

Hydrogenation of benzene and toluene over supported rhodium and rhodium-gold catalysts

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Abstract. Rhodium and rhodium-gold catalysts supported on amorphous aluminosilicates (ASA), titanium dioxide (rutile, TiO₂) was prepared in two different ways: by the absorption and colloidal method. The catalysts were characterized by an inductively coupled plasma optical emission spectrometer (ICP-OES), transmission electron microscopy (TEM) and X-ray diffraction (XRD). The activity and selectivity of the prepared catalysts were tested by the hydrogenation of benzene and toluene. Hydrogenation was conducted at a pressure of 4 MPa and a temperature 80 °C. The bimetallic Rh-Au/ASA catalyst prepared by the absorption method showed high activity in the benzene hydrogenation reaction, the same catalyst prepared by the colloidal method demonstrated high activity in the toluene hydrogenation reaction.

1 Introduction

The content of aromatic compounds formed during the reforming of gasoline reaches 50%, of which 10% is benzene. Incomplete combustion of benzene-containing gasoline engines forms a carcinogenic compound called benzopyrene inside the exhaust gases. Euro standard insists that the benzene content in gasoline should not exceed 1%. One effective way to remove small amounts of benzene is to selectively hydrogenate benzene to cyclohexane. From this point of view, it is necessary to create catalysts that selectively hydrogenate benzene and in the presence of other aromatic compounds (toluene, xylene, cumene, etc.).

The most active metal from platinum group for the hydrogenation of aromatic compounds is rhodium, precipitated on various supports. [1-9]. The authors of [1] studied the possibility of adsorption of an aromatic ring on the Rh (III) faces during hydrogenation and found out what is adsorbed at 20 degrees, earlier studies had 32 degrees. [2] It was found that the aromatic ring, in which rhodium was planted on traditional carriers SiO₂, Al₂O₃, and TiO₂ and adsorbed on rhodium, does not desorb at the molecular level, and the surface coverage of benzene and toluene was found. [3] The authors used various rhodium salts, embedded it in silicon dioxide, and prepared bimetallic rhodium-palladium catalysts. [4] Rhodium is embedded in polyvinylpyrrolidone. [5] The authors planted rhodium in nanocrystalline hydroxapatite. [6] Rhodium was planted on well-known TiO₂ carriers in the form of anatase and rutile. After analyzing these studies, we prepared active catalysts for the selective hydrogenation of benzene with the planting of rhodium on various carbon supports [7], as a result of which depleted carbon supports with a surface area of more than 500 m² / g turned out to be active and selective catalysts that allow selective hydrogenation of benzene in the presence of other aromatic compounds. [8] The authors achieved high catalytic activity in

the hydrogenation of benzene to cyclohexane by catalysis [TPPTS = $P(C_6H_4\text{-}m\text{-}SO_3Na)_3$] with a water-soluble Rh / TPPTS system in an aqueous / organic two-phase system. The influence of several parameters of the system on the hydrogenation reaction of biphasic benzene was investigated. The highest catalytic activity in this reaction was observed at a low volumetric ratio of the water-gasoline phase, i.e., at 0.4. [9] The authors obtained rhodium (0) nanoparticles embedded in cerium (RhNPs) by oxidation of Rh^{3+} ions on the cerium surface in an aqueous medium. The RhNPs / CeO_2 catalyst exhibited high activity in benzene hydrogenation under light conditions. The hydrogenation of this benzene without solvent was carried out at a circulation frequency of 495 h^{-1} , a hydrogen gas pressure of ~ 0.3 MPa, at a temperature of $25.0 \pm 0.1^\circ\text{C}$. RhNPs / CeO_2 was more active than RhNPs planted on titanium, zirconium and hafnium.

In this article, we present information about a rhodium catalyst prepared for the selective hydrogenation of benzene, supported on amorphous aluminosilicate and titanium oxide, developed in the surface regions, as well as about bimetallic rhodium-gold catalysts.

2 Experimental part

2.1 Materials

$RhCl_3$ and $HAuCl_4$ (Sigma Aldrich) were used as the starting compounds of Rh and Au. Titanium dioxide (rutile, TiO_2) and amorphous synthetic aluminosilicate (ASA) called "Siral" were used as carriers. In the colloidal method, PVA (Sigma Aldrich, $M = 10000$) and $NaBH_4$ (Sigma Aldrich) were used as stabilizing and reducing reagents. For the joint impregnation of the catalysts, aqueous solutions of $RhCl_3$ or $HAuCl_4$ were used.

