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Structure activity relationship in Pd/hydrotalcite: effect of calcination of hydrotalcite on palladium dispersion and phenol hydrogenation

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Abstract

Hydrotalcites (HTs) are prepared by low supersaturation and high supersaturation methods containing Mg^{2+} and Al^{3+} cations in the brucite-like sheets and having interlayer CO_3^{2-} anions. Pd/HT with Pd^{2+} in the brucite layer was also prepared for comparison. Catalysts containing 1 wt% of Pd are prepared by impregnation method using different Pd precursors. HT and Pd on HT samples are well characterised by XRD and surface area analysis. CO chemisorption is used to estimate the dispersion and metal area of Pd. The supported metal catalysts are evaluated for phenol hydrogenation. Metal dispersion and catalytic activity depend on the calcination temperature of the HT support. © 1999 Elsevier Science B.V. All rights reserved.

Keywords: Hydrotalcite; Palladium dispersion; Phenol hydrogenation

1. Introduction

Supported metal catalysts are widely being used in various organic transformation reactions, especially hydrogenation. Among supported noble metal catalysts, palladium is one of the most frequently used metals for hydrogenation reactions at laboratory level as well as industrial scale. The supported metal systems are usually characterised by several techniques to measure metal dispersion and its availability because the hydrogenation reaction depends on them. In spite of the vast information available on the supported metal system, there is always a growing interest in finding new supports and adopting new techniques to disperse the metal more efficiently and improve the

catalytic activity and selectivity. Selective hydrogenation of molecules involving C=C and C=O is important in producing speciality chemicals. Therefore, the design and development of specific supported metal catalysts is a challenging task.

In recent times, a new class of materials namely layered double hydroxides (LDHs) are gaining importance as catalysts for base catalysed reactions and also as supports for dispersing metals [1]. Pd and Pt supported over stabilised magnesia derived from LDH precursors have shown high aromatic selectivity in reforming reactions [2–4]. The electronic properties of the metals supported on stabilised MgO have been probed by calorimetry and IR spectra of adsorbed CO on catalysts [5,6]. The studies also gave evidence for the electronic effect of the support on the metal [6]. Basile et al. [7] have demonstrated the homogeneous distribution of Rh^{3+} and Ru^{3+} inside the brucite-like

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layer which on calcination and reduction gave rise to well-dispersed stable metal particles. These materials have been successfully tested for partial oxidation of methane. From the studies reported on HT supported metal systems, it is evident that the preparation method of the support, calcination and reduction temperatures and the metal precursors affect the dispersion of metal to a different extent. The methodology adopted in preparing HT and HT supported metal catalysts are so varied and there is a lack of systematic investigation. In this study, we have attempted to investigate the effect of a few variables which can change the physico-chemical properties of HT such as M^{2+} and M^{3+} ions, their ratios, the morphology of HT and metal dispersion. The basic support materials are well characterised by XRD and surface area measurements. The supported metal catalysts are further characterised by CO chemisorption and are evaluated for industrially important phenol hydrogenation to produce selectively cyclohexanone. Pd/HT systems are also being tried [8] for another useful reaction, viz., acetone to methyl isobutyl ketone (MIBK).

2. Experimental

2.1. Preparation of HTs and PDHTs

2.1.1. HTA and HTB

Hydrotalcite is prepared according to the method given in [9], by co-precipitating from required volumes of aqueous solutions of $Mg(NO_3)_2 \cdot 6H_2O$ (1 mol) and $Al(NO_3)_3 \cdot 9H_2O$ (0.5 mol) ($x=Al(III)/(Al(III)+Mg(II))=0.33$) with a solution of NaOH (3.5 mol) and Na_2CO_3 (1 mol), at $pH > 13$ (high supersaturation). The salt solution is added to the base solution with stirring. Crystallisation was done at 333 K for 18 h and 473 K for 45 h, filtered and washed several times with hot distilled water until the pH became neutral and were designated as HTA and HTB, respectively.

