

ORIGINAL PAPER

ArF laser photolytic deposition and thermal modification
of an ultrafine chlorohydrocarbon[‡]^aJosef Pola*, ^aAnna Galíková, ^bJan Šubrt, ^cAkihiko Ouchi*^aLaboratory of Laser Chemistry, Institute of Chemical Process Fundamentals, ASCR, 16502 Prague, Czech Republic^bInstitute of Inorganic Chemistry, ASCR, 25068 Řež, Czech Republic^cNational Institute of Advanced Industrial Science and Technology, AIST Tsukuba, Ibaraki 305-8565, Japan

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MW ArF laser irradiation of gaseous *cis*-dichloroethene results in fast decomposition of this compound and in deposition of solid ultrafine Cl- and H-containing carbonaceous powder which is of interest due to its sub-microscopic structure and possible reactive modification of the C—Cl bonds. The product was characterized by electron microscopy, and FTIR and Raman spectra and it was revealed that HCl, H₂, and C/H fragments are lost and graphitic features are adopted upon heating to 700 °C.

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Introduction

There is great interest in laser-induced chemical vapor deposition of nanoscopic materials due to many unique properties which they can offer. Various carbon-based particles or coatings like amorphous hydrogenated (e.g. Pola et al., 1996; Lindstam et al., 2001), graphitic (e.g. Kitahama, 1988), highly Csp³-based (Dischler & Bayer, 1990), or H-rich unsaturated (e.g. Stenberg et al., 1997) carbon films, graphitic carbon nanopowders (e.g. Morjan et al., 2003; Galvez et al., 2002), shell-shaped carbon nanoparticles (Choi et al., 2004), carbon clusters and soot particles (Ehbrecht et al., 1993) were obtained by laser-induced photolysis and thermolysis of a number of gaseous hydrocarbon precursors.

We have recently reported on chemical vapor deposition of carbonaceous and silica-poly(oxocarbosilane)- and chaoite-containing carbonaceous materials and shown that these nanostructured materials can be pre-

pared by highly intense (MW) irradiation of gaseous aromatic hydrocarbons from excimer lasers (Pola et al., 2007, 2008a, 2008b).

To explore the possibilities of laser photolytic formation of carbon-based materials from chlorinated alkenes became of interest. These compounds are considered to belong to hazardous materials and their carbonization to a variety of cokes (Mochida et al., 1996) also mechanistic studies of their thermal decomposition (Wu & Won, 2003) have attracted only limited attention. There are numerous photolytic studies on these compounds aimed at the recognition of the primary steps (cleavage of HCl, Cl₂, and H₂ (e.g. Berry, 1974; Umamoto et al., 1985; He et al., 1995; Chandra et al., 2006; Hua et al., 2010)) and of the initial volatile products, but there have been no attempts to elucidate these photolyses as for structure and composition of the final solid products.

In this paper we report on the formation of solid Cl- and H-substituted carbonaceous product

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obtained from MW ArF laser photolysis of *cis*-1,2-dichloroethene. We assumed that this high-molecular material is formed through the recombination of earlier assumed but unspecified intermediary C/H/Cl fragments. We also revealed that this carbonaceous solid undergoes cleavage of C—Cl and C—H bonds and C/H fragments upon heating to 700 °C and transforms to graphitic carbon.

Experimental

Laser irradiation experiments were carried out using gaseous *cis*-1,2-dichloroethene (20 kPa) in argon (total pressure 100 kPa) introduced to a reactor described previously (Pola et al., 2007). The dichloroethene sample was irradiated with an LPX 210i excimer (ArF) laser (Coherent, USA) operating at a repetition frequency of 10 Hz. The laser pulses (fwhm 23 ns, 280 mJ) were focused to an incident area of 0.5 cm × 1.0 cm (fluence of 560 J cm⁻²). Progress of the dichloroethene photolysis was monitored directly in the reactor by FTIR spectroscopy (Shimadzu FTIR IR Prestige-21 spectrometer, Japan) using the diagnostic absorption band at 580 cm⁻¹. Aliquots of the irradiated reactor content were sampled by a gastight syringe (Dynatech Precision Sampling, USA) and analyzed by gas-chromatography-mass spectroscopy (Shimadzu QP 5050 mass spectrometer, Japan), a 60 m capillary column Neutrabond-1, programmed temperature of 30–200 °C. The deposited ultrafine material was analyzed by FTIR spectroscopy and electron microscopy and thermal properties were determined by thermogravimetric analysis (TGA).

