Highly Selective Pt–Cr/C Alloy Catalysts for Single-step Vapour Phase Hydrogenation of Phenol to give Cyclohexanone†

S. T. Srinivas and P. Kanta Rao*

Catalysis Section, Physical and Inorganic Chemistry Division, Indian Institute of Chemical Technology, Hyderabad-500 007, India

Carbon supported platinum–chromium alloy catalysts have been found to be active for the direct hydrogenation of phenol with total selectivity to give cyclohexanone; the hydrogen uptake on alloy catalysts correlates directly with the phenol conversion.

Cyclohexanone is an industrially important intermediate in the production of both caprolactam for nylon 6 and adipic acid for nylon 66. Commercially cyclohexanone is manufactured by dehydrogenation of cyclohexanol. Copper based catalysts are mainly used for the conversion of cyclohexanol into cyclohexanone.[1,2] Cyclohexanol is obtained by air oxidation of cyclohexane or catalytic hydrogenation of phenol. Hydrogenation of phenol over a nickel catalyst gives cyclohexanol selectively, which on dehydrogenation over zinc catalyst yields cyclohexanone.[3] Usually the reaction is carried out in liquid phase conditions using noble metal catalysts.[4] However, a direct single-step vapour phase hydrogenation of phenol to give cyclohexanone is more advantageous in which the endothermic step of cyclohexanol dehydrogenation can be avoided. Supported platinum catalysts are the traditional catalysts of choice for a variety of hydrogenation reactions.[5] More recently bimetallic or alloy catalysts are replacing monometallic Pt catalysts because of their unique catalytic properties.[6–8] In this communication we report for the first time the single-step vapour phase hydrogenation of phenol giving cyclohexanone with total selectivity using novel Pt–Cr alloy catalysts supported on carbon.

A carbon-supported monometallic platinum catalyst with 5 wt.% platinum loading was prepared by the incipient wetting method using an aqueous solution of $H_2PtCl_6{\cdot}6H_2O$ (Fluka) of required concentration on carbon [Vulcan XC-72, Brunauer–Emmett–Teller (BET) surface area 250 $m^2\,g^{-1}$, pore volume 3.0 ml g^{-1}]. The sample was oven dried at 383 K for 16 h and then reduced in a flow of hydrogen–nitrogen mixture (3 : 1) at 523 K until the catalyst gave a negative test for chlorides. The 5 wt.% Pt/C catalyst was then impregnated with appropriate amounts of chromium acetylacetonate (Fluka) dissolved in methanol to give the required chromium loadings (0.5–4 wt.%). Excess solvent was evaporated on a water bath with continuous agitation. The samples thus obtained were oven dried at 393 K for 6 h and then heated in a quartz reactor at 1033 K for 5 h in flowing hydrogen. The alloying between platinum and chromium was confirmed by X-ray diffraction (XRD). The catalysts were characterized by H_2 chemisorption at room temperature (298 K) and N_2 physisorption at 77 K to determine Pt dispersion and BET surface areas, respectively.[9] A fixed bed micro-catalytic reactor was employed to carry out the phenol hydrogenation reaction. About 0.3 g of catalyst sample was taken and pretreated at 773 K for 2 h in hydrogen and then cooled to reaction temperature (473 K). The reactant feed consisting of phenol dissolved in cyclohexane (1 : 4 wt. : wt.) with a hydrogen : phenol mole ratio of 4.7 was fed into the reactor using a microprocessor controlled Secura (B.Bruan, Germany) syringe pump. The reaction products were analysed by GLC using 30% SE-30 on a chromosorb column kept at 453 K and a flame ionisation detector.

BET surface areas, H_2 uptake, dispersion, crystallite size, phenol conversion and selectivity of the catalysts are given in Table 1. It can be seen from Table 1 that a big drop in hydrogen chemisorption capacities is taking place upon addition of chromium to Pt/C and that with a further increase in chromium loading the hydrogen uptake is decreasing only to a much lesser extent. It can also be observed from Table 1 that with the addition of chromium crystallite size is increasing resulting in low dispersion of platinum. Formation of a chromium adlayer may make some of the platinum surface sites inaccessible for hydrogen chemisorption. Formation of an ordered Cr_3Pt alloy phase was confirmed by XRD studies.[10] A continuous decrease of BET surface areas may be seen as a result of alloying of Pt and Cr to form a second layer of chromium upon Cr addition.

