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To 5.06.2008
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Applied Catalysis A

Dear **Sir**

Sub: Submission of manuscript for publication in Applied catalysis A- reg.

I am herewith enclosing the manuscript of our research article entitled **"Hydrogenation of nitrobenzene over palladium supported catalysts - Effect of support"** in electronic version according to the author guidelines. I shall be thankful to you if you could take speedy action for publication of this article in Applied Catalysis A

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*** Graphical Abstract**

Hydrogenation of nitrobenzene over palladium supported catalysts- Effect of support

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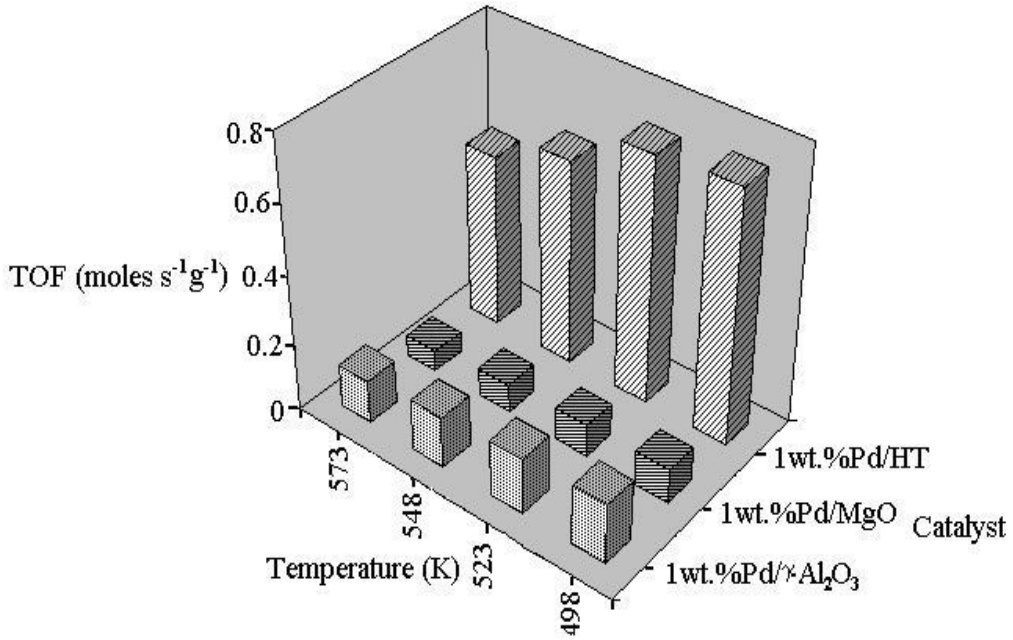

Vapor phase hydrogenation of nitrobenzene is reported on 1 wt.% Pd supported on hydrotalcite, MgO and γ-Al_2O_3 catalysts. The catalysts were prepared in the laboratory using wet impregnation method and were characterized by XRD, BET surface area, TPR, TEM, XPS and CO Chemisorption studies. Turn over frequency for HT supported Pd was found to be higher than on MgO and γ-Al_2O_3 supported catalysts. Thus, hydrotalcite has been found to be an effective support for Pd catalyst, for aniline formation from nitrobenzene via hydrogenation.

* Manuscript

Hydrogenation of nitrobenzene over palladium supported catalysts- Effect of support

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Abstract

Vapor phase hydrogenation of nitrobenzene is reported on 1 wt.% Pd supported on hydrotalcite, MgO and γ-Al_2O_3 catalysts. The catalysts were prepared in the laboratory using wet impregnation method and were characterized by XRD, BET surface area, TPR, TEM, XPS and CO Chemisorption studies. The conversion of nitrobenzene was studied in the temperature region of 498-573 K and compared on all the catalysts. An impressive catalytic performance of nitrobenzene conversion was observed on hydrotalcite supported Pd catalyst. CO chemisorption and TEM results evidence the fact that palladium disperses well on hydrotalcite support when compared with other conventional supports such as MgO and γ-Al_2O_3 which is responsible for high conversion of nitrobenzene.

Keywords: Hydrotalcite; MgO; γ-Al_2O_3; Palladium; Hydrogenation.

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1. Introduction

The catalytic hydrogenation of nitrobenzene is an industrially important reaction for the production of aniline. About 85% of global aniline is produced by catalytic route.[1,2] Aniline is mainly used for the synthesis of methylene diphenyl diisocyanate (MDI), and as an additive for rubber processing. It has also been used as pesticides and herbicides. Supported metals are generally employed as catalysts for hydrogenation reaction.[3] Noble metal supported on basic carriers is known to possess unusual catalytic properties. Hydrotalcite - type layered double hydroxides which are basic in nature display a lamellar structure consisting of brucite like layers and compensating anions.[4] These hydrotalcites (HT) have been tried as supports for dispersing noble metals such as palladium, platinum, rhodium etc. Upon controlled thermal treatments, HT decomposes to M^{II} (M^{III}) O mixed oxides thereby exhibiting high surface area, homogenous inter-dispersion and synergetic effects between the elements.[5,6]

Active carbons were used as supports for palladium in the liquid medium hydrogenation of nitrobenzene to aniline.[7] It is found that dispersion of Pd on carbon remains appreciable even after oxidizing treatment of active carbon and 5 % Pd impregnated on active carbon exhibited high activity. The hydrogenation of nitrobenzene was carried out over three Pd/Carbon catalysts using methanol and isopropanol as solvents.[8] It is reported that hydrogenation proceeds more rapidly in methanol than in isopropanol. Liquid phase hydrogenation of nitrobenzene was studied over Pd-B/SiO_2 amorphous catalyst.[9] It is reported that the promoting effect of the SiO_2 support was mainly attributed to the stabilization of the Pd-B amorphous structure and the dispersion of the Pd active metal. Polymer anchored metal complex of Pd (II) catalysts were

synthesized using styrene divinyl copolymer with 2% as well as 8% cross linking and were tested for the hydrogenation of nitrobenzene.[10] It is reported that the catalyst with 8% cross linking showed high activity due to dispersion of more metal ions on the surface of the polymer. Pt/C catalyst in supercritical carbon dioxide and ethanol have been employed for the hydrogenation of nitrobenzene and the effects of pressure, solvent and metal particle size[11] were studied. The catalytic activity in supercritical carbon dioxide is found to be higher than in ethanol. The overall hydrogenation of nitrobenzene has been found to be structure sensitive in ethanol in which the turnover frequency tends to decrease with an increase in the degree of Pt dispersion. On the contrary, it is structure insensitive in supercritical carbon dioxide.

Recently, Pd supported on Mg-Al hydrotalcite with different Pd loadings prepared by incipient wet impregnation method has been used as catalyst for the vapor phase hydrogenation of nitrobenzene and reported that very low wt.% Pd is sufficient to load on the support for achieving high yield of aniline.[12] There is a considerable scope for understanding of the hydrogenation of nitrobenzene which depends on the various physical factors and mainly on dispersion of active metal on the various supports such as hydrotalcite, MgO and γ- Al_2O_3.

