Tungsten(VI) Oxide Supported Rhodium(0) Nanoparticles Used as Catalyst in Hydrogenation of Benzene at Room Temperature

Oda Sıcaklığında Benzen Hidrojenlenmesinde Katalizör Olarak Kullanılan Tungsten(VI) Oksit Destekli Rodyum(0) Nanoparçacıkları

Research Article

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ABSTRACT

Rhodium(III) ions were first impregnated on the surface of tungsten(VI) oxide (WO_3) in aqueous solution and reduced with aqueous $NaBH_4$ to form rhodium(0) nanoparticles (Rh NPs) on the surface of WO_3. After the isolation of the Rh NPs/WO_3 catalyst by centrifugation, it was characterized by advanced analytical techniques. The results reveal the successful formation of Rh NPs on the surface of WO_3. Rh NPs/WO_3 catalyst with a turnover frequency value of 131 $^{h-1}$ was found to be very active in hydrogenation of neat benzene at 25.0±0.1ºC.

Key Words
Tungsten(VI) oxide, rhodium nanoparticles, benzene, hydrogenation.

ÖZ

Rodyum(III) iyonları ilk önce sulu çözelti içinde tungsten(VI) oksit (WO_3) üzerine tutturulmuş ve WO_3 yüzeyi üzerinde rodyum(0) nanoparçacıkları (Rh NPs) oluşturmak için sulu $NaBH_4$ ile indirgenmiştir. Rh NPs/WO_3 katalizörü santrifüjleme ile ayrıldıktan sonra gelişmiş analitik tekniklerle tanımlanmıştır. Sonuçlar Rh NPs'nin başarılı bir şekilde WO_3 yüzeyinde oluştuğunu göstermektedir. Rh NPs/WO_3 katalizörünün 131 $^{h-1}$ çevrim frekansı değeri ile 25.0±0.1ºC' de solventsiz benzen hidrojenlenmesinde çok aktif olduğu bulunmuştur

Anahtar Kelimeler
Tungsten(VI) oksit, rodyum nanoparçacıkları, benzen, hidrojenlenme.

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INTRODUCTION

Hydrogenation of benzene to cyclohexane has attracted great attention due to the use of cyclohexane for the production of nylon 6 and nylon 6.6 [1,2]. On the other hand, benzene is a toxic component of gasoline [3], which makes the hydrogenation of benzene in gasoline crucial. Therefore, there is a need for the development of highly active catalysts for the hydrogenation of benzene. Ruthenium [4], rhodium [1,3,5], platinum [6], iridium [7] nanoparticles are found to be effective catalysts for this industrially important reaction.

Since the metal nanoparticles tend to aggregate, various supporting materials such as carbon nanotube, silica, alumina and ceria are used to improve the catalytic activity and stability of these nanoparticles [8]. Tungsten(VI) oxides (WO_3) are also considered as a suitable supporting material for metal nanoparticles. Indeed, ruthenium, palladium, rhodium and platinum nanoparticles were successfully formed on WO_3 based supporting materials [9,10]. Since tungsten(VI) oxides are simply prepared and provide high chemical stability [11] they are widely used in many catalytic reactions such as oxidative desulfurization [12], dehydration of 2-Butanol [13], pentane isomerization [14], acetalization [15]. Recently, the promoting effect of WO_3 on noble NPs used as catalysts in ethanol [16,17], methanol [18] and CO [19] oxidations have been confirmed. On the other hand, tungsten(VI) oxides are considered to be used in hydrogenation reactions because the dissociation of H_2 molecules to $H^{\delta+}$ ionic species could easily be stabilized on WO_3 structure [17].

Herein, the preparation, characterization and catalytic use of rhodium(0) nanoparticles (Rh NPs) supported on WO_3 were reported. Rhodium(III) ions impregnated on the surface of tungsten(VI) oxide were reduced by $NaBH_4$ forming the Rh NPs/WO_3 which was used as catalyst in hydrogenation of neat benzene. Rh NPs/WO_3 was isolated from the reaction solution by centrifugation and characterized by ICP-OES, XRD, TEM, TEM-EDX and BET techniques. Rh NPs were successfully prepared on the surface of WO_3.

MATERIALS and METHODS

Materials

Rhodium(III) chloride trihydrate ($RhCl_3.3H_2O$), tungsten(VI), (WO_3, particle size ≈ 100 nm), sodium borohydride ($NaBH_4$, 98%) and benzene (99.9 %) were purchased from Aldrich.

