Selectivity dependence on the alloying element of carbon supported Pt-alloy catalysts in the hydrogenation of phenol[†]

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Abstract

Single step vapour phase hydrogenation of phenol over Pt-M/C (M = Cr, V and Zr) alloy catalysts was investigated at atmospheric pressure and 200°C. The alloying element shows a significant effect on the product selectivities. While Pt–Cr/C and Pt–V/C catalysts are highly selective for hydrogenation of phenol to cyclohexanone, the Pt–Zr/C catalysts are predominantly selective to cyclohexanol.

Key words: alloys; phenol hydrogenation; platinum; selectivity (cyclohexanol/cyclohexanone)

1. Introduction

Catalytic hydrogenation of phenol is an important industrial reaction. Cyclohexanone and cyclohexanol are obtained as major products along with cyclohexane, cyclohexene and benzene [1]. Among these cyclohexanone is an important intermediate in the production of both caprolactam for nylon 6 and adipic acid for nylon 66 [2]. Hydrogenation of phenol over a nickel catalyst gives selectively cyclohexanol, which on dehydrogenation over a zinc catalyst yields cyclohexanone. The reaction is also carried out under liquid-phase conditions using noble metal catalysts [2]. However, a direct single-step vapour-phase hydrogenation of phenol to give cyclohexanone is more advantageous, as the endothermic step of cyclohexanol dehydrogenation would be avoided.

Supported platinum is the traditional catalyst of choice for a variety of hydrogenation processes [3]. For better selectivity, platinum catalysts can be promoted by the addition of

metallic salts or through alloying [4]. More recently bimetallic and alloy catalysts are replacing monometallic catalysts because of their improved selectivities and higher activity as well as longer life [5]. This paper reports the results on the single-step vapour-phase hydrogenation of phenol over carbon supported Pt and Pt–M (M = Cr, V and Zr) alloy catalysts to yield mainly cyclohexanone or cyclohexanol.

2. Experimental

A 5 wt.-% Pt/C catalyst was prepared by incipient wetting of carbon (Vulcan XC-72, BET SA 250 m^2 g^{-1}; pore volume 3 ml g^{-1}) using an aqueous solution of $H_2PtCl_6 \cdot 6H_2O$ (Fluka) of required concentration. The sample was oven dried at 110°C for 16 h and then reduced in a flow (40 ml/min) of a $H_2:N_2$ gas mixture (3:1) at 250°C until the catalyst gave a negative test for chlorides. Then the Pt–M/C alloy catalysts were prepared with varying amount of M (0.5–4.0 wt.-%) by impregnating the 5 wt.-% Pt/C with appropriate amounts of relevant organometallic precursors [$Cr(C_5H_7O_2)_3$, $V(C_5H_7O_2)_3$ and $Zr(C_{12}H_{28}O_4)$] (all Fluka make) dissolved in methanol to give the required metal loadings in the final catalyst. Excess solvent was evaporated on a waterbath with continuous agitation. The samples thus obtained were oven dried at 120°C for 6 h and then heated in a quartz reactor (at 760°C for Pt–Cr, 960°C for Pt–V and 1200°C for Pt–Zr) for 5 h in a flowing $H_2:N_2$ (3:1) gas mixture (30–40 ml min^{-1}). The alloy formation was confirmed by X-ray diffraction. The alloy catalysts were characterized by hydrogen chemisorption at 25°C and nitrogen physisorption at −196°C to measure platinum dispersion and BET surface areas, respectively [6].

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 500°C for 2 h in hydrogen and then cooled to reaction temperature (200°C). The reactant feed, consisting of phenol dissolved in cyclohexane (1:4 wt./wt.) with a hydrogen-to-phenol mole ratio of 4.7, was fed into the reactor using a microprocessor controlled Secura (B. Braun, Germany) syringe pump. The reaction products were condensed in cold traps after steady-state conditions were attained (2 h) and were analysed by gas-liquid chromatography (GLC) using 30% SE-30 on a chromosorb W column (3 mm × 2 m) kept at 180°C and a flame ionisation detector.

