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Letter

Selective vapour-phase hydrodechlorination of chlorobenzene over alumina supported platinum bimetallic catalysts [1]

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Abstract

The influence of addition of a second metal (V, Mo or W) on the activity and selectivity of Pt/Al_2O_3 catalysts was studied in vapour-phase hydrodechlorination of chlorobenzene. While Pt/Al_2O_3 shows a linear decrease in activity with time, the bimetallic catalysts are found to be resistant to deactivation. $Pt–V/Al_2O_3$ enhances the selectivity to cyclohexane, whereas $Pt–Mo/Al_2O_3$ and $Pt–W/Al_2O_3$ improve the selectivity for benzene formation.

Keywords: Hydrodechlorination; Chlorobenzene; Platinum; Bimetallic catalysts

1. Introduction

Catalytic hydrodechlorination is an important process for waste water treatment, disposal or recycling of chlorinated hydrocarbons and in the manufacture of fine chemicals [1–3]. Chlorobenzene is often chosen as a model compound in studying the hydrodechlorination reaction since it represents the halogenated species found in many organic wastes. Noble metals are the catalysts of choice for hydrodechlorination reactions carried out both in liquid and gaseous phases. Pd/C [4], Pd/Al_2O_3 and Rh/Al_2O_3 [5] catalysts have been reported for hydrodechlorination of chlorobenzene. Catalyst deactivation due to poisoning by

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hydrogen chloride produced during the reaction is a normal problem encountered while using monometallic catalysts. Much attention has been focused recently on bimetallic catalysts to achieve longer life (maintaining higher activity) and higher product selectivity compared to that of monometallic catalysts [6]. However, Bodnariuk et al. [7] have reported hydrodechlorination of chlorobenzene in the vapour phase over Pd–Rh/Al_2O_3 and Pd–Sn/Al_2O_3 bimetallic catalysts where a decrease in activity compared to the monometallic catalyst was observed. Ni–Mo/Al_2O_3 [3] catalysts possessing better resistance to deactivation have been reported for this reaction but they work at higher temperatures and pressures.

In the hydrodechlorination of chlorobenzene, benzene and cyclohexane are obtained as the main products along with small quantities of chlorocyclohexane. In view of the industrial application it is always desirable to get cyclohexane from chlorobenzene rather than benzene. In this present communication we report the vapour phase hydrodechlorination of chlorobenzene over Pt–M/Al_2O_3 (M = V, Mo or W) bimetallic systems, which are found to be more stable and selective for the formation of cyclohexane and benzene compared to the monometallic Pt/Al_2O_3 catalyst.

2. Experimental

The platinum catalyst was prepared by impregnating the alumina support (Harshaw, S.A. 196 m^2/g) with an aqueous solution of chloroplatinic acid of the required concentration (Arora-Matthey). The impregnated material was then dried at 110°C for 12 h and calcined in air at 400°C for 6 h. Bimetallic catalysts were prepared by impregnating Pt/Al_2O_3 with an aqueous solution of ammonium metavanadate or ammonium heptamolybdate or ammonium metatungstate (all Fluka) depending on the bimetallic system desired. The resulting solids were dried at 110°C for 12 h and then calcined in air at 500°C for 6 h. For characterization and activity studies one sample of the dried Pt/Al_2O_3 catalyst was calcined at 500°C for 6 h. X-ray powder diffraction (XRD) patterns of the calcined and reduced (500°C for 4 h at a hydrogen flow rate of 60 ml/min) samples were recorded on a Philips PW 1051 diffractometer by using Ni-filtered Cu Kα radiation. The BET surface area of the prepared catalysts was determined by the nitrogen adsorption method at liquid nitrogen temperature.

Catalytic tests were performed in a previously described fixed bed microreactor system at atmospheric pressure [8]. About 0.4 g of catalyst was placed in a glass tubular reactor of 6 mm I.D. and pretreated at 500°C for 4 h in hydrogen at a flow rate of 60 ml/min and cooled to reaction temperature. A space velocity of 8000 h^{-1} (GHSV) was maintained throughout the reaction study. Chlorobenzene 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 (4 h) and were analyzed by GLC using 10% carbowax 20M column and a flame ionization detector.

3. Results and discussion

Catalyst composition and BET surface areas of the catalysts are presented in Table 1. It can be noted that the surface area of Al_2O_3 has decreased upon impregnation by Pt and the second metal M (V, Mo or W). This observation is expected since, upon impregnation of the active phase, pore blocking takes place. However, the decrease is about 7–15% which indicates that the active phase is well dispersed on the support. This observation is also corroborated by the X-ray diffraction patterns of the calcined and reduced catalysts which have shown no diffraction lines due to crystalline Pt phase or compounds between Pt and M or MO_x.

