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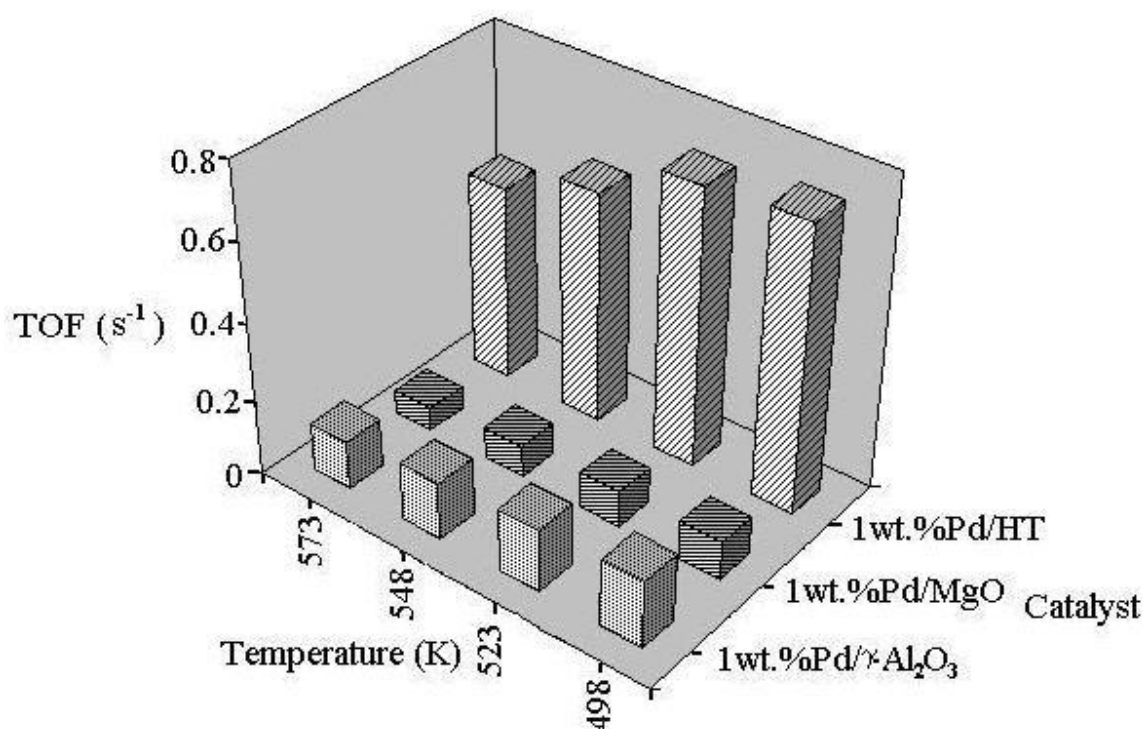
Hydrogenation of nitrobenzene over palladium-supported catalysts- Effect of support

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Vapor phase hydrogenation of nitrobenzene is reported on 1 wt.% Pd supported on hydrotalcite, MgO and γ -Al₂O₃ catalysts. The catalysts were prepared in the laboratory using a wet impregnation method and were characterized by XRD, BET surface area, TPR, TEM, XPS and CO chemisorption studies. The Turnover frequency for HT-supported Pd was found to be higher than on MgO and γ -Al₂O₃ supported

catalysts. Thus, hydrotalcite has been found to be an effective support for Pd catalyst, for aniline formation from nitrobenzene via hydrogenation.

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Abstract

Vapor phase hydrogenation of nitrobenzene is reported on 1 wt.% Pd supported on hydrotalcite, MgO and γ -Al₂O₃ catalysts. The catalysts were prepared in the laboratory using a 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 prove that palladium disperses better on hydrotalcite supports when compared with other conventional supports such as MgO and γ -Al₂O₃, which is responsible for the high conversion of nitrobenzene.

Keywords: Hydrotalcite; MgO; γ -Al₂O₃; 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 routes [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 a pesticide and herbicide. Supported metals are generally employed as catalysts for hydrogenation reactions [3]. Noble metals supported on basic carriers are 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 and rhodium. 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; 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/SiO₂ amorphous catalyst [9]. The promoting effect of the SiO₂ support was mainly attributed to the stabilization of the Pd-B amorphous structure and the dispersion of the Pd active metal.

Polymer-anchored metal complexes 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]. 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.

The earlier work published in J.Mol.Catal. [12] essentially deals with the catalyst system Pd supported on Mg-Al hydrotalcite for the hydrogenation of nitrobenzene. The variable considered is the extent of Pd loading, whereas the present work examines supports like hydrotalcite, MgO and γ - Al₂O₃ for Pd dispersion towards the hydrogenation of nitrobenzene in order to formulate guidelines for more active and more selective catalyst systems. Secondly, the aim of the present communication is to elucidate the necessary factors for effectively dispersing Pd on the supports.

