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LETTERS

Low-Temperature (553 K) Catalytic Growth of Highly Ordered Carbon Filaments during Hydrodechlorination Reactions

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In the gas-phase hydrodechlorination of chlorobenzene to benzene over Ni/SiO_2, a pretreatment of the catalyst with HCl or HBr gas induced the growth of highly ordered carbon filaments from the catalyst surface. This filamentous growth was observed to occur at 553 K, i.e., at least 150 K less than that reported previously in the literature for the catalytic formation of graphitic carbon. The hydrogen halide pretreatment also resulted in an appreciable increase in the average nickel particle size and a suppression of hydrodechlorination activity. In the absence of this pretreatment the catalyst exhibited stable hydrodechlorination activity and there was no evidence of any filamentous carbon growth. Analysis of the halide-treated samples revealed the presence of potassium that was not evident in the freshly activated catalyst but was introduced as a result of a corrosive attack of the hydrogen halide gas on the microreactor unit. The source of our low-temperature ordered carbon growth must be electronic in nature and is attributed to an intimate combination of halogen/alkali metal on the catalyst surface that facilitates a restructuring of the active sites where a destructive chemisorption of chlorobenzene precedes the dissolution of carbon and precipitation in an ordered fashion.

Introduction

As part of an ongoing program of “environmental catalysis”, we have been examining the catalytic hydrodehalogenation of a range of halogenated aromatics in the gas phase over supported nickel catalysts.[1−3] Catalytic hydrodehalogenation represents a nondestructive, low-energy treatment whereby known hazardous compounds are transformed into recyclable products in a closed system with negligible associated toxic emissions. Chlorobenzene has emerged as a favored model reactant where hydrodechlorination yields HCl that can serve to induce catalyst deactivation possibly via the formation of an unreactive surface $NiCl_2$ species.[4] In our studies of hydrodehalogenation we probed such effects by contacting a freshly activated Ni/SiO_2 catalyst directly with the pertinent hydrogen halide, monitoring the subsequent catalytic activity and comparing it with the reproducible conversions achieved using the untreated catalyst. We observed a dramatic loss of activity that was unexpectedly accompanied by the growth of filamentous carbon from the surface of the catalyst. The growth of such carbonaceous materials is certainly well established either by an arc discharge method or by catalytic decomposition of hydrocarbons over both supported and unsupported metal surfaces, but each route typically requires temperatures in excess of 723 K.[5,6] In our system, the catalytic step was conducted at 553 K; i.e., appreciable carbon filament growth was achieved at a temperature at least 150 K lower than that quoted for related catalyst

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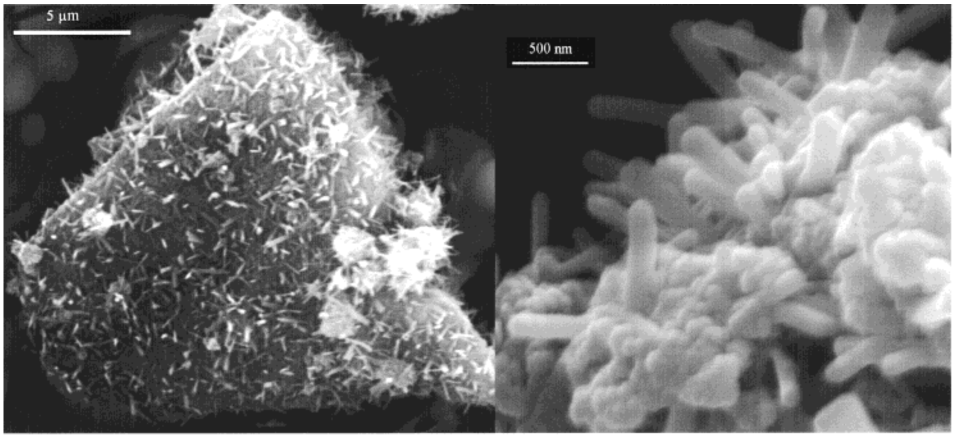

Figure 1. Low- and high-magnification SEM micrographs of the carbon filaments formed during the hydrodechlorination of chlorobenzene over HBr-pretreated Ni/SiO_2.

systems. We are unaware of any published account of ordered carbonaceous filament growth at such a low temperature. In this Letter, we report our experimental observations, provide some preliminary characterization results for the filamentous carbon growth that we have generated in this serendipitous manner and identify a possible combination of promoters for this growth.

