A graphite oxide-based nickel catalyst for reductive dechlorination of polychlorinated aromatic hydrocarbons

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Heterogeneous Ni-containing catalysts based on graphite oxide were prepared and their activity in the dechlorination of polychlorinated aromatic hydrocarbons by different organosilanes was studied.

Key words: nickel-containing catalyst; graphite oxide; dechlorination; polychlorinated aromatic hydrocarbons.

Polychlorinated aromatic hydrocarbons (PAH) contained in electrical and chemical industrial wastes are sources of highly toxic substances, polychlorinated dioxins and dibenzofurans.[1] Complete dechlorination giving relatively nontoxic aromatic hydrocarbons appears to be the most promising method among the known methods of PAH detoxification. Dechlorination can proceed on treatment with sodium naphthalide, dispersed alkali metals, molten aluminum, or organohydridesilanes in the presence of catalysts.[2—6] Unlike alkali metals or molten aluminum, organosilicon hydrides are nonpyrophoric, nonexplosive, and nontoxic compounds, readily available as commercial products.

The collidal nickel catalyst prepared by the reduction *in situ* of anhydrous $NiCl_2$ with organosilicon hydrides is known[4—7] to catalyze complete dechlorination of chlorobenzene (CB), 4,4′-dichlorodibenzyl (DCB), tetrachlorobenzene (TCB), and Sovol (a mixture of polychlorinated biphenyls containing, on the average, five Cl atoms per biphenyl molecule). The efficiency of dechlorination depends on both the way of preparation of the catalyst and the number of Cl atoms in the PAH. It has been shown[5,6] that, when the PAH molecule contains many Cl atoms (for example, TCB or Sovol), the catalyst should be prepared from a mixture of organosilicon hydrides and $NaBH_4$ and dechlorination requires the use of organosilicon hydrides whose boiling points are higher than that of triethylsilane (TES). In all studies, the catalyst was used only once, because, after separation from the reaction mixture, it was inactive (perhaps, due to oxidation in air) and was not regenerated on treatment with organohydridesilanes. In addition, colloidal nickel is pyrophoric, which makes the procedure more complicated.

We investigated methods of development of a reusable stable catalyst for complete dechlorination of PAH. For this purpose, we attempted to prepare a heterogeneous catalyst in which nickel is supported on the surface of a graphite-based carbon material. The low number of functional groups in graphite precludes fixing of a sufficiant amount of metal on its surface. Conversely, graphite oxide (GO) can serve as a support that combines the properties of oxide and carbon supports because it contains a large number of oxygen-containing functional groups (C—OH, COOH, *etc.*) able to anchor cationic complexes or small transition metal clusters due to cation-exchange reactions and coordination.[8,9]

Experimental

$C_4O_{2.33}H_{1.53}$ (primitive formula) was prepared by the modified Hummers method.[10] The C : O ratio, found from the primitive formula after subtraction of H and O in amounts corresponding to H_2O, is 2.55 (see Table 1) and the interplanar spacing is 6.7 Å, which is consistent with published data.[11] According to DTA, GO partially decomposes in air in the 180—240 °C range to give CO, CO_2, and H_2O and at 420—580 °C, the carbonaceous residue is oxidized by atmospheric oxygen.[12] The IR spectrum of GO exhibits a broad absorption band at about 3400 cm^{-1} (stretching vibrations of OH groups participating in hydrogen bonds) and an absorption band at 1730 cm^{-1} due to the stretching vibrations of the C=O bonds of the carboxy group. The weak absorption band at 1620 cm^{-1} can be assigned to both deformation vibrations of H_2O [15] and vibrations of the carbonyl groups in the quinoid system.[15] The IR spectrum also contains weak absorption bands at about 1380 cm^{-1}, which were assigned to the deformation vibrations of the tertiary C—OH groups, and broad bands in the region of 1000—1100 cm^{-1}, assigned to the stretching vibrations of the C—O bonds of aliphatic alcohols.[13]

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The catalyst was prepared by supporting nickel chloride from an ethanolic solution onto dried graphite oxide followed by drying and treatment with TES with refluxing. This gave non-hygroscopic (unlike the initial graphite oxide) hydrophobic samples, stable during long-term storage in air and containing 3—10% Ni.[15] The compositions of the resulting catalysts are summarized in Table 1.

TES was prepared from $EtCl_2SiH$ by the Grignard reaction with EtBr. $Et(Bu^iO)_2SiH$ was synthesized by treatment of $EtCl_2SiH$ with isobutyl alcohol. Anhydrous nickel chloride was prepared by refluxing $NiCl_2 \cdot 6H_2O$ with thionyl chloride for 4 h followed by evaporation of excess thionyl chloride and drying the product *in vacuo* for 7 h at ~20 °C.