2.1.2. HTC

Precipitation was carried out by simultaneously adding a solution containing calculated amounts of $Mg(NO_3)_2 \cdot 6H_2O$ (1 mol) and $Al(NO_3)_3 \cdot 9H_2O$ ($x=0.33$), and a solution containing NaOH (2 M) and Na_2CO_3 (0.2 M) [10]. The pH was maintained

between 9 and 10 (low supersaturation) by adjusting the addition of the salt and the base solution. Crystallisation was done at 333 K for 18 h. The material was washed with hot distilled water until the pH became neutral and was designated as HTC.

2.1.3. HTD, HTE and HTF

HTs D–F with different Al contents, $x=0.15$, 0.20 and 0.30, respectively, were prepared by co-precipitation at high supersaturation. A solution of 128.2 g of $Mg(NO_3)_2 \cdot 6H_2O$ (0.5 mol) and 33.1–101 g of $Al(NO_3)_3 \cdot 9H_2O$ (0.08–0.27 mol) taken in 350 cm^3 distilled water is added to a solution of 60 g of NaOH (1.5 mol) and 50 g of Na_2CO_3 (0.47 mol) in 500 cm^3 distilled water. For the HTD sample, at the end of precipitation, a solution containing 6 g of $Al(NO_3)_3$ is added drop wise with stirring. This is done in order to introduce an impure alumina phase. The precipitates obtained are crystallised at 333 K for 18 h. The slurry is cooled to room temperature, filtered and washed several times with hot distilled water until the pH is neutral.

2.1.4. PDHT with Pd^{2+} in the brucite-like sheet, HTG

Hydrotalcite (HTG) is prepared by co-precipitating from required volumes of aqueous solutions of $Mg(NO_3)_2 \cdot 6H_2O$, $Al(NO_3)_3 \cdot 9H_2O$ and $Pd(NO_3)_2$, with a solution containing NaOH and Na_2CO_3 , at high supersaturation. Palladium nitrate was taken in such a way to get 1 wt% of palladium on the support after calcination. Crystallisation was done at 313 K for 18 h. The incorporation of the Pd^{2+} in the brucite-like sheet is confirmed by XRD.

2.1.5. Pd supported on HT (PDHTs)

Onto HT supports (except HTG), prepared by various methods, $PdCl_2$ acidified with HCl (to effect the complete dissolution of the salt) was impregnated so as to get 1 wt% of Pd. Ca. 1 wt% Pd was also loaded on HTA support calcined at different temperatures and was used for chemisorption and catalysis experiments. $Pd(NH_3)_4Cl_2$ palladium precursor was also used to load 1 wt% of Pd on the calcined HT supports. Calcination is done in air at 723 K for 18 h.

Table 1
Preparation conditions of HTs and their surface area

Code	Mg ²⁺ /Al ³⁺	$x = \text{Al(III)}/(\text{Al(III)} + \text{Mg(II)})$	Crystallisation temperature (K)	Phases present by XRD	Surface area (m ² g ⁻¹)
HTA	Mg ²⁺ /Al ³⁺	0.33	333	HT	54
HTB	Mg ²⁺ /Al ³⁺	0.33	473	HT	17
HTC	Mg ²⁺ /Al ³⁺	0.33	333	HT	66
HTD	Mg ²⁺ /Al ³⁺	0.15	333	HT, boehmite	107
HTE	Mg ²⁺ /Al ³⁺	0.20	333	HT	61
HTF	Mg ²⁺ /Al ³⁺	0.30	333	HT	47
HTG	Pd ²⁺ , Mg ²⁺ /Al ³⁺	0.30	313	HT	65

All HTs are prepared at high supersaturation condition (pH \geq 13) except HTC (pH \approx 10). All HTs are crystallised for 18 h except HTB (45 h).