The present work deals with the influence of support for Pd catalyst towards hydrogenation of nitrobenzene to aniline. The effects of various reaction parameters such as temperature, time on stream were studied. The physico-chemical properties of Pd Supported catalysts are correlated with the rate of nitrobenzene conversion to aniline.

2. Experimental

2.1. Preparation of Support

Mg-Al hydrotalcite was prepared according to the method reported by Reichle et al.[13] Solution A was prepared by dissolving 256 g of Mg $(NO_3)_2.6H_2O$ (1 mol) and 185.7 g of Al $(NO_3)_3.9H_2O$ (0.5 mol) in 700 cm^3 distilled water, maintaining a Mg/Al molar ratio of 2. Solution B was prepared by dissolving 280 g of 50% NaOH (140 g in 140 cm^3 distilled water) and 100 g of Na_2CO_3 in 1000 cm^3 distilled water. HT was prepared by adding solution A to solution B in 3-4 h with constant stirring while maintaining the pH between 11-13. The resulting gel was transferred to an autoclave and allowed to crystallize at 333 K for 18 h. The sample was filtered and washed several times with hot distilled water until pH of the filtrate is neutral and also to remove any free sodium ions that may be present. The sample was dried in an oven for 12 h at 373 K and then calcined at 723 K in air for 18 h.

2.2. Preparation of catalyst

1 wt.% Pd on HT support was prepared by incipient wet impregnation method, using an aqueous solution of palladium chloride acidified with HCl (to effect the complete dissolution of the salt). Required amount of palladium chloride was taken so as to obtain the desired Pd concentration on support and the solution was mixed with support in distilled water. The resulting slurry was stirred well for removing excess water and subsequently dried in an oven at 373 K for 12 h. The solid residue was then crushed and calcined in air at 723 K for 5 h. Similarly 1 wt.% Pd/ MgO (Harshaw) and 1 wt.% Pd/γ-Al_2O_3 (Harshaw) were prepared.

2.3. Characterization

BET surface area was obtained on Autosorb Automated Gas Sorption System (M/s. Quantachrome, USA) with N_2 as adsorbate at liquid nitrogen temperature. X-ray powder diffraction (XRD) patterns of all catalysts were recorded on a Rigaku Miniflex (M/s. Rigaku Corporation, Japan) X-ray diffractometer using Ni filtered Cu Kα radiation (λ= 1.5406 Å) with a scan speed of 2° min^{-1} and a scan range of 2-80° at 30 kV and 50 mA. Temperature programmed reduction (TPR) profiles of the catalysts were generated on a home made on-line quartz micro reactor interfaced to a thermal conductivity detector (TCD) equipped with a gas chromatograph (Varian CP 3800 USA) and the profiles were recorded using GC software. H_2/Ar (10 vol.% of H_2 and balance Ar) mixture was used as the reducing gas while the catalyst was heated at a linear heating ramp of 10 $Kmin^{-1}$ from 303 K to 850 K.

X-ray Photoelectron Spectroscopy is recorded on Kratos Axis 165 XPS Spectrometer, with Mg-Kα radiation (1253.6 eV). In the ESCA study, C 1s – binding energy value of 285 eV is taken as reference level. Prior to the ESCA studies, all the catalysts has been reduced in 6 % H_2 balance He flow at 673 K for 3 h. Transmission Electron Microscopy (TEM) is recorded on TECNAI FE1 G^{12} Philips instrument using LaB_6 filament at 120 kV. CO chemisorption was carried out at 303 K on a homemade pulse reactor to evaluate the dispersion and metal particle size. In a typical experiment, about 100 mg of the catalyst sample was placed in a micro-reactor of 8 mm i.d., and 250 mm long quartz reactor and the catalyst sample was first reduced under a hydrogen flow at 673 K for 2 h, pre-treatment at 673 K for 1 h under He flow and finally was cooled in He flow up to 303 K. The outlet of the reactor was connected to a micro-thermal

conductivity detector (TCD) equipped GC-17A (M/s. Shimadzu Instruments, Japan) through an automatic six-port valve (M/s. Valco Instruments U.S.A). After cooling, pulses of 10% CO balance He were injected at room temperature through a 1ml loop connected to the six-port valve until no further change in the intensity of the outlet CO (from GC- software). Assuming CO: Pd stoichiometry of 1 : 1, dispersion, particle size and metal area of Pd were calculated using Pd metal cross sectional area as 7.874 nm^2.[14]

2.4. Nitrobenzene hydrogenation

Vapour phase hydrogenation of nitrobenzene reaction was performed in a fixed-bed tubular reactor (10 mm i.d., 300 mm long glass reactor) using 0.5 g catalyst at atmospheric pressure at different temperatures ranging from 498-573 K. The catalyst sample was diluted with quartz beads with same amount of catalyst and packed at the center of reactor between two plugs of quartz wool. The catalyst has been reduced in a flow of H_2 at 673 K. Nitrobenzene (1 ml/h) is injected with the help of a syringe pump (Secura FT, B. Braun Germany) with H_2 flow (1 lh^{-1}). The product mixture was collected every hour in a trap and analyzed by a GC (GC-17A, M/s. Shimadzu instruments, Japan) using a Zebron ZB-WAX capillary column of 0.53 mm dia. and 30 m long.

3. Results and Discussion

3.1. Characterisation

BET surface area of calcined Pd supported catalysts are given in Table 1. Calcined hydrotalcite support has a surface area of about 214 m^2g^{-1}, the surface area of MgO and γ- Al_2O_3 is found to be 40 m^2g^{-1} and 240 m^2g^{-1} respectively. When palladium is loaded onto the support a decrease in surface area is observed in all the catalysts which may be due to pore blocking. However, deposition of Pd on MgO does not decrease the

surface area significantly as in the case of hydrotalcite. During the preparation of Pd/MgO catalyst migration of Cl^- ion onto MgO surface might have occurred, and hence there is no drastic decrease in the surface area.[15] XRD pattern of reduced HT catalyst in 1 wt.% Pd/HT shows the presence of metallic Pd phases (ICDD No. 87-0653, *d* = 2.25, 1.95, 1.38) and MgO periclase (ICDD No. 87-0638, *d* = 2.25, 1.95, 1.38) shown in Fig. 1b. 1 wt.% Pd/MgO reduced catalyst shows the presence of MgO periclase (ICDD No. 87-0638, *d* = 2.25, 1.95, 1.38) and also the presence of metallic Pd phases (ICDD No. 87-0653, *d* = 2.25, 1.95, 1.38) shown in Fig 1c. In the case of 1 wt.% Pd /γ-Al_2O_3 catalyst, the phase corresponding to γ- Al_2O_3 is present ($2\theta = 45^\circ$ with d value 1.99, $2\theta = 36.1^\circ$ with d value 2.46) and due to the amorphous nature of the catalyst the metallic Pd phases are not seen clearly in XRD, but a broad peak due to Pd is found to occur around $2\theta = 40^\circ$ with d value 2.25 (Fig 1a).

