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Gas-phase hydrodechlorination of chlorobenzenes over silica-supported palladium and palladium–ytterbium[†]

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A 5% w/w palladium loading on silica has been achieved via impregnation of the support with $Pd(C_2H_3O_2)_2$ and $\{(DMF)_{10}Yb_2[Pd(CN)_4]_3\}_\infty$ precursors to deliver monometallic (Pd/SiO_2) and bimetallic ($Yb-Pd/SiO_2$) catalyst systems respectively. The catalytic action of each has been assessed in the continuous gas-phase hydrodechlorination (HDC) of chlorobenzene (CB) and 1,2-dichlorobenzene (1,2-DCB) ($T = 423$ K, inlet chlorine/palladium mol ratio of 5×10^3 h^{-1}) and the hydrogenation of benzene ($T = 423$ K, inlet C_6H_6/palladium mol ratio of 35 h^{-1}). Activation of both catalysts delivered similar palladium crystallite size distributions with an average palladium diameter of 5–6 nm where the ytterbium component (in $Yb-Pd/SiO_2$) was present as a thin surface coating. The Pd–Yb bimetallic exhibited significantly higher HDC and hydrogenation activities, the former manifested by significantly greater fractional dechlorinations and benzene selectivities/yields. Yb/SiO_2 proved inactive in terms of promoting hydrogen scission or addition and the promotional effect of ytterbium in $Yb-Pd/SiO_2$ is discussed in terms of electron donation and hydrogen transfer via surface YbH_2. Under identical reaction conditions, a lower HDC activity was recorded for 1,2-DCB compared with CB, a response that is attributed to steric constraints allied to the deactivating effect of the second chlorine substituent. Both Pd/SiO_2 and $Yb-Pd/SiO_2$ exhibited a decline in HDC activity with time-on-stream, but the bimetallic was significantly more resistant to deactivation. Copyright © 2003 John Wiley & Sons, Ltd.

KEYWORDS: hydrodechlorination; hydrogenation; Pd/SiO_2; $Yb-Pd/SiO_2$; bimetallic catalyst; chlorobenzene; 1,2-dichlorobenzene

INTRODUCTION

Chlorinated benzenes have found widespread use as organic solvents, heat transfer agents, oil additives and in the synthesis of pesticides/insecticides and dyes.[1,2] The release of any associated chlorinated waste is stringently regulated due to mounting evidence of ecological and atmospheric damage, and a major impetus is now in place to eliminate toxic halogenated hydrocarbon emissions. The present methods employed for the disposal of halogenated compounds include incineration, catalytic combustion and biotreatment. Incineration requires temperatures in excess of 1200 K, and can lead to the formation of more toxic by-products, such as polychlorinated dibenzodioxins and polychlorinated dibenzofurans.[3] Catalytic combustion is also destructive and although the use of catalysts can drastically reduce the operating temperature (to <700 K), this approach is still prohibitively energy demanding.[3] Biotreatment involves aerobic or anaerobic degradation, where the chlorinated feed can serve as the sole carbon energy source,[2,4] but inhibition of bacterial growth is typical and the overall rate of chlorine removal is very low. Hydrodechlorination (HDC) is an alternative methodology that is less sensitive to feed composition and facilitates the recovery/reuse of valuable chemical feedstock. Although >99.9% destruction of the chloro-feed can be achieved by thermal HDC,[5] the

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process is highly energy demanding and does not represent an effective use of resources. Catalytic HDC represents a more progressive green processing strategy, and the advantages of this approach[6] have provided the impetus for this research. We have assessed the performance of Pd/SiO_2 and Yb–Pd/SiO_2 (derived from a novel organometallic precursor) in promoting the gas-phase HDC of chlorobenzene (CB) and 1,2-dichlorobenzene (1,2-DCB) and report herein the results of our study.