FTIR spectra were obtained on thin layers of the deposited powders accommodated between KBr plates using a Nicolet Impact 400 spectrometer (USA).

SEM analyses were conducted using a Philips XL 30 CP scanning electron microscope (The Netherlands) equipped with an energy dispersive analyzer EDAX DX 4 with a PV 9760/77 detector of X-ray radiation (USA). Quantitative determination of C, O, and Cl elements was performed using this assembly. For image acquisition, a Robinson detector of BS elec-

trons able to work in low vacuum mode (65 Pa) was used.

Thermogravimetric analysis of the solid deposit (sample mass 0.5 mg) was conducted by heating the sample up to 700 °C at the rate of 4 °C min⁻¹ in a stream of argon using digital recording balances Cahn D-200 (CAHN Instruments, INC, Cerritos, USA). Composition of the outgoing gases was analyzed by a quadrupole mass spectrometer (VG Gas Analysis LTD, Middlewich, England) enabling multiple (16 channel) ion monitoring as a time-dependent plot.

cis-1,2-Dichloroethene (Tokyo Chemical Industry, Japan, purity higher than 99 %) was distilled prior to use.

Results and discussion

ArF laser irradiation of gaseous *cis*-1,2-dichloroethene (20 kPa) leads to visible luminescence, depletion of dichloroethene, efficient formation of HCl and a number of volatile products, and to a dark fog that fills the reactor and deposits on its surface as ultrafine powder. The observed visible luminescence in the pulse spark is consistent with multiple photon dissociation and plasma formation. Volatile products are HCl, chloroethyne, 1,1-dichloroethene, *trans*-1,2-dichloroethene, trichloroethene, trichloromethane, 1,1,2,2-tetrachloroethane, 1,1,1,3,-tetrachloropropene, and 1,2,3,3-tetrachloro-1-propene (Fig. 1).

These compounds confirm that photolysis is a complex process involving isomerization of the initial *cis*-1,2-dichloroethene to *trans*-1,2-dichloroethene, HCl elimination to chloroethyne, and cleavage and addition (or rearrangement) of H and Cl leading to 1,1-dichloroethene. Other plausible reactions are: a three-center elimination of HCl and isomerization of chloroethyne, both leading to chlorovinylidene which is capable, when added to dichloroethenes and chloroethyne, of yielding three-membered cyclic compounds that further rearrange to unsaturated three-membered linear compounds. Thus, it was assumed that the earlier observed H and Cl formation and Cl₂, HCl, and H₂ elimination (Umemoto

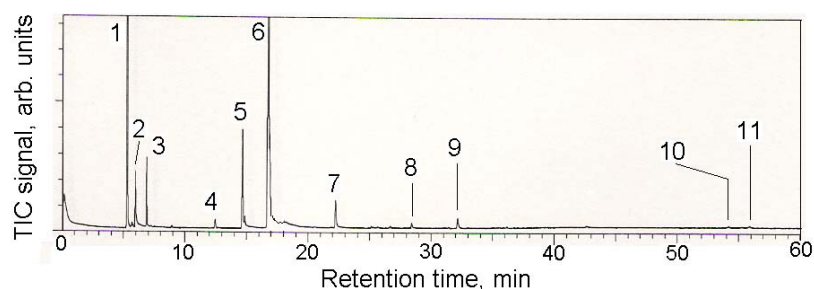


Fig. 1. GC/MS trace analysis of volatile products in ArF laser photolysis of *cis*-1,2-dichloroethene. Peak designation: 1 – Ar, 2 – HCl, 3 – chloroethyne, 4 – 1,1-dichloroethene, 5 – *trans*-1,2-dichloroethene, 6 – *cis*-1,2-dichloroethene, 7 – trichloroethene, 8 – trichloromethane, 9 – 1,1,2,2-tetrachloroethane, 10 – 1,1,1,3,-tetrachloropropene, 11 – 1,2,3,3-tetrachloro-1-propene.

