Effect of support modification on the chlorobenzene hydrodechlorination activity on Pt/Al_2O_3 catalysts *

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Received 5 November 1996; accepted 7 November 1997

Al_2O_3 was modified with TiO_2 and ZrO_2 using organometallic precursors and is used in the preparation of supported platinum catalysts. The catalysts have been characterised by nitrogen adsorption, hydrogen chemisorption and X-ray diffraction and were tested for their activity in the hydrodechlorination of chlorobenzene. The investigations show that support modification controls the catalyst deactivation remarkably and the catalysts were found to be highly active and selective.

Keywords: modified alumina, supported platinum catalysts, H_2 chemisorption, BET area, XRD, hydrodechlorination, chlorobenzene

1. Introduction

Supported platinum catalysts are extensively used in hydrogenation, dehydrogenation and oxidation reactions and platinum supported on alumina and zeolites form bifunctional catalysts for isomerisation in the reforming of naphtha to give high octane gasoline [1,2]. Generally supports ensure better dispersion of metal and the stability of the metal sites by influencing their catalytic properties through electronic interactions. At the metal–support interface the supporting oxide can offer sites which might intervene in the transformation of reacting molecules [3]. However, the problem normally encountered while using platinum catalysts supported on Al_2O_3, SiO_2, TiO_2 etc., is catalyst deactivation due to poisoning and/or sintering. Further, TiO_2, ZrO_2 and MgO when used as supports show lower activities and/or coke deposition because of their low surface area and unsuitable acid–base properties [4]. Recently Al_2O_3 modification by rare earth oxides like La_2O_3, CeO_2, alkali and alkaline earth metals [5,6] have shown that incorporation of the additives to the supports changes the dispersion of metal, after metal–support interaction, and changes distribution of acid sites, as well as physical properties like surface area, pore structure and mechanical strength as well as thermal stability. Clearly, a better understanding of the effect of the support modification on catalytic behaviour is important and may provide guidance in choosing or designing a better catalyst for a specific reaction. The present communication reports the effect of support modification on the dispersion and activity of Pt/Al_2O_3 catalysts where Al_2O_3 is modified with TiO_2 and ZrO_2. The activity of prepared catalysts was evaluated in the hydrodechlorination of chlorobenzene. The catalysts were characterised by XRD, H_2 chemisorption and BET area in order to correlate the activity with the physicochemical characteristics of the catalysts.

2. Experimental

The modified Al_2O_3 supports were prepared by impregnating Al_2O_3 (Harshaw SA = 196 m^2 g^{-1}) with requisite amount of $(C_{12}H_{22}O_4)Ti$ and $(C_{12}H_{22}O_4)Zr$ to yield 10 wt% of TiO_2 and ZrO_2 on Al_2O_3, respectively. Hydrolysis of organometallic precursors was done by using methanol and the excess solvent was evaporated to dryness on a water bath. The samples were dried at 110°C for 12 h followed by calcination at 450°C for 4 h. A series of platinum catalysts supported on modified Al_2O_3 were prepared by impregnating with appropriate amounts of H_2PtCl_6 solution to yield 1–5 wt% Pt loading. The impregnated samples were dried at 110°C for 12 h and calcined at 400°C for 4 h. Actual metal loadings in the catalysts were determined by DC plasma emission spectroscopy.

X-ray powder diffraction patterns were recorded on a Philips PW 1051 diffractometer using Cu K_α radiation. BET surface areas of the catalysts were determined by using nitrogen adsorption at liquid nitrogen temperature in a conventional glass high-vacuum unit. The same unit was used to carry out H_2 chemisorption experiments at ambient temperature. The double isotherm method was employed to determine H_2 chemisorption capacities of the catalysts [7]. In a typical experiment about 1 g of the dry catalyst was loaded in a pyrex U-shaped sample cell

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attached to a high-vacuum glass system equipped with a McLeod gauge. The catalyst was reduced in situ at 250°C (low-temperature reduction – LTR) and at 500°C (high-temperature reduction – HTR) respectively for 2 h and then the samples were heated at the same temperature for 1 h under vacuum (10^{-6} Torr, 1 Torr = 133 Pa) and then brought to ambient temperature.

