

Preparation and characterization of Pt/ γ -Al₂O₃ nanocatalyst fabricated by green colloid – Microwave assisted method and its application in hydrogenation of the phenol

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Abstract

There is interest in minimizing or eliminating the dependency on the use of non-recyclable, expensive and homogeneous catalysts. This can be achieved by replacing them with more durable nanoheterogeneous catalysts, which offer high catalytic performance and easy recoverability. Designing highly active and stable heterogeneous catalysts for the selective hydrogenation of phenol is still a challenge. In this study, a novel type of Pt/ γ -Al₂O₃ nanocatalyst is elaborately designed and prepared using a clean and green colloid-Microwave assisted synthetic method. The obtained nanocatalyst was characterized using TEM and BET analysis. The results of TEM and chemisorption characterization results confirm that the confined nanocatalyst possesses stronger Pt-Al₂O₃ interaction, with an excellent monodispersity of Pt nanoparticle on the surface of solid support. The prepared nanocatalyst exhibited enhanced catalytic activity and stability for the hydrogenation of phenol to cyclohexanone compared to the unsupported nanocatalyst. Cyclohexanone is widely used in pesticides, coatings, dyes, lubricants, and other industries due to its low volatility and high solubility. At 1 MPa, 3 hours, and 80 °C, a selectivity of 92.6 % and complete conversion of phenol to cyclohexanone were achieved.

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Keywords: Pt/ γ -Al₂O₃ nanocatalyst, Colloid, Microwave, Hydrogenation, Phenol

1. Introduction

To reduce the dependency on the use of non-recyclable, expensive and homogeneous catalysts, synthetic chemists based on the nanotechnology are searching for more durable nanoheterogeneous catalysts [1]. So, to meet the rising demand for fine chemicals nanoheterogeneous catalysts due to their high catalytic performance and easy recoverability [2]. Nanocatalysts have proved beneficial for application in heterogeneous catalysis compared to the bulk catalyst and offer improved physicochemical properties such as high active sites, surface-to-volume ratio, surface energy, and better composition-based selectivity towards particular reaction pathways [3]. However, the nanocatalysts synthesis on high surface area solid supports (metals/metal oxides/hybrids) is gaining attention considering their durability and discrete nano-dispersibility [4]. Transition metals (Pd, Pt, Au and Ag), have been considered ideal for heterogeneous nanocatalysts in a variety of organic and biorthogonal synthesis due to they can easily donate and accept electrons from molecules [5]. As a main drawback, the obtained nanoparticles are prone to aggregation, thereby reducing their potential for long-term preservation and application [6]. To overcome the aggregation of nanoparticles, an alternative way based on the implanting or anchoring of nanoparticles as active sites on inert low-density solid supports has been proposed for the deterioration of catalytic activity [7]. It is clear that the solid supports limit the leaching of metal ions and help to maintain the shape, size, and morphology of the metal nanoparticles which are favorable for achieving enhanced catalytic activity and durable performance [8]. Cyclohexanone is widely used in coatings, pesticides, dyes, lubricants, and other industries due to its high solubility and low volatility, but designing highly active and stable heterogeneous catalysts for selective hydrogenation of phenol to cyclohexanone is a still challenge [9]. Wang and Yang prepared Pt nanoparticles confined in TiO₂ nanotubes with enhanced catalytic performance for phenol hydrogenation by atomic layer deposition. They reported the high activity and good stability under the mild reaction conditions of this confined catalyst that may have application prospect in industrialization [10].

In this work, a unique combination of green colloid system and Microwave (MW)-assisted method, was studied for the first time for the synthesis of solid-supported Pt/ γ -Al₂O₃ nanocatalyst as fast and clean approach and devoted characterization as well as application in catalyzing of phenol to cyclohexanone as hydrogenation reaction. This work can open a research window for applications of nanoheterogeneous catalysts in multiphase reactions. The nanoheterogeneous structure provided the advantages of high stability and conversion.