Experimental Procedure

The catalyst was prepared by the homogeneous precipitation/deposition of nickel (15.2% w/w) onto a Cab-O-Sil 5M silica (BET surface area = 194 $m^2\ g^{-1}$) and dried in air at 383 K for 20 h.[7] The catalyst precursor, sieved in the mesh range 150−125 μm, was activated by heating at 5 K min^{-1} in a 100 $cm^3\ min^{-1}$ stream of dry hydrogen (99.9%) to 673 K, maintaining this temperature for at least 14 h. All the catalytic reactions were carried out in situ under atmospheric pressure in a fixed bed glass reactor[8] (i.d. = 15 mm) at 553 K. A Model 100 (kd Scientific) microprocessor-controlled infusion pump was used to deliver the chloroaromatic feed at a fixed molar rate ($6 \times 10^{-3}\ h^{-1}$, partial pressure = 0.04 atm), which was carried through the catalyst bed in a stream of purified hydrogen. In the case of the HCl/HBr pretreatments, the catalyst was contacted with flowing HCl and HBr gas (in the range 20−150 $cm^3\ min^{-1}$ for 0.25−5 min) at 548 K; HCl/HBr contact was exothermic and gave rise to an increase in the catalyst bed temperature of up to 34 K. The pretreated catalyst was then flushed with hydrogen (100 $cm^3\ min^{-1}$) for 2 h prior to catalysis. The catalyst system was operated with negligible internal or external diffusion retardation of the reaction rate, and heat transport effects can be ignored. The reactor effluent was frozen in a liquid nitrogen trap for subsequent analysis, which was made using an AI Cambridge GC94 chromatograph equipped with a flame ionization detector and employing a DB-1 50 m × 0.20 mm i.d., 0.33 μm capillary column (J&W Scientific). All the reactants were AnalaR grade and were used without further purification.

The freshly activated and hydrogen halide pretreated catalyst samples were analyzed by transmission electron microscopy (TEM) using a Philips CM20 TEM/STEM equipped with a UTW energy-dispersive X-ray (EDX) detector (Oxford Instruments) operated at an accelerating voltage of 200 keV. The specimens were prepared by suspending the catalyst in isopropyl alcohol with ultrasound and evaporating a drop of the resultant suspension onto a holey carbon support grid. Scanning electron microscopic (SEM) analysis was performed on a Hitachi S700 field emission SEM where the sample was deposited on a standard SEM holder and double coated with gold. The nature of the carbon deposition was examined by temperature-programmed oxidation (TPO). The demineralized sample was ramped (10 K min^{-1}) to 1248 K in a 5% v/v O_2/He mixture, and the effluent gas was analyzed by on-line TCD; the sample temperature was independently monitored using an on-line data logging system (Pico Technology, model TC-08).

TABLE 1: Effect of Contacting the Ni/SiO_2 Catalyst with HCl and HBr on the Resulting Hydrodechlorination Rate (*r*), the Weighted Average Supported Nickel Particle Size (*d*), and the Observed Range of Nickel Particle Sizes

	freshly activated catalyst	HCl-pretreated catalyst	HBr-pretreated catalyst
r, mol $h^{-1}\ g_{Ni}^{-1}$	1.5×10^{-4}	8.0×10^{-6}	7.9×10^{-6}
d, nm	1.6	23	75
size range, nm	0.4−3.3	11−50	10−180

Results and Discussion

The catalytic hydrogen treatment of chlorobenzene generated benzene as the sole product, and there was no detectable ring reduction; i.e., the process is 100% selective in terms of hydrodechlorination. Conversion was stable with respect to time for up to 6 h on stream, and there was no evidence of any short-term catalyst deactivation with the untreated catalyst. Steady state hydrodechlorination rates with and without HCl/HBr pretreatment are recorded in Table 1, where it is clear that contacting the catalyst with the hydrogen halide resulted in a marked loss of activity. The latter proved to be irreversible in that a catalyst regeneration in flowing hydrogen at elevated temperatures was ineffective in restoring the original activity. The freshly activated Ni/SiO_2 was characterized by a narrow distribution of the supported nickel metal particle size, as noted elsewhere;[7] selected area electron diffraction (SAED) and dark field imaging have revealed that the nickel particles are crystalline. The hydrogen halide treatment induced an appreciable growth of the nickel crystallites, where the shift in the average size was significantly greater in the case of the HBr treatment (see Table 1). Moreover, the treated samples were characterized by a wide size distribution of geometrically shaped (square/hexagonal) nickel particles. An agglomeration of nickel particles (supported on carbon) after a HCl treatment has been noted elsewhere[9] and was attributed to a surface mobility of Ni−Cl species. Indeed, larger nickel metal particles are typically generated with a nickel chloride precursor, regardless of the nature of the support or reduction temperature due to crystallite