Supported palladium has been successfully employed in a wide range of hydroprocessing applications.[7,8] HDC of aromatic chlorides has been studied both in the liquid[9–14] and vapor phases[1,15,16] with an array of transition metals (nickel, palladium, platinum, rhodium) anchored to such supports as Al_2O_3, activated carbon, SiO_2, Nb_2O_5 and synthetic zeolites. Catalyst deactivation has been a common feature of these studies, and this is attributed to a surface poisoning by the HCl by-product and/or carbon deposition.[17–20] It should, however, be noted that Lingaiah *et al*.[21] observed no loss of activity during the HDC of CB over Ni/C. A search through the literature did not unearth any reports of Yb–Pd/SiO_2 (the focus of this study) use in the HDC of chloroarenes. Nevertheless, previous studies have revealed a higher activity associated with Pd–Yb relative to palladium in the reduction of NO by CH_4[22] and in the hydrogenation of phenol.[23] Imamura *et al*.[24] have ascribed enhanced propyne hydrogenation rates over palladium/lanthanide catalysts to a higher concentration of reactive hydrogen on the supported bimetallic. A number of bimetallic catalyst systems have been employed to promote HDC reactions.[25–33] Lingaiah and co-workers recorded lower CB HDC activities for Fe–Pd supported on silica,[25] magnesia[26] and alumina[27] when compared with the corresponding monometallic palladium systems and explained this effect on the basis of a dilution of the active palladium sites with possible (inactive) Pd–Fe alloy formation. Bonarowska and co-workers examined the HDC of dichlorodifluoromethane (CFC-12) over Au–Pd/C[28,29] and Au–Pd/SiO_2[30] and observed greater selectivity for the target CH_2F_2 due to the presence of gold, whereas rhenium[31] incorporation had no effect on selectivity. Ohnishi *et al*.,[32] in the HDC of 1,1,2-trichlorotrifluoroethane (CFC-113) over Bi–Pd/SiO_2 and Tl–Pd/C, recorded enhanced selectivity toward trifluoroethene and chlorotrifluoroethene over the bimetallic systems. Moreover, Heinrichs *et al*.[33] observed quite distinct selectivities in the HDC of 1,2-dichloroethane over Ag–Pd/SiO_2 and Pd/SiO_2. The one related study of ytterbium use to modify hydrogenolysis activity is given by Bihan and Yoshimura,[34] who used Pd–Pt/Yb-modified USY zeolite to promote hydrodearomatization/hydrodesulfurization and noted a greater stability of the catalyst, in that palladium sintering was limited by the presence of ytterbium, which resulted in a greater dispersion of palladium on the ytterbium-stabilized support.[34] The existing database of HDC activities/selectivities for supported bimetallics is, as yet, insufficient to draw any generic conclusions. Nonetheless, it is generally accepted that catalytic HDC, in common with most hydrogenolysis reactions, is strongly influenced by the electronic structure of the active metal sites.[35] From the outset of this study, it was anticipated that electron donation from electropositive ytterbium could influence the intrinsic HDC activity of the palladium sites, an effect that is probed in this report.

EXPERIMENTAL

Catalyst preparation and activation

The palladium–ytterbium complex $\{(DMF)_{10}Yb_2[Pd(CN)_4]_3\}_\infty$, which served as the bimetallic catalyst precursor, was prepared using a procedure previously described by Shore and co-workers.[36] A solution of the bimetallic complex in dimethyl formamide (DMF) was contacted with a sample of fumed SiO_2 (Aldrich, surface area >200 m^2 g^{-1}) to deliver a 5% w/w palladium loading. The DMF was removed from the metal-impregnated SiO_2 under vacuum over a period of 12 h at room temperature. The resulting white solid was removed in air and placed (in a quartz boat) in a furnace and flushed with hydrogen for *ca* 10 min and reduced under a steady hydrogen flow with incremental temperature increases of 25 K, approximately every 10 min, to a final temperature of 523 K, which was maintained for 30 min. The sample was then flushed in helium and passivated in a 1% v/v oxygen in helium flow at room temperature. A 5% w/w Pd/SiO_2 was prepared by contacting the same SiO_2 substrate with the acetate precursor (in DMF) and activated/passivated as above. A 5% w/w ytterbium on SiO_2 was prepared as follows. Weighed amounts of SiO_2 and ytterbium powder were charged into a reaction flask in a drybox. Liquid ammonia was then vacuum-transferred into this flask at 195 K, the mixture was stirred for *ca* 3 h and the liquid ammonia was then pumped away. Each sample was sieved (ATM fine test sieves) into a batch of 75 µm average particle diameter and subjected to a second reduction step (prior to catalysis) in a fixed-bed tubular glass reactor (i.d. 1.25 cm) by heating (10 K min^{-1}) in a 60 cm^3 min^{-1} stream of dry hydrogen (99.999%), monitored using a Humonics (Model 520) flow meter to a final temperature of 573 K that was maintained for 12 h.