2.2. Characterisation

X-ray powder diffraction patterns of HT samples were recorded with a Philips 1051 X-ray diffractometer with nickel filtered Cu K α radiation ($\lambda = 1.5405 \text{ \AA}$). SEM pictures were taken using Hitachi S-800. Surface area was measured by using Micromeritics Pulse Chemisorb 2700 instrument. CO uptake was measured at room temperature on the reduced Pd/HT sample (1 wt% Pd/HT catalysts are reduced in flowing hydrogen at 573 K for 3 h) in an all glass high vacuum constant volume apparatus as described earlier [11,12]. A stoichiometry of CO:Pd=1 for dispersion calculations was assumed. Crystallite size is calculated on the basis of spherical particles of Pd and surface density of 1.27×10^{19} atoms/m² [13].

Table 1 gives the description of preparation conditions of HTs, Al contents in the brucite layer (x values), the XRD phases present and the surface areas.

2.3. Phenol hydrogenation

Vapour phase hydrogenation of phenol was carried out over ca. 0.1–0.2 g of Pd/HT catalysts at 453 K in a vertical down flow reactor. Before catalysis, the fresh sample was reduced in hydrogen at 573 K for 3 h. The reaction mixture containing phenol and the diluent cyclohexane (1:4 w/w) was added from the top of the reactor at a controlled rate, 4.5 ml/h, with the help of a calibrated motorised syringe. H₂/phenol mole ratio was maintained at 4. The reaction products were analysed on a Chemito 3865 chromatograph with an Apiezon L treated with 2% KOH (2 m long) column. The experimental set-up and conditions are described elsewhere [11,12].

3. Results and discussion

The XRD patterns of some of the HT samples prepared by the authors are shown in Fig. 1. A well-crystallised HT structure is present in all the samples without any significant impurity phase. HTB was hydrothermally treated at 473 K in an autoclave and it showed more intense peaks than the samples crystallised at 333 K. HTC prepared at pH=10 showed the presence of relatively broad basal reflection ($d_{(0\ 0\ 3)}$ and $d_{(0\ 0\ 6)}$) indicating disorder in the stacking of the layer. Sample HTD shows an impurity phase corresponding to that of aluminium oxyhydroxide (Fig. 1(d), *).

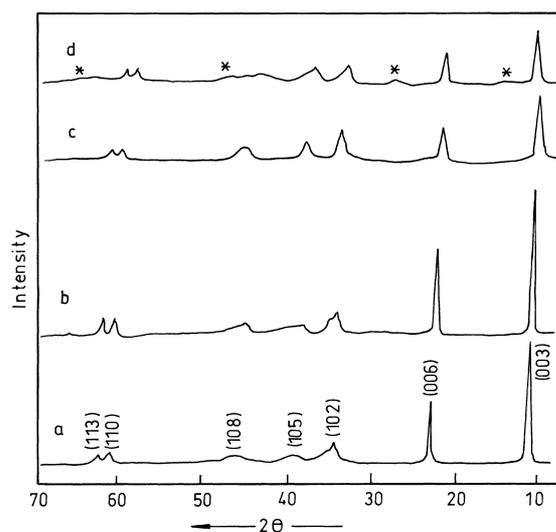


Fig. 1. XRD patterns of: (a) HTA, (b) HTB, (c) HTC, and (d) HTD.

Table 2
Adsorption and catalytic properties of 1 wt% Pd/HTs

Catalyst	CO uptake (cm ³ g ⁻¹ cat)	Pd dispersion (%)	Crystallite size (nm)	Phenol conversion (%)	Cyclohexanone selectivity (%)
Pd/HTA	1.22	58	1.9	98	92
Pd/HTB	0.96	46	2.4	70	93
Pd/HTC	0.60	29	3.8	50	98
Pd/HTD	0.90	43	2.6	75	95
Pd/HTE	0.93	44	2.5	86	95
Pd/HTF	1.20	58	1.9	94	93

Uncalcined HTs dried at 373 K. Weight of the catalyst for reaction=0.200 g. WHSV=0.037 mol h⁻¹ g⁻¹ cat.