TPR profiles of supported palladium catalysts are shown in Fig. 2. A two-stage reduction is observed in 1 wt.% Pd/HT catalyst (Fig.2a). The first stage reduction gives rise to a strong positive hydrogen consumption peak at T_{max}~ 425 K. This represents PdO reduction and/or hydrogen chemisorption on the metallic palladium that is formed and/or hydrogen adsorption that is known to occur directly on the support as well as spillover species. The second stage reduction at T_{max} ~760 K indicates further consumption of hydrogen on all the catalysts, which may be attributed to the spill over of the hydrogen activated on metallic palladium on to the support.[16,17] No negative peak corresponding to β-PdHx decomposition is observed over Pd/HT catalysts. The reason may be due to high dispersion of palladium over the support.[18] In 1 wt.% Pd/MgO (Fig.2b), a negative peak is observed around 350 K. In hydrogen atmosphere,

$PdCl_2$ or PdO gets reduced easily at ambient temperature to Pd metal, and further interacts with hydrogen forming PdHx which appears to have occurred during the passage of reducing gas prior to the start of the temperature program.[15] The intensity of this peak is high, which may be attributed to lower Pd dispersion in this catalyst. In 1 wt.% Pd/γ- Al_2O_3 a negative peak corresponding to β-PdHx is observed around 450 K (Fig. 2c).

XPS spectra of calcined and reduced palladium catalysts are shown in Figs. 3 and 4. In calcined 1 wt .% Pd/HT catalyst (Fig.3a) the binding energy value of Pd $3d_{5/2}$ is found to be around 337.2 eV which indicates the presence of $Pd^{2+.}$ Two peaks, corresponding to Pd $3d_{3/2}$ and Pd $3d_{5/2}$ are found in reduced Pd/HT, Pd/Al_2O_3 and Pd / MgO catalysts (Figs 3b, 4a and 4b). The binding energy value of Pd $3d_{5/2}$ and Pd $3d_{3/2}$ peaks in all the reduced catalysts is found to be around 335 eV and 341.5 eV respectively which indicates the presence of Pd in metallic form as reported in the literature.[18,19] It is also noted that the peak due to Pd $3d_{5/2}$ in alumina is broader than that due to Pd in MgO and hydrotalcite. This broadening of peak due to Pd $3d_{5/2}$ in alumina is an indication for the deposition of Pd in bulk.

TEM images of reduced catalysts are shown in Fig. 5. Pd particles are found to be well dispersed in 1 wt.% Pd/HT (Fig. 5a) and the metal particles are found to be evenly distributed on the HT support. However, in the case of 1wt. % Pd/γ-$Al_2O_{3,}$ particle size of Pd metal is found to be large as shown in Fig 5b. The Pd metal particles are found to be agglomerated in 1 wt.% Pd/MgO (Fig.5c). The chemisorption of carbon monoxide on palladium has attracted much attention because CO is an interesting probe molecule to characterize adsorption sites.[20] Number of surface palladium sites is assumed to be equal

to the number of CO moles adsorbed per gram of the catalyst. Pd dispersion, metal surface area and particle size calculated from CO chemisorption are given in Table 1. It is clear from the results that palladium disperses well on hydrotalcite support than other conventional supports such as MgO and γ-alumina which is in accordance with the literature report.[21] The carbon content of all the spent catalysts 1 wt.% Pd/HT, 1 wt.% Pd/MgO and 1 wt.% Pd/γ-Al_2O_3 is calculated from CHNS analysis and the values are given in Table 2. Among all the three catalysts the carbon content is found to be higher for alumina supported palladium catalyst (17.26%) than 1 wt.% Pd/MgO (3.50%) and 1 wt.% Pd/HT (2.27%). This is attributed due to acidic nature of alumina support.

3.2. Catalytic Activity

3.2.1. Effect of temperature

The vapor phase hydrogenation of nitrobenzene to aniline was studied over 1 wt. % Pd on different supports such as hydrotalcite, MgO and γ-Al_2O_3 in the temperature region of 498-573 K. Fig. 6 shows the influence of temperature for the rate of hydrogenation of nitrobenzene over palladium catalysts. As temperature is increased the rate of nitrobenzene conversion is found to decrease in all the catalysts. This may be due to coke formation or poisoning due to water generated during the reaction. Thus a lower temperature was preferred (498 K) for maximum rate of conversion for all the catalysts

3.2.2. Effect of time on stream

Fig. 7 shows variation in rate of nitrobenzene hydrogenation with time over supported palladium catalysts at 498K. The reaction is studied for 5 h on all the catalysts. The rate of conversion of nitrobenzene was found to be same upto 3 h and then it is found to decrease in the subsequent period on all the catalysts. The

decrease in the rate of conversion of nitrobenzene may be due to water or coke formed during the course of reaction which acts as a poison. In the case of 1 wt.% Pd/HT, the decrease in activity may be attributed only due to absorption of water vapor which is released in the reaction as a byproduct. This is understood from XRD results as there is a reconstruction of hydrotalcite phases ICDD No., *d* = 7.84, 3.90, 2.57) which regains its hydrotalcite structure back by memory effect.[22] The decrease in rate of conversion of nitrobenzene in the case of MgO and γ-Al_2O_3 supported Pd catalysts may be due to coke formation as confirmed from CHNS analysis (Table 2). The carbon content is found to be higher on Al_2O_3 than HT and MgO supported spent catalyst.

3.3.3. Effect of support

Hydrogenation activity of various Pd supported catalysts have been compared in terms of TOF values in the region 498-573 K and presented in a three dimensional diagram (Fig. 8). The effect of support for hydrogenation of nitro benzene is evaluated by turn over frequency (TOF) of nitrobenzene conversion on each catalyst and it is defined as the number of molecules of nitrobenzene converted per Pd atom per second. It is calculated as,

$$\text{TOF} = \frac{\text{Number of moles of nitrobenzene passed per second} \times \text{fractional conversion}}{\text{Number of surface Pd sites}}$$

Number of surface palladium sites is assumed to be equal to the number of CO moles adsorbed per gram of the catalyst. Turn over frequency for HT supported Pd was found to be higher than on MgO and γ-Al_2O_3 supported catalysts. Thus, hydrotalcite supported palladium catalyst has been found to be an effective catalyst for the synthesis of aniline from the hydrogenation of nitrobenzene when compared with other catalysts

viz.,1 wt.% Pd/γ-Al_2O_3 and 1 wt.% Pd/MgO. The high activity of HT supported Pd catalyst may be attributed to high dispersion of Pd (72%) on hydrotalcite support as evident from CO chemisorption studies, where there is a large uptake of CO (Table 1). Palladium disperses well on hydrotalcite support than on other conventional oxides such as MgO and γ-Al_2O_3. 1 wt.% Pd/HT shows higher activity at lower temperature 498 K when compared with 1 wt.% Pd/MgO and 1 wt.% Pd/γ-Al_2O_3. However, the very low activity of 1 wt.% Pd/γ-Al_2O_3 may be attributed due to coke formation as evident from CHNS analysis.