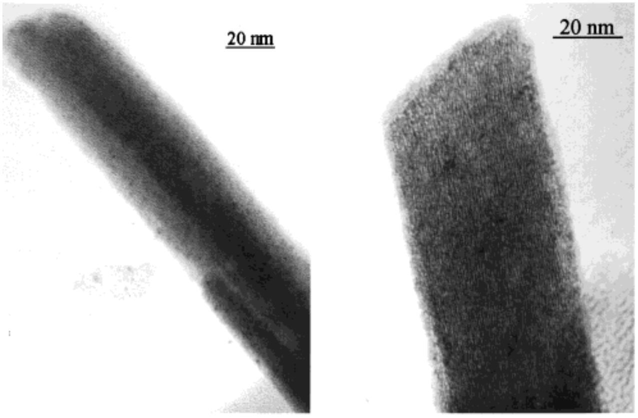

Figure 2. Representative TEM micrographs of the carbon filaments formed during the hydrodechlorination of chlorobenzene over HBr-pretreated Ni/SiO_2.

growth involving volatile nickel chloride in the presence of hydrogen and hydrogen chloride.[10]

While the growth of nickel crystallites in the presence of hydrogen halide was not altogether unexpected, the presence of an appreciable carbon deposition on these samples was certainly curious, particularly as this carbon was in the form of a "hedgehog-like" filamentous growth from the catalyst surface, as shown by the SEM micrographs presented in Figure 1. The filaments, which range in diameter from between 10 and 180 nm, appear, from TEM analysis, to be highly ordered and exhibit little or no curvature; this ordered structure is evident in the representative TEM micrographs shown in Figure 2. In addition to this highly ordered form of carbon, a small amount (ca. 5% w/w) of amorphous carbon, deposited along the filament edges, was observed along with trace quantities of carbon nanotubes. Nickel metal particles, with a high degree of dispersion, were observed on the surface of these carbon filaments. It is now generally accepted that the growth of filamentous carbon from a hydrocarbon feedstock on supported metal catalysts involves adsorption of the hydrocarbon with decomposition on specific faces of the metal followed by a dissolution of the carbon atoms into the metal particle and diffusion to precipitate at other faces as graphitic layers.[6,11] The growth and characteristics of the carbon are very much dependent on catalyst composition and the reaction conditions. Carbon deposition can be bidirectional in nature on opposite faces of the metal particle, which then remains within the carbon fiber throughout the growth process. Alternatively, deposition may be monodirectional where the metal particle is either carried at the tip of the growing fiber or remains attached to the substrate with the fiber growing from an exposed face.[11] In our case, while there is some evidence of particle fragmentation, the nickel metal crystallites largely remain anchored to the support during carbon growth. The latter effect can be attributed to the strong metal support interaction(s) associated with Ni/SiO_2 catalysts prepared by precipitation/deposition.[7] The "hedgehog-like" growth, however, serves to occlude the active metal face(s), and this may be responsible, at least in part, for the dramatic loss of hydrodechlorination activity. Given the involvement of electron-withdrawing halogens, the promotion of filamentous carbon growth at such a low temperature must be linked to electronic effects. Indeed, prolonged and continuous use of Ni/SiO_2 catalysts in hydrodechlorination processes has been shown to result in a disruption of the hydrogen chemisorption characteristics as a result of Cl/catalyst electronic interactions.[3] The STEM/EDX elemental maps of the "hedgehog" (HBr-treated) sample, shown in Figure 3, highlight the dispersion of nickel particles on both the catalyst and the carbon filaments while the halogen component (from both the pretreatment and reaction steps) is also present on the catalyst and the carbonaceous growth. It must be pointed out that the untreated catalyst after extended use (in excess of 200 h on stream) did exhibit an appreciable carbon content and preliminary XPS analysis has revealed the presence of a nickel carbide species. Temperature-programmed oxidation of the used and demineralized catalyst samples revealed an amorphous carbon content of up to 8% w/w. In the absence of a pretreatment with HCl or HBr there was no evidence of any graphitic carbon formation on the used catalysts regardless of the reaction conditions, i.e. contact time, temperature, aromatic/hydrogen partial pressure(s), etc. The direct interaction of hydrogen halide with the catalyst must then induce a reconstruction of the metal crystallites to expose orientations that promote the growth of ordered carbon. Yang and Chen[12] have shown that the specific orientation of surface metal particles influences the crystallinity of the carbon deposits. It is certainly the case that the HCl/HBr treatment brings about an appreciable change in metal dispersion and this surface reconstruction may well generate an arrangement that favors dissociative chemisorption of chlorobenzene. Indeed, Chambers and Baker[13] have noted that the presence of trace quantities of chlorine in an ethylene feed promoted the carbon deposition activity (at 673 K) of cobalt and iron powders.