2. Experimental

2.1. Materials

Ammonium hexachloroplatinate (IV) (99.99%) ($(\text{NH}_4)_2\text{PtCl}_6$) as a convenient and economic platinum (Pt) precursor was purchased from MiliporeSigma. γ -alumina powder (99.99%) with particle size 0.1 micron was purchased from Sigma-Aldrich. Phenol ($\text{C}_6\text{H}_5\text{OH}$) GR for analysis ACS (50 g/l, H_2O , 20 °C) and polyethylene glycol (PEG 6000, 98%) as surfactant to stabilize Pt nanoparticles were purchased from Merck.

2.2. Green and MW assisted method for the preparation of the Pt/ γ - Al_2O_3 nanocatalyst

$(\text{NH}_4)_2\text{PtCl}_6$ solution (0.02 M, 5 mL) was put into a 25 mL beaker, then 0.15 g PEG surfactant was added and stirred for 2 h to form a clear solution. This section was done three times in three beakers, separately. A certain amount of γ - Al_2O_3 were suspended in three above aqueous solutions and were ultrasonically dispersed for 30 min, then magnetically stirred for 3 h. Then the obtained mixtures heated up to 110 °C in a microwave oven using an optimized heating rate. The solids to increase the porosity, was left to soak for 16 h, and dried overnight at 60 °C, separately. The resulting powders were heated and calcined under an air flow (30 °C/min) to 500 °C and maintained at that temperature for 5 h to remove the surfactant and any remaining water. Based on the used solid support, four types of nanocatalysts were produced as 0.5, 1.0, 2.0 and 2.5 Wt.% Pt in Pt/ γ - Al_2O_3 nanocatalyst. This experiment was done without the usage of γ - Al_2O_3 as an unsupported nanocatalyst that was used as a control sample to study the role of solid support in catalytic activity.

2.3. Characterization

The morphology and particle size of the nanostructure Pt/ γ - Al_2O_3 catalyst were observed by Transmission Electron Microscopy (TEM) analyzer (Carl Zeiss AG - Zeiss EM900). Surface areas (S_{BET}) of the nanostructure Pt/ γ - Al_2O_3 catalyst was calculated by applying the BET equation from the adsorption branch using (Micromeritics- ASAP2010). Barrett, Joyner and Halenda's (BJH) method was used to calculate particle size distributions using the from desorption branch of the isotherms.

2.4. Catalytic Experiments

In a typical reaction, firstly, a 500 mL aqueous solution of phenol (22 g/L) was prepared by dissolving phenol in deionized water. In a three-necked flask in three different experiments, 50 mL of the phenol and 10 Wt.% of Pt in nanocatalyst (Pt/ γ - Al_2O_3) relative to phenol was placed and was connected to the flask to store the hydrogen. Prior to the reaction, the system was flushed with hydrogen several times to remove air [11]. The mixing was heated/stirred at 80 °C for 3 h. After 3 h, a sample was taken and analyzed to monitor the progress of the hydrogenation reaction.

A gas chromatograph (Varian CP-3800 GC With FID (PN 3800/3380)) equipped with a Flame Ionization Detector (FID) and TraceGOLD TG-5MS, 20 m \times 0.15 mm \times 0.15 μm column was used to investigate the reaction products. The GC conditions were summarized in Table 1.

This procedure was performed for all catalyst and Pt nanoparticles as an unsupported control sample.

Table 1. The GC conditions for analyzing the reaction products in the phenol hydrogenation reaction at 80 °C for 3 h.

Injection temperature (°C)	detector temperature (°C)	temperature ramping rate (°C/min)
220	240	10

3. Results and discussion

3.1. Textural characteristics

Surface characteristics of Pt/ γ - Al_2O_3 (2 Wt.%) nanocatalyst was studied through N_2 adsorption–desorption isotherms at 196 C, as depicted in Fig. 1(a). Pore analysis was carried out by applying the BJH method, where the pore size distribution (PSD) curves are illustrated in Fig. 1(b).

