

Letter

# Highly active hydrotalcite supported palladium catalyst for selective synthesis of cyclohexanone from phenol

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## Abstract

Hydrogenation of phenol was studied over uncalcined and calcined hydrotalcite supported palladium catalysts and compared with the conventional  $\Gamma$ - $\text{Al}_2\text{O}_3$  and MgO supported catalysts. Pd on uncalcined hydrotalcite support (Pd/UHT) showed very high conversions ( $\geq 95\%$ ) and high selectivities ( $\geq 85\%$ ) towards cyclohexanone. These catalysts maintained their activity for nearly 4 h and the results are presented.

*Keywords:* Palladium; Hydrotalcite; Supported catalyst; Phenol hydrogenation

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## 1. Introduction

Cyclohexanone is an important intermediate for the production of caprolactum and nylon. More than 80% of the world's production of cyclohexanone is carried out by the oxidation of cyclohexane.

This process requires high temperatures and high pressures and also produces undesirable side products. Cyclohexanone can also be produced by hydrogenation of phenol either in the liquid or the vapour phase [1]. The vapour phase hydrogenation involves a two-step process which is energy intensive and expensive and has been replaced by a low cost phenol to cyclohexanone process [2]. As part of our involvement in the hydrogenation of aromatic hydrocarbons and functional aromatics, we have been studying the hydrogenation of phenol over several supported Ni catalysts [3,4]. Our approach to the catalyst develop-

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ment is mainly to enhance the cyclohexanone selectivity with good conversion of phenol. In this connection we have been experimenting with anionic clays as supports for metals such as Pd, Ni, and Pt for phenol hydrogenation.

Anionic clays, particularly hydrotalcites (HT), have attracted much attention in recent years because of their use in base catalysed reactions [5]. HTs have brucite-like positively charged layers of magnesium and aluminium hydroxide octahedra sharing edges and have interstitial carbonate anions to compensate the charges. The anionic clays can be synthetically made and the modification of the clay is possible by substitution of the  $\text{Mg}^{2+}$  with other cations. The structural modification can also be affected by calcination. HT materials containing Ni in place of Mg have been found to be good hydrogenation catalysts [6]. Hydrogenation of phenol is a well known and an important industrial reaction where the selectivity for the cyclohexanone is a primary objective especially if it can be achieved in a single step. Several supported metal catalysts such as Ni on  $\gamma\text{-Al}_2\text{O}_3$  or C or precious metal containing catalysts such as Pd or Pt supported on oxides, zeolites or carbon have been studied for this reaction [3,4,7–9]. Even though the selectivity towards cyclohexanone has been reported to be nearly 100% the conversion levels have not been as high as reported in this communication. To the best of our knowledge there is no information available as such on using HT materials as support for dispersing palladium. In this communication phenol hydrogenation over palladium supported on uncalcined and calcined hydrotalcite is reported for the first time. The results are compared with Pd/MgO and Pd/ $\text{Al}_2\text{O}_3$  catalysts.

## 2. Experimental

HT is prepared as per the method described by Reichle et al. [10]. The chemicals used are of GR grade from Loba chemie. Solution A was prepared by dissolving 250 g  $\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  (1 mol) and 187.5 g  $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$  (0.5 mol) in 700  $\text{cm}^3$  distilled water. Solution B was prepared by dissolving 280 g of 50% aqueous NaOH (3.5 mol) and 100 g of anhydrous  $\text{Na}_2\text{CO}_3$  (0.943 mol) in 1000  $\text{cm}^3$  distilled water. Solution A was added to solution B in about 6 h at room temperature under vigorous stirring. After complete addition the contents were heated to  $338 \pm 5$  K for about 18 h under good stirring. The contents were cooled and washed with distilled water thoroughly until the pH was neutral. The white crystalline material was dried in an oven at 373 K for 24 h. This is termed as uncalcined hydrotalcite (UHT). The UHT was then calcined in air at 723 K for 18 h to get its oxide form. This is termed calcined hydrotalcite (CHT). UHT, CHT, MgO (Harshaw, Surface area 40  $\text{m}^2 \text{g}^{-1}$ ) and  $\gamma\text{-Al}_2\text{O}_3$  (Harshaw Al 111-61E, surface area 240  $\text{m}^2 \text{g}^{-1}$ ) in powdered form were all impregnated with an aqueous solution of  $\text{PdCl}_2$  acidified with a drop of conc. HCl in order to make sure the complete dissolution of the salt. The surface area of the support