The surface area of the HT samples except HTB and HTD are in the region 47–66 m² g⁻¹. Except HTD and HTE, the samples have the Al(III)/(Al(III)+Mg(II)) ratio of around 0.30. The samples HTB and HTD differ widely in their surface area. The low surface area of HTB (17 m² g⁻¹) may be attributed to the hydrothermal treatment which might have resulted in high crystallinity as evidenced from XRD. The HTD sample has a large surface area of 107 m² g⁻¹. The HTD sample has a lower Al content in the brucite layer (lower *x* value) compared to others and it has also got boehmite impurities. According to XRD, the sample is not very crystalline. The impure phase and also the amorphous nature of the sample might have contributed to the large surface area.

Adsorption and catalytic properties of 1 wt% Pd supported on HTs are given in Table 2. Although the catalysts contain 1 wt% of palladium, the CO uptake per gram of the catalyst varies from 0.6 to 1.22 cm³ g⁻¹ cat. There seems to be no dependence of surface area on palladium dispersion. For example, Pd on HTB having a surface area of 17 m² g⁻¹ and Pd on HTD with a surface area of 107 m² g⁻¹ show a dispersion of 46% and 43%, respectively. Therefore, the differences in the CO uptake can only be explained by the differences in the Al(III)/(Al(III)+Mg(II)) ratio and the structural differences arising from the preparation conditions. The differences in dispersion could also be due to the morphology and crystallinity of the hydroxalcite support. For example, XRD and SEM reveal that the morphology of HTC prepared at low supersaturation condition is completely different [10]. When acidified PdCl₂ solution is impregnated over HT having CO₃²⁻ interlayer anion, PdCl₄²⁻ replaces the anion at the edges leading to a good dispersion of palladium on reduction [12]. HTA with

Al content 0.33 (*x*) prepared at high supersaturation and having small crystallites have more number of CO₃²⁻ sites at the edges helping palladium dispersion. On the other hand, HTC with Al content 0.33 (*x*) prepared at low supersaturation condition shows a larger crystallite morphology and therefore exposes less number of CO₃²⁻ anions. Furthermore, HTC shows layer disorder as evidenced by XRD. Therefore, most of the palladium precursor probably are deposited on the surface contributing to a low dispersion of 29%. The increase of Al(III)/(Al(III)+Mg(II)) ratio from 0.15 to 0.30 increases the palladium dispersion. The high Al content contributes to the number of CO₃²⁻ anion sites which seem to have a bearing on palladium dispersion.

Phenol conversion over the catalysts varies from 50% to 98%, which seems to be related to the palladium dispersion and the availability of palladium for the reaction. Irrespective of the conversion level, cyclohexanone selectivity is always greater than 90%. The palladium supported on HT catalysts showed better conversion and stabilities compared to the conventional Pd/Al₂O₃ and Pd/MgO catalysts [11,12].

Phenol hydrogenation was carried out on the catalysts reduced at 573 K for 3 h. The reduction treatment contributes to the destruction of the layered structure. The surface area of the catalyst after reduction is slightly higher than that of the parent HT by about 10 m² g⁻¹. The XRD patterns of the reduced samples show characteristic HT peaks as well as diffused MgO peaks. The metal dispersion measurements are made on the reduced samples and therefore, the phenol conversion can be directly related to the metal availability.

In Fig. 2(A), the change in surface area of HTA sample due to calcination is shown. The samples are