It is evident that the obtained adsorption–desorption isotherms for Pt/ γ - Al_2O_3 (2 Wt.%) nanocatalyst as a typical sample (Table 2) (S_{BET} ($\text{m}^2 \text{g}^{-1}$) =104.52, V_{P} ($\text{cm}^3 \text{g}^{-1}$) =0.2135, r_{p} (nm) =18.95) is of type IV, being mainly characteristic for mesoporous materials [12]. They are all associated with H_2 type of hysteresis loops, in the relative pressure (p/p_0) range of 0.55–0.95, usually related to the ink bottle pores with a wide orifice of the border inner parts.

Table 2. The Surface characteristics of Pt/ γ - Al_2O_3 (2 Wt.%) nanocatalysts was studied through N_2 adsorption–desorption isotherms.

S_{BET} ($\text{m}^2 \text{g}^{-1}$)	V_{P} ($\text{cm}^3 \text{g}^{-1}$)	r_{p} (nm)
104.52	0.2135	18.95

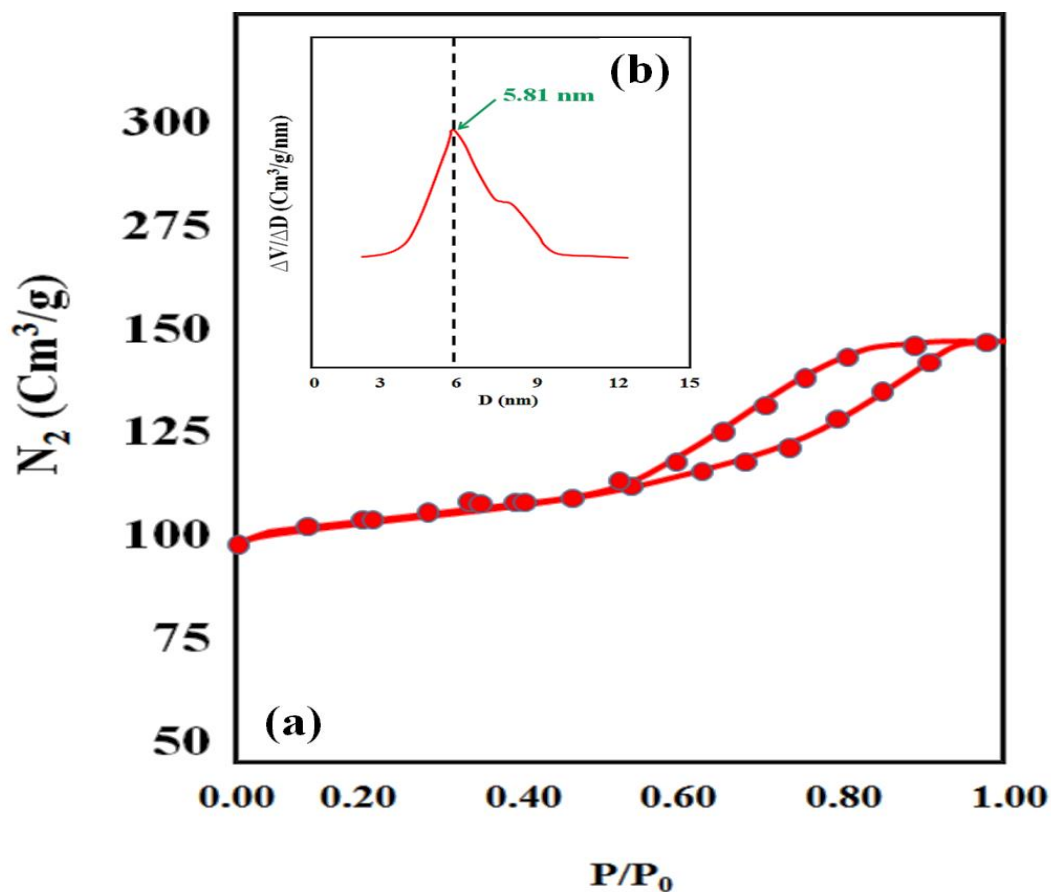


Fig. 1. (a) N₂ adsorption–desorption isotherms, (b) Pore size distribution curve of of Pt/γ-Al₂O₃ (2 Wt.%) nanocatalyst.

