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Hydrogenation of ortho-nitrochlorobenzene on activated carbon supported platinum catalysts

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Abstract: Platinum/carbon catalyst is one of the most important catalysts in hydrogenation of ortho-nitrochlorobenzene to 2,2′-dichlorohydrazobenzene. The preparation process and the supports of catalysts are studied in this paper. Raw materials and preparation procedure of the activated carbon have great influences on the compositions and surface structure of platinum/carbon catalysts. Platinum catalysts supported on activated carbon with high purity, high surface area, large pore volume and appropriate pore structure usually exhibit higher activities for hydrogenation of ortho-nitrochlorobenzene to 2,2′-dichlorohydrazobenzene. The catalyst prepared from H_2PtCl_6 with pH=3 shows greater catalytic performance than those prepared under other conditions.

Key words: Platinum/carbon catalyst, Hydrogenation, Ortho-nitrochlorobenzene, 2,2′-dichlorohydrazobenzene, Activated carbon
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INTRODUCTION

2,2′-dichlorohydrazobenzene (DHB) is a commercially important intermediate, and is conventionally manufactured by zinc reduction of ortho-nitrochlorobenzene (Xu, 1996). The major disadvantage of this process is the generation of large amounts of sludge in reduction. A single step catalytic hydrogenation of ortho-nitrochlorobenzene to DHB using supported noble metal catalyst in the presence of aqueous sodium hydroxide medium becomes more important, because it is environmentally acceptable and the byproduct aniline is also a valuable product.

Brenner was the first person to disclose the method of using platinum/carbon catalyst and a sodium hydroxide (Brenner and Pricheet, 1964). Sulfides platinum/carbon catalyst has also been reported for the hydrogenation reaction (Baessler and Fuchs, 1980). Many other patents described the conditions which enhance the rate of hydrogenation and the selectivity to DHB (Joachim, 1980). The process using platinum/carbon catalyst consists of initial reduction of ortho-nitrochlorobenzene to ortho-subnitrochlorobenzene, further to ortho-hydroxylamine-chlorobenzene and finally the formation of DHB in the presence of sodium hydroxide. Formation of ortho-chloroaniline is the main competing side reaction as shown in Fig.1 (Peter *et al.*, 1997).

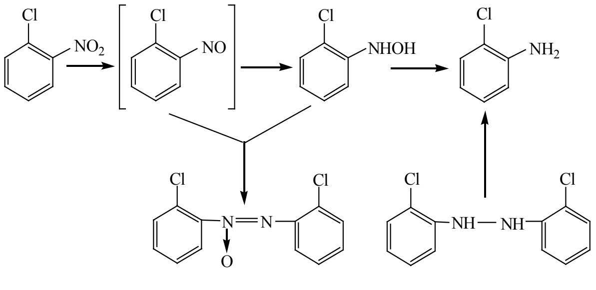


Fig.1 Hydrogenation of ortho-nitrochlorobenzene to 2,2′-dichlorohydrazobenzene

Platinum/carbon catalyst is the most important factor in this process. The supports and the preparation process of catalysts were investigated in this work.

EXPERIMENTAL DETAILS

Materials and apparatus

The active carbon (C1: SH767, C2: SH660, C3: SH602, C4: SH772) was purchased from the Shanghai Activated Carbon Co. Ltd. (China), (pH around 5.3). Hydrogen gas with purity >99.9% was supplied by the Shanghai Pujiang Hydrogen Co. Ltd. (China) and ortho-nitrochlorobenzene was from Changshan Chemical Co. Ltd. (China). Toluene, sodium hydroxide, and formaldehyde were purchased from the Shanghai Chemical Reagent Co. Ltd. (China). All hydrogenation experiments were carried out in a 1000 cm^3 hastelloy reactor. The reactor system supplied by the Xinchang Deli Chemical Instrument Co. Ltd. (China) consisted of an agitated vessel equipped with gas inlet and outlet system, cooling coil, automatic temperature controller, variable agitation speed controller and safety rupture disc.

Catalyst preparation

Platinum/carbon catalyst (1 wt.%) was prepared by wet impregnation of commercial active carbon with H_2PtCl_6 solution, followed by reduction with formaldehyde at 80 °C. The liquid was filtered and the catalyst was stored in packed bottle.