Preparation of Rh NPs supported on WO_3

In a 250 mL round bottom flask 400 mg of WO_3 was added to a solution of $RhCl_3.3H_2O$ (5.2 mg) in 100 mL H_2O. This slurry was stirred at room temperature for 24 h, then $NaBH_4$ (6 mM in 10 mL H_2O) solution was added dropwise. After 1 h stirring Rh NPs/WO_3 were formed and the sample was isolated by centrifugation (at 8000 rpm) and washed with 50 mL of distilled water and the remnant was dried under vacuum at 60 °C for 12 h. Rhodium content, determined by ICP-OES, was found as 0.39% wt. for Rh NPs/WO_3. The sample was also characterized by XRD, TEM, TEM-EDX and BET techniques as described in a recent report [20].

Hydrogenation Apparatus

Hydrogenation reactions were carried out using a Fischer-Porter pressure bottle which are modified with Swagelock TFE-sealed quick connects. The reactor was connected to a H_2 gas tank. The gas pressure in the reactor was measured with a pressure transducer (Omega PX-302) coupled with a digital transmitter (Omega D1131) and RS-232 module. The data were transferred to a computer and the change of H_2 pressure in the reactor was followed on Lab View 8.0 program.

Hydrogenation of Neat Benzene Using Rh NPs Supported on WO_3

Hydrogenation of neat benzene was performed by following the procedure described elsewhere [21]. Before the hydrogenation experiments, the catalyst and the substrate were transferred into the reactor in the oxygen free dry box. In a typical experiment, 80 mg Rh NPs/WO_3 (0.39% wt. Rh) catalyst, 0.6 mL of neat benzene and magnetic stir bar were transferred into a test tube in the Fischer-Porter pressure bottle. After sealing the Fischer-Porter bottle in the oxygen free drybox, it was connected to the oxygen free hydrogenation line via its Swagelock connects. The temperature of the reaction was controlled by a water bath (25.0±0.1 °C). The hydrogenation reaction was followed on the computer using Lab View 8.0 program. The conversion of neat benzene was monitored by the hydrogen pressure loss in the reactor. The complete conversion of benzene was also confirmed by ^{1}H-NMR. It is noteworthy that WO_3 nanopowders without rhodium nanoparticles are found to be catalytically inactive in the hydrogenation of benzene at 25.0±0.1ºC.

Reusability of Rh NPs/WO_3 in Hydrogenation of Neat Benzene

After the complete hydrogenation of benzene started with 0.6 mL of neat benzene and 80 mg of Rh NPs/WO_3 (0.39% wt. Rh) at 25.0±0.1ºC, the Fischer-Porter bottle was taken into the dry box and kept there until the catalyst settle down at the bottom of the reactor. The supernatant was separated from the catalyst via a pipette and then 0.6 mL of neat benzene was transferred again into the reactor. Second run of the hydrogenation of benzene at 25.0±0.1ºC was started again as described above.

RESULTS and DISCUSSION

Rhodium(0) nanoparticles supported on WO_3 were prepared by the impregnation of Rh^{3+} ions on the surface of WO_3, followed by their reduction with aqueous solution of $NaBH_4$. Rh NPs/WO_3 was isolated from the reaction solution by centrifugation and characterized by ICP-OES, XRD, BET, TEM and TEM-EDX.

The XRD patterns of WO_3 and Rh NPs/WO_3 show that there is no change in the position of the characteristic diffraction peaks of tungsten(VI) oxide after Rh loading (Figure 1). This observation indicates that WO_3 remains intact after the impregnation and reduction of Rh^{3+} ions on the surface of tungsten(VI) oxide powder. However, there exists no XRD peaks attributed to the rhodium NPs in Fig.1 due to the low Rh loading on WO_3 powder. Indeed, the rhodium loading determined by ICP-OES was found as 0.39% wt. which is below than the detection limit of XRD.