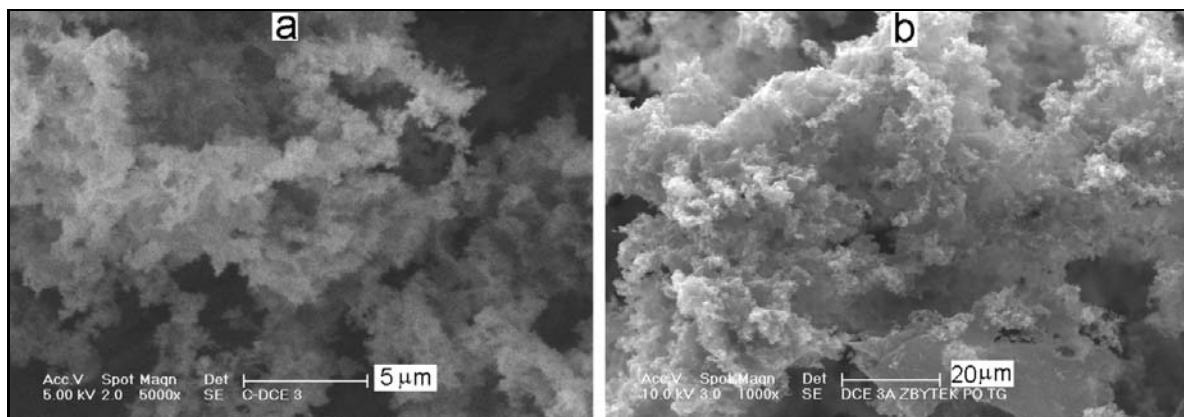


Fig. 2. SEM images of ultrafine powder obtained after deposition (a) and subsequent heating to 700 °C (b).

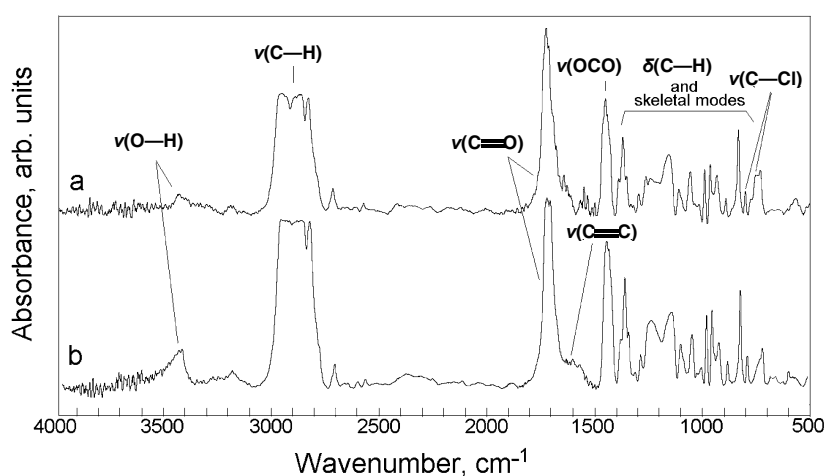


Fig. 3. FTIR spectrum of ultrafine powder obtained after deposition (a) and subsequent heating to 700 °C (b).

et al., 1985; He et al., 1995; Chandra et al., 2006; Hua et al., 2010), along with the formation and rearrangement of the three-membered cyclic compounds, are followed by further C—H and C—Cl bond homolyses, rearrangements, molecular (Cl_2 , HCl, and H_2) elimination, and carbene additions allowing the formation of high-molecular C/H/Cl unsaturated compounds. The observed 1,1,2,2-tetrachloroethane, 1,1,1,3-tetrachloropropene, and 1,2,3,3-tetrachloro-1-propene serve as examples of intermediate products arising from an addition of carbenes and/or addition/recombination of C-centered radicals; the observed trichloromethane illustrates the possibility of cleavage of bonds between carbon atoms in these intermediate products.

