

Synthesis and Characterization of Carbon Nanotube Supported Pt-Au Catalyst and Its Microwave Assisted N-Hexane Decomposition Measurements

Mohammed Ali Salih¹, Aykut Çağlar¹, Arif Kivrak², Hilal Kivrak^{1,*}

¹Chemical Engineering Department, Van Yüzüncü Yıl University, Van, Turkey

²Department of Chemistry, Van Yüzüncü Yıl University, Van, Turkey

*Corresponding author: hilalkivrak@gmail.com, hilalkivrak@yyu.edu.tr

Abstract Herein, CNT supported Pt and Pt-Au catalysts were carefully synthesized via NaBH₄ reduction method. Pt-Au catalysts were obtained at varying ratios. For all of these CNT supported Pt and Pt-Au catalysts, BET, EDX, and XRD measurements were performed. The atomic ratio of the catalyst was obtained by EDX analysis. Surface area was defined via BET and crystal structure was examined by XRD. For microwave assisted n-hexane reforming measurements, microwave reactor was used to investigate the decomposition of n-hexane on CNT supported bimetallic Pt-Au catalysts. After applying microwave heating during the reaction time, the volume change is defined and read out. As a result, it was observed that Pt-Au catalysts prepared at 50:50 atomic ratio gives the best catalytic activity.

Keywords: Pt, Pt-Au, CNT, nanocatalyst, n-hexane, decomposition, microwave assisted heating

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1. Introduction

Energy is important and permanent needs for human kind. Fossil fuels such as oil, coal and natural gas are the currently used fuels. Nevertheless, it is predicted that fossil fuel will exhaust in the near future. According to the Hubbert theory, the global production of fossil fuels will start to decrease by 2020 [1]. Thus, the researchers are intensively studying on the alternative energy sources [2-7]. In that context, heterogeneous catalysis is also crucial for these studies to provide a promising means to develop alternative energy technologies. In this regard, catalysts having high activity and high selectivity should be produced [8].

Gasoline is a mixture of hydrocarbons. It could be used as a fuel in internal combustion engines (ICEs). Due to its high extent consumption in automobile industry, the request for the gasoline is increasing globally [9,10]. The catalytic reforming is an important process. During the catalytic reforming of n-hexane, naphtha was converted into high-octane reformates [11]. Hydrocarbons or naphtha have low octane number. Hence, it is not suitable to use them directly for direct gasoline blending. Therefore, catalytic reforming of naphtha and isomerization of light alkanes are required to enhance the gasoline quality (>70). High octane numbers relate to good engine performance [12].

Heterogeneous catalysts consisting of metal nanoparticles onto supports could be synthesized via various techniques.

Furthermore, their catalytic activity could be investigated in a number of catalytic chemical reactions. One could note that activity could be enhanced greatly by varying the size, shape and composition of nanoparticle [13]. For instance, it was reported that when pure mesoporous silica (MCF-17) was modified with Aluminum, Lewis acid sites were created. This material is not active for the n-hexane catalytic reforming. When it is modified with colloidal synthesized platinum nanoparticles, the catalyst showed enhanced activity [8,14,15]. Ni and Pt-Ni were also used to increase the activity of catalytic reforming [12]. It was reported that the bimetallic catalysts presented a higher activity in the isomerization of n-hexane compared to the monometallic ones.

N-hexane decomposition is an important parameter for the n-hexane catalytic reforming process. At present, n-hexane decomposition was examined on CNT supported Pt and Pt-Au bimetallic catalysts under microwave irradiation. In our previous, microwave irradiation was also used for different applications [16,17]. CNT supported Pt and Pt-Au catalysts were prepared by NaBH₄ reduction method, characterized via BET, EDX, and XRD.