The BET nitrogen adsorption analysis (Figure 2) gave the surface area of WO_3 and Rh NPs/WO_3 (0.39% wt. Rh) as 9.7 m^2/g and 11.2 m^2/g, respectively. The larger surface area of Rh NPs/WO_3 may be attributed to the presence of Rh NPs on the surface of WO_3 powder. The presence of Rh NPs on WO_3 was also investigated by TEM and TEM-EDX analyses. Indeed, the TEM image of Rh NPs/WO_3 (0.39% wt. Rh) given in Fig.3a shows that Rh NPs were successfully formed on the surface of WO_3. TEM-EDX (Figure 3b) provides the confirmation of the existence of Rh NPs on WO_3.

The catalytic activity of Rh NPs/WO_3 was tested in hydrogenation of neat benzene under ~3 bar pressure of H_2 gas at 25.0±0.1ºC. The hydrogenation of solvent free benzene was monitored by hydrogen uptake which was converted to the loss of benzene concentration (Figure 4) using stoichiometric calculations. The total conversion of benzene to cyclohexane was achieved after 45 h at 25.0±0.1ºC.

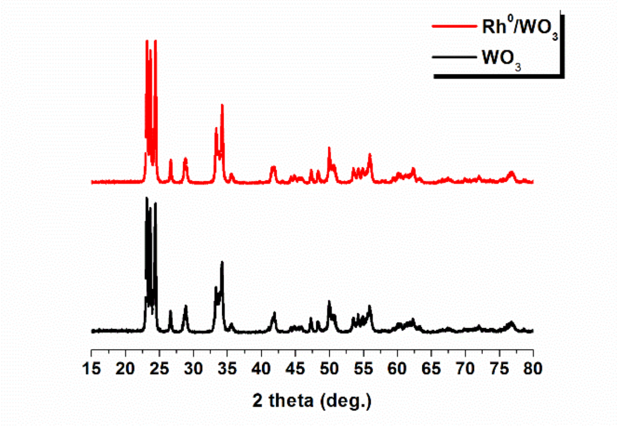

Figure 1. XRD patterns of WO_3 and Rh NPs/WO_3 (0.39% wt. Rh).

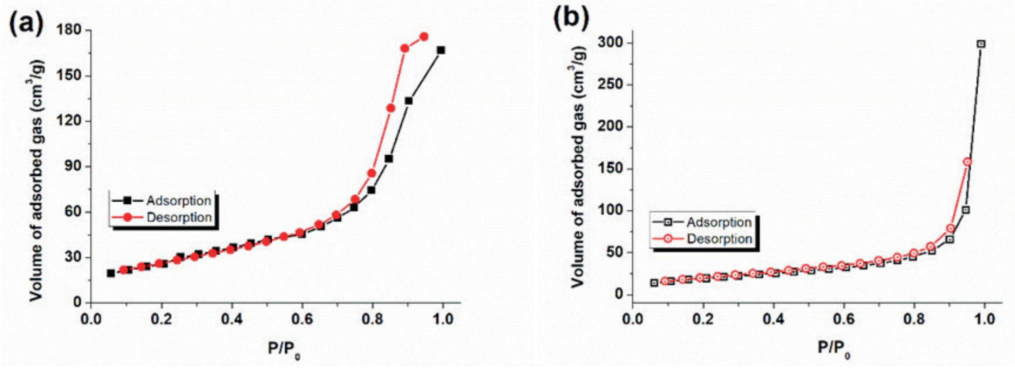

Figure 2. The nitrogen adsorption-desorption isotherms of (a) WO_3 and (b) Rh NPs/ WO_3 (0.39% wt. Rh).