Approximately 38 mg of the ultrafine powder was accumulated in five runs, each carried out using 8 min irradiation and driving the photolysis to the progress of about 50 %. Scanning electron microscopy confirmed fluffy submicron structures merged to larger spongy agglomerates (Fig. 2a) and SEM-energy dispersive X-ray (EDX)-derived stoichiometry $\text{C}_{1.00}\text{Cl}_{0.098}\text{O}_{0.050}$ revealed chlorocarbon structure with

the C to Cl mole ratio of about 10 and tiny incorporation of O. The substantial decrease in the Cl content in the deposit as compared to the initial amount of dichloroethene is related to the efficient cleavage of C—Cl bonds. Low incorporation of O in the deposit is compatible with the reactivity of the deposit towards atmospheric oxygen.

The FTIR spectra (Fig. 3a) showed absorption maxima at 3440 cm^{-1} , $2840\text{--}2970\text{ cm}^{-1}$, 1730 cm^{-1} , and 1460 cm^{-1} and bands at $1370\text{--}970\text{ cm}^{-1}$ and $744\text{--}600\text{ cm}^{-1}$ which could be assigned to $\nu(\text{O—H})$, $\nu(\text{C—H})$, $\nu(\text{C=O})$, $\nu(\text{O—C—O})$, $\delta(\text{C—H})$, and skeletal and $\nu(\text{C—Cl})$ vibrations, respectively. These spectra confirm the presence of the C—H and C—Cl bonds as well as the incorporation of oxygen in the C=O and O—H groups.

Raman spectrum of the deposited powder (Fig. 4a) showed D and G bands of unsaturated sp^2 carbon at 1350 cm^{-1} and 1600 cm^{-1} , respectively. The G band reflects bond stretches of all pairs of sp^2 atoms in rings and chains, and the D band corresponds to the breathing modes of the rings (e.g. Dillon et al., 1984; Schwan et al., 1996).

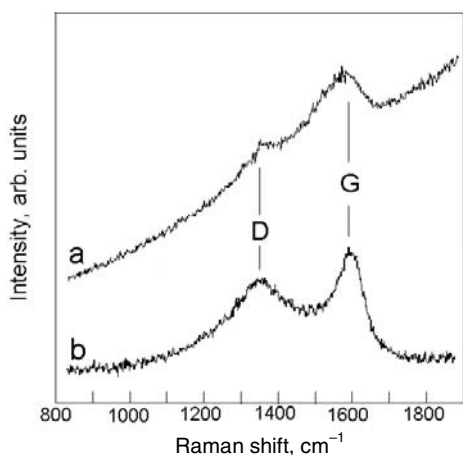


Fig. 4. Raman spectrum of the deposit before (a) and after (b) heating to 700 °C.

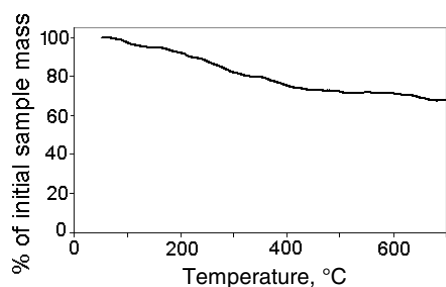


Fig. 5. TGA of the deposited powder.

High molecular mass of the deposit was confirmed by the low volatility at high temperatures: thermogravimetric analysis (Fig. 5) revealed that the deposit experiences a continuous but small (ca. 30 %) decrease in mass when heated to 700 °C. Major diagnostic single-ion peaks of the gaseous decomposition products at m/z 2 (H_2), 27 (a C_2H_3 fragment), 36 (HCl), 37 (a C_3H fragment), and 70 (Cl_2) (Fig. 6) confirm the cleavage of C—C, C—Cl, and C—H bonds in the high-molecular mass (hydrogenated) Cl-substituted carbonaceous network.