2. Materials and Methods

2.1. Catalyst Preparation

In this research, the synthesis weight 0.1 g of Carbon Nano Tube (CNT) support dissolved in 40 ml water and

stirrer for 10 min. Then, $\text{H}_2\text{Cl}_6\text{Pt}_6 \cdot x\text{H}_2\text{O}$ precursor was added to the catalyst solution for absorbent CNT to Pt stay in ultrasonic bath about 20 min. Following this, the different amount of NaBH_4 was added to the solution for reduction after 20 min in ultrasonic. As a result, the obtained precipitate was filtrated, washed with by-distilled water and dried at oven vacuum 75°C . By this method, CNT supported Pt catalysts was obtained. The synthesis details of the CNT supported Pt catalysts were given Table 3.1. For the synthesis of CNT supported Pt-Au catalysts, 0.1 g of CNT support was used and dissolved in the water. Then, this mixture was ultrasonicated and stirred for 10 min and $\text{H}_2\text{Cl}_6\text{Pt}_6 \cdot x\text{H}_2\text{O}$ precursor was dissolved in the same kind of solvent for absorbent CNT to Pt. These two solution were mixed, ultrasonicated and stirred for 20 min. Then NaBH_4 was added to reduce this solution and ultrasonicated for reduction after 20 min in ultrasonic bath. Following this, AuCl was added to this solution and further reduction was performed. A precipitate was obtained, filtrated, washed with by-distilled water and dried under 75°C an oven vacuum. As a result, Pt-Au catalysts was obtained at varying ratios. The synthesis details of the CNT supported Pt-Au catalysts were given Table 1.

Table 1. Details of the preparation method on CNT supported Pt and Pt-Au catalysts prepared by NaBH_4 reduction method

No	Catalyst	%Pt	Metal ratio (Pt: Au)	Pt: NaBH_4 mol ratio
1	Pt/CNT	10	100:0	100
2	Pt-Au/CNT	10	90:10	100
3	Pt-Au/CNT	10	80:20	100
4	Pt-Au/CNT	10	70:30	100
5	Pt-Au/CNT	10	60:40	100
6	Pt-Au/CNT	10	50:50	100
7	Pt-Au/CNT	10	40:60	100
8	Pt-Au/CNT	10	30:70	100
9	Pt-Au/CNT	10	20:80	100
10	Pt-Au/CNT	10	10:90	100

2.2. Catalyst Characterization

The atomic ratio of the CNT supported Pt and Pt-Au catalysts was obtained by EDX analysis using a scanning electron microscope Phillips XL30 with a 20 keV electron beam. X-ray diffraction (XRD) analyses were performed using a Rigaku diffractometer model Miniflex II using $\text{Cu K}\alpha$ radiation source. The diffractograms were recorded from $2\theta = 50^\circ$ to 85° with a step size of 0.05° and a scan time of 2 s per step. All the catalysts and the characterization methods used for these catalysts were given in Table 2.

2.3. N-Hexane Decomposition Measurements

In this study, a Microwave Anton Paar reactor was used to investigate the decomposition of n-hexane on CNT bimetallic catalysts. 0.05 g catalyst was inserted in 20 ml reactor tube. Furthermore, 10 ml n-hexane was added in to the reactor tube. Then, this mixture was heated to 150°C and its temperature was kept constant at this temperature for 30 min. At the end of the 30 min, the tube was cooled and removed from the reactor. The volume change is defined and read out.

Table 2. Details of the characterization methods on CNT supported Pt and Pt-Au catalysts

No	Catalyst	Pt: Au metal ratio	Characterization
1	Pt/CNT	100:0	BET, EDX
2	Pt-Au/CNT	90:10	BET, EDX
3	Pt-Au/CNT	80:20	BET, EDX
4	Pt-Au/CNT	70:30	BET, EDX
5	Pt-Au/CNT	60:40	BET, EDX
6	Pt-Au/CNT	50:50	BET, EDX, XRD
7	Pt-Au/CNT	40:60	BET, EDX
8	Pt-Au/CNT	30:70	BET, EDX
9	Pt-Au/CNT	20:80	BET, EDX
10	Pt-Au/CNT	10:90	BET, EDX

3. Results and Discussion

Characterization results of these catalysts were given on Table 3. The elemental compositions of these catalysts investigated using EDX spectroscopy were given in Table 3. Considering all CNT supported Pt and Pt-Au catalysts, the nominal weight percent of Pt is 10% and the EDX results show that weight percentage of Pt is around 10% similar to the nominal values. Furthermore, BET surface areas were also given on Table 3. According to these values, BET surface areas decrease by increasing metal loading.

