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Study on hydrodechlorination of polychlorinated biphenyls during reductive pyrolysis in the presence of a catalyst

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Abstract

For the first time an experimental set-up, called atmospheric pressure temperature programmed reduction (AP-TPR) applied in the speciation study of sulphur compounds in coal, has been used in the hydrodechlorination study of polychlorinated biphenyls (PCBs) with several specifically designed catalysts. Quantitative results concerning the degree of dechlorination were obtained using a potentiometric detection system equipped with a Cl^- selective electrode. Using a MS detection system, qualitative interpretation of the hydrodechlorination process (HDCl) of PCB as a function of the systematical increasing temperature could be formulated. Highly chlorinated organic compounds, i.e. decachlorobiphenyl (CB 209) and a technical mixture of PCBs (Aroclor 1254), were subjected to reductive pyrolysis in a flow of hydrogen in the presence of a catalyst. A number of nickel catalysts on carbon and silica were prepared using an optimized spray drying technique. A commercial carbon supported palladium catalyst was also tested.

Pd/C leads to a complete removal of chlorine from CB 209 and to a smaller extent from Aroclor 1254 and at a much lower temperature than for the NiC catalysts. The HDCl of Aroclor 1254 and CB 209 catalysed by Ni/C starts at 300 and 350 °C, respectively. The highest removal of chlorine is achieved using Ni/C catalyst with the lowest amount of NiO being 3 wt%. While nickel on silica support is found to be inactive for the HDCl reaction under the conditions of AP-TPR analysis. AP-TPR-MS study shows that biphenyl structure is decomposed to benzene, toluene, styrene and propenyl benzene with a maximum evolution temperature higher than the HDCl process but depending on the catalyst and PCBs. It can be concluded that AP-TPR method can be considered as a simple method for preliminary testing the activity of catalysts for HDCl process.

Keywords: Polychlorinated biphenyls; Reductive pyrolysis; Catalyst; Hydrodechlorination

1. Introduction

PCBs have been manufactured by the chlorination of biphenyl with anhydrous chlorine using Lewis acids as a catalyst [1]. The resulting product is a complex mixture of congeners with different number of chlorine atoms per molecule and their isomers. Theoretically, 209 PCB congeners are possible, but only about 130 congeners are likely occur in commercial products. The PCBs have been used commercially since 1930, especially as insulating fluids, hydraulic and lubricating fluids, heat exchanger fluids, and as additives in adhesives and paints. They have found widespread applications because of their general stability and inertness as well as their excellent dielectric properties [2]. Since more and more reports appeared about their toxicity, European actions are being taken for their total elimination by 2010. This class of chlorinated hydrocarbons is considered as priority pollutant due to its widespread presence in the environment and tendency to accumulate in the fatty tissues of humans and other animals. The disposal of PCB containing products generates considerable environmental problems. At present, PCBs are principally being destroyed by high-temperature incineration. However, this method may promote to form more toxic polychlorinated dibenzofurans and polychlorinated dibenzodioxins [2,3]. Therefore a broad research has been developed for non-thermal oxidation methods of degrading PCBs with simultaneous recovery of the hydrocarbons

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formed and their 'recycling' use as valuable products. The catalytic hydrodechlorination (HDCl) may be such an alternative representing an environmental friendly method.

Noble and transition metal catalysts on alumina, silica and carbon supports have been generally employed to promote HDCl reactions. The dechlorination of organic chlorinated compounds such as chlorinated benzenes and chlorinated phenols using supported Pd, Pt, Rh and Ni has been widely reported [4–14]. Most studies on the HDCl process of PCB were carried out using commercial hydroprocessing catalysts, mainly NiMo/Al_2O_3 and CoMo/Al_2O_3 [15–20]. These catalysts are found to be more resistant to deactivation by HCl formed compared to nobel metal based catalysts, however, the former operate at more severe conditions (250–350 °C, high pressure of hydrogen). NiMo catalysts can be used in their oxide or sulfide forms. It was reported that sulfided NiMo/Al_2O_3 catalyst shows a higher activity than its oxide form [21]. Compared to catalytic process, the thermal hydrogenolysis of chloroarene including PCBs in an atmosphere of hydrogen requires much higher temperatures in the range of 700–925 °C [22].