There is a considerable scope for understanding the hydrogenation of nitrobenzene, which depends on various physical factors and mainly on the dispersion of active metal on the various supports such as hydrotalcite, MgO and γ - Al₂O₃. The present work deals with the influence of the support for Pd catalyst on the hydrogenation of

nitrobenzene to aniline. The effects of various reaction parameters such as temperature and time on stream were studied.

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 $\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (1 mol) and 185.7 g of $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ (0.5 mol) in 700 cm^3 of 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 of distilled water) and 100 g of Na_2CO_3 in 1000 cm^3 of distilled water. HT was prepared by adding solution A to solution B over 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 the pH of the filtrate became 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 an incipient wet impregnation method, using an aqueous solution of palladium chloride acidified with HCl (to effect the complete dissolution of the salt). The required amount of palladium chloride was taken so as to obtain the desired Pd concentration on the support and the solution was mixed with the 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 an Autosorb Automated Gas Sorption System (M/s. Quantachrome, USA) with N₂ 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 K α radiation ($\lambda = 1.5406 \text{ \AA}$) with a scan speed of 2° min^{-1} and a scan range of $2\text{-}80^\circ$ 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. A H₂/Ar (10 vol.% of H₂ 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 results are recorded on a Kratos Axis 165 XPS Spectrometer, with Mg-K α 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 % H₂ balance He flow at 673 K for 3 h. Transmission electron microscopy (TEM) results are recorded on a TECNAI FE1 G¹² Philips instrument using an LaB₆ filament at 120 kV. CO chemisorption was carried out at 303 K on a homemade pulse reactor to evaluate the dispersion and the metal particle size. In a typical experiment, about 100 mg of the catalyst sample was placed in a reactor of 8 mm i.d., and the catalyst sample was first reduced under a hydrogen flow at 673 K for 2 h,

then pre-treated at 673 K for 1 h under He flow and finally 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, we calculated the dispersion, particle size and metal area of Pd using a Pd metal cross sectional area of 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 the 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 on a GC (GC-17A, M/s. Shimadzu instruments, Japan) using a Zebron ZB-WAX capillary column 0.53 mm in dia. and 30 m long.

3. Results and Discussion

3.1. Characterisation

BET surface areas of calcined Pd supported catalysts are given in Table 1. Calcined hydrotalcite support has a surface area of about $214 \text{ m}^2\text{g}^{-1}$; the surface area of MgO and $\gamma\text{-Al}_2\text{O}_3$ is found to be $40 \text{ m}^2\text{g}^{-1}$ and $240 \text{ m}^2\text{g}^{-1}$ 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^- ions onto the MgO surface might have occurred, and hence there is no drastic decrease in the surface area [15]. The 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, $d = 2.25, 1.95, 1.38$) as 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, $d = 2.25, 1.95, 1.38$) as 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 $T_{\text{max}} \sim 425$ 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 $T_{\text{max}} \sim 760$ K indicates further consumption of hydrogen on all the catalysts, which may be attributed to the spillover of the hydrogen activated on metallic palladium onto the support [16,17]. No negative peak corresponding to β -PdHx decomposition is observed over Pd/HT

catalysts. The reason may be due to the 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, PdCl₂ or PdO gets reduced easily at ambient temperature to Pd metal, and further interacts with hydrogen, forming PdH_x, 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 - Al₂O₃, a negative peak corresponding to β -PdH_x 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 Pd²⁺. Two peaks, corresponding to Pd 3d_{3/2} and Pd 3d_{5/2}, are found in reduced Pd/HT, Pd/Al₂O₃ and Pd / MgO catalysts (Figs 3b, 4a and 4b). The binding energy values of Pd 3d_{5/2} and Pd 3d_{3/2} peaks in all the reduced catalysts are found to be around 335 eV and 341.5 eV respectively; such values indicate 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 -Al₂O₃, the 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]. The 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 better on hydrotalcite support than on other conventional supports such as MgO and γ -alumina, which is in accordance with the literature report [21]. The carbon contents of all the spent catalysts: 1 wt.% Pd/HT, 1 wt.% Pd/MgO and 1 wt.% Pd/ γ -Al₂O₃ are calculated from CHNS analyse; the values are given in Table 2. Among the three catalysts, the carbon content is found to be higher for alumina-supported palladium catalyst (17.26%) than for 1 wt.% Pd/MgO (3.50%) and 1 wt.% Pd/HT (2.27%). This is attributed to the acidic nature of the 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 -Al₂O₃ in the temperature region of 498-573 K. Figure 6 shows the influence of temperature on 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 to 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. The product selectivity towards aniline is around 98 % for all the catalysts. There may be a possibility of other products appearing during nitrobenzene

hydrogenation. However, the analysis of reaction products by GC has revealed that the major identifiable product is only aniline.

3.2.2. Effect of time on stream

Figure 7 shows the variation in the rate of nitrobenzene hydrogenation with time over supported palladium catalysts at 498 K. The reaction was studied for 5 h on all the catalysts. The rate of conversion of nitrobenzene was found to be same up to 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 would act as a poison. In the case of 1 wt.% Pd/HT, the decrease in activity may be attributed only 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 by a memory effect [22]. The decrease in rate of conversion of nitrobenzene in the case of MgO and γ -Al₂O₃-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 Al₂O₃ than on HT and MgO-supported spent catalyst.