The high activity of 1 wt.% Pd/HT can also be accounted in terms of particle size measured from TEM image. From TEM images, it is observed that Pd particles are well dispersed and are evenly distributed (Fig 5a) on the HT support. Pd particles are found to be agglomerated on MgO support (Fig.5c). However, in the case of γ-Al_2O_3 supported Pd catalyst, particle size of Pd is found to be bigger than other supports (Fig 5b). Also Pd dispersion, metal surface area and particle size values calculated from both CO chemisorption studies and TEM images agree well with each other. Further, XPS peak due to PdO in Al_2O_3 is broader than in MgO and HT (Figs 3 and 4). The peak broadening of Pd $3d_{5/2}$ peak in XPS also indicated the presence of large amount of Pd in the bulk rather than on the surface which is not beneficial for hydrogenation activity. Such a broadening of peak is not observed on HT and MgO supported Pd catalysts. Hence, XPS result also supports the fact that Pd is finely dispersed on hydrotalcite support when compared with other supports. Carbon deposit estimated on the spent catalysts 1 wt. % Pd/HT, 1 wt. % Pd/MgO and 1 wt. % Pd/γ-Al_2O_3 (Table 2) also reveals the difference in the nature of support. γ-Al_2O_3 being an acidic support found to possess

large amount of carbon deposit. The other two supports being basic in nature possess low amount of carbon deposit. The reason for high activity of HT supported Pd may also be attributed due to the high basic nature of the support.

4. Conclusion

The effect of dispersion, particle size and metal area of Pd on various supports has been presented for the catalytic hydrogenation of nitrobenzene. It is observed that Pd is well dispersed on HT support. Hydrotalcite supported Pd catalyst has been found to be more active than MgO and γ-Al_2O_3 supported Pd catalysts. The reason for the high activity has been attributed to the presence of more number of finely dispersed Pd particles on the surface and high basic nature of hydrotalcite support. Thus, hydrotalcite has been found to be an effective support for Pd catalyst, for aniline formation from nitrobenzene via hydrogenation.

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Supplementary Material

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Table(s)

Table. 1: Surface area, Dispersion, and Particle size of supported palladium catalysts

Catalyst	Surface area (m^2g^{-1})	CO Uptake ($\mu mol\ g^{-1}$)	[a]Dispersion (%)	[b]Metal Area (m^2/g)	[c]Particle size (nm)
1wt.%Pd/HT	183 (220)*	68	72	3.223	1.63
1wt.%Pd/MgO	34 (40)*	36	38	1.706	3.08
1wt.%Pd/γ-Al_2O_3	221 (240)*	13	14	0.616	8.5

***** Supports without Pd loading

[a] % Dispersion = [CO uptake ($\mu mol\ g^{-1}$) X 100]/ [total Pd ($\mu mol\ g^{-1}$)]

[b] Metal area = Metal Cross Sectional Area X No. of Palladium atoms on surface
Metal cross sectional area of Pd is 7.87 nm^2

[c] Particle size (nm) = 6000/[metal area (m^2 g Pd^{-1}) X ρ]
[Pd density (ρ) = 11.4 g cm^{-3}]

Table 2: Analysis of Carbon content by CHNS

Spent catalyst	Carbon content (%)
1wt.%Pd/HT	2.27
1wt.%Pd/MgO	3.50
1wt.%Pd/γ-Al_2O_3	17.26

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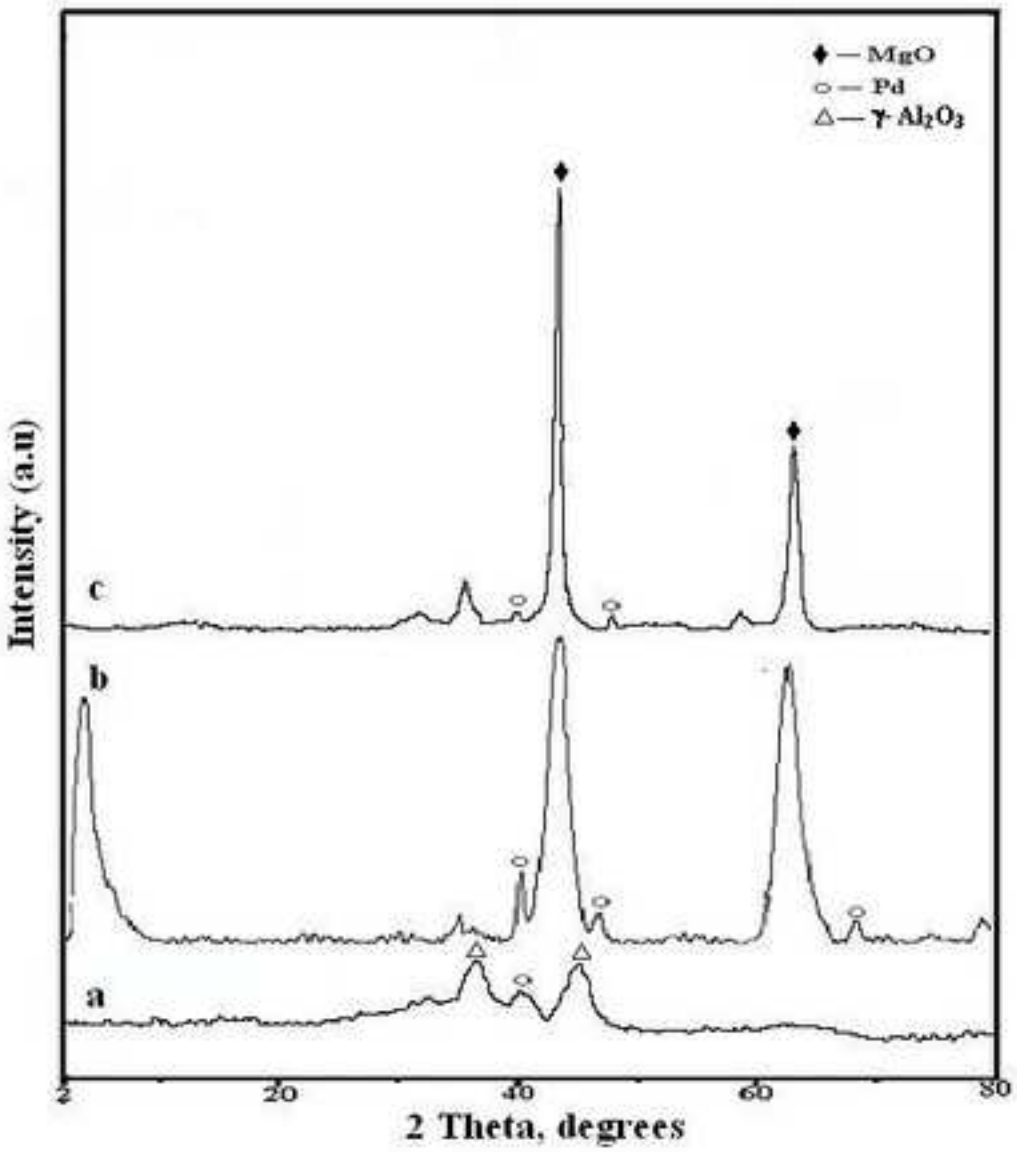