The IR spectra of samples pressed in pellets with KBr were recorded on a Bruker JFS-113V Fourier transform spectrometer, and X-ray diffraction patterns were obtained on a DRON-3 diffractometer ((Cu-Kα) radiation, Ni filter).

Preparation of graphite oxide. Electric-carbon graphite (20 g) and concentrated H_2SO_4 (600 mL) were placed in a three-necked 2-liter flask equipped with a mechanical stirrer and a thermometer. Concentrated HNO_3 (10 mL) was added with stirring and the mixture was heated on a water bath (45 °C) until blue-colored graphite bisulfate appeared. The mixture was cooled to 10—15 °C and $KMnO_4$ (60 g) was added in portions over a period of 1 h, the temperature being maintained below 20 °C. After the addition had been completed, the mixture was slowly cooled with stirring to 40 °C and left overnight. Then the mixture was cooled again to 10—15 °C and 1 L of water was added in portions with continuous stirring, the temperature being maintained below 50 °C. The resulting suspension was poured into a 3-liter beaker and concentrated H_2O_2 (50 mL) was slowly (due to foaming) added with stirring. The warm mixture was centrifuged, the precipitate was separated and suspended in 1 L of 3% HCl, and the suspension was centrifuged. The procedure was repeated 4—5 times. Then GO was diluted with water to 25 L and washed with decanting until the pH of the wash water was ≥4.0 and SO_4^{2-} or Cl^- ions were not detected. The washed suspension was centrifuged and dried in a steam of warm air (60 °C) under atmospheric pressure and then the sample was ultimately dried to a constant weight at a pressure of 0.01 Torr and a temperature of 56 °C.

Preparation of the catalysts. Graphite oxide (1 g) was placed in a three-necked flask and an ethanolic solution of nickel chloride (0.07 g of $NiCl_2$ for GO—Ni-1 and 0.39 g of $NiCl_2$ for GO—Ni-2) was added with stirring. The mixture was concentrated *in vacuo* at ~20 °C, TES (3 g) was added, and the mixture was refluxed for 20 h; during this period, it was purged with air at intervals in order to remove the HCl evolved. The precipitate was filtered off and extracted with ether in a Soxhlet apparatus and the solution was dried *in vacuo* at 56 °C until a constant weight was attained (the compositions of the catalysts are given in Table 1).

Reductive dechlorination of DCB with TES. *A.* The GO—Ni-1 catalyst (310 mg, 0.147 mmol of Ni) and TES (1430 mg, 12.327 mmol) were placed in a two-necked flask and the mixture was refluxed for 0.5 h. Then DCB (88.6 mg, 0.353 mmol) was added and the mixture was refluxed for 3 h. According to GLC, dibenzyl was formed in a quantitative yield.

B. A mixture of GO—Ni-2 (111 mg, 0.193 mmol of Ni) and TES (522 mg, 4.500 mmol) was refluxed for 0.5 h, DCB (113.1 mg, 0.450 mmol) was added, and the mixture was refluxed for 3 h. The yields of dibenzyl determined by GLC after 1, 2, and 3 h were 24, 64, and 99%, respectively. The catalyst was filtered off, washed three times with ether, dried *in vacuo*, and used in three more cycles of dechlorination of DCB with TES. Dibenzyl was formed in a quantitative yield in all cases.

Reductive dechlorination of DCB with TOS. A mixture of GO—Ni-2 (109.2 mg, 0.190 mmol of Ni) and TOS (913.5 mg, 5.570 mmol) was refluxed for 0.5 h, DCB (41.4 mg, 0.165 mmol) was added, and the mixture was refluxed for 6 h. Dibenzyl was formed in a quantitative yield.

Reductive dechlorination of TCB with TOS. A mixture of GO—Ni-2 (381.3 mg, 0.665 mmol of Ni) and TOS (1560 mg, 9.512 mmol) was refluxed for 0.5 h, TCB (47.9 mg, 0.222 mmol) was added, and the mixture was refluxed for 6 h. According to GLC, the yield of benzene was quantitative.

Then TOS (510 mg, 3.110 mmol) and TCB (52.3 mg, 0.242 mmol) were added and the mixture was refluxed for 6 h. The yield of benzene was quantitative.

Additional TOS (400 mg, 2.439 mmol) and TCB (51.1 mg, 0.237 mmol) were added to the mixture and the mixture was refluxed for 6 h. The yield of benzene was quantitative.

Reductive dechlorination of Sovol with $Et(Bu^iO)_2SiH$. Sovol (10.1 mg, 0.031 mmol) and $Et(Bu^iO)_2SiH$ (473.3 mg, 2.320 mmol) were added to GO—Ni-2 (168.1 mg, 0.293 mmol of Ni). The mixture was heated for 15 h at 190 °C. According to GLC, the yield of diphenyl was quantitative.