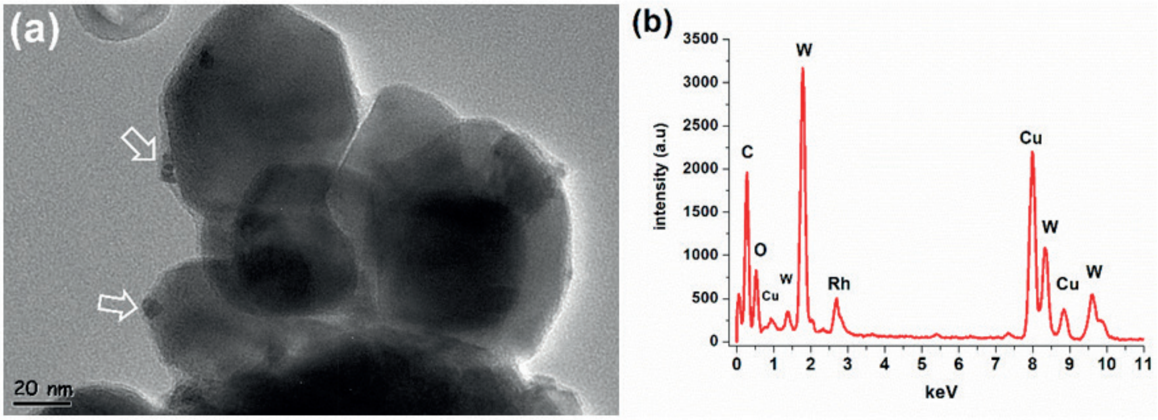

Figure 3. (a) TEM image and (b) TEM-EDX of Rh NPs/WO_3 (0.39% wt. Rh) (White arrows in figure a represent the Rh NPs).

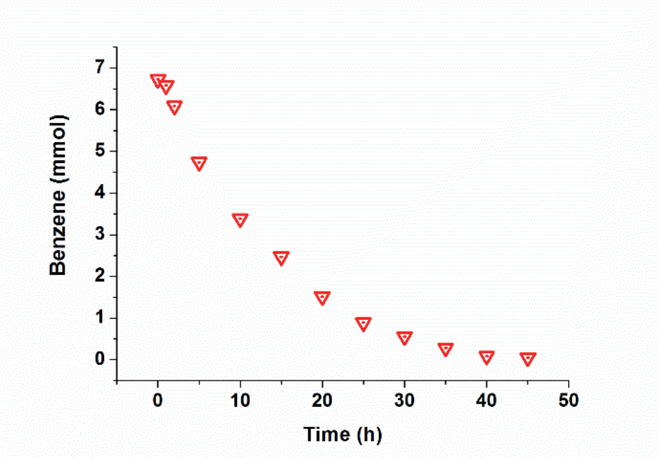

Figure 4. The plot of benzene consumption versus time using 80 mg of Rh NPs/WO_3 (0.39% wt. Rh) catalyst and 0.6 mL of neat benzene under 3 bar H_2 pressure at 25.0±0.1°C.

Rh NPs/WO_3 catalyst provided a TOF value of 131 h^{-1} at 25.0±0.1°C during 5 h in this reaction. Indeed, Rh NPs/WO_3 was found to be highly active catalyst as compared to most of the reported catalyst given in Table 1 such as Rh/fluorous hybrid silica [31], Rh/CNT [26], Rh/BMI.PF_6 [33], Rh/SiO_2 [27], $[Rh(COD)Cl]_2$ [32], PtO_2 [43] and Pt NPs [43]. It is noteworthy that the reaction conditions such as temperature, pressure and solvent show variations for the reported catalysts, which makes the comparison of the catalytic activities of these catalysts difficult. However, the catalytic activity of the Rh NPs/WO_3 catalyst under low pressure, low temperature in solvent free medium makes Rh NPs/WO_3 advantageous over most of the reported catalysts.

Table 1. Catalytic performance of various catalysts for benzene hydrogenation. Turnover frequency (TOF) values in references were described as (mol cyclohexane) × (mol metal)$^{-1}$× h^{-1}

Catalyst	Temperature (°C)	Pressure of H_2 (bar)	TOF (h^{-1})	Solvent	Ref.
2%Rh/NZ-CP	60	10	25765.5	neat benzene	1
Rh/HAp	25	3	1770	neat benzene	2
Rh/AlO(OH)	75	4	1700	neat benzene	3
Rh/MWNTs	20	10	1038	neat benzene	4
Pd-Rh/CNT	20	10	592.6	neat benzene	5
Rh/TiO_2	25	1	476	water/benzene	6
Rh NPs/CDG	50	4	310	neat benzene	7
Rh/PVP	30	7	250	water/benzene	8
Rh NPs/CDG	25	4	228	neat benzene	28
Rh/ Fe_3O_4/SiO_2-NH_2	25	6	196	neat benzene	9
Rh NPs/WO_3	25	3	131	neat benzene	This study
Rh/CNT	20	10	118.1	neat benzene	26
Rh/SiO_2	25	1	113	water/benzene	27
Rh (2 mol%) / fluorous hybrid silica	60	1	111	2-propanol	10
Rh(COD)Cl]$_2$ (rhodium nanoparticles)	25	1	16	neat benzene	11
Rh/BMI.PF_6	75	4	11	BMI.PF_6/benzene	12
$Ru_{0.04}Ni_{0.96}$/C(30)	60	53	13522.4	neat benzene	13
Ru/Mesoporous Carbon	110	40	35112	neat benzene	14
Ru@graphite oxide	100	10	34331	neat benzene	15
Ru-B/MIL-53(AlCr)	30	10	23040	ethanol	16
Ru/CNTs	80	40	6983	neat benzene	17
Ru/porous carbon	110	40	5544	neat benzene	18
0.27%Ru/Zeolite	25	2.9	5430	neat benzene	4
Ru/SiO_2	100	20	5000	neat benzene	19
Ru-MOF_Mt	160	60	3478	neat benzene	20
Ru/SBA-15	110	40	974	neat benzene	35
Ru (2 mol %) / fluorous hybrid silica	60	1	29	2-propanol	31
Ir/Graphite oxide	100	10	10000	neat benzene	21
Ir/Zeolite	25	3	3190	neat benzene	21
Pt(0) NPs	75	4	28	neat benzene	22
PtO_2	75	4	2	neat benzene	43