High-purity H_2 gas was employed at pressures between 10 and 400 Torr for the determination of the total amount of both weakly and strongly chemisorbed H_2. After this step, the samples were evacuated to 10^{-6} Torr at ambient temperature for the removal of the weakly adsorbed H_2 and a second adsorption isotherm was generated under identical conditions. The difference between the two adsorption isotherms after extrapolation to zero pressure provides the amount of strongly chemisorbed H_2. The platinum dispersion was estimated assuming dissociative adsorption of H_2 on the metal.

Catalytic runs were carried out in a previously described fixed-bed microreactor [8]. About 0.4 g of the catalyst was taken in a glass reactor and pretreated at 250°C (LTR) or 500°C (HTR) for 2 h in H_2 at a flow rate of 60 ml/min^{-1} and cooled to reaction temperature (140°C). A space velocity of 8000 h^{-1} (GHSV) was maintained throughout the reaction run. Chlorobenzene was fed into the reactor using a microprocessor controlled SECURA (B. Braun, Germany) syringe pump. The reaction effluents were condensed in cold traps after steady-state conditions were attained (4 h) and were analysed by GLC equipped with FID using 10% Carbowax 20M column.

3. Results and discussion

X-ray powder diffraction patterns of Al_2O_3, Pt/Al_2O_3, TiO_2–Al_2O_3, ZrO_2–Al_2O_3 and Pt supported on modified Al_2O_3 catalysts are presented in figure 1. The X-ray pattern of the Al_2O_3 sample shows mainly phases which are characteristic of γ-Al_2O_3. On the other hand in TiO_2-modified Al_2O_3, TiO_2 is in the anatase form which may be due to the calcination conditions (450°C for 4 h) and the organometallic precursor of TiO_2 employed in the preparation. In ZrO_2-modified Al_2O_3, ZrO_2 obtained from its organometallic precursor is present as a mixture of both monoclinic and tetragonal phases. The experimentally observed interplanar distances of the phases obtained from XRD patterns, Al_2O_3 (d = 1.98, 2.39, 1.39), TiO_2 (d = 3.5) and ZrO_2 (d = 3.13, 1.53, 1.81) are closer to the characteristic values of Al_2O_3 and TiO_2 (anatase) and ZrO_2 (monoclinic + tetragonal) phases [9]. This observation shows