3. Results and discussion

Alloying between platinum and the second metal in the catalysts was detected from the respective characteristic d values in the X-ray diffraction (XRD) data [7]. Pt–Cr/C catalysts have shown phases due to Pt ($d = 2.27$) and Cr_3Pt ordered alloy phase ($d = 1.92$). Pt–V/C catalysts have shown alloy phases due to PtV_3 ($d = 3.41$) and PtV ($d = 3.22$). PtZr ($d = 2.57$) and $Pt_{11}Zr_9$ ($d = 2.40$) were observed in Pt–Zr/C catalysts with Zr loadings of 0.5 and 1 wt.-%. The ZrO_2 phase ($d = 2.96$) is observed in catalysts with Zr loading of 2 and 4 wt.-%. A 5 wt.-% Pt loading on carbon was selected for alloying with Cr, V or Zr as this platinum loading gave maximum selectivity to cyclohexanone in phenol hydrogenation

during preliminary investigations on catalysts with different platinum loadings [8]. It may be mentioned here that hydrogen chemisorption and phenol hydrogenation activity are practically nil on the carbon support alone. Catalyst composition, hydrogen chemisorption data, BET surface areas of the catalysts and phenol conversion are given in Table 1. It can be seen from this table that a steep drop in hydrogen chemisorption capacities is taking place upon addition of M to Pt/C and that with further increase in M loading the hydrogen uptake is decreasing only to a lesser extent. This may be attributed to the seggregation of platinum particles after alloying which causes a considerable loss of exposed platinum area. Similar trends can be seen in the H/Pt value. This is expected since they result from the hydrogen chemisorption capacities of the catalysts. A continuous decrease in BET surface areas may be seen as a result of blocking of pores by platinum alloy ensembles and possible sintering of Pt/C particles at the high temperatures employed for alloying. It can also be seen from Table 1 that even though a large decrease in the hydrogen uptake after alloying is observed the decrease in phenol conversion is relatively small. The phenol conversion in the alloy catalysts is in the order of Pt–Cr > Pt–V > Pt–Zr. From a close observation of the data in Table 1, it appears that the sites titrated by hydrogen chemisorption are responsible for phenol hydrogenation.

The selectivities of cyclohexanone and cyclohexanol for various catalysts are illustrated in a bar diagram (Fig. 1). In the case of 5 wt.-% Pt/C, about 84% selectivity to cyclohexanone was obtained. Significantly, on Pt–Cr/C alloy catalysts total selectivity to cyclohexanone is obtained [9], phenol becoming directly hydrogenated to cyclohexanone. It appears that further hydrogenation of cyclohexanone to cyclohexanol is not occurring on Pt–Cr/C catalysts unlike on monometallic platinum catalysts to some extent. Cyclohexane used as solvent in this reaction was unaffected after the reaction (formation of benzene was not observed) confirming that dehydrogenation of cyclohexane is not occurring on the catalysts under the experimental conditions employed in this study. On Pt–V/C catalysts cyclohexanone selectivity increased from 79 to 96% with increase in V loading from 0.5 to

Table 1
Hydrogen uptake, H/Pt values, BET surface area and phenol conversion of various catalysts

| Catalyst composition (wt.-%)	H_2 uptake, (μ mol·$g_{cat.}^{-1}$)	H/Pt	BET SA ($m^2 g^{-1}$)	Phenol conversion (%)
5 Pt	81.7	0.64	228	64.5
5 Pt–0.5 Cr	26.7	0.21	192	55.0
5 Pt–1.0 Cr	22.3	0.17	178	52.5
5 Pt–2.0 Cr	17.8	0.14	131	49.9
5 Pt–4.0 Cr	15.2	0.12	111	50.1
5 Pt–0.5 V	23.2	0.18	211	51.1
5 Pt–1.0 V	19.6	0.15	183	49.8
5 Pt–2.0 V	17.9	0.14	159	45.8
5 Pt–4.0 V	9.8	0.12	118	50.0
5 Pt–0.5 Zr	20.1	0.16	178	45.1
5 Pt–1.0 Zr	17.9	0.14	160	42.0
5 Pt–2.0 Zr	13.4	0.10	147	38.5
5 Pt–4.0 Zr	8.9	0.07	129	35.5
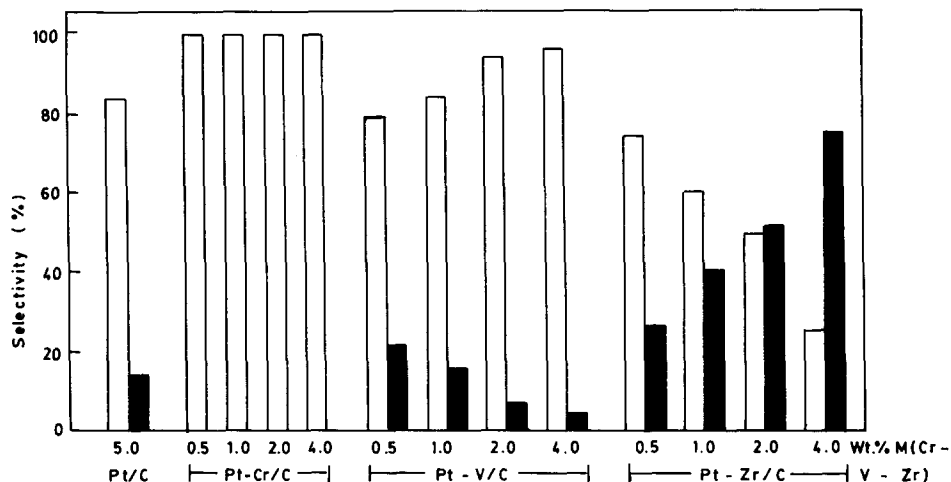
Fig. 1. Selectivity to (□) cyclohexanone and (■) cyclohexanol on various carbon supported Pt–M (M = Cr, V, Zr) alloy catalysts in the hydrogenation of phenol.