2.2 Catalyst preparation

Mono and bimetallic catalysts were prepared using moisture absorption («imp») and colloidal («coll»). The resulting solutions were added drop wise to the supports, and then heated at 80°C for 3 h, dried at 100°C , and oxidized for 3 h at 250°C in a stream of H_2 . During the manufacture of bimetallic catalysts, Au and Rh were absorbed sequentially (first Au, then Rh). In the colloidal method, metal salts were oxidized with a strong reducing agent sodium borohydride ($NaBH_4$) in their aqueous solutions to obtain fine-grained particles. A stabilizing agent, polyvinyl alcohol (PVA), was added to an aqueous solution of a metal salt with a relative mass ratio ($mPVA / m(Au + M) = 1.2$). Then an excess amount of $NaBH_4$ was added in the case of solid mixing ($nNaBH_4 / n(Au + M) = 5$). After 1 hour, the remaining $NaBH_4$ residue was added to the support after complete removal, and also acidified with the addition of 10-2M HCl solution for sol-immobilization. Depending on the required experimental conditions, the pH was adjusted to 1.0 or 3.5. For the bimetallic catalyst in both different methods, the total weight of the metal was 3% (by weight) and 50:50 (by percentage).

2.3 Hydrogenation unit

The hydrogenation of benzene and toluene was carried out in a high-pressure kinetic unit capable of maintaining a constant temperature and pressure during the reaction. The autoclave part of the unit is equipped with an ultra-thermostat layer, has a turbulent mixer to prevent the formation of waves, and a tubular neck, which allows the sample to be obtained during the reaction.

2.4 Research methods

The catalysts were characterized by sequential methods of inductively coupled plasma-optical emission spectroscopy (ICP-OES), transmission electron microscopy (TEM) and parallel application of X-ray diffraction (XRD) methods.

3 Results and discussion

Two different methods have been used to absorb rhodium and gold from their salts. In the first method, rhodium and gold were absorbed sequentially, and in the second, a mixture of gold and rhodium salts was absorbed together. Table 1 shows the results of the ICP-OES analysis of the composition of the prepared catalysts.

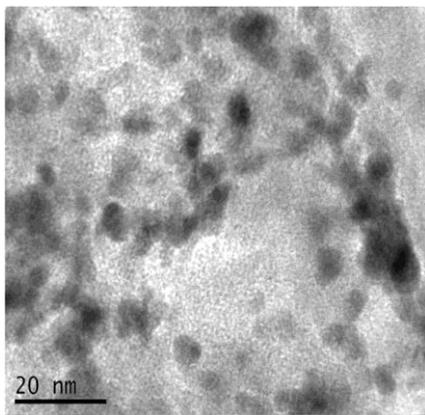
Table 1. Chemical composition of Au-Rh / TiO₂ (wt. %) catalyst

Catalysts	Method of preparation	Au	Rh	Cl
Au@Rh	Sequential absorption	2.1	0.73	0.31
Au+Rh	Parallel absorption	2.33	0.73	0.3
Au@Rh	Colloidal sequent	1.59	0.76	0.35
Au+Rh	Colloidal row	1.5	0.71	0.38

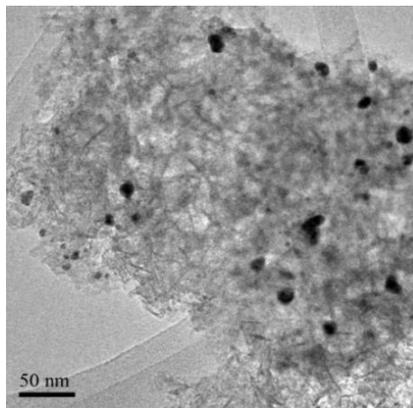
It can be seen from this table that the amount of absorbed gold in the sequential absorption method is higher than in the colloidal sequent method, where gold is 2.1 and 1.59; the rhodium content is vice versa, i.e., 0.73 and 0.76. In the parallel absorption method, the amount of gold and rhodium is also higher than in the colloidal method, i.e., 2.33 and 0.73 (gold 1.5 and 0.71). This indicates the not similar activity of catalysts.