In the temperature range (140–200°C) studied, similar conversion and selectivity traces have been obtained in the hydrodechlorination of chlorobenzene on all the catalysts. The change in conversion of chlorobenzene with time at a reaction temperature of 140°C was studied on various catalyst systems. Fig. 1 shows the results of the time on stream studies on mono- and bimetallic catalysts carried out for 16 h under similar reaction conditions. It can be seen that the activity of Pt/Al_2O_3 steadily decreased with time, whereas the bimetallic catalysts exhibited stable activity after 4 h on-line with conversions remaining fairly constant throughout the period of study. The initial decrease in activity before attaining the steady state observed on bimetallic catalysts may be attributed to the interaction between metal and HCl (produced in the reaction) forming a stable surface chloride species [5]. Selectivities for benzene and cyclohexane remained fairly stable on all the catalysts after 4 h. While the selectivity for cyclohexane decreased initially that for benzene increased correspondingly. Fig. 1 shows that the bimetallic catalysts are resistant to deactivation compared to the monometallic catalysts.

The change in conversion and selectivity as a result of changes in the partial pressure of H_2 or chlorobenzene (+25% of the stoichiometric requirement), at a

Table 1
Composition and BET surface areas of various platinum bimetallic catalysts

Sample	Pt content (wt.-%)	M content (wt.-%)	BET S.A. (m^2/g)
Al_2O_3	–	–	196
Pt/Al_2O_3	3	–	182
$Pt\text{-}V/Al_2O_3$	3	3	178
$Pt\text{-}MO/Al_2O_3$	3	3	169
$Pt\text{-}W/Al_2O_3$	3	3	166

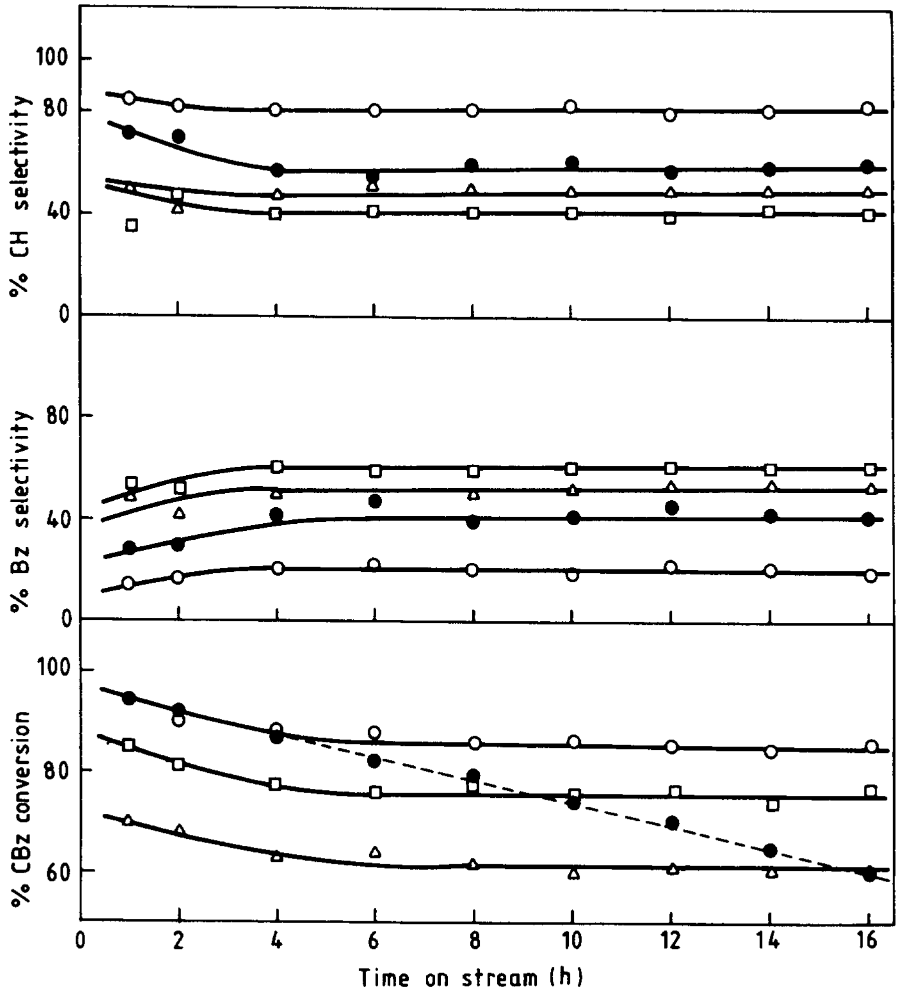

Fig. 1. Time on stream studies on mono- and bimetallic catalysts. (●) Pt/Al_2O_3, (○) Pt–V/Al_2O_3, (□) Pt–Mo/Al_2O_3, (△) Pt–W/Al_2O_3.

constant reaction temperature of 140°C, was also studied. A typical set of activity and selectivity data, obtained after 4 h on stream, is presented as a bar diagram in Fig. 2. It can be seen in Fig. 2 that the chlorobenzene conversion decreased with the addition of M to Pt/Al_2O_3 except on Pt–V/Al_2O_3. The chlorobenzene conversion obtained on the alumina supported catalysts followed the order Pt = Pt–V > Pt–Mo > Pt–W.