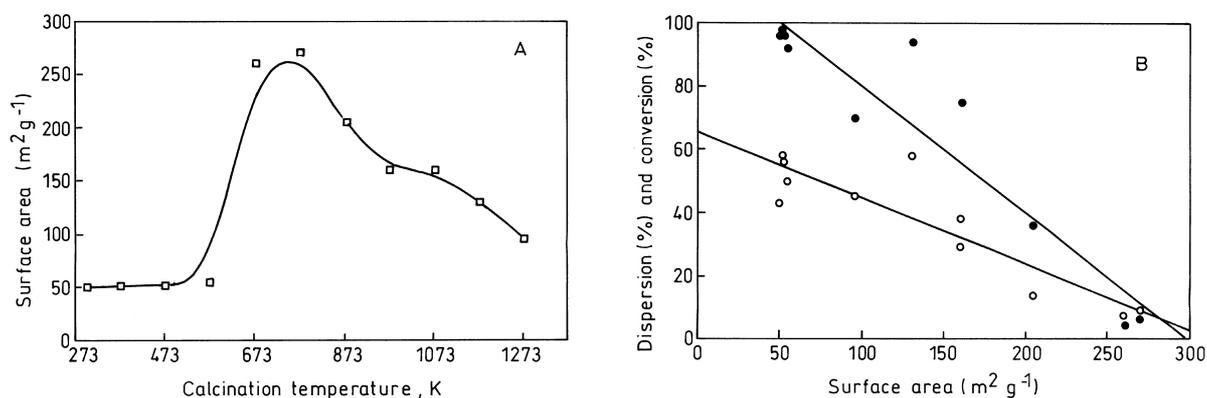


Fig. 2. (A) Effect of calcination temperature of HTA on surface area (\square), and (B) relationship between surface area, dispersion (\circ) and phenol conversion (\bullet).

calcined at different temperatures for 4 h. The surface area is nearly the same, around $50 \text{ m}^2 \text{ g}^{-1}$ upto a calcination temperature of 573 K beyond which it increases and reaches a maximum of about $300 \text{ m}^2 \text{ g}^{-1}$ around 700 K. With further calcination, the surface area falls. The change in surface area may be explained based on the changes in structural features of HT. Calcination disturbs the layered structure with the formation of $\text{MgO-Al}_2\text{O}_3$ mixed oxide phase which is amorphous and contributes to the surface area. It is also possible that during calcination, the carbonate anions (CO_3^{2-}) are removed as CO_2 accompanied by dehydroxylation. This creates voids and contribute to the surface area. With further calcination beyond 873 K, it is likely that the surface MgAl_2O_4 spinels and crystalline MgO are formed, contributing to the decrease in surface area [12].

1 wt% Pd was loaded onto the HTA samples calcined at different temperatures. It is expected that a large surface of the support would contribute to better dispersion. However, it is found that (Fig. 2(B)) the HTA sample calcined around 700 K shows a low dispersion of 10%, even though the surface area of the support is about $300 \text{ m}^2 \text{ g}^{-1}$. The samples calcined at lower temperatures (273–573 K) as well as the samples calcined beyond 873 K show higher dispersion. It may be derived that surface area is not the only factor which decides the dispersion and the structural properties of HT support also influence the metal dispersion.

As we said earlier, the carbonate interlayer anions may help dispersion when the support is calcined at

low temperature and the layered structure is maintained. It appears that the crystalline MgO phase in combination with spinel MgAl_2O_4 also favours palladium dispersion. Phenol hydrogenation is in conformity with the variation in dispersion calculated by CO chemisorption. Phenol conversion and cyclohexanone selectivity are $>90\%$ and this trend is maintained for 4 h on PdHTA having layered structure (low calcination temperature) compared to Pd on HTA with crystalline MgO and MgAl_2O_4 phases having low surface area formed because of high calcination temperatures. The possibility of agglomeration of Pd when supported over crystalline material is high.

Different HTs (HTA to HTF) varying in Al content and precipitation conditions are subjected to calcination at 723 K for 18 h. As observed in Fig. 2(A) for HTA, the surface area of all the calcined HTs increased 4–5 times. Ca. 1 wt% Pd was loaded onto these calcined samples using $\text{Pd}(\text{NH}_3)_4\text{Cl}_2$. In spite of the large surface area of calcined samples, Pd dispersion is less compared to the corresponding uncalcined HT (Table 2). The availability of Pd has been measured by CO uptake. Crystallite size of Pd samples are large because of low Pd dispersion.

