise the catalyst: The specific surface area in the Akusorb device was determined by the BET method by adsorption of nitrogen molecules. Chemical composition was determined using scanning electron microscopy (JSM-6460LV (JEOL, SEM).

Results and Discussion

Table 1 summarises the Rh/BAC catalyst, meso, micro pore volumes and pore diameters. The rhodium cations mentioned above are still metallic and enter the pores during adsorption, based on their volume diameters. Therefore, these parameters can be considered as evidence that the catalysts prepared by the adsorption method are not active in the hydrogenation of benzene.

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>V_pore, cm³/g</th>
<th>S_BET, m²/g</th>
<th>D_pore, nm</th>
</tr>
</thead>
<tbody>
<tr>
<td>Rh/BAC</td>
<td>0.298</td>
<td>934.0</td>
<td>0.6–0.8</td>
</tr>
<tr>
<td>Reduced Rh/BAC</td>
<td>0.319</td>
<td>988.0</td>
<td>0.6–0.9</td>
</tr>
</tbody>
</table>

The SEM image of Rh/BAC catalysts is shown in Figure 1. The figure shows different types of birch activated carbon granules taken at different scales. However, the rhodium granules are not visible. At the same time, pores are not visible in the images.

Figure 1. Scanning electron microscope (SEM) images of 1 % Rh/BAC catalysts:
1 — ×100; 2 — ×1000; 3 — ×3000; 4 — ×10000
Table 2 presents the chemical compositions. Rhodium was detected at points 3, 4, 7, and 10 out of ten used for its determination. At point 10, rhodium was discovered to be 0.1 %, and at points 3 and 4, it was 0.2 %. At point 7, it was identified as 0.41 %. Rhodium was not detected in other points, which suggests that its volume is lower than before, and the metallic rhodium atoms are not on the surface of the carbon. The aggregate comprises mixed carbon microgranules, resulting in an uneven distribution of rhodium volume throughout.

The table indicates that rhodium chloride salt and its associated chlorine anions are present in conjunction with the rhodium. Additionally, elements such as potassium, magnesium, calcium, sulfur, and oxygen were found on the Birch activated carbon (BAC) surface, which is believed to have originated from it. During the hydrogenation of benzene, analogous kinetic curves were observed on catalysts with a moisture capacity and an adsorption method, as depicted in Figures 2 and 3. The reaction rate for catalysts produced using the moisture capacity method is less than 10 mL/min, compared to only 1.8 mL/min for catalysts obtained by the adsorption method. The moisture capacity method is known for producing catalysts with a high rate of reaction.

![Figure 2](image-url)

**Figure 2.** Kinetic curve for benzene hydrogenation using 1 % Rh/BAC catalyst.

Reaction conditions: 0.1 g of catalyst (moisture capacity), 60mL of ethanol, 1 mL of benzene, at 60 °C, 40 MPa
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Figure 3. Kinetic curve for benzene hydrogenation using 1% Rh/BAC catalyst. Reaction conditions: 0.1 g of catalyst (adsorption), 60 mL of ethanol, 1 mL of benzene, at 60 °C and 40 MPa pressure.

We believe that this trait is linked to the process of adsorption. Rhodium cations adsorb salt deep within the pores, thereby increasing its solubility. Even after hydrogen with reduction, the catalyst does not entirely vanish within the pore, leading to surface adsorption of hydrogen molecules. This makes it difficult for the benzene molecule to be adsorbed and enter the pores, resulting in a low hydrogenation rate.

Figure 4 illustrates the kinetic curve of benzene hydrogenation on catalysts that were prepared using the moisture capacity method with 1% Rh/BAC. Nevertheless, certain alterations were observed during the pretreatment. After annealing the first catalyst (1) without reduction, the second catalyst (2) was used in the hydrogen flow. Despite the high initial rate on the first catalyst, the reaction was stopped for not more than half of the counted amount of absorbed hydrogen. On the second catalyst, with a low initial rate, the reaction proceeded until all hydrogen was completely absorbed.

Figure 4. Kinetic curve of benzene hydrogenation. Experiment conditions: 0.1 g, 1% Rh/BAC (moisture capacity), 60 mL of ethanol, 1 mL of benzene, at 60°C, 40 MPa. 1 — not reduced; 2 — reduced by hydrogen.

This phenomenon can be explained as follows: when the instantaneous hydrogenation catalyst is used without reduction in a hydrogen atmosphere, rhodium transitions from the cationic type to the metallic form occur through autocatalysis. Concurrently, the metallic surface that is formed undergoes hydrogenation. Consequently, the atoms in metallic rhodium take the shape of clusters. Additionally, due to the abundance
of metal atoms in rhodium, its initial rate is higher. The reaction achieves completion as the metals begin to cluster more slowly.

Figure 5. Kinetic curve of benzene hydrogenation with 1 % Rh/BAC.

Experiment conditions: 0.1 g of catalyst (moisture capacity), 60 mL of ethanol, 1 mL of benzene, at 60 °C, 40 MPa.

I — moisture capacity; 2 — adsorption.

Figure 5 illustrates the hydrogenation kinetic curves of catalysts for benzene production using different methods. On the first curve (green), the volume of hydrogen calculated is completely washed out on the catalyst, obtained by using the moisture capacity method with 1 % Rh/BAC. On the second catalyst (red curve), the reaction commences gradually at a rate of 1.8 mL/min and terminates entirely after eliminating 230 mL of hydrogen from the catalyst. As stated above, rhodium cations from the rhodium salt penetrate and remain as metals in the micropores. It is hypothesized that the reaction does not occur because the benzene molecule cannot reach this site.

**Conclusions**

Rhodium catalysts, supported on carbon materials, were created using adsorption and wet impregnation methods in this study. Liquid-phase benzene hydrogenation was conducted in a batch reactor. The physicochemical characteristics of the rhodium catalysts on carbon materials were characterised using SEM and N₂ adsorption-desorption analysis. The catalysts’ benzene hydrogenation activity is dependent on the method of creation. The catalyst obtained through adsorption is considerably inferior to that produced via the moisture capacity method. The catalyst itself, which has moisture capacity, is easily pre-treated. The reaction is completed by the reduced catalyst, but not by the unreduced catalyst.

**References**


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