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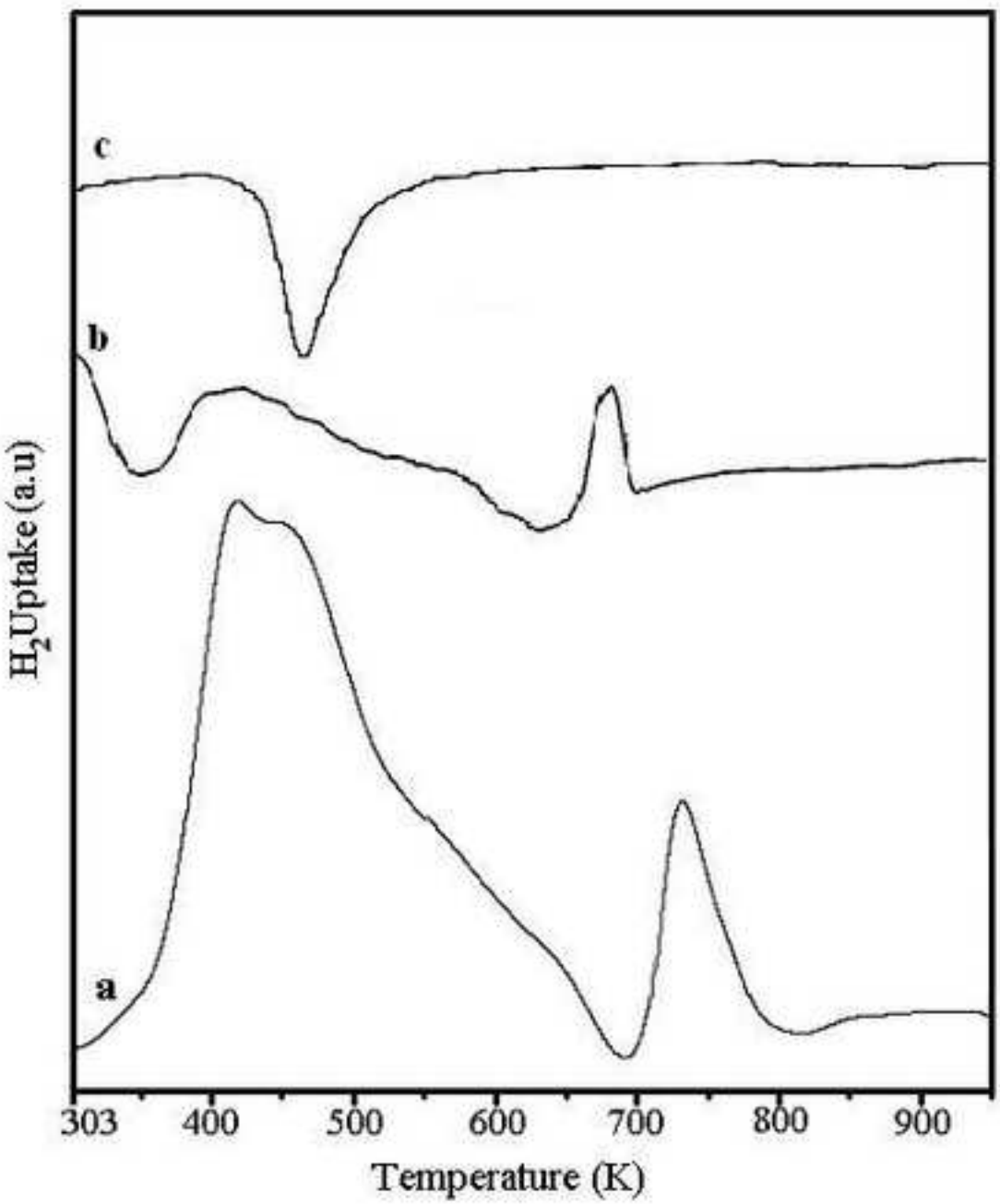

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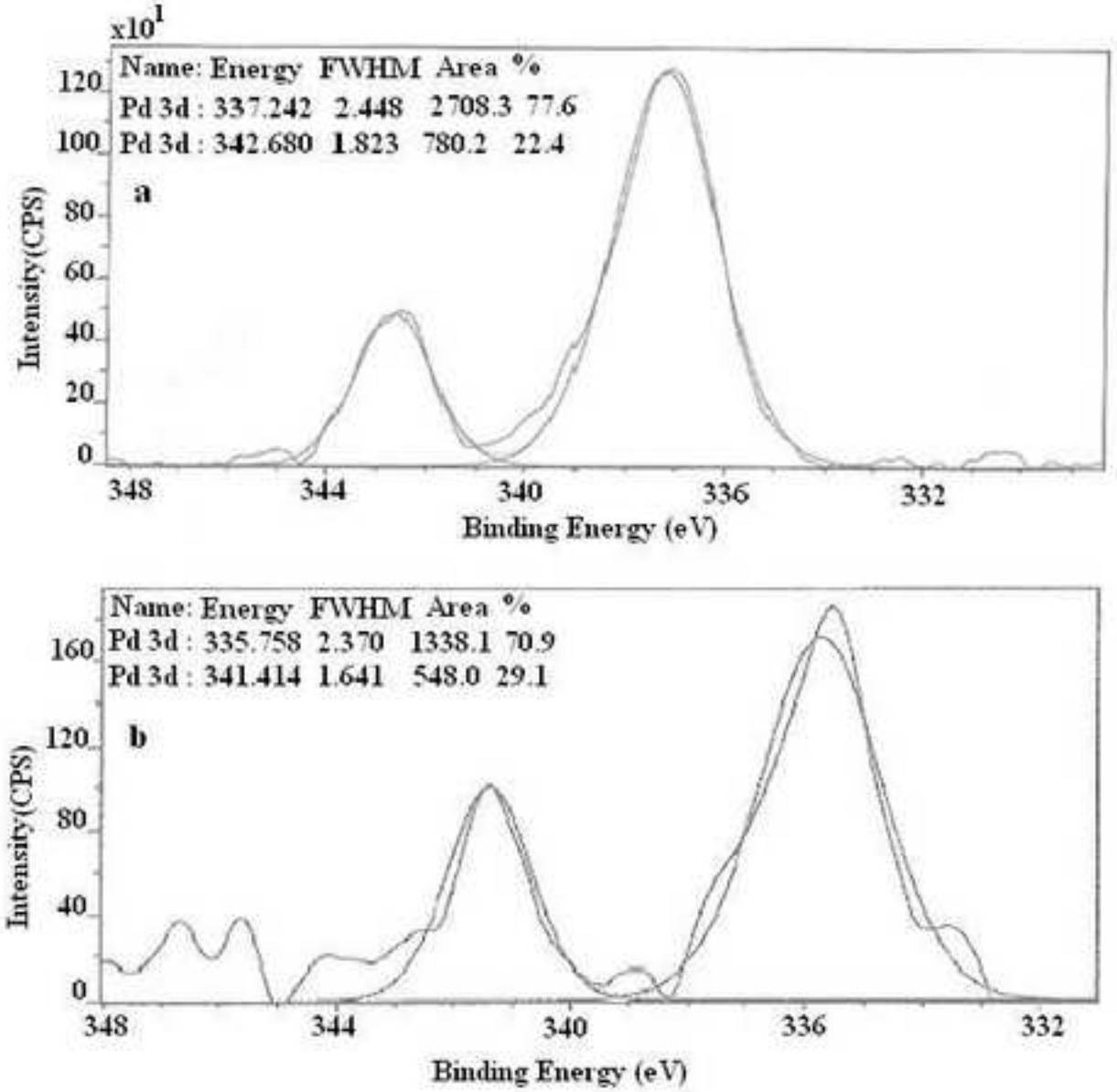