It has to be noted that the very sensitive TGA technique (Galíková & Pola, 2008) permits the detection of traces of O_2 . The peak observed at m/z = 32 cannot, however, correspond to O_2 because typical signal of O_2 under similar conditions (argon flow, temperature increase, sample mass) is by 2–3 orders of magnitude lower. It can thus be assumed that the peak at m/z = 32 corresponds to the formation of methanol via hydrogenation of CO and CH_2O produced by thermal cleavage of the superficially oxygenated carbon framework.

The above assignments of single ion peaks are in agreement with spectral properties of the heated powder. The SEM-EDX analysis showed that the heated powder retains its morphology (Fig. 2b) and that it lacks Cl. The FTIR spectrum (Fig. 3b) confirmed the

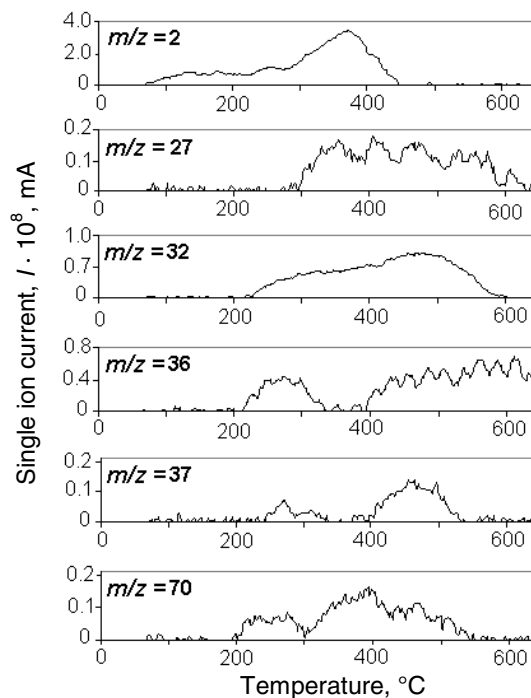


Fig. 6. Diagnostic single-ion traces obtained upon heating of the deposit.

depletion of the C—Cl bands and the growth of the C=C band. The latter feature is supported by the Raman spectrum (Fig. 4b) showing better developed D and G bands; the sharper G and more intense D band are accountable for by a more pronounced sp^2 bonding of the carbon network and a higher content of ring structures.

Spectral and EDX-SEM analyses of the deposited powder are thus in agreement with the carbonaceous structure and some content of H—C and C—Cl bonds, whereas the spectral changes and TGA analysis revealed that the deposited powder undergoes cleavage of the C—Cl and C—H bonds and transforms to graphitic carbon.

It was observed that the deposited submicroscopic chlorohydrocarbon has a potential for the synthesis of nanoscopic carbonaceous materials with organic functional groups because it may undergo reactions with various reagents like nucleophiles, chlorosilanes, or hydridosilanes and replace thus the —Cl substituent by e.g. —OH, —OR, and alkoxy-silyl groups (Komuro et al., 2002; Bykovchenko et al., 1965; Okamoto et al., 2001).

Conclusions

ArF laser photolytic decomposition of *cis*-dichloroethene yields gaseous HCl and a number of volatile chlorohydrocarbons, and it allows concomitant deposition of an ultrafine solid Cl- and H-containing carbonaceous deposit.

SEM-determined morphology of the deposited powder is described as sub- μ m-sized fluffy agglom-

erates and SEM-EDX-elemental composition corresponds to $C_{1.00}Cl_{0.098}O_{0.050}$ reflecting low incorporation of O upon the exposition of the powder to atmosphere.

TGA analysis of the powder revealed a small sample mass decrease due to the elimination of HCl, H_2 , and H/C fragments.

FTIR and Raman spectra of the deposited and subsequently TGA-heated powder are consistent with structural modification of the heated powder and development of graphitic features.

The deposited chlorohydrocarbon has a potential for substituting the C—Cl bonds by other functional groups.

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