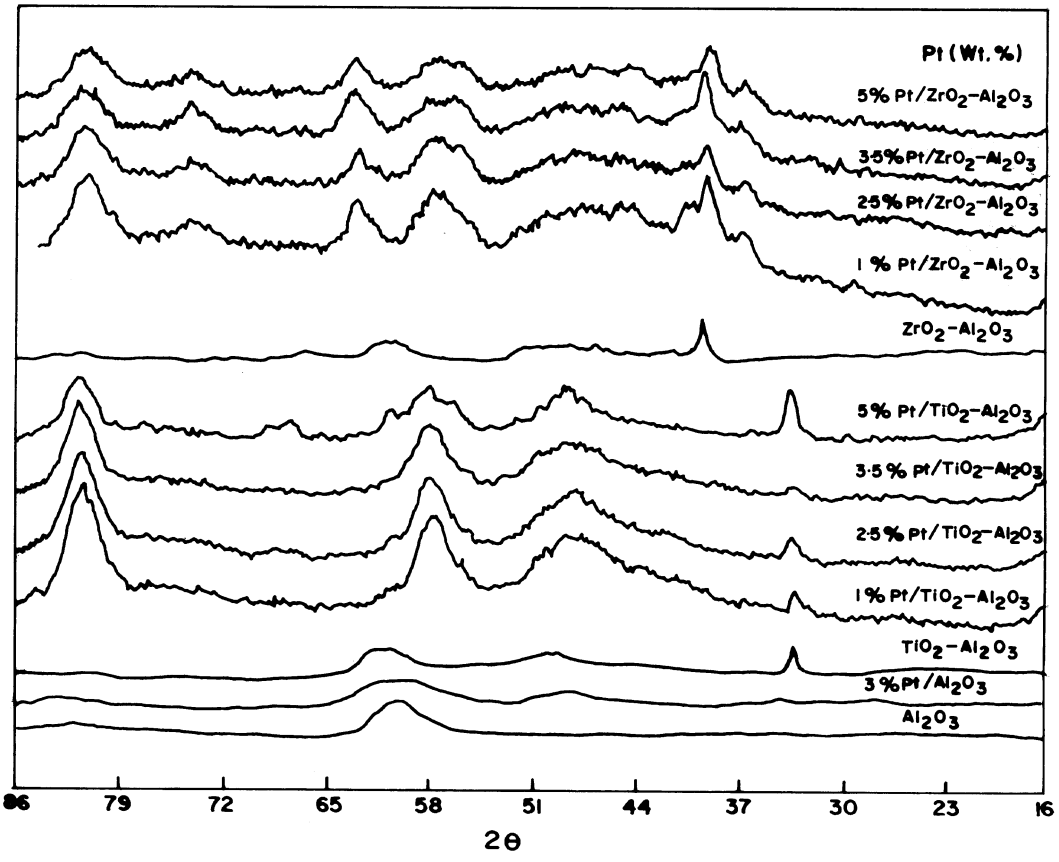

Figure 1. X-ray powder diffraction patterns of the catalysts.

that both TiO_2 and ZrO_2 are spread over Al_2O_3 rather than forming internal compounds considering the fact that they are about 10 wt% on Al_2O_3. In Pt/Al_2O_3 as well as Pt supported on TiO_2–Al_2O_3 and ZrO_2–Al_2O_3, no characteristic peaks due to Pt were observed at all Pt loadings which shows that Pt is in well dispersed form in all the catalysts. Even if Pt crystallites are formed they are too small to be detected by X-rays, i.e. below 40 Å size. In HTR-treated TiO_2-modified Al_2O_3 catalysts TiO_2 remained in anatase form and did not change to rutile phase. The BET surface areas of the catalysts as presented in table 1 show that the surface area of the support, Al_2O_3, has decreased with the addition of TiO_2 and ZrO_2 and also upon the impregnation of Pt. This observation is expected since, upon impregnation of the additives active phase pore blocking takes place which affects the total surface area. The hydrogen chemisorption capacities of various Pt-loaded modified Al_2O_3 catalysts are given in table 1. It can be seen from table 1 that the H_2 uptake is continuously increasing with increase in Pt loading. This shows that the available active Pt metal area is increasing with Pt loading. On the other hand the H/Pt or dispersion value which is translated from H_2 chemisorption shows a decreasing trend with increase in Pt loading. It may be noted here that H_2 chemisorption on supports alone was found to be negligible. All the catalysts were prereduced at 250°C (LTR) and 500°C (HTR) before chemisorption and activity studies. In case of Pt supported on ZrO_2–Al_2O_3 no notable difference of H_2 chemisorption was observed for LTR- and HTR-treated catalysts (table 1), whereas in the case of Pt/TiO_2–Al_2O_3 catalysts a significant decrease in H_2 chemisorption can be seen. This may be ascribed to the so-called strong metal–support interaction (SMSI) phenomenon [10]. However, at HTR conditions the determination of Pt dispersion becomes irrelevant especially when there is an uncertainty as to the interaction between the Pt–Ti is concerned [11].