The nature of palladium dispersion was probed by high-resolution transmission electron microscopy (HRTEM) analysis using a Philips CM200 FEGTEM microscope equipped with a UTW energy dispersive X-ray (EDX) detector (Oxford Instruments) and operated at an accelerating voltage of 200 kV. The specimens were prepared by ultrasonic dispersion in 2-butanol, evaporating a drop of the resultant suspension onto a holey carbon support grid. The mean palladium particle sizes quoted in this paper are based on a measurement of over 500 individual particles. A secondary-ion mass spectrometry (SIMS) analysis (VG ESCALAB) of each activated catalyst (pressed into indium foil) revealed only the presence of silicon, oxygen, palladium or (in the case of the supported bimetallic) ytterbium on the surface.

Nitrogen BET surface area measurements were carried out at 77 K (Micromeritics TriStar) on freshly reduced samples.

Catalytic system

The reactions were conducted *in situ* (after catalyst activation) with a co-current flow of the aromatic feed in hydrogen. A layer of glass beads above the catalyst bed ensured that the reactants were vaporized and reached reaction temperature before contacting the catalyst.[18] A Model 100 (kd Scientific) microprocessor-controlled infusion pump was used to deliver the aromatic feed, via a glass–Teflon air-tight syringe and Teflon line at a fixed calibrated flow rate, which was carried through the catalyst bed in a stream of dry hydrogen. All the HDC reactions were carried out at 423 K, where isothermal operation was ensured by diluting the catalyst bed with ground glass (75 μm). The ground glass was mixed thoroughly with catalyst before insertion into the reactor. CB (Aldrich, 99.9%), 1,2-DCB (Aldrich, 99%) and methanol (Merck, 99.8%), which served as solvent, were used without further purification. The HDC reaction was monitored at an inlet hourly chlorine/palladium mole ratio of 5×10^3 and a contact time of 0.02 min. Hydrogenation activity was also monitored by examining the reduction of benzene (as feed) at 423 K: inlet hourly benzene/palladium mole ratio of 35. The catalyst was activated as above, benzene conversion was followed over 3 h on stream, the catalyst was then contacted with 0.3 mol 1,2-DCB over 24 h and the benzene feed was reintroduced with product analysis. In a series of blank tests, passage of each reactant in a stream of hydrogen through the empty reactor, i.e. in the absence of catalyst, did not result in any detectable conversion. The reactor effluent was frozen in a liquid-nitrogen trap for subsequent analysis, which was undertaken using a Perkin–Elmer Auto System XL chromatograph equipped with a split/splitless injector and a flame ionization detector, employing a DB-1 50 m × 0.20 mm i.d., 0.33 μm capillary column (J&W Scientific). The overall level of HDC/hydrogenation was converted to mol% conversion using detailed calibration plots for each feedstock. Quantitative analysis was based on relative peak area with acetone as solvent, where analytical repeatability was better than ±0.4% and the detection limit typically corresponded to a feedstock conversion of less than 0.1 mol%. HDC performance is quantified in terms of fractional dechlorination X_{Cl}

$$X_{\mathrm{Cl}} = \frac{[\mathrm{Cl}]_{\mathrm{in}} - [\mathrm{Cl}]_{\mathrm{out}}}{[\mathrm{Cl}]_{\mathrm{in}}} \tag{1}$$

where it has been demonstrated previously[18–20] that HCl is the only inorganic product with no detectable Cl_2 production. The percentage selectivity of benzene S_{benzene} from a 1,2-DCB feed is given by

$$S_{\mathrm{benzene}}(\%) = \frac{[\mathrm{benzene}]_{\mathrm{out}}}{[1{,}2\text{-DCB}]_{\mathrm{in}} - [1{,}2\text{-DCB}]_{\mathrm{out}}} \times 100 \tag{2}$$

and the percentage yield of benzene Y_{benzene} can be calculated from

$$Y_{\mathrm{benzene}}(\%) = \frac{[\mathrm{benzene}]_{\mathrm{out}}}{[1{,}2\text{-DCB}]_{\mathrm{in}}} \times 100 \tag{3}$$

