Structural influence of hydrotalcite on Pd dispersion and phenol hydrogenation

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An interesting structure dispersion relationship of Pd/hydrotalcite is studied by changing the calcination temperature of hydrotalcite support and evaluated for phenol hydrogenation.

Efforts are being directed towards searching for new and efficient supports for dispersing noble metals. Hydrotalcites (HTs) have brucite-like positively charged layers of magnesium and aluminium octahedra sharing edges and have interstitial carbonate anions.[1] Supported metal hydrotalcites have created much scientific interest because of their interesting properties in catalytic reforming.[2,3] However, not much attention has been paid to the characterization of hydrotalcite supported metals. We have investigated the high phenol hydrogenation activity of Pd/HT to cyclohexanone,[4] which is an important raw material for the production of caprolactam. Here we discuss, for the first time, the interesting changes in properties of the HT support with calcination and its influence on metal dispersion and hydrogenation activity.

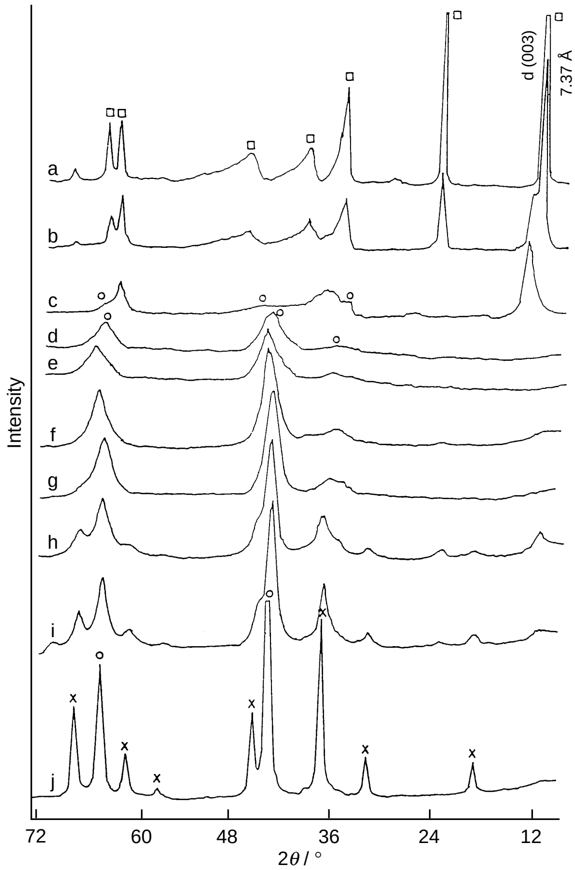

Fig. 1 XRD patterns of the hydrotalcites calcined at different temperatures (K): (a) 373, (b) 473, (c) 573, (d) 673, (e) 773, (f) 873, (g) 973, (h) 1073, (i) 1173 and (j) 1273. (□) HT, (○) MgO, (×) $MgAl_2O_4$.

HT was prepared according to the method described by Reichle *et al.*[5] HT was calcined in air for 4 h in the temperature range 473–1273 K and XRD patterns were recorded in air. Apart from calcined HTs, γ-Al_2O_3 and $MgAl_2O_4$ were also used as supports for loading 1 mass% of Pd. Impregnation was done with a standard $PdCl_2$ solution acidified with HCl. Surface area of the support and CO chemisorption on 1 mass% Pd/HT were measured. Phenol hydrogenation was carried out at 453 K over *ca.* 0.2 g of the catalyst at a phenol WHSV of 0.037 mol g^{-1} h^{-1}. The experimental details are given elsewhere.[4]

Fig. 1 shows XRD patterns of calcined HTs. The sample dried at room temperature (not shown) and 373 K showed the same diffraction patterns and $d_{(003)}$ basal spacing (7.37 A°) indicating retention of interlayer water. At 473 K, owing to the loss of gallery water, the basal spacing decreased by 0.56 Å. The patterns showed both anhydrous and hydrated HT, the latter might have formed owing to fast rehydration of HT.[6] The sample calcined at 573 K showed a basal spacing of 6.6 Å indicating dehydrated HT of low crystallinity along with MgO peaks. Between 373 and 573 K, the intensity of $d_{(003)}$ peak decreased, broadened and shifted towards higher 2θ values indicating the progressive destruction of the layered structure. Beyond 573 K, broad and diffuse peaks corresponding to mixed oxides of MgO are observed. With increase in calcination temperature the MgO peaks intensify and at 1073 K HT showed peaks representing a mixture of crystalline MgO and spinel $MgAl_2O_4$. At 1273 K mainly $MgAl_2O_4$ along with crystalline MgO are formed.

The surface area remained almost the same (Fig. 2) up to a calcination temperature of 573 K, indicating that the layered structure of HT is predominantly present. Beyond 573 K and up to 773 K, there is an increase in surface area. This is due to the loss of water and CO_2 which creates craters in the metal oxide sheet.[5] Above 773 K, there is a progressive decrease in surface area as the crystallinity of the material increases.

Fig. 2 shows the effect of calcination temperature of HT on dispersion and catalytic activity of Pd. Two maxima in dispersion (*ca.* 60%) and conversion ($\geqslant$90%) can be seen when

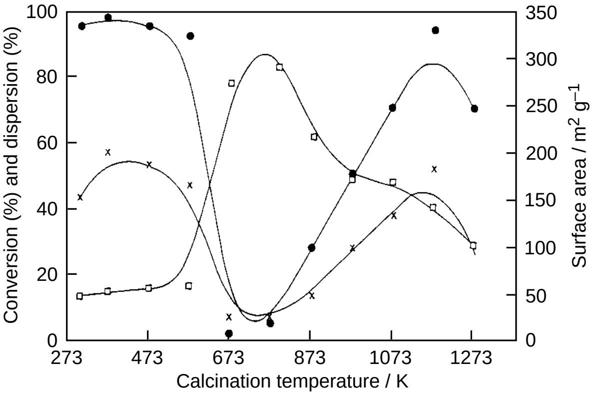

Fig. 2 Effect of calcination on surface area of HT, metal dispersion and activity of 1 mass% Pd/HT. (□) Surface area, (●) conversion (%), (×) dispersion (%).