Results and Discussion

PAH was dechlorinated in the presence of catalysts with nickel contents of 2.79% (GO—Ni-1) or 10.2% (GO—Ni-2). It was found that refluxing of GO—Ni-1 with TES for 3 h results in quantitative dechlorination of DCB. However, in this case, the required amounts of the catalyst and TES per unit weight of the substrate (3.5 and 16.1 $g\,g^{-1}$, respectively) should be large because TES acts as both the reducing agent and the solvent. Dechlorination of DCB in the presence of GO—Ni-2 also gives dibenzyl in a quantitative yield; however, in this case, substantially smaller amounts of the catalyst and TES with respect to DCB are needed (1 and 4.6 $g\,g^{-1}$, respectively); in addition, TES is consumed only in 12—14% excess relative to its stoichiometric amount and the unreacted silane can be recycled. The

Table 1. Composition of graphite oxide and the catalysts

Sample	Found (%)					C : O	Molecular formula
	C	H	Ni	Cl	Si		
GO*	54.37	1.73	—	—	—	2.55	$C_4O_{2.33}H_{1.53}$
GO—Ni-1	70.00	2.28	2.79	1.96	3.17	6.18	$C_4O_{0.87}H_{0.45}Ni_{0.04}Cl_{0.04}A_{0.09}$**
GO—Ni-2	42.48	2.53	10.23	10.95	0.96	3.30	$C_4O_{2.42}H_{2.42}Ni_{0.21}Cl_{0.37}A_{0.04}$**

* Ash content 1.6%. ** A = Et_3SiO.

catalyst can be reused after separation from the reaction mixture, washing with ether, and drying,. Three more cycles of dechlorination of DCB were carried out; the yield of dibenzyl remained quantitative in all cases.

The prepared catalysts are stable not only in alkylsilicon hydrides but also in alkoxysilicon hydrides, which are inexpensive commercial products. Hence, the latter can be used for dehydrochlorination of PAH. Since the H atom in alkoxysilicon hydrides is much less active than that in alkylsilicon hydrides,[16] these compounds cannot be used to reduce $NiCl_2$ at the step of the catalyst preparation. However, preliminary treatment of the catalyst with organohydridesilanes (for example, TES) affords active oxidation-resistant catalysts that can be used repeatedly for complete dechlorination of DCB when commercially available triethoxysilane (TOS) is used as the dechlorinating agent (refluxing for 6 h at 133 °C, which is the boiling point of TOS).

In the presence of the GO—Ni catalyst, unlike collidal nickel,[5] TCB does not undergo dechlorination on refluxing with TES, apparently because of the low boiling point of TES. Indeed, the replacement of TES by TOS, which contains less active hydride ion but has a higher boiling point, made it possible to perform complete TCB dechlorination over a period of 6 h. The catalyst activity was retained after the addition of fresh portions of TCB and TOS to the reaction mixture; on the one hand, this implies the possibility of repeated use of the catalyst and, on the other hand, this allows substantial decrease in the consumption of TOS.

Sovol, which contains more Cl atoms in the molecule than TCB, cannot be dechlorinated by treatment with TES and TOS in the presence of GO—Ni. However, the use of a higher-boiling silane $Et(Bu^iO)_2SiH$ (b.p. 111—113 °C/52 Torr) results in complete dechlorination of Sovol over a period of 15 h at 190 °C.

The reduction of PAH in the presence of GO—$NiCl_2$ yields chlorosilanes, which are fixed by the catalyst so tightly that the catalyst still contains silicon even after prolonged extraction with ether in the Soxhlet apparatus (see Table 1).

In addition, treatment of GO—$NiCl_2$ with triethylsilane results in the partial reduction of GO. This is indicated by the comparison of the C : O ratios in the initial GO and in GO—Ni (see Table 1). This ratio for GO—Ni was determined in the same way as for GO; however, processing of the results of chemical analysis was based on the assumption that O and H occur as H_2O molecules and some O atoms exist as Et_3SiO^-. It follows from Table 1 that the C : O ratio in GO—Ni is higher than that in the initial GO, apparently, due to the elimination of oxygen from the support during the reduction of GO—$NiCl_2$. This reduction appears to account for the fact that the GO—Ni catalysts, unlike GO and GO—$NiCl_2$, are hydrophobic. The reduction of GO is also confirmed by an increase in the thermal stability of the catalysts. Indeed, the DTA curve of GO—Ni-2 does not exhibit the first exothermic effect corresponding to the decomposition of GO; an exothermic effect associated with the oxidation of the carbon support by atmospheric oxygen is observed only in the 470—590 °C temperature range. These results are consistent with published data.[12] The presence of all bands corresponding to oxygen-containing functional groups of GO in the IR spectra of the GO—Ni catalysts points to the partial reduction of graphite oxide.

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