In fig. 1 shows the TEM images of the Au-Rh / ASA catalyst, based on these data (Fig. 1-a, b), the size of the catalyst particles prepared by the colloidal method is 20 nm, the size of the particles formed by the absorption method is 50 nm.

TEM images (Fig.2-a, b) describe that the Au-Rh/TiO₂ catalyst is supported by rutile nanotubes. The sizes of metal particles in catalysts prepared by colloidal and absorption methods are 20 and 50 nm, respectively.



a. Colloidal method



b. Absorption method

Fig.1. TEM images of the Au-Rh/ASA catalyst

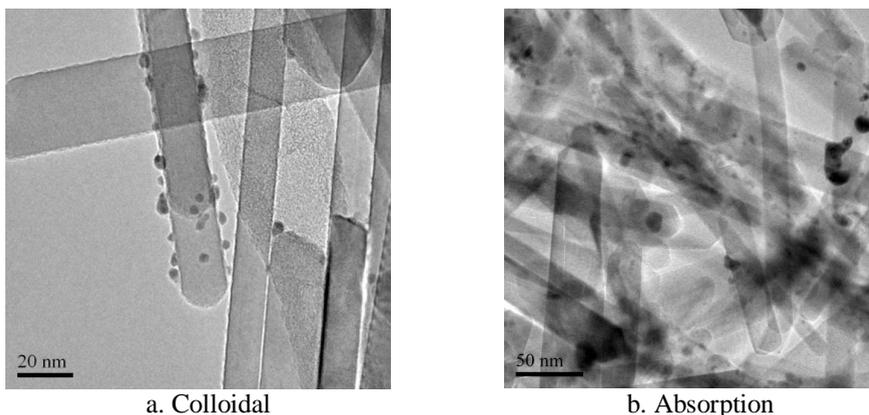
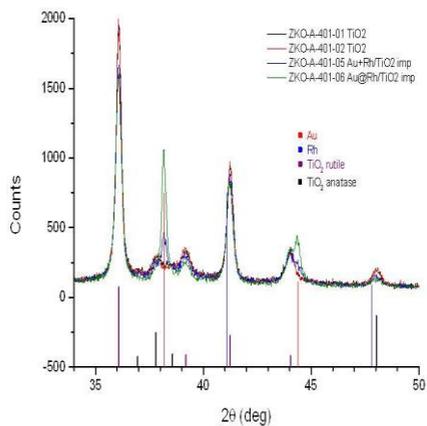


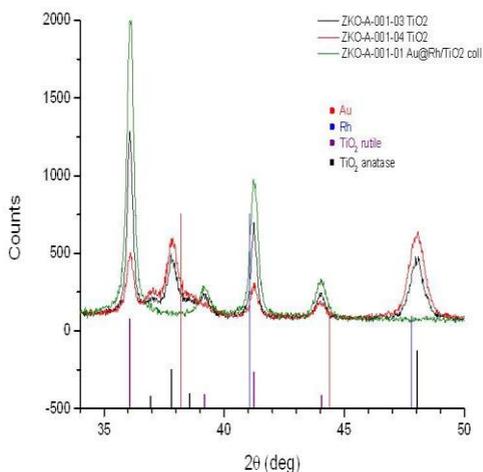
Fig. 2. TEM images of the Au-Rh/TiO₂ catalyst

XRD images of the Au-Rh/TiO₂ catalyst are shown in Fig.3. By analyzing XRD with high definition, the metallic phase of gold and rhodium can be seen separately, TiO₂ is observed as rutile with a small amount of anatase impurity.

Although the XRD spectra are the same, there may be differences in composition or



a. Absorption



b. Colloidal

Fig.3. XRD spectrum of the Au-Rh/TiO₂ catalyst

phases. In catalysts made by the impregnation method, phases of gold and rhodium can be observed; while in the colloidal method, these peaks deviate somewhat from pure metals, which can be explained by the presence of bimetallic particles of rhodium and gold as a solid solution and the presence of a methanome (intermetallic) state in it.

To prepare a catalyst for the selective hydrogenation of benzene in the presence of other aromatic compounds, experiments were developed on the individual hydrogenation of benzene and toluene with these catalysts, following the principle that if a catalyst can selectively hydrogenate benzene in the presence of toluene, then xelol, cumene can retain selectivity in the presence of other aromatic compounds.