3.2. TEM image

The TEM micrograph of the nanocatalyst (2 Wt.%) as a typical sample is present in Fig. 2. TEM image show the formation of Pt nanoparticles with spherical morphology with a fine particle size of the size 10-15 nm and good monodispersity on the surface of Al₂O₃ support.

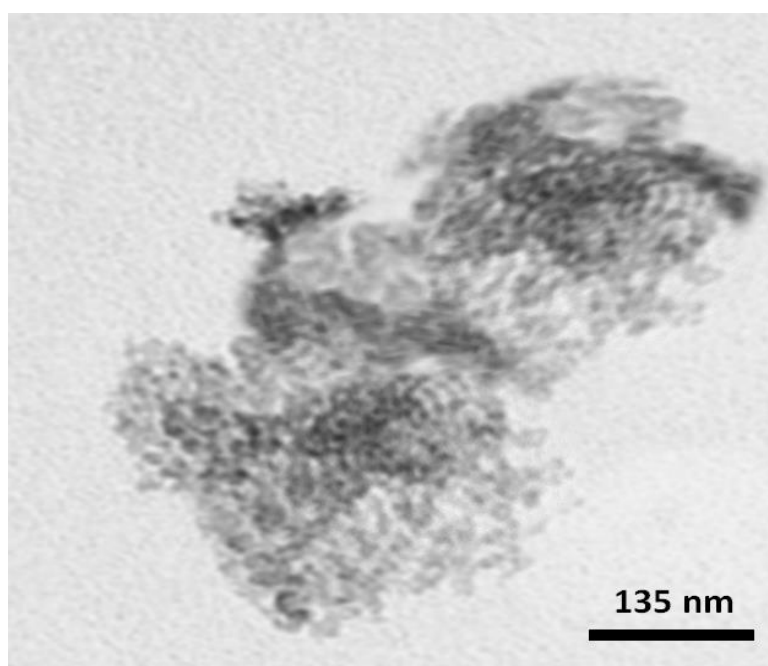


Fig. 2. The TEM image of the Pt/γ-Al₂O₃ (2 Wt.%) nanocatalyst

3.3. Catalytic performance test

In this study, different types of nanocatalysts were tested and the obtained results are shown in Fig. 3. The conversion of phenol hydrogenation increased by 92.6 % with Pt nanoparticles loading in nanocatalyst (to 2 Wt.% Pt) and only cyclohexanone was detected at 8 h indicating 100% selectivity. The cyclohexanone conversion was decreased slightly to 81% at 8 h in nanocatalyst (2.5 Wt.%). The reason for this phenomenon may be presented with Pt nanoparticle aggregation in solid support in a high dosage of Pt nanoparticle sample.

