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Catalytic hydrodechlorination over Pd supported on amorphous and structured carbon

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Abstract

The gas phase catalytic hydrodechlorination (HDC) of chlorobenzene has been studied ($T = 423$ K) over Pd (8 ± 1wt%) supported on activated carbon (Pd/AC), graphite (Pd/graphite), and graphitic carbon nanofiber (Pd/GNF). The activated carbon (875 $m^2\ g^{-1}$) and graphite (11 $m^2\ g^{-1}$) substrates were obtained from a commercial source, but the carbon nanofibers (74 $m^2\ g^{-1}$) were synthesized by ethylene decomposition over unsupported Ni to yield a mean fiber diameter of 225 nm. Under identical reaction conditions, the following initial HDC activity sequence was established: Pd/GNF $\approx$ Pd/AC $>$ Pd/graphite. HDC activity declined with time-on-stream (four reaction cycles were considered), where Pd/GNF maintained a significantly higher fractional HDC and Pd/AC activity decreased continually to converge with Pd/graphite at a common residual conversion. The prereaction and postreaction catalyst samples were characterized by BET area/pore size analysis, temperature-programmed reduction, transmission electron microscopy, scanning electron microscopy, H_2 chemisorption/temperature-programmed desorption (TPD), X-ray diffraction (XRD), and acid/base titration. Pd size distribution is given in each case where surface area-weighted Pd diameter increased in the order: Pd/graphite $<$ Pd/GNF $<$ Pd/AC. The spent catalysts exhibited lower H_2 uptake with a disruption to the TPD profiles. Pd on each support adopted (on the basis of XRD analysis) an exclusive cubic geometry, but whereas the particles on AC were globular in nature, faceted Pd particles predominated on the graphite and (to a lesser extent) GNF supports. HDC activity and temporal behavior is rationalized on the basis of metal–support interactions, Pd particle size, and H_2 uptake/release characteristics.

Keywords: Hydrodechlorination; Chlorobenzene; Supported Pd; Activated carbon; Graphite; Carbon nanofibers

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1. Introduction

The release of halogenated organics into the environment is associated with stratospheric ozone depletion, smog formation, global warming, and a range of human health effects [1]. Although such releases have been curtailed through stringent environmental regulations, chlorinated compounds still find widespread use (in, e.g., the manufacture of pesticides and degreasing agents) [2]. In previous reports [3–5], we demonstrated the viability of catalytic hydrodechlorination (HDC) over supported Ni as a nondestructive, low-energy method of converting toxic haloarene gas streams into recyclable raw materials. Chlorinated waste treatments based on electrochemical, radiation, photochemical, and biotechnological processes [6,7] result in low conversions and impractical scale-up. Thermal methods, including pyrolysis (>1200 K) and hydrogenolysis (>800 K), have high energy requirements [8,9]. Incineration can generate harmful dioxins/furans [1,6,7]. Catalytic HDC has now been reported in both liquid and gas phases over an array of catalysts, notably supported Pt [10–12], Ni [3–16], Rh [11,12], Ru [12,17], Ni–Mo [18], and Fe [19,20]. Group VIII noble metals are known to be effective in hydrogenolysis, and Pd has been demonstrated to deliver higher specific HDC rates [11,21]. Accordingly, we have adopted Pd as a model cat-

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alytic agent in this fundamental study of the role of different forms of carbon support in determining Pd HDC performance.