It is worth mentioning that the support Al_2O_3 and the reduced catalysts V_2O_5/Al_2O_3, MoO_3/Al_2O_3 and WO_3/Al_2O_3 have been tested and found to be inactive for the hydrodechlorination reaction under the conditions employed in this study. The decrease in the dechlorination activity with the addition of a second metal M to the noble metal may be a consequence of one or more of the

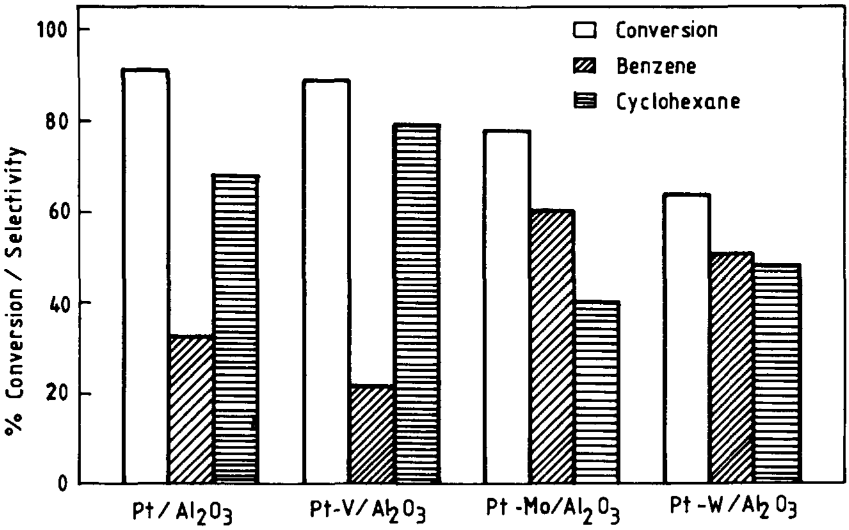

Fig. 2. Activity and selectivity data during the hydrodechlorination of chlorobenzene on mono- and bimetallic catalysts. (Reaction temperature: 140°C, GHSV: 8000 h^{-1}, partial pressure of H_2: 120 mmHg and partial pressure of chlorobenzene: 640 mmHg).

following factors [7]; (i) dilution of the platinum surface by the less active metal, (ii) surface enrichment of the less active metal in the presence of HCl and (iii) interaction of HCl with the support leading to structural changes in the catalyst. The first two factors reduce the surface density of Pt metal sites whereas the third may affect the properties of the active species in terms of change in crystallite size and dispersion leading to reduced activity. The amorphous nature of the active species (as revealed by XRD data) and marginal change in the surface area of the support after impregnation suggest that the dilution effect is more prominent in the bimetallic catalyst systems.

It can also be observed from Fig. 2 that the selectivity towards cyclohexane is enhanced on Pt–V/Al_2O_3 (79%) compared to that on Pt/Al_2O_3 (68%). On the other hand, cyclohexane selectivity decreased on Pt–Mo/Al_2O_3 and Pt–W/Al_2O_3, giving higher selectivity to benzene (60 and 51%, respectively). Formation of chlorocyclohexane is not observed on these catalysts. These contrasting trends in product selectivities may be attributed to the added element which may modify the adsorptive capacities of the reactants and intermediate products on the Pt sites. Electronic interaction between Pt and M are hypothesized to reduce the bond strength between the hydrocarbon (or its fragments) and the metal surface with consequent activity and selectivity changes [9]. The higher selectivity to cyclohexane on Pt–V/Al_2O_3 may be due to higher reducibility of VO_x than MoO_x or WO_x, in the presence of Pt [10,11].

For the hydrodechlorination of chlorobenzene, mainly two reaction schemes are prominent. Lapiere et al. [12] have reported a Langmuir type reaction mechanism where the reaction between the adsorbed hydrogen and chlorobenzene is the rate determining step. The second, step-wise mechanism, proposed by Coq et al. [5] is similar to that of the oxidation of hydrocarbons. The latter mechanism envisages interaction of chlorobenzene with the metal surface forming a metal chloride and regeneration of the metal surface by hydrogen. Both the rates of surface chlorination and reduction are reported to decrease with the decrease in metal particle size. In the present investigation it is assumed that the second metal dilutes the Pt sites leading to smaller particles. Decrease in particle size imparts electron deficient character to the small metal aggregates and thus decreases the activity, as suggested by Coq et al. [5]. Though with the available data, it is not possible to arrive at a conclusion, it may be assumed that the second mechanism is more probable.

4. Conclusion

In conclusion, it may be stated that the addition of a metal oxide (MO_x, M = V, Mo or W) to Pt improves its stability during the hydrodechlorination of chlorobenzene. $Pt–V/Al_2O_3$ seems to be a more promising catalyst for obtaining cyclohexane selectively in the hydrodechlorination of chlorobenzene. This study clearly demonstrates that by changing the second metallic element (V, Mo or W), it is possible to change the properties of monometallic Pt sites and achieve the required product selectivity. A detailed investigation to find out the effect of metal (V, Mo or W) loading and its implications on the electronic modification of platinum and its influence on the hydrodechlorination of chlorobenzene are under way in the authors' laboratory.

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