The hydrodechlorination of chlorobenzene (CBz) was studied at a reaction temperature of 140°C and 1 atm pressure on all catalysts. It is worth mentioning here that no chlorobenzene hydrodechlorination activity was found on Al_2O_3 and modified Al_2O_3 supports alone. In hydrodechlorination of chlorobenzene (CBz), benzene (Bz) and cyclohexane (CH) are obtained as major products along with chlorocyclohexane (CCH). In this study chlorocyclohexane selectivity was negligible, i.e., less than 2%. In figure 2 chlorobenzene hydrodechlorination activity for all the catalysts is presented. From the H_2 chemisorption data the number of accessible Pt surface atoms are calculated and used to give catalyst activity in terms of turn over numbers (TON mol site^{-1} s^{-1}). It can be seen from figure 2 that the specific activity, i.e. TON, shows the following trend with respect to support as well as catalyst pretreatment: Pt/TiO_2–Al_2O_3(HTR) > Pt/TiO_2–Al_2O_3(LTR) > Pt/ZrO_2–Al_2O_3 = Pt/Al_2O_3. This implies that a similar activity contribution from Al_2O_3, TiO_2–Al_2O_3 and ZrO_2–Al_2O_3 is occurring. This shows that support modification is not affecting the catalyst activity in chlorobenzene hydrodechlorination reaction. These observations are more pronounced in figure 3A where conversion and product selectivities are plotted as a function of Pt loading in the catalysts. It can be seen in figure 3A that the chlorobenzene conversion is lower above and below 2.5 wt% Pt loading, even though H_2 chemisorption capacities have increased continuously with increase in Pt loading in all the catalysts. The product selectivities (figure 3A) show that in case of TiO_2-modified catalysts the selectivity to benzene is decreased with increase in Pt loading and cyclohexane selectivity has shown an opposite trend. Similarly for ZrO_2-modified catalysts a decrease in benzene selectiv-

Table 1
Catalyst composition, BET surface area and H_2 chemisorption data of Pt/Al_2O_3 catalysts

Sample [a]	Pt loading (wt%)	BET SA ($m^2\ g^{-1}$)	H_2 chemisorption (μmol g^{-1} cat)		H/Pt	
			LTR	HTR	LTR	HTR
A	–	196	–	–	–	–
TA	–	160	–	–	–	–
ZA	–	152	–	–	–	–
PA	3.0	175	63.0	65.2	0.81	0.84
PTA-1	1.0	145	28.5	4.5	0.55	0.08
PTA-2	2.5	121	35.8	11.4	0.28	0.09
PTA-3	3.5	110	46.5	10.0	0.25	0.01
PTA-4	5.0	99	55.0	16.0	0.21	0.02
PZA-1	1.0	146	33.0	34.2	0.64	0.66
PZA-2	2.5	139	42.1	43.5	0.33	0.34
PZA-3	3.5	130	50.0	51.8	0.27	0.28
PZA-4	5.0	113	61.7	62.0	0.24	0.24

[a] A = Al_2O_3, TA = TiO_2–Al_2O_3, ZA = ZrO_2–Al_2O_3, PA = Pt/Al_2O_3, PTA = Pt–TiO_2–Al_2O_3 and PZA = Pt–ZrO_2–Al_2O_3.

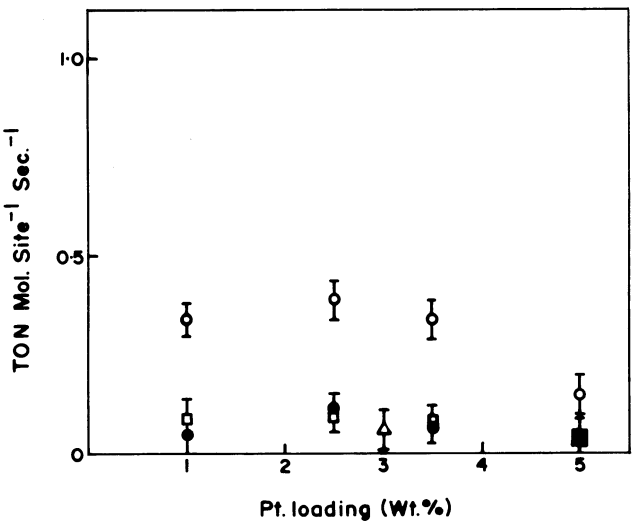

Figure 2. Chlorobenzene hydrodechlorination activity of the catalysts.

ity was observed with increase in Pt loading and cyclohexane selectivity increased. In all the catalysts a maximum benzene selectivity of 63% was obtained for LTR-treated TiO_2-modified catalyst at 1 wt% Pt loading. And a maximum selectivity for cyclohexane (98%) was obtained for HTR-treated TiO_2-modified catalyst at 5 wt% Pt loading. However, a comparison of chlorobenzene conversion and product selectivities for 3 wt% Pt/Al_2O_3 with TiO_2-, ZrO_2-modified catalysts shows that, rather than support modification, the metal (Pt) loading is influencing the reaction.