The stability of catalyst in the HDCl reaction is also related to the kind of support used. It is well known that activated carbon is resistant to HCl, which is not true for alumina, allowing to maintain high activity for long time. Moreover, the use of carbon as support allows to recover the precious metal by burning off the used catalyst.

The overall aim of this work was to develop a simple method for testing the activity of catalysts for HDCl process of highly chlorinated organic materials. Herein, we report the use of reductive pyrolysis to determine the transformation of PCBs, i.e. dechlorination and decomposition, in the presence of palladium and nickel catalysts under atmospheric H_2 gas conditions. A series of silica and carbon supported nickel catalysts were prepared by a spray-drying (SD) method. Recently, spray-drying has been successively applied for the synthesis unsupported bismuth molybdate catalyst for selective oxidation of propylene [23]. For the first time, a technique analogous to atmospheric pressure temperature programmed reduction (AP-TPR), widely used in the study of sulfur functionalities in coal [24–26], has been applied for monitoring chlorine evolution during heat treatment up to 1000 °C. A Cl^--ion selective electrode (ISE) was used as a potentiometric detection system. Moreover, the AP-TPR reactor was combined with another detection system, i.e. a mass spectrometry (MS), to follow not only HCl but also hydrocarbon products formed on catalytic decomposition of PCBs.

2. Experimental

2.1. Materials

2,2′,3,3′,4,4′,5,5′,6,6′-decachlorobiphenyl (CB 209) of chemical grade was purchased from Sigma-Aldrich and a standard PCB mixture of known chlorine content (Aroclor 1254) were used as reagents. Table 1 shows selected physicochemical properties of the PCBs used.

Table 1
Characteristics of CB 209 and Aroclor 1254

PCB	Cl wt%	Melting point °C	Boiling temperature °C	Density g/cm^3
Aroclor 1254	54.0	305.6–307.8	365–390	1.495
CB 209	71.0	10	–	–

A number of different nickel catalysts were prepared by spray-drying technique on powdered activated carbon (AC) support (SX Ultra Cat 3719-1 produced by NORIT) and silica (SiO_2, silicagel 60 F_{254} from Merck). $Ni(NO_3)_2\cdot 6H_2O$ was used in the spray-drying method to introduce the active NiO phase onto the support. The catalyst preparation was described elsewhere [27]. The commercial carbon supported palladium catalyst containing 5% Pd was delivered by Engelhard Corporation (Pd5/C).

2.2. Procedures/apparatus

Fig. 1 shows the AP-TPR set-up combined with potentiometric system for a Cl^- detection (for more general technical details see Ref. [24]). The potentiometric detection system is held at constant temperature of 20 °C. The detection beaker is filled with an ionic strength adjuster (ISA) solution of 5 M $NaNO_3$ for optimal detection condition for the Cl^--ISE. The calibration of this ISE results in a Nernstian behaviour with a linear relationship of the measured potential and the ln of the Cl^--concentration [$E = -22.378 \times \ln(Cl^-) + 50.007$; with $R^2 = 0.9989$ and $T = 20$ °C). The AP-TPR reactor is also coupled on-line with a MS (Fisons-VG Thermolab MS, 0-300 amu) via a heated capillary (170 °C).

For the AP-TPR analysis, CB 209 as a solid, was directly mixed with 30 mg of a catalyst. Aroclor 1254, which is a dense liquid, was dissolved in isooctane (to ensure good contact with the catalyst particles) and mixed with 30 mg of a catalyst. In order to evaporate isooctane, this mixture was dried at 60 °C for the nickel catalyst and at ambient temperature for the palladium catalyst both in an helium atmosphere before putting into the reactor.

For all AP-TPR experiments the conditions were the same. The sample was heated with a heating rate of 5 °C/min in the range of 25–1000 °C. Hydrogen was used as sweep and reducing gas with a flow rate of 100 cm^3/min. The degree of chlorine removal was calculated from potentiometrically measured amount of HCl as Cl^- using the ISE. Each AP-TPR experiment was repeated at least twice.