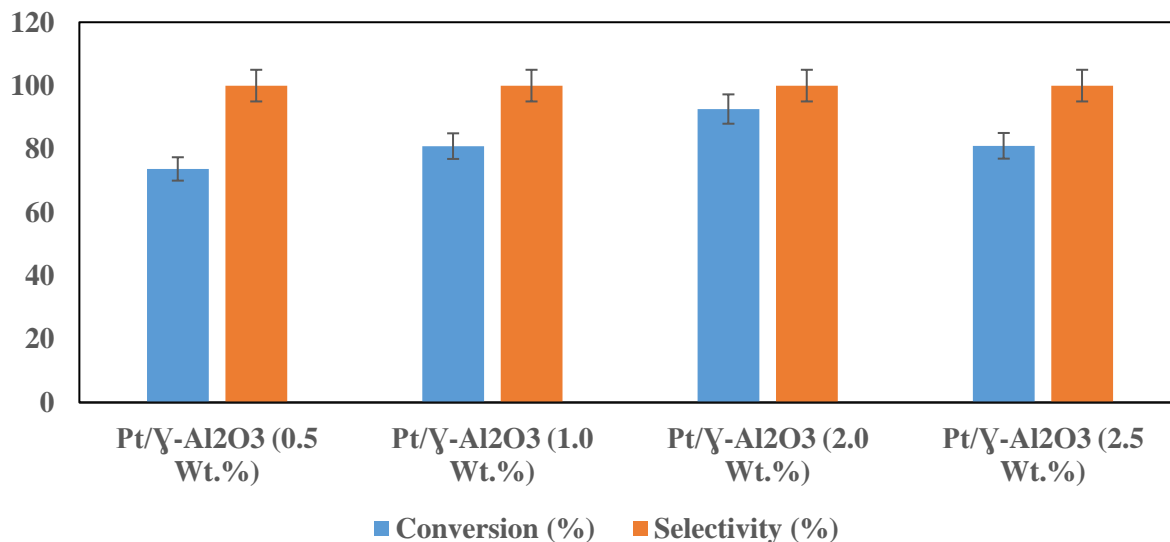


Fig. 3. The effect of Pt/γ-Al₂O₃ nanocatalyst types in hydrogenation of phenol

3.4. The effect of catalyst amount

To study the effect of catalyst amount, different amounts of Pt/γ-Al₂O₃ (2 Wt.%) nanocatalysts as the most effective catalyst in hydrogenation reaction under optimized reaction conditions, were tested as shown in Fig. 4. First, 5 and 10 wt% of Pt/γ-Al₂O₃ with respect to phenol was tested. Conversion of phenol increased with the amount catalyst to 10 wt% of Pt/γ-Al₂O₃ and was 92.6 % in 8 h. Only cyclohexanone was detected with 100% selectivity. the amount of Pt/γ-Al₂O₃ was increased to 25 wt% with concerning phenol and the phenol conversion achieved was 63.4 % in 3 h. The increase in the conversion with an increase in the catalyst weight can be attributed to an increase in the availability of the number of catalytically active sites required for this reaction. On further increasing the amount of catalyst, there is no appreciable change in conversion. The high cyclohexanone selectivity is attributed to an excellent monodispersity of Pt nanoparticles on the solid support.

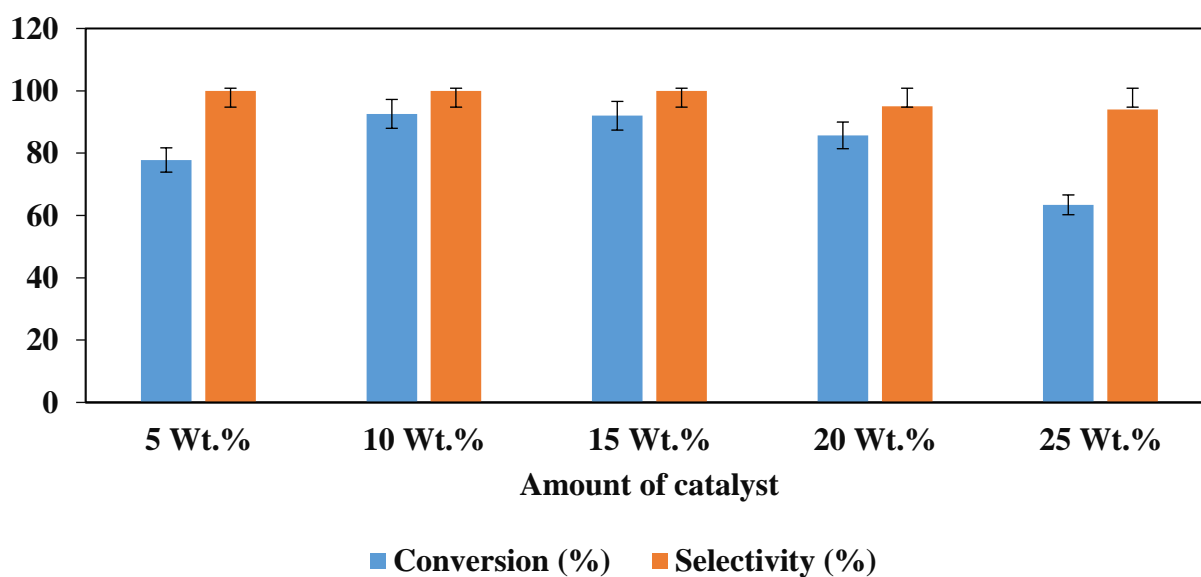


Fig. 4. The effect of catalyst amount (different amounts of Pt/γ-Al₂O₃ (2 Wt.%) nanocatalyst in hydrogenation of phenol