RESULTS AND DISCUSSIONS

The BET surface area and palladium particle size characteristics are included in Table 1. The surface-weighted average palladium particle was slightly smaller in the case of the bimetallic, albeit the range of palladium sizes was wider. The use of the $\{(\mathrm{DMF})_{10}\mathrm{Yb}_2[\mathrm{Pd(CN)}_4]_3\}_\infty$ precursor represents a novel means of simultaneous addition of a lanthanide and noble metal to the silica support. We have shown previously[23] that the ytterbium component is present as a thin coating spread over the catalyst's surface with no evidence of any distinct clustering or particles of ytterbium in the Yb–Pd/SiO_2 sample. This spreading of ytterbium across the SiO_2 surface can explain the lower overall (BET) surface area. Long-term (up to 18 h on-stream) catalytic HDC activity/selectivity was monitored with a total inlet chlorine to palladium mole ratio of 1×10^5, which represents very demanding catalyst testing conditions. The HDC of CB over Pd/SiO_2 generated benzene as the only organic product with no evidence of further hydrogenation to cyclohexane. A secondary ring reduction has been reported elsewhere for reaction over Pt/Al_2O_3[9] and Pt/H–BEA zeolite.[17] CB consumption showed a continual decline with time, as illustrated in Fig. 1, a response that has been noted previously.[16,20] Reaction over Yb–Pd/SiO_2 (under identical conditions) delivered an initial conversion that was 25 times greater when compared with that of the monometallic catalyst. Reaction over Yb–Pd/SiO_2 generated benzene as the principal product but cyclohexane was formed in trace amounts (selectivity <1%). The bimetallic also exhibited an initial loss of activity but an appreciably higher level of dechlorination was maintained compared with Pd/SiO_2. The temporal response of the fractional dechlorination X_{Cl} can be expressed in terms of the empirical relationship

$$X_{\mathrm{Cl}} = X_0 \Delta t^n \exp(-\alpha \Delta t) \tag{4}$$

and the goodness of the fit to the experimentally determined X_{Cl} values can be seen in Fig. 1. Fit convergence yielded

Table 1. Nitrogen BET surface areas, surface-weighted average palladium particle sizes and range of sizes associated with Pd/SiO_2 and Yb–Pd/SiO_2

	Pd/SiO_2	Yb–Pd/SiO_2
N_2 BET surface area ($m^2\ g^{-1}$)	181	153
Average Pd diameter (nm)	6.0	5.1
Pd diameter range (nm)	<2 to 18	<2 to 25

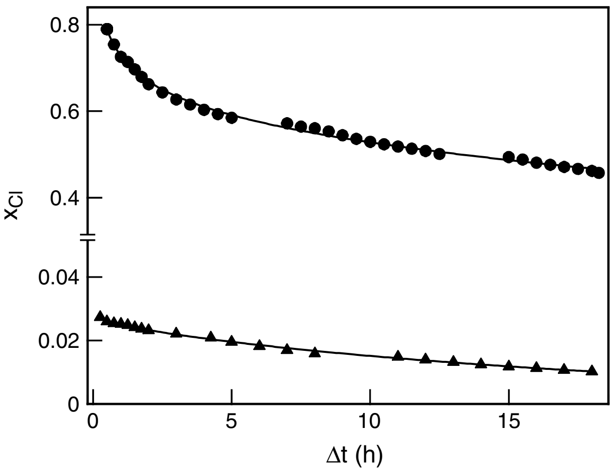

Figure 1. Fractional dechlorination of CB (X_{Cl}) as a function of time-on-stream over Pd/SiO$_2$ (▲) and Yb–Pd/SiO$_2$ (●) at 423 K; inlet Cl/Pd mole ratio is 5×10^3 h^{-1}. Note: lines represent fits to Eqn (4), correlation coefficients >0.996.