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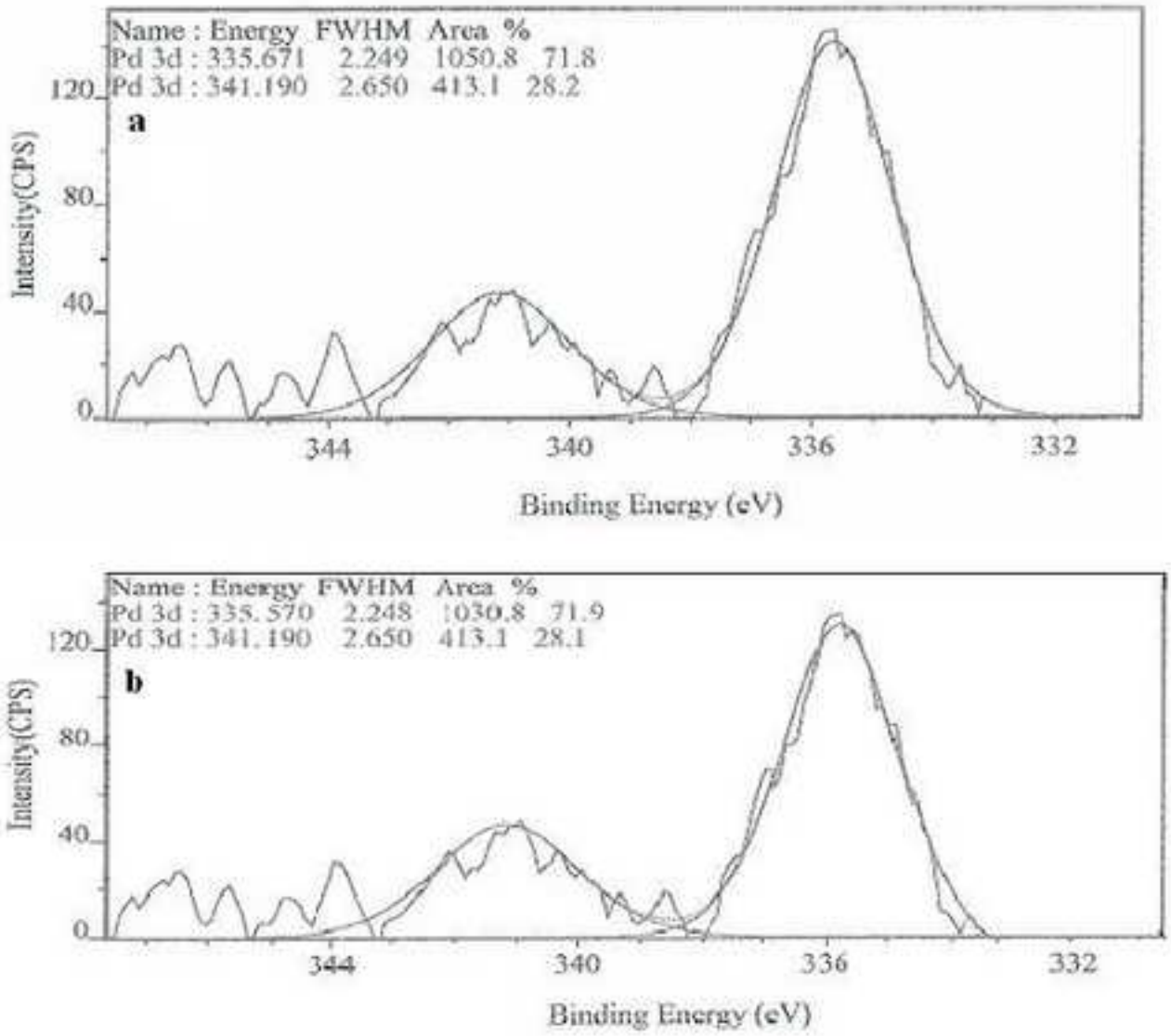