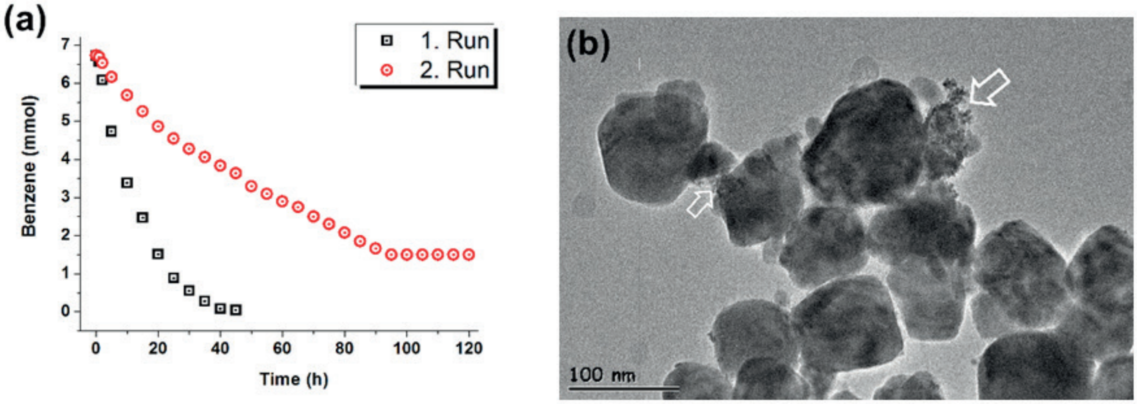

Figure 5. (a) Graph of benzene consumption versus time for the first and second use of Rh NPs/WO_3 (0.39% wt. Rh) catalyst in hydrogenation of benzene at 25.0±0.1°C, (b) TEM image of Rh NPs/WO_3 catalyst (0.39% wt. Rh) taken after the second use (White arrows in figure b represent the aggregation of Rh NPs).

The reusability of Rh NPs/WO_3 catalyst was also investigated in hydrogenation of neat benzene under 3 bar H_2 pressure at 25.0±0.1°C. The reusability test reveals that Rh NPs/WO_3 catalyst loses its activity during the second use (Figure 5a). It provides no activity after 90 h. After the second use, Rh NPs/WO_3 catalyst was isolated from the reaction solution by removing supernatant via a pipette and dried under vacuum at 60°C for 12 h. The TEM image of Rh NPs/WO_3 catalyst taken after the second use shows the agglomeration of Rh NPs (Figure 5b), which could be the main reason of the catalytic activity loss.

CONCLUSIONS

Rhodium(0) nanoparticles supported on WO_3 was successfully prepared and characterized by using advanced analytical techniques such as ICP-OES, BET, XRD, TEM and TEM-EDX. Rh NPs/WO_3 catalyst with a TOF value of 131 h^{-1} was found to be highly active in solventless hydrogenation of benzene to cyclohexane at 25.0±0.1°C. However, Rh NPs/WO_3 catalyst provided poor reusability due to the aggregation of rhodium nanoparticles on the surface of WO_3 after the first catalytic use. The facile and environmentally friendly preparation of the catalyst followed in this work can be extended to prepare other tungsten(VI) oxide supported noble or non-noble metal catalysts such as ruthenium, palladium, cobalt and nickel.

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