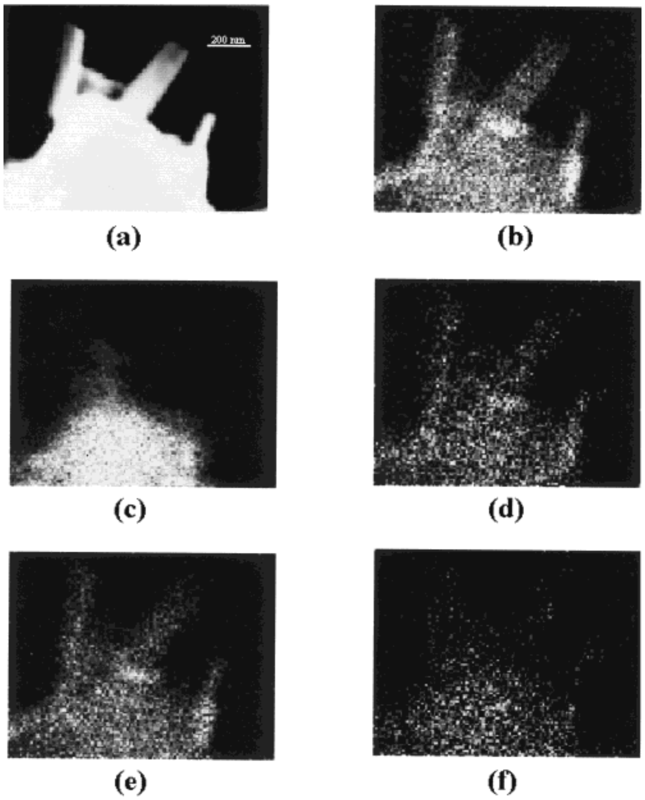

Figure 3. STEM/EDX elemental maps of the "hedgehog" sample showing (a) a STEM annular dark field image of the catalyst exhibiting growth of a number of individual carbon filaments together with EDX maps illustrating the distribution of (b) Ni, (c) Si, (d) Cl, (e) Br, and (f) K on the sample.

The EDX analysis also revealed the unexpected presence of potassium that was largely associated with the catalyst rather than the carbon filaments (see Figure 3). Potassium (even in trace amounts) was not detected in the freshly activated sample, and its presence must arise as a serendipitous impurity introduced through a corrosive leaching from the walls of the microreactor unit in the flow of HBr gas. It is well established that alkali metal doping markedly affects the reactivity of supported metal catalysts via an electronic effect. The possible involvement of the potassium "impurities" in promoting the formation of graphitic carbon does find a precedence in the recent work of Stevens et al.[14,15] involving the interaction of cesium with nanoporous carbon. They observed that their Cs/C system had a high affinity for hydrogen and promoted the splitting of the very energetic C−H bond in benzene where electropositive cesium provides electrons necessary to initiate the process and the carbon stabilizes the intermediate radical anions.[14] In addition, the presence of cesium was found to promote a nanostructuring of amorphous carbon even at room temperature.[15] It seems that we have hit upon a combination of halogen/alkali metal on our active surface where the interplay of electropositive and electronegative elements facilitate a reconstruction of the active sites to provide a chemically modified pathway to destructive chemisorption of chlorobenzene in the presence of hydrogen under relatively mild conditions. Moreover, the modified active sites promote the dissolution of carbon and precipitation in a highly ordered fashion. We are now attempting to synthesize Ni/SiO_2 catalysts with varying "built-in" alkali metal/halogen combinations as a first step to optimize the filamentous carbon growth process.

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