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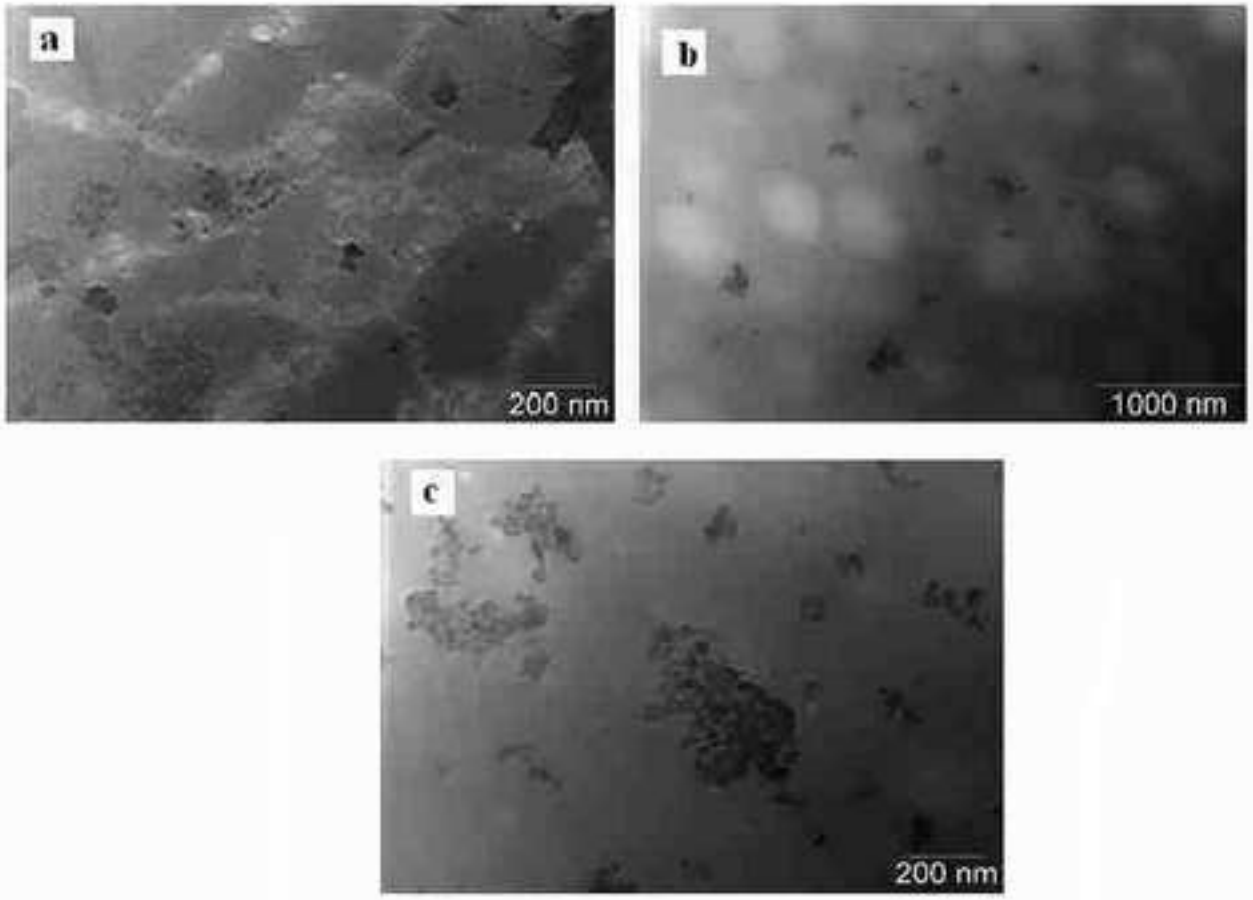

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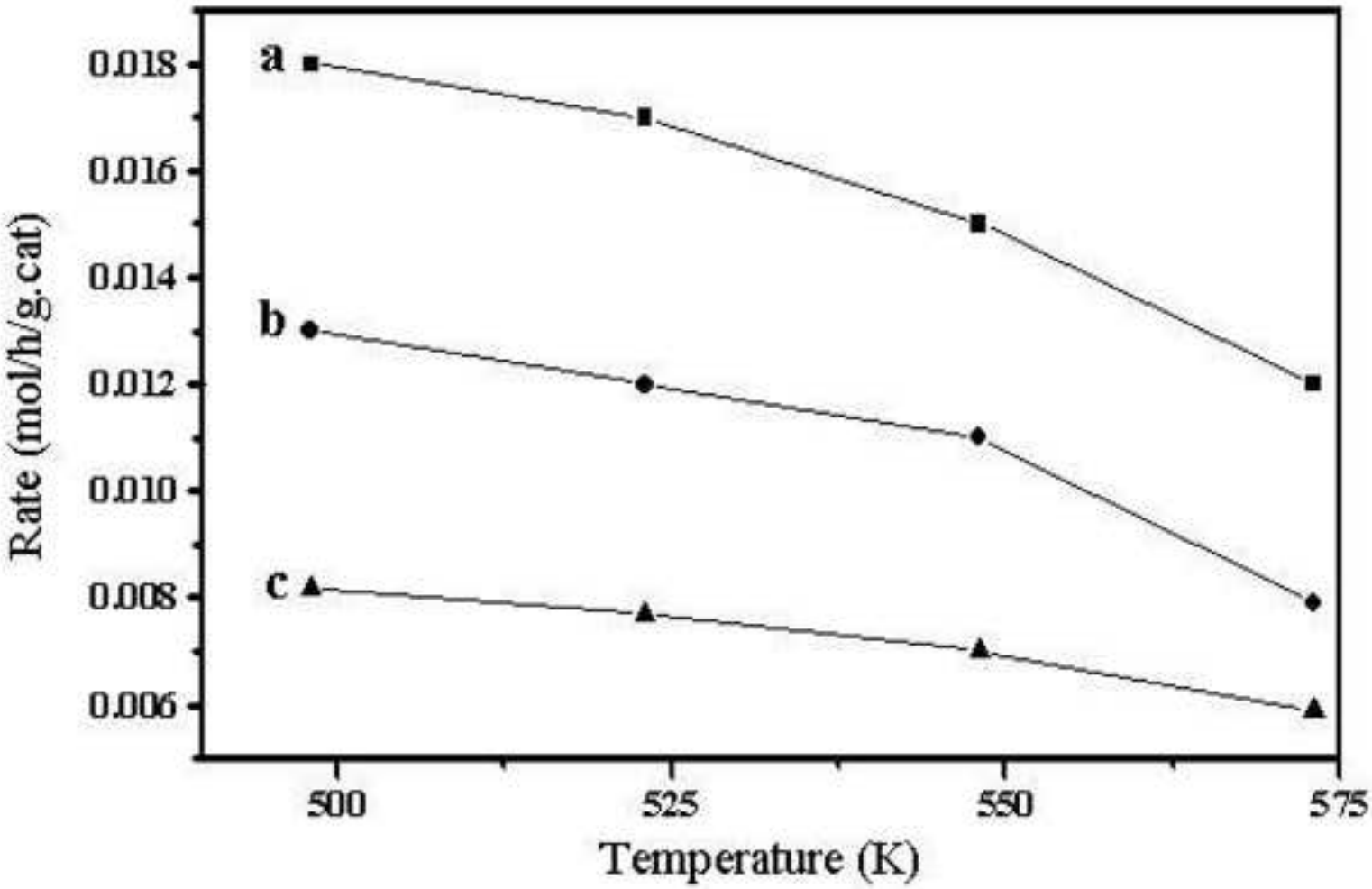