However, a close observation of figure 2 and figure 3A shows that the HTR-treated TiO_2-modified catalysts are the most active. Taken into account that on HTR-treated TiO_2 catalysts the number of accessible Pt atoms is much reduced, it is obvious that a strong metal–support interaction (SMSI) is taking place [12]. A number of phenomena are associated with SMSI behaviour brought about in metal/TiO_2 systems by an HTR step, such as (i) electron transfer from the support to the metal, (ii) morphological changes in the metal particles, (iii) decoration of the metal surface by TiO_x species, (iv) formation of intermetallic compounds and (v) hydrogen spillover [12,13]. After assessing these factors for their capabilities to enhance catalyst activity in hydrogenation reactions Sen and Vannice [12] explained the higher activity and TON values on HTR-treated Pt/TiO_2 catalysts to an increase in the number of active sites in the Pt–TiO_2 interface region. These active sites, which are electron-deficient in nature are in close proximity to Pt and may be responsible for the higher activity exhibited by HTR-treated TiO_2–Pt catalysts. Accordingly we feel that the additional sites created at the Pt–TiO_2 interfacial region may be contributing for the higher activities obtained on HTR-treated Pt/TiO_2–Al_2O_3 catalysts. In LTR-treated TiO_2-modified catalysts and ZrO_2-modified catalysts the decrease in conversion beyond 2.5 wt% Pt may be due to the poisoning of active Pt sites by HCl produced in the reaction [14]. If the increasing trend of H_2 uptake with Pt loading is attributed to hydrogen spillover, it should help to increase the specific activity of the catalyst [15]. In spite of the increasing H_2 uptake with Pt loading, particle size is also increasing and it may be influencing the reaction by way of inhibiting the facile adsorption of chlorobenzene beyond 2.5 wt% Pt loading [3].

Figure 3B shows the results of time on stream studies on 3 wt% Pt/Al_2O_3 catalyst, TiO_2- and ZrO_2-modified 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 TiO_2- and ZrO_2-modified catalysts exhibited stable activity after 4 h online with conversions remaining fairly constant throughout the period of study. The initial decrease in the activity before attaining the steady state in the modified catalysts may be attributed to the interaction between metal and HCl (produced in the reaction) forming a stable metal chloride species [16]. Selectivities to 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. Figure 3B clearly shows that TiO_2- and ZrO_2-modified Pt/Al_2O_3 catalysts are resistant to deactivation compared to the unmodified Pt catalyst. Kanta Rao and co-workers [8] have studied the influence of addition of a second metal (V, Mo or W) on the activity and selectivity of Pt/Al_2O_3 catalysts in hydrodechlorination of chlorobenzene in vapor phase. While Pt/Al_2O_3 showed a linear decrease in activity with time, the bimetallic catalysts are found to be resistant to deactivation. These investigations clearly demonstrate that by support modification or by addition of a second metal to Pt, it is possible to modify the properties of the Pt sites to resist deactivation.

According to a formal mechanism, chlorobenzene conversion is similar to that of oxidation of hydrocarbons: chlorobenzene and HCl (produced in the reaction) interact with the metal surface to form a surface metal chloride and H_2 cleans the metal surface. Hydrogenation of the aromatic ring can occur by the parallel conversion of chlorobenzene to chlorocyclohexane or the consecutive conversion to benzene and cyclohexane [16,17]. Since chlorine removal from chlorobenzene is a highly selective process, chances of hydrogenation of the aromatic ring to chlorocyclohexane represent less than 2% on the catalyst systems studied here.

In conclusion, this study shows that the modification of alumina increases deactivation resistance of Pt/Al_2O_3 catalysts in the hydrodechlorination of chlorobenzene. A near total selectivity (98%) was obtained in the case of Pt/Al_2O_3 catalyst modified with TiO_2. Further investigations are in progress to ascertain the reaction mechanism and structure and activity relationships in Pt supported on modified Al_2O_3 catalysts.