was measured by the single point BET method using Micromeritics 2700 pulse chemisorb instrument. CO uptake was measured in an all glass high vacuum system capable of producing  $1 \cdot 10^{-6}$  torr. Before adsorption the catalysts were reduced for 3 h at 573 K and evacuated at that temperature for 2 h. CO adsorption isotherms were constructed at room temperature on the degassed catalysts. The irreversible CO chemisorption was used for calculating the CO uptake of the catalysts. XRD patterns of the support as well as Pd loaded HTs were taken in a Philips instrument using  $\text{CuK}_\alpha$  radiation. Vapour phase phenol hydrogenation was carried out at 453 K over 0.5 g of powdered catalyst packed between layers of quartz wool and glass beads in a vertical tubular quartz reactor of 2 cm diameter and 40 cm long. The reaction mixture containing phenol and cyclohexane (1:4 wt./wt.) was added from the top of the reactor at a controlled rate with the help of a motorised syringe. Hydrogen was used as a reductant and a carrier gas. The feed rate was altered and H/phenol was maintained at 4. The liquid products collected at the bottom of the reactor was analysed by a gas chromatograph fitted with Apiezon L column of 2 m length and 3 mm diameter in a programmed mode in the temperature region 393–433 K at a heating rate of  $20^\circ\text{C min}^{-1}$ . The products were identified as cyclohexanone, cyclohexanol and unreacted phenol. The reported conversions and selectivities are based on gas chromatographic analysis.

### 3. Results and discussion

The surface area and pore volume of UHT are  $90 \text{ m}^2 \text{ g}^{-1}$  and  $0.7 \text{ cm}^3$ , respectively. On calcination at 723 K the surface area and pore volume have increased to  $220 \text{ m}^2 \text{ g}^{-1}$  and  $1.1 \text{ cm}^3$ , respectively. The loss of interstitial water and the loss of carbon dioxide and water due to decarbonation and dehydroxylation leads to amorphous oxide with high surface area [10]. The UHT support did not show any change in surface area due to the addition of acidified  $\text{PdCl}_2$  for the preparation of Pd/UHT by impregnation. The Pd/UHT catalyst used for reaction (reduced at 573 K before carrying out reaction at 453 K) showed an increase in surface area from  $90 \text{ m}^2 \text{ g}^{-1}$  to  $120 \text{ m}^2 \text{ g}^{-1}$ .

X-ray examination of the prepared fresh samples is comparable with that of hydrotalcite. The CHT showed the XRD peaks corresponding to those of MgO. The XRD pattern of the Pd/UHT is similar to that of UHT indicating no change in the structure. Pd/UHT showed sharp XRD peaks at  $2\theta = 11.5$  and  $22.7$ . Pd/UHT used for reaction, showed a broadened peak at  $2\theta = 11.5$  with the disappearance of a peak at  $2\theta = 22.7$ . The broad peak at  $2\theta = 11.5$  could be characterised due to the partial dehydroxylation/decarbonation or HT of poor crystallinity. This is also evident from the increase in surface area of the used Pd/UHT catalyst.

In Table 1, the CO uptake of the supported palladium catalysts, which is a

Table 1  
Conversion and selectivity of various catalysts

Catalyst	CO uptake % (cm <sup>3</sup> g cat <sup>-1</sup> )	Conversion	Selectivity <sup>a</sup> (%)	
			=O	-OH
1 wt.-% Pd/UHT <sup>b</sup>	1.80	98	87	13
2 wt.-% Pd/UHT <sup>b</sup>	2.00	98	86	13
1 wt.-% Pd/CHT	0.55	40	97	3
2 wt.-% Pd/CHT	1.43	65	94	6
3 wt.-% Pd/CHT	1.70	79	89	11
5 wt.-% Pd/CHT	2.30	90	84	16
2 wt.-% Pd/MgO	0.56	20	98	2
2 wt.-% Pd/Al <sub>2</sub> O <sub>3</sub>	0.38	10	100	0

<sup>a</sup> =O, cyclohexanone; -OH, cyclohexanol.

<sup>b</sup> These two catalysts were reduced at 573 K and the others were reduced at 623 K.

reflection of the metal surface area along with the phenol conversions and selectivities are given. Pd/UHT catalysts showed large CO uptake compared to that of Pd on CHT, Al<sub>2</sub>O<sub>3</sub> or MgO. The conversion follows the same trend as that of CO uptake. 2 wt.-% Pd supported on  $\Gamma$ -Al<sub>2</sub>O<sub>3</sub> and MgO shows a conversion of about 10–20% only even though the selectivity for cyclohexanone is nearly 100%. HT supported Pd catalysts on the other hand, show comparatively very high conversions ( $\geq 95\%$ ) with a good selectivity for cyclohexanone (84–97%). Among the HT catalysts, the UHT catalysts show higher conversions compared with the corresponding CHT supported Pd catalysts. On increasing Pd content from, say, 1 to 5 wt.-% the CHT shows equally good conversion of nearly 90% with high selectivity for cyclohexanone.