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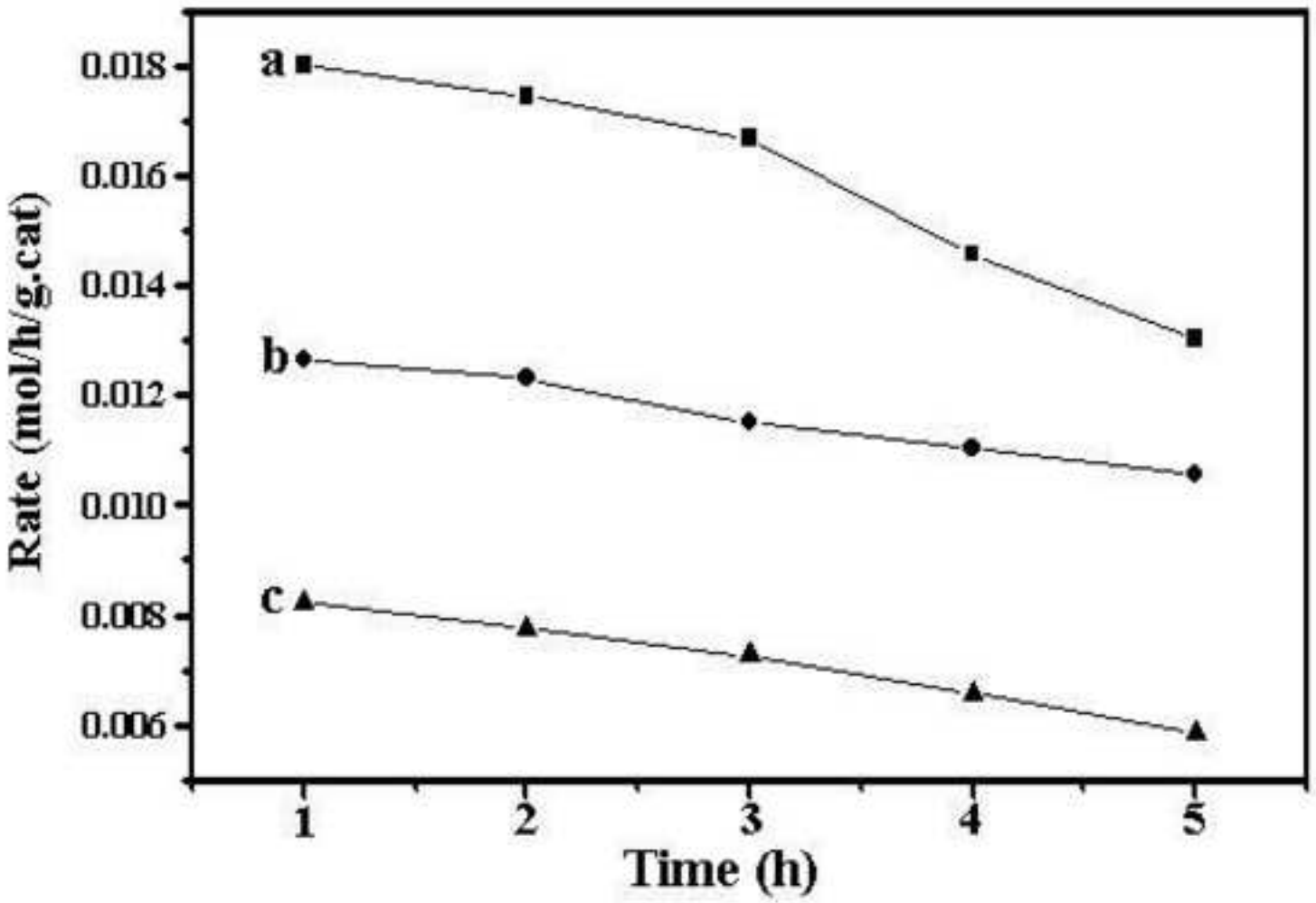

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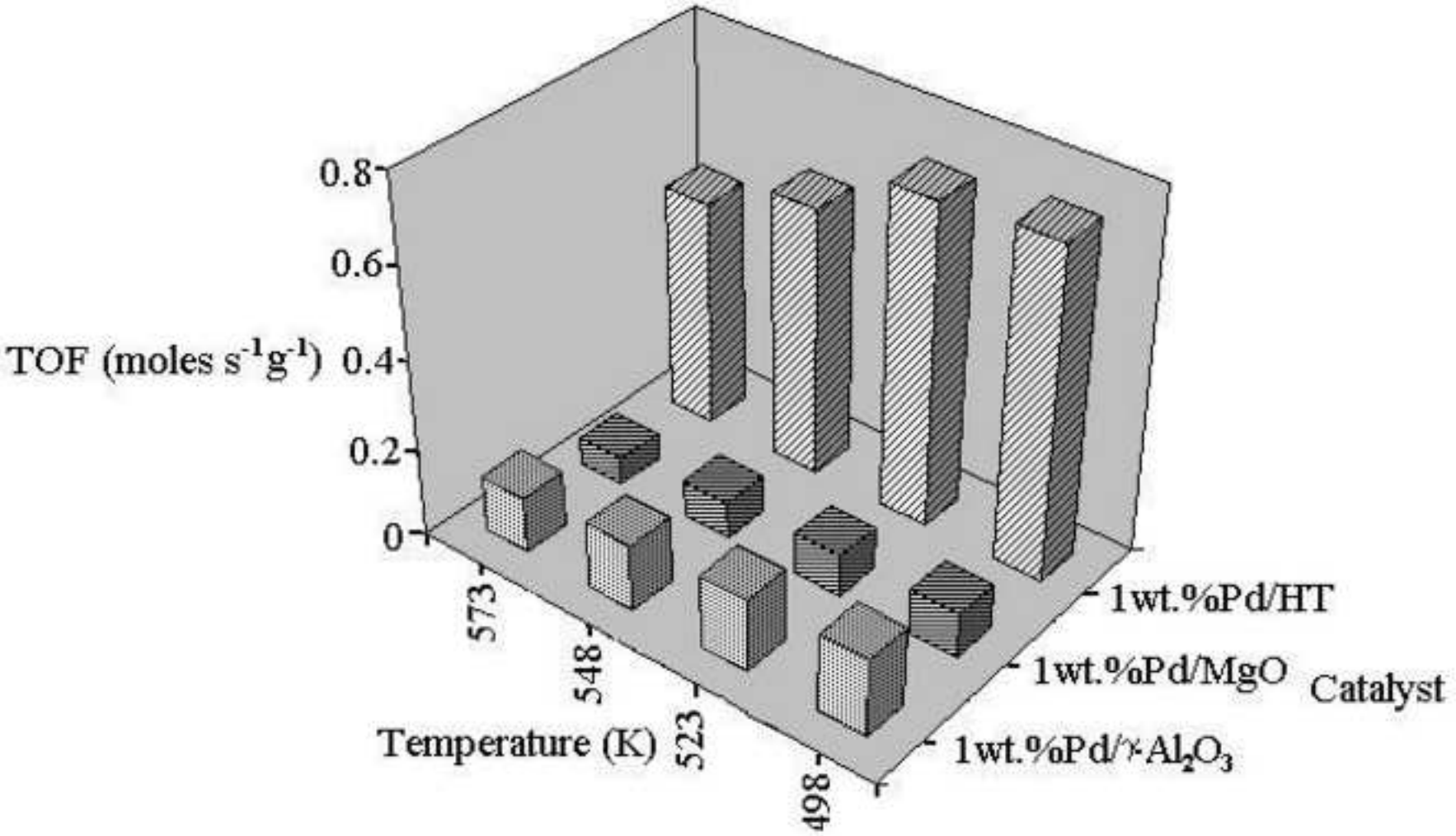
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