4 wt.-% and correspondingly the cyclohexanol selectivity decreased. Alloying of platinum with zirconium has an opposite effect. While the selectivity decreased from 74% at 0.5 wt.-% Zr to 25% at 4 wt.-% Zr, the cyclohexanol selectivity increased from 26 to 75%, respectively. This shows that alloying of Zr to Pt has a negative effect on the cyclohexanone selectivity. No other side products were obtained along with cyclohexanone and cyclohexanol. These contrasting trends in product selectivities can be attributed to the effect of the alloying element. The alloy formation in the catalysts results in a strong metal–metal interaction between platinum and the alloying elements [10]. The Joyner–Shpiro model for Pt–Cr alloying in H-ZSM-5 proposes a platinum enrichment at the surface with a chromium enrichment in the sub-surface layer [11]. Consequently the fraction of Pt (δ+) state decreases in Pt–Cr/H-ZSM-5 with respect to Pt/H-ZSM-5. This platinum–chromium electronic interaction, rather than simple dilution, is said to be responsible for both hydrogenolysis and aromatisation of lower alkanes. The platinum–chromium interaction is assumed to reduce the bonding strength between the hydrocarbon or its fragments and the metal surface with consequent activity and selectivity changes [12,13]. The different activity and selectivity behaviour in the hydrogenation of phenol to cyclohexanone and cyclohexanol on Pt–Cr/C, Pt–V/C and Pt–Zr/C may thus be explained as being due to different extents of platinum–metal (Cr or V or Zr) interaction affecting the Pt (δ+) state and strength of bonding between the reactants and products. However, Aduriz et al. [14] attributed the selectivity behaviour in valyene and isoprene hydrogenation to the dilution effect of palladium sites in palladium alloyed with germanium, tin, lead or antimony. More recently, Masson et al. [15] computed the relative adsorption equilibrium constants for consecutive reactions to study the selectivity criteria in acetophenone hydrogenation on chromium promoted Raney nickel alloy catalysts.

All alloy catalysts used in our study may oxidize in air (upon drying, upon transfer in air, perhaps also by phenol). Thus the catalysts used here are actually an alloy, with some platinum exposed, covered by CrO_x, VO_x and ZrO_x species. Specifically these oxides may

activate the –C–OH or C=O group for hydrogenation. Beard and Ross [16] observed TiO_x species in Pt–Ti/C alloy catalysts apart from ordered Pt–Ti alloy phases. Recently it has been reported that phenol converts to cyclohexanone, which further hydrogenates to cyclohexanol on Pt and Pd supported on Al_2O_3 and zeolite LTL [17]. Indeed, much work needs to be done to explore the mechanism of the reaction. However, in our opinion three probable routes exist for phenol hydrogenation. First, hydrogenation of phenol to cyclohexanone and further hydrogenation to cyclohexanol. Secondly, direct hydrogenation of phenol to cyclohexanol and dehydrogenation to cyclohexanone. A third possible route is formation of intermediate cyclohexene-1-ol and tautomerisation to cyclohexanone owing to its greater stability. Thus, by changing the alloying element (Cr, V and Zr) and composition of these alloy catalysts, as well as the pretreatment conditions, it is possible to tailor the structure of the metallic platinum phase. In this way catalytic activities and selectivities in the hydrogenation of phenol can be controlled in order to yield preferentially a desired product. The activity and selectivity in the reaction was found to be constant in a 16 h run on all three platinum alloy catalyst systems showing that the catalysts are stable during the period of study.

4. Conclusions

It was found that the Pt–M/C (M = Cr, V and Zr) alloy catalysts are active for direct hydrogenation of phenol to cyclohexanone or cyclohexanol. Cyclohexanone is obtained (100% selectivity) in single step on Pt–Cr/C alloy catalysts. Pt–Cr/C and Pt–V/C systems seems to be promising for single-step vapour-phase hydrogenation of phenol to cyclohexanone. On the other hand, Pt–Zr/C catalysts yield predominantly cyclohexanol.

Acknowledgements

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