Hydrogen-assisted dechlorination of aliphatic compounds has received much attention in the literature, with a particular focus on the conversion of chlorofluorocarbons [22,23] and chloroalkanes/chloroalkenes [10,24,25]. A distinction must be made between HDC and dehydrochlorination; the latter involves the internal elimination of HCl and is applicable to the dechlorination of aliphatic chloro compounds [26], where an external H_2 source is not necessary but can serve to limit deactivation [27]. HDC of chloroarenes has been considered to a lesser extent, but there are data available on the conversion of chlorobenzenes (CBs) [10,28], chlorophenols [29,30], and polychlorinated aromatics [31,32]. Catalyst deactivation is a feature of HDC in both liquid [33–36] and gas phase [21,37–44] operations, as a result of HCl interactions that poison the active metal [11,21,33,35,36,38,40,41]. The catalyst parameters that influence HDC performance include synthesis route [33,34], support [10,11,21,33,35], metal dispersion [11,33,34,38], metal loading [44], activation procedure [19,28,34,42,43], incorporation of additives [12,35,36,45], solvent [12,14,46], and the presence of a second metal (bimetallic catalysts) [19,21,28,39,41–43]. There is some evidence that the support can inhibit HCl poisoning [11,33]; in any case, the support must be resistant to the corrosive effects of high HCl concentrations generated at elevated temperatures [21]. Carbon [10,28] and inorganic supports, such as Al_2O_3 [10,37,42], SiO_2 [19,41], MgO [43], Nb_2O_5 [34], and AlF_3 [10], have been used in gas phase HDC of CB. The existing literature on chloroarene HDC over carbon-supported Pd is summarized in Table 1, where feasible, we relate our results to the trends that have emerged from the tabulated studies. We first note some reports that considered a series of supported Pd catalysts in CB HDC applications. Prati et al. [10] reported a clear dependence of activity on the nature of the support, yielding the following gas phase activity sequence: $Pd/C > Pd/Vycor$ (porous glass) $> Pd/Al_2O_3 > Pd/AlF_3$. In the liquid phase, Benitez et al. [11] compared the HDC performance of supported Pd at a similar dispersion (7–10%), where $Pd/SiO_2 > Pd/Al_2O_3 > Pd/C$. In contrast, Halligudi et al. [44] reported the following order of decreasing 1,2-dichlorobenzene HDC: $Pd/Al_2O_3 > Pd/C > Pd/SiO_2 > Pd/MgO$. These results point to a support effect, but the source/cause has not yet been established.

The present study was conducted to couple characterization and catalytic data to probe the role of carbon structural characteristics in determining Pd HDC performance. Three carbonaceous supports were considered: conventional activated carbon, graphite, and GNFs. Carbon nanofibers, produced by the catalytic decomposition of carbon-containing gases at high temperatures, exhibit a high-aspect ratio with ordered parallel graphene layers arranged in a specific conformation [56,57]. Interest in GNF as a catalyst support has risen over the last decade, due largely to reduced mass transfer constraints when compared with conventional activated carbon, which exhibits variable structural characteristics when produced from disparate sources [56,58–61]. The use of GNF supports in hydrogenation reactions [56,57,60,62,63] and ammonium synthesis [64] has been recorded in the literature, but there has been no published study of catalytic HDC. In addition, there are no reports of Pd/graphite use in HDC. Here we provide the first account of Pd/graphite- and Pd/GNF-promoted CB HDC.

2. Experimental

2.1. Catalyst preparation and activation

The activated carbon (G-60, 100 mesh) was obtained from NORIT (UK), and the graphite (synthetic 1- to 2-µm powder) was obtained from Sigma–Aldrich. The GNF support was synthesized by the catalytic decomposition of ethylene over unsupported Ni, as described in detail previously [57]. The catalytically generated GNF product was contacted (agitation at 500 rpm) with dilute mineral acid ($1\ \mathrm{mol\,dm^{-3}}$ HNO_3) for 7 days, to remove the parent catalyst particles. This step was necessary to avoid any contribution to HDC from residual Ni; the commercial activated carbon and graphite samples were also subjected to the same demineralization. The carbon supports were thoroughly washed with deionized water (until pH approached 7) and oven-dried at 383 K for 12 h. The GNF sample was subjected to partial oxidation (in a 5% v/v O_2/He mixture) at 673 K for 2 h to remove the amorphous carbon content. The carbon-supported (8 ± 1 wt%, ca. 1 at% Pd) Pd precursor samples were prepared by standard impregnation, in which a 2-butanolic $Pd(NO_3)_2$ solution was added dropwise at 353 K to the substrate with constant agitation (500 rpm), then air-dried at 393 K for 16 h. Aqueous solutions were not used, because carbon support materials are known to have hydrophobic properties leading to difficulties with surface wetting that may adversely affect the ultimate Pd dispersion. Moreover, the acid washing/partial oxidation can modify the wetting characteristics to provide anchoring sites for the supported metal [56,65]. The Pd loading (reproducible to within ±4%) was determined by ICP-OES (Vista-PRO, Varian). Before its use in catalysis, the precursor, sieved (ATM fine test sieves) into a batch of 75 µm average particle diameter, was reduced directly in a $60\ \mathrm{cm^3\,min^{-1}}$ stream of ultrapure dry H_2 at $10\ \mathrm{K\,min^{-1}}$ to 523 ± 1 K, which was maintained for at least 12 h.

2.2. Catalyst characterization

Specific BET surface area and BJH pore volume analyses were performed using the commercial Micromeritics TriStar 3000 unit; N_2 at 77 K served as sorbate. Before measurement, the samples were outgassed at 433 K for 16 h. Bulk tap densities of the carbonaceous supports were obtained from a gravimetric measurement of