A 5 wt.% Pt loading on carbon was selected for alloying with chromium, as this platinum loading gave maximum selectivity to cyclohexanone in hydrogenation of phenol during preliminary investigations on catalysts with different platinum loadings.[11] From Table 1, it is clear that even though a large decrease in H_2 uptake after alloying is observed the decrease in phenol conversion is relatively small. Thus, it appears that the intrinsic activity of the phenol hydrogenation sites on Pt/C catalysts is increased significantly upon alloying with chromium. From a close observation of the data, it is clear that the sites titrated by hydrogen chemisorption are responsible for phenol hydrogenation. It is significant that alloying of platinum with chromium resulted in 100% selectivity to cyclohexanone in hydrogenation of phenol while that on unalloyed platinum was about 84%. On Pt–Cr/C catalysts phenol is directly hydrogenated to cyclohexanone and its further hydrogenation to cyclohexanol does not occur unlike on monometallic platinum catalyst. It is of note that when cyclohexane was used as the solvent phenol was found unaffected after the reaction, thus confirming that dehydrogenation of cyclohexane does not occur on these catalysts.

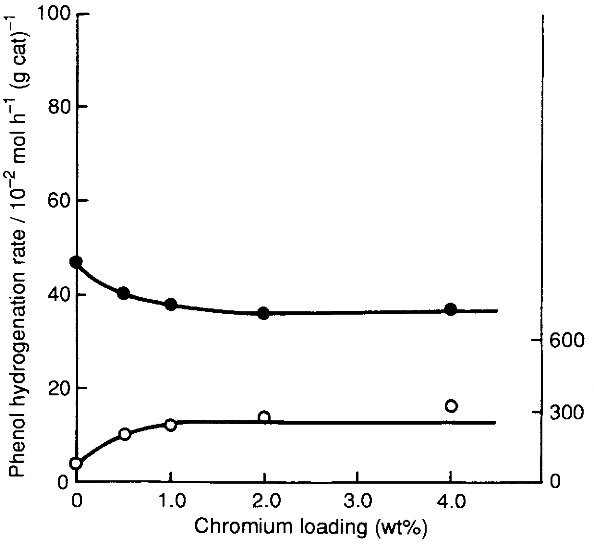

Fig. 1 Effect of chromium loading in 5 wt.% Pt/C catalyst on the phenol hydrogenation rate and turnover number. (●) Phenol hydrogenation rate; (○) TON.

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Table 1 H_2 uptake, dispersion, crystallite size, BET surface areas, phenol conversion and product selectivities of various catalysts

Catalyst composition (wt.%)	H_2 uptake/ µmol (g cat)$^{-1}$	Dispersion (%)	Crystallite size (d)/Å	BET SA/ m^2 (g cat)$^{-1}$	Phenol conversion (%)	% Selectivity Cyclohexanone	% Selectivity Cyclohexanol
5 Pt/C	81.7	64	13.3	228	64.5	83.9	14.2
0.5 Cr–5 Pt/C	26.7	21	41.0	192	55.0	100	—
1 Cr–5Pt/C	22.3	17	49.0	178	52.5	100	—
2 Cr–5 Pt/C	17.8	14	61.1	131	49.9	100	—
4 Cr–5 Pt/C	15.2	12	71.7	111	50.1	100	—

Phenol hydrogenation rate and turnover number (TON) are plotted as a function of chromium loading in the catalysts in Fig. 1. It can be seen from Fig. 1 that the rate decreases up to a chromium loading of 1 wt.% beyond which it remains almost constant. The TON also remains constant on Pt–Cr/C alloy catalysts indicating that the reaction is structure insensitive on these catalysts. The improved selectivity of alloy catalysts may be ascribed in part to a dilution effect of the platinum sites. The isolation of active sites upon alloying produces a significant improvement in the dissipation of the heat of reaction resulting in high selectivity to cyclohexanone and the modifier may also selectively block the sites that would be responsible for the unselective hydrogenation.[12,13] Alloying of the 5 wt.% Pt/C catalyst with Cr has thus improved the cyclohexanone selectivity from 84 to 100% in the hydrogenation of phenol without any other side products.

The catalyst, 1 wt.% Cr–5 wt.% Pt/C was tested on stream for 16 h continuously and the activity and cyclohexanone selectivity, monitored every hour were found to be constant throughout. This is a significant observation.

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