Figure 4 shows the curves of benzene hydrogenation using a rhodium catalyst (curve-1) mounted on an amorphous aluminosilicate (ASA) carrier and a rhodium-gold catalyst (curve-2) mounted on the same carrier. The catalysts are prepared by impregnation. The shapes of the conversion curves are the same, the activity of individual rhodium is higher, i.e., it reaches 100% conversion in 220 minutes, and with the Au-Rh catalyst it reaches 100% conversion in 240 minutes. It can be seen from this that with the same preparation method, the active metal of the catalyst is rhodium, the gold compound does not play an effective role.

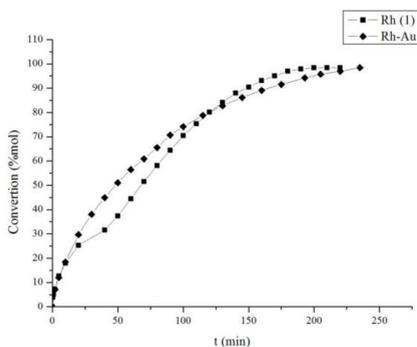


Fig.4. Curves of benzene hydrogenation in the presence of Rh/ASA (1) and Au-Rh/ASA (2) catalysts prepared by the absorption method in ethanol 4.0 MPA, 40°C

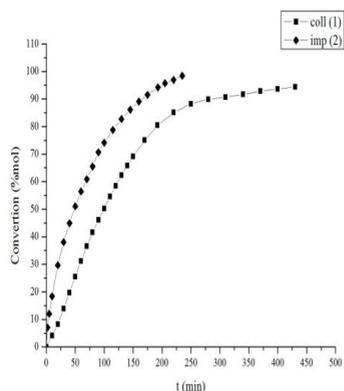


Fig.5. Curve of benzene hydrogenation in catalyst Au-Rh/ASA, 4.0 MPA and 80 oC, ethanol: 1-colloidal method; 2-absorption method.

The conversion curves of benzene hydrogenation with Au-Rh/ASA catalysts prepared by different methods are shown in Fig.5. It can be seen from the curves that they have the same shapes but exhibit different activity. While the complete conversion on the impregnated Rh-Au/ASA catalyst took 240 minutes, this colloidal catalyst took 430 minutes and only 95% conversion was achieved.

This can be explained by the state of the metal formed during the manufacture of the catalysts and the conditions for the formation of the active media of the catalysts. Firstly, when using the method of absorption, absorption of gold and rhodium ions into supports and its subsequent processing, they pass into the metallic state, and with the colloidal method, already formed metal particles (micelle nuclei) in a colloidal solution of rhodium and gold are planted into the supports. Secondly, when an aqueous solution of a metal salt is absorbed by amorphous silicon-aluminum, macro, micro and mesoporous deeper metal ions are formed. During the adsorption of the reduced metal from the colloidal solution, accumulations of metals are formed on the surface of the support. Thus, monodisperse metal clusters are obtained, but the mutual influence on the surfaces is limited due to the formation of coordinate bonds. The mutual influence arising from the absorption and pretreatment of the embedded catalysts leads to the formation of various phases, solid solutions, and spinel. During the oxidation of catalysts, all this affects the formation of a metal cluster and the state of charge of the active metal. As a result, it causes unequal activity and selectivity of the catalysts.

The hydrogenation conversion curves in Rh-Au/ASA Rh-Au/TiO₂ catalysts prepared by colloidal and absorption methods of benzene are shown in Fig.6 - 7.

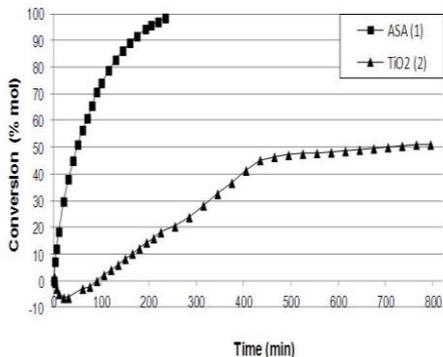


Fig.6. hydrogenation of benzene in ethanol at 4 MPa and 80 °C on the catalyst Au-Rh/ASA (1) Au-Rh / TiO₂ (2) prepared by the absorption method