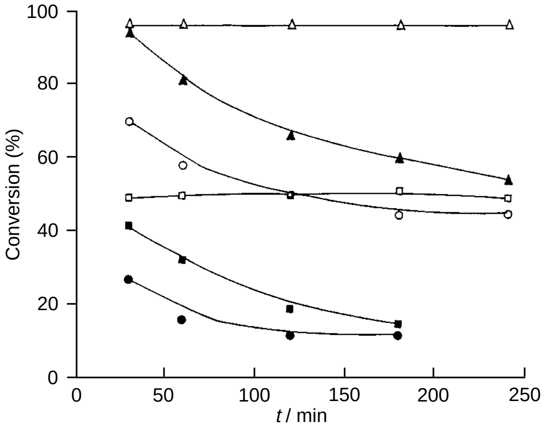

Fig. 3 Effect of time on stream over 1 mass% Pd/support. HT support calcined at different temperatures (K): (△) 373, (□) 973, (○) 1073 and (▲) 1173, (●) 1 mass% Pd/Al_2O_3, (■) 1 mass% Pd/$MgAl_2O_4$.

the support is calcined in the region of room temp. to 573 K and at 973–1173 K. The dispersion of Pd slightly increases when the support is dried at 373 K and calcined at 473 K compared to the support dried at room temp. and calcined at 573 K. There is an abrupt decrease in CO uptake when the support is calcined between 673 and 773 K, and CO uptake progressively increases up to a calcination temperature of 1173 K and again decreases thereafter. Despite a large surface area of HT having the MgO phase, the dispersion of Pd is low on these supports. There is no direct relationship between surface area of the support, which exists in different phases, and Pd dispersion indicating that the structural properties are playing a major role in metal dispersion. Phenol conversion follows the same trend as that of dispersion and metal area. The selectivity towards cyclohexanone is ⩾95%.

Acidification of $PdCl_2$ leads to $PdCl_4^{2-}$ anion which on impregnation replaces the carbonate anion at the external edge surface of the non-porous HTs. This interaction results in a fine dispersion of palladium precursor which on reduction gives highly dispersed palladium. The replacement of carbonate anion in the internal surface sites can be ruled out as there is no change in the basal spacing of the palladium-loaded HT (XRD not shown). The physically adsorbed water in room-temperature dried HT inhibits CO_3^{2-} access to $PdCl_4^{2-}$; therefore the deposition of the precursor is relatively more on the surface. This results in less dispersion of palladium compared to the sample dried at 373 K. The dispersion over HT dried at 373 K and calcined at 473 K is almost the same. This indicates that the structural water did not alter the dispersion as the precursor is mostly deposited by ion-exchange of CO_3^{2-} on the external edge surface. The dispersion is less over HT which is partially decarbonated and dehydroxylated and includes both the phases of MgO and HT. Even though aluminium is distributed uniformly throughout the HT layer, on calcination, alumina segregates out to the surface and as the calcination temperature increases the concentration of alumina on the surface increases. The increase in crystallinity of MgO and the segregation of Al_2O_3 to the surface with increase in calcination temperature in the range 673–973 K, improves the dispersion of Pd though the role of these two phases is not very clear. The dispersion of Pd on HT calcined in the range 1073–1273 K increases with the increase in $MgAl_2O_4$ phase and decreases over the support containing a large amount of crystalline MgO and $MgAl_2O_4$. The decrease in dispersion could be due to sintering of Pd on this highly crystalline phase. From Fig. 1 and 2 it is observed that there exists a correlation between dispersion of Pd and MgO/$MgAl_2O_4$ ratio with a maximum dispersion at an optimum ratio.

Fig. 3 shows time on stream over Pd/HT, Pd/Al_2O_3 and Pd/$MgAl_2O_4$. Pd/Al_2O_3, Pd/$MgAl_2O_4$ deactivate due to the formation of coke by the acid sites of alumina.[7] Pd/HT in which the support was calcined upto to 973 K did not show any appreciable deactivation. Spectroscopic techniques show that, on calcination of HT, a small portion of octahedral Al is converted to tetrahedral Al possibly residing on the surface and the amount increases with calcination temperature.[8] This alumina is in a local oxidic environment that does not favor the acid-catalysed reaction that typically occurs over alumina.[9] The stability of the catalyst, in which the HT is calcined up to 973 K, against coke formation could be explained based on the above observation. The role of impurities which may surface during calcination in preventing the catalyst from deactivation can not be ruled out. Above calcination at 973 K the HT shows a spinel $MgAl_2O_4$ phase and there is appreciable deactivation. The rate of deactivation increases with increase in spinel phase in the support.

Some interesting observations have been made in this study. Pd dispersion depends on the HT structure. Palladium is highly dispersed over HT having a layered structure with carbonate interlayer anions and also on a mixture of crystalline MgO and $MgAl_2O_4$ spinel. In spite of partial segregation of alumina to the surface during calcination it did not show appreciable deactivation in phenol hydrogenation which is a problem with acidic alumina. In summary HTs are attractive alternative supports for noble metals.

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Footnote and References

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