3.3.3. Effect of support

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

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

The number of surface palladium sites is assumed to be equal to the number of CO moles adsorbed per gram of the catalyst. The turnover frequency for HT-supported Pd was found to be higher than on MgO and γ -Al₂O₃ 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 -Al₂O₃ 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 better on hydrotalcite support than on other conventional oxides such as MgO and γ -Al₂O₃. 1 wt.% Pd/HT shows higher activity at a lower temperature of 498 K when compared with 1 wt.% Pd/MgO and 1 wt.% Pd/ γ -Al₂O₃. However, the very low activity of 1 wt.% Pd/ γ -Al₂O₃ may be attributed to coke formation, as is evident from CHNS analysis.

The high activity of 1 wt.% Pd/HT can also be accounted for in terms of particle size measured from TEM images. These images show 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 supports (Fig. 5c). However, in the case of γ -Al₂O₃-supported Pd catalyst, the particle size of Pd is found to be bigger than those for other supports (Fig. 5b). Also values of Pd dispersion, metal surface area and particle size calculated from both CO chemisorption studies and TEM images agree well with each other. Further, the XPS peak due to PdO in Al₂O₃ is broader than those in MgO or HT (Figs. 3 and 4). The

peak broadening of Pd 3d_{5/2} peak in XPS also indicated the presence of a large amount of Pd in the bulk rather than on the surface, which is not beneficial for hydrogenation activity. Such a broadening of the peak is not observed on HT- and MgO-supported Pd catalysts. Hence, such XPS results also support the conclusion that Pd is more finely dispersed on hydrotalcite support when compared with other supports. Carbon deposits estimated on the spent catalysts 1 wt. % Pd/HT, 1 wt. % Pd/MgO and 1 wt. % Pd/ γ -Al₂O₃ (Table 2) also reveal the difference in the nature of the supports. γ -Al₂O₃ being an acidic support is found to possess large amounts of carbon deposit. The other two supports being basic in nature possess low amounts of carbon deposit.

Hydrotalcite support is basic in nature. Palladium gets anchored on the hydrotalcite support, and because of the anchored Pd, the possibility for agglomeration or aggregation of Pd on hydrotalcite support is reduced. Finely dispersed Pd particles on hydrotalcite support may be responsible for the observed reactivity. The detailed mechanistic aspects of the reaction is under investigation.

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 -Al₂O₃ supported Pd catalysts. The reason for the high activity has been attributed to the presence of a larger number of finely dispersed Pd particles on the surface and to the highly basic nature of the 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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Figure Captions**Figure 1** : XRD patterns of reduced catalystsa: 1wt.% Pd/ γ -Al₂O₃, b: 1wt.% Pd/HT, c: 1wt.% Pd/MgO**Figure 2** : TPR profiles of calcined catalystsa: 1wt.% Pd/HT, b: 1wt.% Pd/MgO, c: 1wt.% Pd/ γ -Al₂O₃**Figure 3** : XPS spectra of 1 wt.%Pd/HT catalysts

a: Calcined, b: Reduced

Figure 4 : XPS spectra of reduced catalystsa: 1wt.% Pd/MgO, b: 1wt.% Pd/ γ -Al₂O₃**Figure 5** : TEM images of reduced catalystsa: 1wt.% Pd/HT, b: 1wt.% Pd/MgO, c: 1wt.% Pd/ γ -Al₂O₃**Figure 6** : Effect of temperature on rate of nitrobenzene hydrogenationa: 1wt.% Pd/HT, b: 1wt.% Pd/MgO, c: 1wt.% Pd/ γ -Al₂O₃Catalyst: 0.5 g, GHSV: 1500 h⁻¹, H₂flow: 1 lh⁻¹**Figure 7** : Effect of time on stream on rate of nitrobenzene hydrogenationa: 1wt.% Pd/HT, b: 1wt.% Pd/MgO, c: 1wt.% Pd/ γ -Al₂O₃T: 498 K, Catalyst: 0.5 g, GHSV: 1500 h⁻¹, H₂flow: 1lh⁻¹**Figure 8** : Turnover frequency for hydrogenation of nitrobenzeneCatalyst = 0.5 g, GHSV = 1500 h⁻¹, H₂ flow = 1 lh⁻¹

Table. 1: Surface area, dispersion, and particle size of supported palladium catalysts

Catalyst	Surface area (m ² g ⁻¹)	CO Uptake (μmol 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 ₂ O ₃	221 (240)*	13	14	0.616	8.5

* Supports without Pd loading

^a % Dispersion = [CO uptake (μmol g⁻¹) X 100]/ [total Pd (μmol 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 nm²

^c Particle size (nm) = 6000/[metal area (m² 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 ₂ O ₃	17.26

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