a value for the initial fractional dechlorination X_0[37] that was significantly higher for Yb–Pd/SiO$_2$ (0.73) than for Pd/SiO$_2$ (0.026). Ytterbium supported on silica (Yb/SiO$_2$) did not exhibit any aromatic HDC or hydrogenation activity under the same reaction conditions. Although ytterbium alone has no hydrogen addition/scission capability, it does serve to promote the HDC activity of the noble metal. Given the similar palladium particle sizes (and overall range of sizes) associated with both Pd/SiO$_2$ and Yb–Pd/SiO$_2$, a particle size effect is unlikely to contribute strongly to the observed enhanced dechlorination. HDC activity may, however, be sensitive to changes in the electronic structure of the supported palladium where, on the basis of the catalytic data, the presence of the electropositive ytterbium acts, through electron donation, to raise hydrogen scission activity. Such an effect can be facilitated through the intimate association of the lanthanide component as a thin film over the palladium phase dispersed on silica. HDC promotion may also be due to the established (by X-ray diffraction and magnetic susceptibility measurements) property of ytterbium as a hydrogen source in the form ytterbium dihydride (YbH$_2$) that is generated at ambient temperature and atmospheric pressure.[38] Indeed, orthorhombic YbH$_2$ has been detected as a thin film at room temperature,[39] which is the form that may well prevail on the activated Yb–Pd/SiO$_2$ catalyst. It has been shown[40] that the hydrogen associated with Yb–H films is highly mobile, with hydrogen release at elevated temperatures. The presence of this additional source of reactive hydrogen in Yb–Pd/SiO$_2$ may be the predominant source of the observed superior dechlorination activity. Both monometallic and bimetallic catalysts exhibited a loss of activity with extended use, which can, drawing on the available literature, be attributed to active site poisoning by the HCl by-product and/or carbon deposition.[17–20] However, on the basis of the fit to Eqn (4), the time required for the fractional dechlorination delivered by Yb–Pd/SiO$_2$ to decay to one-half its initial value ($\Delta t_{1/2} = 40.5$ h) is considerably greater than that which is necessary ($\Delta t_{1/2} = 12.7$ h) for Pd/SiO$_2$; the bimetallic exhibits a higher degree of tolerance. As an addendum to the HDC studies, we examined the hydrogenation of benzene (to cyclohexane) over the same two catalysts in order to establish a possibly generic enhanced 'hydroprocessing' capability for the Yb–Pd system. The cyclohexane yield from the freshly activated bimetallic was significantly higher, as recorded in Table 2. Moreover, this high cyclohexane yield over Yb–Pd/SiO$_2$ was largely maintained after prolonged contact with a chlorine-containing gas stream, whereas Pd/SiO$_2$ (after the same treatment) exhibited negligible conversion. The latter confirms a greater resistance of the bimetallic to chlorine-induced deactivation allied to an enhanced hydrogen addition performance, as we demonstrated previously for the hydrogenation of phenol.[23]

The HDC of 1,2-DCB can proceed stepwise with CB as a reactive intermediate or in a concerted fashion with the concomitant scission of both C–Cl bonds, as shown in Fig. 2. The variation of the fractional chlorine removal X_{Cl} from 1,2-DCB as a function of time-on-stream is shown in Fig. 3, wherein the fits to Eqn (4) are also included. Conversion over Pd/SiO$_2$ was very low (<1 mol%) but still with a detectable temporal loss of activity. The bimetallic catalyst again exhibited a higher level of dechlorination, $X_0 = 0.25$ compared with $X_0 = 0.004$ for Pd/SiO$_2$. The bimetallic system also sustained a decline in HDC activity, but X_{Cl} consistently

Table 2. Cyclohexane yield $Y_{cyclohexane}$ from the hydrogenation of benzene at 423 K over Pd/SiO$_2$ and Yb–Pd/SiO$_2$ before (freshly activated) and after 1,2-DCB contact (0.3 mol); inlet C$_6$H$_6$/Pd mole ratio was 35 h^{-1}

	$Y_{cyclohexane}$ (%)	
Catalyst	Freshly activated	After Cl contact
Pd/SiO$_2$	5	1
Yb–Pd/SiO$_2$	38	36

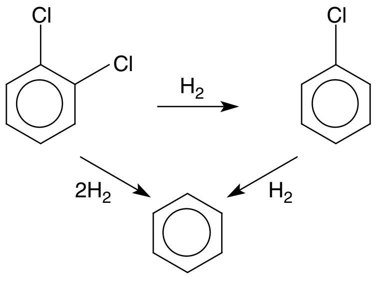

Figure 2. Series/parallel reaction scheme for the HDC of 1,2-DCB to benzene.