Hydrogenation of phenol depends on palladium availability and therefore, the low dispersion of Pd on the calcined sample leads to low conversion of phenol as can be seen from Table 3. The selectivity for cyclohexanone on these samples is around 85%. From the observation of Pd dispersion discussed here as well as the effect of calcination on HTA shown in Fig. 2(A) and (B), it is clear that the large surface area does not

Table 3
Adsorption and catalytic properties of 1 wt% Pd/on calcined HTs

Catalyst	Surface area of HT ($\text{m}^2 \text{g}^{-1}$)	CO uptake ($\text{cm}^3 \text{g}^{-1} \text{cat}$)	Pd dispersion (%)	Crystallite size (nm)	Phenol conversion (%)	Cyclohexanone selectivity (%)
1 Pd/HTA	237	0.30	14	7.9	10	98
1 Pd/HTB	127	0.45	21	5.3	29	75
1 Pd/HTC	240	0.18	9	12.4	5	99
1 Pd/HTD	190	0.61	29	3.8	33	94
1 Pd/HTE	215	0.20	10	11.1	5	100
1 Pd/HTF	223	0.29	14	7.9	8	100

HT calcined at 723 K/18 h, weight of the catalyst=0.200 g. WHSV=0.037 mol h⁻¹ g⁻¹ cat.

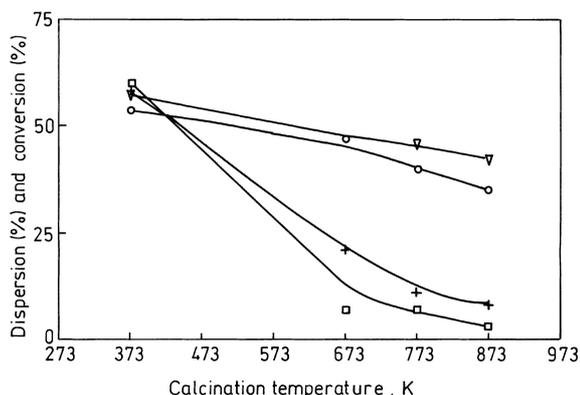


Fig. 3. Effect of calcination temperature of 1 wt% Pd/HTA and 1 wt% PdHTG on dispersion and phenol conversion (weight of the catalyst=0.100 g). Phenol conversion – (○) and (□); Pd dispersion – (▽) and (+).

contribute to the palladium dispersion. It is more likely that the structure of the hydrotalcite before calcination decides the palladium dispersion.

In Fig. 3, we are comparing two catalysts namely 1 wt% Pd/HTA and Pd/HTG containing 1 wt% of Pd. As we described in Section 2, 1 wt% Pd/HTA is prepared by impregnation method and 1 wt% PdHTG is prepared by incorporating Pd during precipitation of hydrotalcite. Therefore in PdHTG, palladium is expected to be in the layered structure and is also confirmed by XRD. These catalysts are subjected to different calcination temperatures (373–873 K) and the Pd dispersions are measured after reduction. The calcined samples are also evaluated for phenol hydrogenation. Both the Pd catalysts show similar dispersion of Pd and phenol hydrogenation properties when dried at 373 K. However, with the increase of calcina-

tion temperature, the Pd dispersion and phenol hydrogenation activity of 1 wt% Pd/HTA decreases more drastically than the 1 wt% of palladium containing HTG catalyst. From this observation, it may be derived that Pd when incorporated in the layered structure is more stable than the impregnated catalyst even when calcined at 873 K. Similarly thermal stability was also observed for Rh³⁺ and Ru³⁺ when isomorphously substituted in HT [7].

4. Conclusions

Palladium hydrotalcite prepared at high supersaturation with Al content of 0.33 ($x \approx 0.33$) can be used as a good support in uncalcined form for palladium dispersion and the supported palladium catalyst shows good phenol hydrogenation with >90% conversion and selectivity for cyclohexanone. More than the surface area, the brucite structure and the carbonate anions are responsible for the palladium dispersion. Though palladium on crystalline MgO and MgAl₂O₄ spinel are also equally active for CO chemisorption and phenol hydrogenation, there is a faster catalytic deactivation with time compared to 1 wt% Pd on uncalcined hydrotalcite. 1 wt% Pd hydrotalcite catalyst with palladium incorporated in the brucite structure during precipitation shows stable dispersion even after high temperature (673–873 K) calcination treatments.

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