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Catalytic destruction of brominated aromatic compounds studied in a catalyst microbed coupled to gas chromatography/mass spectrometry

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Abstract

The capability of solid porous catalysts has been studied for the destruction or modification of halogenated aromatic compounds contaminating the pyrolysis oil of recycled plastics from electronic waste. A fast and simple experimental procedure is carried out using a micropyrolyser coupled to GC–MS in such a way that catalyst microbed was placed in the sample tube of the pyrolyser. The pyrolysis products of polycarbonate blended with a frequently applied flame retardant tetrabromobisphenol A (TBBPA) and epoxy resin containing TBBPA monomer units have been analysed, and the brominated components were compared with the thermal decomposition products of TBBPA and its diallyl ether. When TBBPA vapour passes through molecular sieve 4A a slight debromination and a partial cleavage of bisphenol A into phenols occur. Over molecular sieves of larger pore size (13X and NaY zeolite) an important decrease of TBBPA amount is observed indicating effective trapping ability of these catalysts of basic character for brominated aromatic compounds. A total chemical modification of the vapour was achieved by Al-MCM-41 catalyst that split TBBPA into bromophenols. Analogous results were obtained by carrying out similar experiments on diallyl ether of TBBPA. Moreover, it was revealed that brominated bisphenol A compounds are modified essentially the same way, either evaporated or evolved from a polycarbonate blend or produced by pyrolysis from an epoxy resin.

Keywords: Tetrabromobisphenol A; Catalytic debromination; Pyrolysis–catalysis–GC–MS; Catalyst microbed

1. Introduction

Besides the recovery of useful materials, polluting compounds are also produced in the process of waste recycling by pyrolysis. The electronic and electric equipments represent the most troublesome waste (WEEE) in this respect because of their flame retardant content. Although the use of halogen-containing compounds has been repressed lately, presumably we shall meet with this kind of flame retardants in wastes for several years. The pyrolytic recycling of WEEE is considered as an adequate process for recovering valuable metals, and at the same time for obtaining monomers or oils from the plastic constituents [1]. Unfortunately the halogen-containing flame retardant component of the waste contaminates the pyrolysis oil and gas [2].

Tetrabromobisphenol A (TBBPA) is a widely applied flame retardant in the plastics of electronic industry, such as epoxy and polycarbonate resins, ABS, high impact polystyrene, phenolic resins and others. In printed circuit boards TBBPA content may be more than 30% (w/w). The thermal decomposition of this compound has been studied by thermogravimetry and in a tubular batch reactor [3], and the pyrolysis and combustion products were analysed by Fourier transform infrared (FTIR) spectrometry, gas chromatography (GC) and GC/mass spectrometry (MS) techniques [4,5]. The formation of polybromodibenzodioxin and -dibenzofuran by pyrolysis or combustion from brominated flame retardants blended in plastics was in the focus of several investigations [6–8]. Brominated epoxy resin is an inherent flame retardant plastic as TBBPA is built in its polymer structure shown in Fig. 1. The thermal decomposition of this polymer results in bromobisphenols and bromophenols, in this way the involvement of brominated epoxy in WEEE is also a potential source of environmental pollution [2,9].

The elimination of bromoaromatic products from pyrolysis oils of electronic waste is a troublesome task. Different procedures were examined to extract brominated flame retardants from various polymer materials [10]. Special pyrolysis conditions of WEEE recycling have been proposed in order to reduce the production of bromoaromatic compounds, such as mixing

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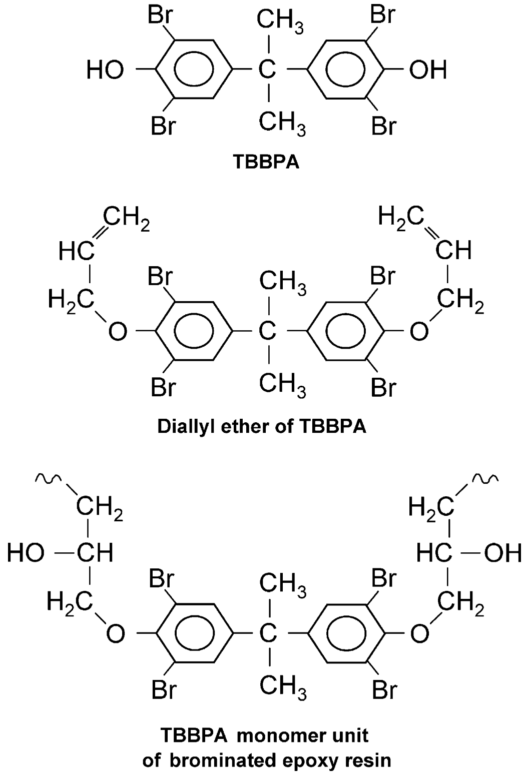

Fig. 1. Chemical formulae of flame retardant materials studied.

with polypropylene [11] or with various metal oxides as catalysts [12]. Considering the increasing demand for the catalytic upgrading of waste pyrolysis oils, a fast analytical method of catalyst evaluation should be particularly helpful in this field.