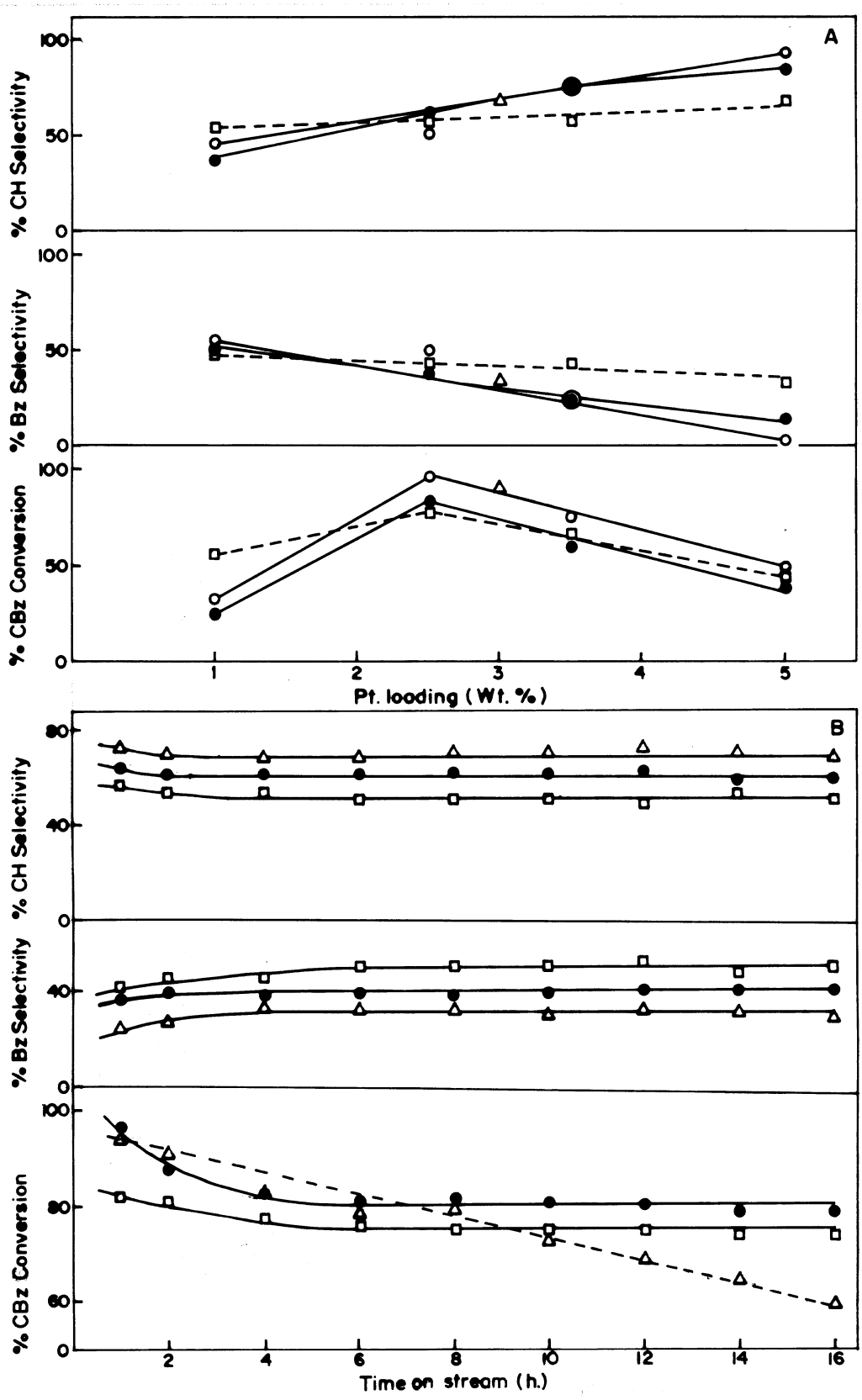

Figure 3. (A) Conversion and product selectivities as a function of Pt loading. (B) Results of time on stream studies.

Acknowledgement

STS thanks the Council of Scientific and Industrial Research, New Delhi, India for the award of a Research Associateship.

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