Activity measurements

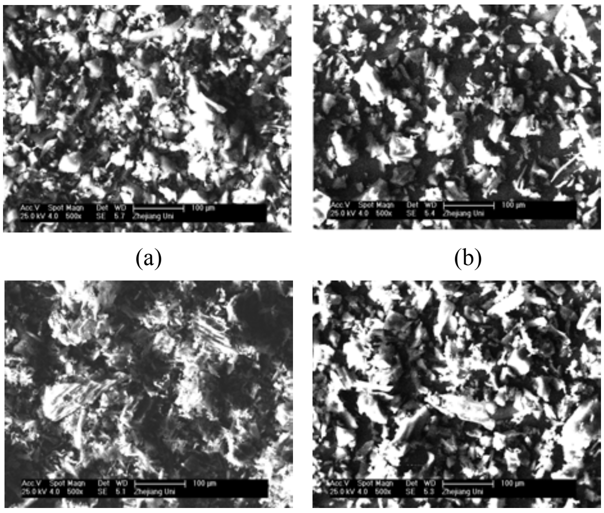
In a typical hydrogenation experiment, 250 g ortho-nitrochlorobenzene, 0.1 g catalyst (calculated by platinum), 20 g sodium hydroxide, 60 g water and 80 ml toluene were put into a clean, dry reactor. The reactor was flushed thrice with hydrogen and then heated to a desired temperature. The intermediate and products were analyzed by liquid chromatography (SHIMADZU model SPD-10A, ultraviolet detector and 125 mm×4 mm C18 column). The mobile phase was acetonitrile and water, volume ratio was 55:45, flow rate was 1.05 ml/min and the detection wavelength was 220 nm.

RESULTS AND DISCUSSION

Supports

Supports are very important to preparation of catalysts. The primary role of the support is to homogeneously disperse and stabilize small metallic particles and thus provide access to a much larger number of catalytically active atoms than in the corresponding bulk metal even when the latter is grounded to fine power. The most important parameters for the catalyst manufacture are the porosity, pore size distribution of the activated carbon and surface area. The particle size distribution of the powder or granulate, the attrition resistance and the ash content are also important parameters (Auer *et al.*, 1998).

The influence of four kinds of activated carbon on the catalyst was compared in this study. Morphology of activated carbon powder as observed by electron microscopy is largely determined by the raw material. Coconut shell, wood and nut based activated carbons are easily recognized, because the nature of the starting material is directly reflected in the final product (Fig.2).



(a) (b) (c) (d)

Fig.2 SEM images of activated carbon, magnification of 500:1 (a) C1; (b) C2; (c) C3; (d) C4

Typical particle of about 50 μm in diameter shows loose structure, partly due to the nature of the raw material used. C1, C2 and C4 taken at higher magnification reveal well developed macroporosity. Through the macropores the reagent molecules reach the small pores and the active centers located inside the carbon particle. C3 shows dense structure.

Peter *et al.*(1997) selected the salts of V, Fe, Co, Cu, Re, Mo as the reduction promoters and studied hydroxylamine accumulation in hydrogenation of nitroarenes. They found that the addition of vanadium as catalytic promoter could increase reaction rate and yield relatively purer products.

In this work, the metal contents of the carbons as determined by IRIS Intrepid II XSP ICP are given in Table 1.

Table 1 Metal content (μg/g) of active carbon

Metal content	C1	C2	C3	C4
Cu	0.113	0.084	0.102	0.086
Fe	1.54	1.55	2.22	1.84
Pb	0.103	0.234	0.109	0.009
Zn	18.01	7.27	6.03	2.53
Ca	607.5	1101	687.4	1055
K	63.2	15.1	60.7	92.0
Mg	135.3	389.5	243.4	294.0
Na	78.3	12.0	198.9	48.8
Ash content	1.10%	1.15%	1.57%	0.80%
Selectivity	88.7%	83.4%	80.5%	77.4%

The results showed that the data were irregular. The reason may be that the contents of metal salts were low, that all active sites were covered by platinum, and that the contents of metal salts had little effect on the course of hydrogenation or had less effect than other factors.

Characterization of the porous structure of the support was carried out by nitrogen adsorption at 77 K in Quanta Chrome apparatus and the total surface area was obtained by using the BET equation. The nitrogen (77 K) adsorption isotherms (amount adsorbed in ml/g vs relative pressure) of the supports shown in Fig.3 indicated that C1 had large surface area and well-developed porosity over the range of pore sizes. The amount of adsorption at low relative pressures was large enough and indicated an important contribution of narrow micropores. Furthermore, at higher relative pressures, the isotherm shows a deviation which indicates the presence of wider micropores, and a linear part with a considerable slope, which is due to the contribution of mesopores (2 nm< *d*<50 nm) to total porosity. C2, C4 show very similar micropore volume. C3 has poorly developed porosity and the lowest volume. The difference of the supports porosity can also be better followed by plotting the nitrogen adsorption data in Dubinin-Radush-kevich (D-R) coordinates (Fig.4). The shapes of the plot are similar. A linear portion at low relative pressures (up to P/P_0=0.1) due to the filling of micropores, and upward deviation at higher relative pressure ascribes to the coverage of the surface of wider pores. Furthermore the amount of adsorption on C3 is even lower.