Table 3. Characterization results on CNT supported Pt and Pt-Au catalysts

No	Catalyst	Pt: Au metal ratio	BET surface area (m^2/g)	EDX % Pt
1	Pt/CNT	100:0	303	9.25
2	Pt-Au/CNT	90:10	298	9.86
3	Pt-Au/CNT	80:20	299	10.27
4	Pt-Au/CNT	70:30	230	10.13
5	Pt-Au/CNT	60:40	225	11.38
6	Pt-Au/CNT	50:50	223	9.12
7	Pt-Au/CNT	40:60	228	10.83
8	Pt-Au/CNT	30:70	150	11.50
9	Pt-Au/CNT	20:80	186	10.12
10	Pt-Au/CNT	10:90	192	8.98

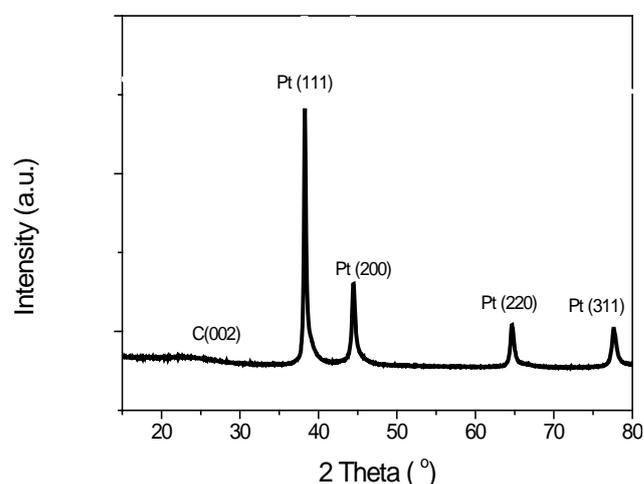


Figure 1. XRD patterns of CNT supported Pt-Au (50:50) catalysts

X-ray diffractograms of Pt-Au (50:50) catalyst were given in Figure 1. XRD pattern of this catalyst exhibited a broad peak at about $2\theta = 25^\circ$ associated to the carbon support material. Furthermore, (111), (200), (220) of face centered cubic (fcc) structure of Pt and Pt alloys were presented at XRD pattern.

N hexane decomposition measurements were performed on Pt and Pt-Au catalysts. The volume change was given for every catalyst on the Table 4. It was observed that Pt-Au catalysts at prepared at 50:50 atomic ratio gives the best catalytic activity.

Table 4. N hexane decomposition results on CNT supported Pt and Pt-Au catalysts

No	Catalyst	Pt:Au metal ratio	N Hexane decomposition (ml)
1	Pt/CNT	100:0	2.5
2	Pt-Au/CNT	90:10	2.8
3	Pt-Au/CNT	80:20	2.6
4	Pt-Au/CNT	70:30	2.6
5	Pt-Au/CNT	60:40	2.9
6	Pt-Au/CNT	50:50	3.2
7	Pt-Au/CNT	40:60	3.1
8	Pt-Au/CNT	30:70	2.9
9	Pt-Au/CNT	20:80	2.6
10	Pt-Au/CNT	10:90	2.4

4. Conclusions

In the light of the experimental results, the following conclusion could be drawn:

- CNT supported Pt and Pt-Au catalysts at different atomic ratios were prepared successfully via NaHB_4 reduction method
- Pt and Pt-Au catalysts were characterized by BET, EDX, and XRD.
- EDX measurements revealed that catalysts were prepared at the desired Pt content.
- BET measurements indicated that Au addition leads to decrease the surface area of bimetallic catalysts.
- XRD pattern of Pt-Au catalyst indicate Pt fcc peaks belonging the Pt-Au structure were observed.
- Best catalytic activity for the n-hexane decomposition reaction was obtained for Pt-Au (50:50)/CNT catalyst.

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