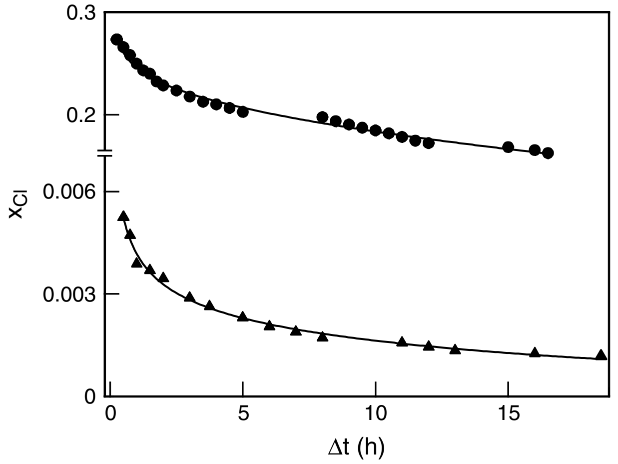

Figure 3. Fractional dechlorination of 1,2-DCB X_{Cl} as a function of time-on-stream over Pd/SiO$_2$ (▲) and Yb–Pd/SiO$_2$ (●) at 423 K; inlet Cl/Pd mole ratio is 5×10^3 h^{-1}. Note: lines represent fits to Eqn (4), correlation coefficient >0.994.

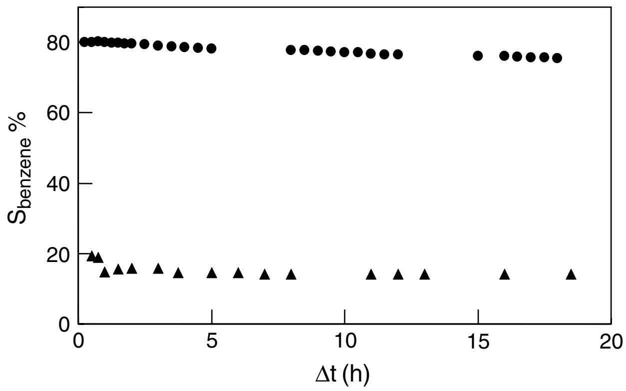

Figure 4. The variation of benzene selectivity $S_{benzene}$ (%) with time-on-stream for the HDC of 1,2-DCB over Pd/SiO$_2$ (▲) and Yb–Pd/SiO$_2$ (●) at 423 K; inlet Cl/Pd mole ratio is 5×10^3 h^{-1}.

Table 3. Benzene yield $Y_{benzene}$ at selected times-on-stream resulting from the HDC of CB and 1,2-DCB over Pd/SiO$_2$ and Yb–Pd/SiO$_2$; inlet Cl/Pd mole ratio was 5×10^3 h^{-1}

	$Y_{benzene}$ (%)			
	CB feed		1,2-DCB feed	
Δt (h)	Pd/SiO$_2$	Yb–Pd/SiO$_2$	Pd/SiO$_2$	Yb–Pd/SiO$_2$
1	2.5	72.2	0.1	22.0
5	2.0	58.3	0.1	17.6
9	1.5	54.2	<0.1	16.5
12	1.4	50.6	<0.1	14.8
15	1.2	49.2	<0.1	14.4
18	1.0	46.1	<0.1	13.3