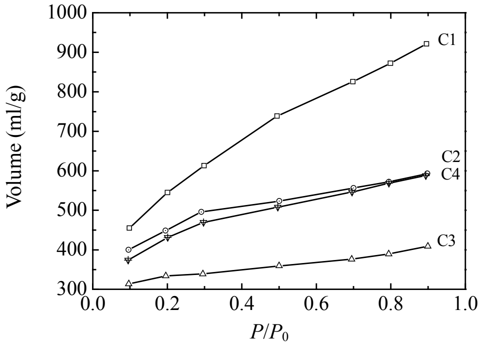


Fig.3 N_2 adsorption isotherms (77 K) of different active carbons

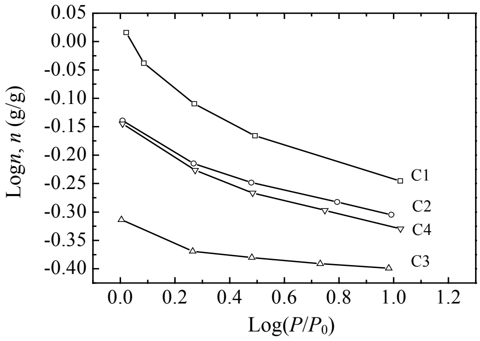


Fig.4 Dubinin-radush-kevich (D-R) plots for N_2 adsorption at 77 K on active carbon

The results in Table 2 show C3 with high purity, large surface area and pore volume and appropriate pore structure usually exhibits high activity for the hydrogenation of ortho-nitrochlorobenzene to 2,2′-dichlorohydrazobenzene.

Table 2 Effects of the supports on the catalysts

Catalyst	*A* (m^2/g)	DHB (%)	*R* (L/min)	Reuse times
Pt/C1	1917.35	88.7	0.89	10
Pt/C2	1476.58	83.4	10.99	3
Pt/C3	980.57	80.5	0.30	0
Pt/C4	1418.27	77.4	0.59	2

Note: *A*: surface area; DHB: 2,2′-dichlorohydrazobenzene; *R*: H_2 consumed rate

Preparation process

The most important step in the preparation process of platinum/C is the metal precursor. The interaction of the support surface between the metal precursors in the impregnation greatly influences the metal adsorption and dispersion of the catalyst. Fuente *et al.*(2001) studied the effects of the preparation on the dispersion of activated carbon supported platinum catalysts using the precursor of H_2PtCl_6 and $Pt(NH_3)_4Cl_2$, and found that the catalysts prepared from H_2PtCl_6 were homogeneously dispersed and showed greater catalytic activities than catalysts prepared from $Pt(NH_3)_4Cl_2$. But when the precursor of H_2PtCl_6 was used, the pH did not have to be taken into account. The influence of five different pH on the catalyst was discussed.

Table 3 shows that the pH of metal precursor solutions has important influence. In metal precursor solutions, the precursor molecules diffuse into the supports and interact with them. If the pH of the solution is higher than that of the aqueous slurry of the support, cationic adsorption is favored. So the adsorption of the $PtCl_6^{2-}$ should be carried out under lower pH. But when too low pH will adversely affects the adsorbed balance of the active carbon.

Table 3 Effects of pH on the catalysts

pH (around)	DHB (%)	*R* (L/min)	Reuse times
7	75.6	0.36	0
5	80.0	0.47	1
3	88.7	0.89	10
2	87.8	0.94	7
1	86.4	0.77	6

Note: *R*: H_2 consumed rate

Catalyst characterization

Fig.5 shows the SEM image of catalysts. It appeared that the distribution of Pt particle size was narrow, which seemed to be connected with an increase of the catalytic activities. The diameters of the particles were about 10 nm, but Pt crystallites on the inert carbon surface could not be detected. The catalytic centers concentrated on the sides, angles and defects of the observed surface.

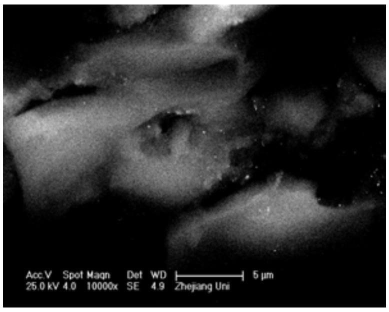


Fig.5 Pt particles on activated carbon derived from wood

CONCLUSION

Raw material and preparation process of the activated carbon have great influence on the compositions and surface structure of platinum/carbon catalysts. Platinum catalysts supported on activated carbon with high purity, large surface area, pore volume and appropriate pore structure usually exhibit high activity for the hydrogenation of ortho-nitrochlorobenzene to 2,2′-dichlorohydrazobenzene. The metal precursors with pH=3 used (in our case prepared from H_2PtCl_6 with supports having a low pH) show high activity, selectivity and long life time. The results of this study showed that the surface area of the specific support has great influence on the performance of the final catalysts.

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