In this work the elimination and/or transformation of TBBPA and its thermal decomposition products evolved from flame retarded plastics were studied over adsorbent and catalyst microbeds of dehalogenation and cracking activity. The method of pyrolysis–catalysis–GC/MS set up earlier [13] was applied.

2. Experimental

2.1. Materials

2.1.1. Flame retardants and flame retarded plastics

The molecular structures of flame retardant materials studied in this work are shown in Fig. 1. 4,4′-Isopropylidenebis(2,6-dibromophenol) (97% purity) (TBBPA) and 2,2′,6,6′-tetrabromobisphenol A diallyl ether (99% purity) (All$_2$TBBPA) were obtained from Aldrich (Milwaukee, WI, USA). To prepare the flame retarded polycarbonate sample 4.0% (w/w) of TBBPA was mechanically mixed into polycarbonate (Bayer, Leverkusen, Germany) at 250 °C in a Brabender EH 50 device. Brominated epoxy resin of 20% (w/w) bromine content was synthesised [9] in the Institute of Macromolecular Chemistry of the Czech Academy of Sciences (Prague).

2.1.2. Catalyst beds

The catalyst bed materials were molecular sieves: catalyst support, sodium Y zeolite powder (Aldrich), 13X (Linde, Pullach, Germany), Union Carbide Type A4 (Fluka, Selze, Germany) and laboratory prepared Al-MCM-41 catalyst with a Si/Al ratio of 20 [14].

2.2. Instruments

Pyrolysis GC/MS measurements were carried out in a Pyroprobe 2000 (CDS Analytical, Oxford, PA, USA) pyrolyser equipped with a platinum coil and quartz sample tube. About 0.2 mg solid sample was put in a quartz sample tube and about 0.5 mg catalyst microbed was placed near to it at both sides, separated by quartz wool, as shown in Fig. 2. The purpose of this arrangement was to prevent volatile pyrolysis products bypass the catalyst bed, when driven also against the carrier gas flow by a fast pressure jump due to flash pyrolysis. The platinum coil of the pyrolyser was heated up at 400 °C/s heating rate. The pyrolysis was carried out at 300 and 500 °C, for 20 s. The products of the catalytic transformation were purged to an Agilent 6890 GC–5973 MSD system (Agilent Technologies, Palo Alto, CA, USA) by the carrier gas directed through the pyrolysis chamber held at 250 °C. The helium carrier gas of 20 ml/min flow rate was split in a ratio of 1:20 before being introduced into the gas chromatograph. The separation was carried out on a HP 5MS (Agilent Technologies) capillary column of 30 m length, of 0.25 mm diameter and of 0.25 μm film thickness; temperature programmed from 50 to 300 °C at 10 °C/min heating rate and held at 300 °C for 5 min. The temperatures of the transfer line of GC–MS and the source of the mass spectrometer were 280 and 180 °C, respectively. The mass spectrometer was operating in electron-impact mode (EI) at 70 eV, in the scan range 14–630 Da.

2.3. MS identification

The EI mass spectra of the decomposition products of TBBPA have been published earlier [2]. Identification of the products of All$_2$TBBPA was based on the typical natural isotope pattern of

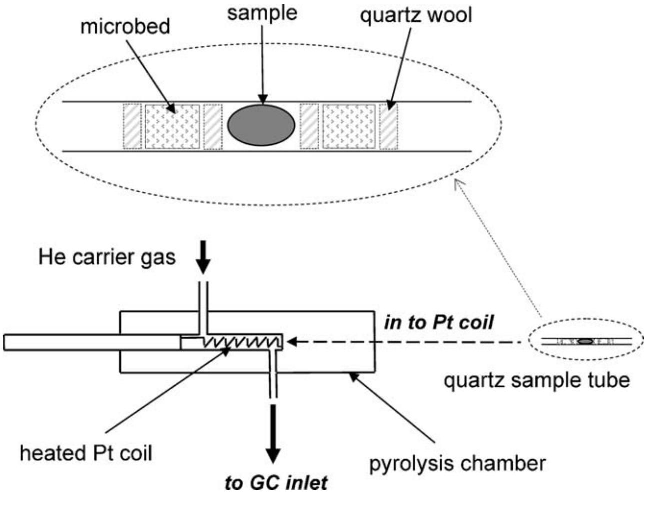

Fig. 2. Sample arrangement in the micropyrolyser for studying catalytic conversion of pyrolysis products.