exceeded that delivered by Pd/SiO$_2$; the Δ$t_{1/2}$ value was again greater due to the presence of ytterbium (31.6 h as opposed to 5.5 h). The improved HDC performance associated with Yb–Pd/SiO$_2$ is clearly illustrated in Fig. 4, where benzene selectivity $S_{benzene}$ is plotted as a function of time-on-stream. It is immediately evident that complete dechlorination to benzene was enhanced (fourfold) over the supported bimetallic. There is a detectable decline in $S_{benzene}$ with extended reaction time that can be linked to the decrease in X_{Cl} (Fig. 3) as the contribution of stepwise chlorine removal (Fig. 2) becomes more significant. Benzene yield $Y_{benzene}$ at selected time-on-stream values resulting from the HDC of CB and 1,2-DCB over both catalysts is recorded in Table 3, wherein the promotional effect of ytterbium is again in evidence. It is noteworthy that (under identical reaction conditions) $Y_{benzene}$ from CB was consistently greater than that from 1,2-DCB. This can be explained on the basis of both steric and electronic effects. HDC of the 1,2-DCB feed is subject to steric constraints, where hindrance due to the proximity of the *ortho*-chlorine substituents renders both chlorine atoms less susceptible to hydrogen cleavage from the ring. The lower degree of HDC of the di-chlorinated reactant is also indicative of an electrophilic mechanism where the presence of the second chlorine substituent (as opposed to a hydrogen atom in the case of CB) serves to deactivate the ring for electrophilic attack via an inductive effect that decreases the electron density of the aromatic ring, i.e. destabilizes the cationic transition state. Similar electrophilic effects have been reported in related heterogeneous catalytic dechlorinations.[8,41] The results plotted in Fig. 5 really serve to demonstrate the appreciable difference in the catalytic performance of both Pd/SiO$_2$ and Yb–Pd/SiO$_2$. The fractional conversion of 1,2-DCB ($X_{1,2\text{-DCB}}$) over the Yb–Pd system is markedly greater and the associated benzene selectivity is so much higher that the two sets of data are far removed with no possible overlap.

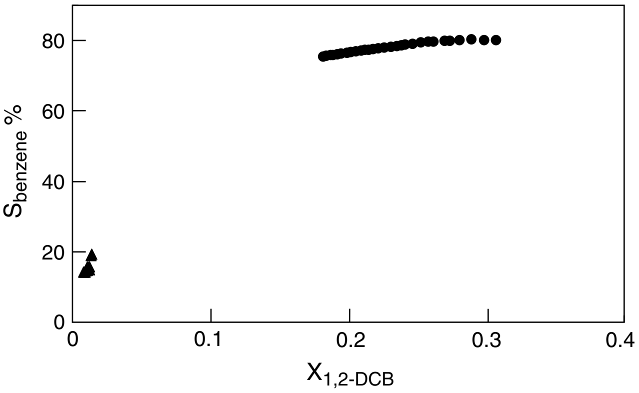

Figure 5. Benzene selectivity $S_{benzene}$ (%) as a function of fractional 1,2-DCB conversion $X_{1,2\text{-DCB}}$ over Pd/SiO$_2$ (▲) and Yb–Pd/SiO$_2$ (●) at 423 K; inlet Cl/Pd mole ratio is 5×10^3 h^{-1}.

CONCLUSIONS

A 5% w/w palladium loading on silica was achieved by impregnating the support with $Pd(C_2H_3O_2)_2$ (monometallic catalyst) and $\{(DMF)_{10}Yb_2[Pd(CN)_4]_3\}_\infty$ (bimetallic catalyst). After reduction in hydrogen, the average palladium crystallite diameter was similar (5–6 nm) for both catalysts. The performance of Pd/SiO_2 and $Yb–Pd/SiO_2$ in promoting the HDC of CB and 1,2-DCB has revealed an appreciably higher HDC efficiency due to the presence of ytterbium. This is manifested by higher fractional dechlorinations and a greater yield of benzene in the conversion of 1,2-DCB. This enhanced activity extends to the hydrogenation of benzene, where the Pd–Yb bimetallic delivered an eightfold higher cyclohexane yield. Yb/SiO_2 is inactive in both hydrogenation and HDC and the promotional effect of ytterbium must be linked to (i) a modification of the intrinsic activity of the palladium sites through electron donation and/or (ii) hydrogen transfer (via YbH_2) to the active palladium sites. The 1,2-DCB reactant was more resistant to HDC when compared with CB, a result that can be explained on the basis of a combined steric hindrance and a deactivating inductive effect. A loss of HDC activity with time-on-stream was observed for both catalysts, but $Yb–Pd/SiO_2$ showed a higher tolerance. Work is now under way to characterize the catalysts, pre- and post-reaction, in order to establish the predominant source of (a) the ytterbium promotional effect and (b) deactivation during HDC.

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