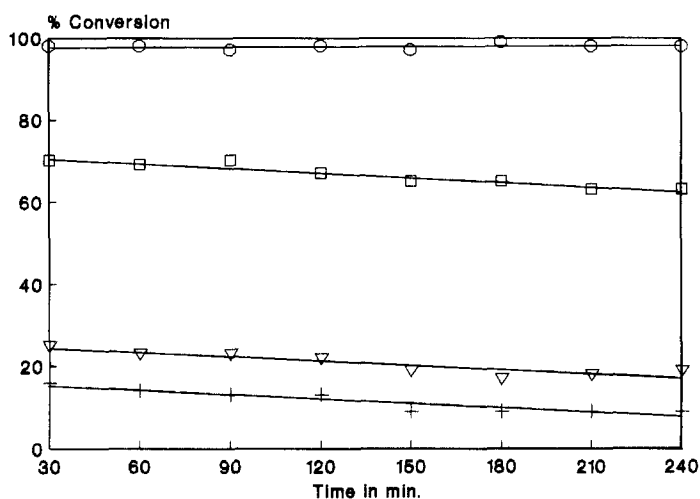


Fig. 1. Effect of time on stream.  $T = 453$  K,  $H/\text{phenol} = 4$ .  $\circ$ , 2 wt.-% Pd/UHT;  $\nabla$ , 2 wt.-% Pd/MgO;  $\square$ , 2 wt.-% Pd/CHT;  $+$ , 2 wt.-% Pd/Al<sub>2</sub>O<sub>3</sub>.

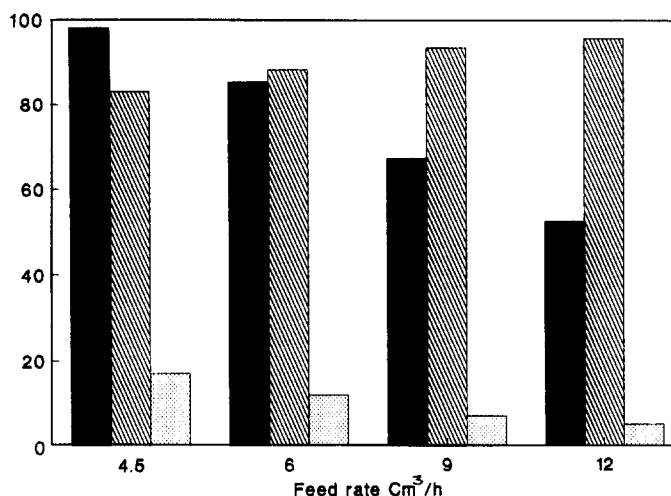


Fig. 2. Effect of feed rate on 2 wt.-% Pd/UHT.  $T = 453$  K,  $H/\text{phenol} = 4$ . Shaded area, conversion; striped area, =O; dotted area, -OH.

Time on stream of 2 wt.-% Pd loaded on different supports viz.,  $\gamma\text{-Al}_2\text{O}_3$ , MgO, CHT and UHT are shown in Fig. 1. The UHT supported catalyst shows stable activity with time on stream compared to  $\gamma\text{-Al}_2\text{O}_3$ , MgO and CHT. In Fig. 2 the effect of contact time in terms of phenol-cyclohexane mixture feed over 2 wt.-% Pd/UHT is given. If the feed rate increases, the conversion decreases and thus the formation of cyclohexanol. Cyclohexanone selectivity increases though slightly (80–95%) at the expense of cyclohexanol.

Further studies are on to find out the dependence of hydrogenation activity on the structure, method of preparation and the influence of anion present in the interlayer of the hydrotalcite.

#### 4. Conclusion

From the foregoing it may be derived that hydrotalcite (HT), an anionic synthetic clay with basic properties may be a good material for supporting metals such as palladium. HT supported catalysts containing palladium (1–5 wt.-%) have been found to be very selective for phenol hydrogenation with a conversion of greater than 95%. This promising observation is presented in this communication for the first time using hydrotalcite supported palladium catalysts.

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