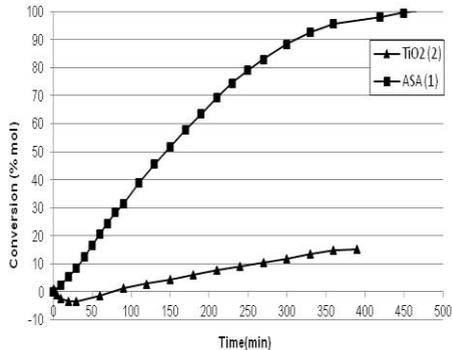


Fig.7. Curve of benzene hydrogenation on catalysts 1-Au-Rh/ASA, Au-Rh/TiO₂, 4 MPa and 80 °C in ethanol prepared by colloidal method

The conversion curve for similar catalysts prepared by the absorption method changes instantly (Fig.6). 100% conversion of benzene via Rh-Au / ASA is carried out within 240 minutes. In the Rh-Au/TiO₂ catalyst, the hydrogenation of benzene is very slow, and the conversion curve is divided into three parts. In the first part, the reverse change in the volume of hydrogen, i.e., the negative velocity gives one hundred. It can be assumed that the reason for this is the movement of hydrogen from the liquid phase into the reaction medium and the beginning of its absorption. After 400 minutes of reaction, you can see that the curve has shown shape. Then the line is interrupted, and again the linear form continues up to 800 minutes. At this time, the conversion of benzene was 50%.

As for the catalysts prepared by the colloidal method (Fig. 7), the conversion of benzene through Rh-Au/ASA approached 95% within 425 min, but barely reached 15% within 420 min in the Rh-Au/TiO₂ catalyst. It can be concluded that these catalysts are unsuitable for the quantitative hydrogenation of benzene.

Comparing the results in the figures (Fig.6,7), we can conclude that the most effective carrier of the active metal is amorphous silicon-aluminum (ASA) of the “Siral” trademark.

The conversion curves of toluene hydrogenation in catalysts prepared by absorption and colloidal methods are shown in Fig.8.

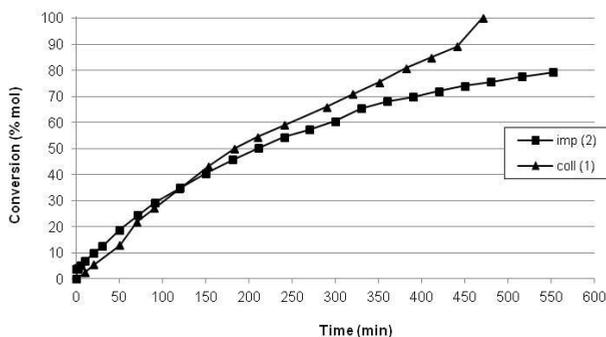


Fig.8. Toluene hydrogenation curve in ethanol on the Au-Rh/ASA catalyst at a temperature of 4.0 MPa and 80°C: 1 - prepared by the colloidal method; 2-prepared by absorption.

Comparing these curves with the curves of benzene hydrogenation (Fig.5), we note that the hydrogenation of toluene on a similar catalyst showed a completely different result. In fig. 8, when 100% conversion of toluene was achieved (curve 1) with the catalyst prepared by the colloidal method, only on the catalyst prepared by the impregnation method, in 550 minutes it was possible to convert toluene by 77% (in Fig. 5, to the complete conversion of benzene on the catalyst Rh-Au/ASA prepared by the impregnation method took 240 minutes), full conversion of toluene was not achieved.

Based on this, we can conclude that Au-Rh/ASA prepared by the absorption method is an effective catalyst for the selective hydrogenation of benzene in the presence of other aromatic compounds.

4 Conclusion

In this work, mono- and bimetallic catalysts Rh and Au-Rh were prepared by two different methods, and their function was tested in hydrogenation reactions. The influence of the preparation method and the nature of the active metal with the support was expressed in the activity and selectivity of these catalysts in the hydrogenation reaction. The hydrogenation activity of benzene and toluene depends primarily on the nature of the active metal. The addition of the second component of gold could not increase the hydrogenation activity. The carrier also plays a role in the activity of the catalyst. It can be concluded that the activity of rhodium and rhodium-gold catalysts embedded in aluminosilicate is slightly higher than that of similar catalysts embedded in titanium oxide, which is explained by the specific surface area. The catalysts prepared by the moisture absorption method are active in the hydrogenation of benzene from those prepared by the colloidal method. Analysis by ICP, TEM and XPS methods showed that bimetallic rhodium-gold particles have a different structure than monometallic particles. These parameters have shown their influence on the selectivity of catalysts with unequal activity in the hydrogenation of benzene and toluene.

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