3.5. The effect of reusability

To investigate the stability and reusability of the catalyst, the solid was recovered after centrifuging the reaction mixture with ethanol and dried at 60 °C for 24 h and obtained nanocatalyst was reused in the next reaction cycle. The nanocatalyst was successfully reused consecutively six times under similar reaction conditions giving the conversion in the range 69–92 %, (Fig. 5). Only cyclohexanone was detected with 100% selectivity for all runs. The conversion was decreased after the three cycles, which may be due to the aggregation of particles of the used catalyst that may block the active sites present on the catalyst.

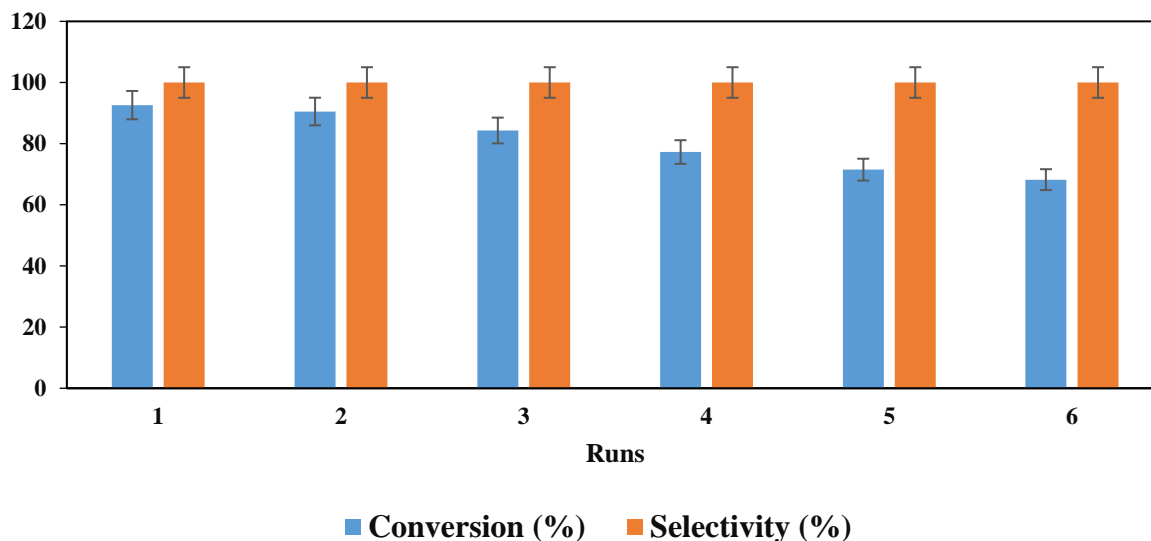


Fig. 5. The effect of reusability of Pt/ γ -Al₂O₃ (2 Wt.%) nanocatalyst in hydrogenation of phenol.

4. Conclusions

Hydrogenation of phenol to cyclohexanone was achieved actively and selectively using a series of Pt/ γ -Al₂O₃ (0.5, 1, 2 and 2.5 Wt.%) supported catalysts. Pt nanoparticles supported on γ -Al₂O₃ (Pt/ γ -Al₂O₃) were synthesized using a unique combination of clean and green colloid-MW assisted synthetic method. The Pt/ γ -Al₂O₃ (2 Wt.%) nanocatalyst directed the reaction toward the desired product leading to high cyclohexanone selectivity and high phenol conversion. The conversion of phenol achieved was 96.2 % with 100 % cyclohexanone selectivity within 8 h using 10 Wt.% of Pt nanoparticles relative to phenol. This paper presents novel research in heterogeneous catalysis using the green colloid template-MW assisted method.

Conflicts of Interest

The author declares no conflict of interest.

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