Combustion synthesis: Towards novel nanomaterials

Andrzej Huczkó 1,*, Agnieszka Dąbrowska 1, Michał Bystrzejewski 1, Łukasz Dobrzycyki 1, Michał Franczak 2, Anar Mukhametzhanova 3, Santosh Tiwari 4, Manoj Pandey 5, Rabisharan Bogati 5, Bhim Kafle 5, Deepak Prasad Subedi 5

Department of Chemistry, Warsaw University, Warsaw, Poland

1. Introduction

The bottom-up approach of the synthesis of nanomaterials involves the generation of building blocks (ions, atoms, radicals, molecules) via the thermal or plasma activation of starting reactants. Here we propose the combustion synthesis (CS) which is an autogenous and strongly exothermic redox reaction between oxidizer and reducing agents and has been well known and explored for many years now [1]. For example, the thermite reaction has been widely used for connecting rails, in military applications and fireworks while CS has been routinely utilized in the generation of emergency oxygen on board the aircraft. Combustion synthesis has been also successfully used to produce different nanomaterials [2]. The CS is here an adaptation of a simple and easier synthesis option bestowed with time and energy saving prospect. Huczkó et al. [3] produced efficiently silicon carbide nanowires (SiCNWs) in the reaction between elemental silicon and halogenated carbon compounds. The CS approach, due to a short reaction duration and fast quench, can be a source of novel nanomaterials. Here we present (i) the CS synthesis of SiC nanowires (SiCNWs) and (ii) the magnesiothermic reduction of the asbestos waste. The resulting raw and purified products were analyzed with different chemical and physicochemical techniques (XRD, SEM, TGA and Raman spectroscopy) to verify its composition and morphology.

Keywords: COMBUSTION SYNTHESIS, MAGNESIOTHERMIC REDUCTION, SiC NANOWIRES, GRAPHENE, NANOSTRUCTURES, WASTE

We present here the results of two series of combustion runs. The silicon reduction of fluorinated graphite was aimed not only at the production of SiCNWs but it was also expected that the defluorination of CFs can lead towards the formation of graphene-like carbon nanostructures. The magnesiothermic reduction of asbestos waste can produce fine silica with some specific surface properties this due to the high temperature and fast quench of the combustion products. The resulting raw and purified products were analyzed with XRD, SEM, EDS, TGA and Raman spectroscopy to verify its composition and morphology.

2. Experimental

Table 1 presents the operational parameters of all runs. The starting stoichiometric components were hand-mixed at ambient temperature prior to introduction into the quartz crucible in reactor before performing the combustion synthesis. The combustion was initiated thermally by ohmic heating of a carbon tape immersed in the reactants following the experimental protocol described elsewhere [11]. The reactor was provided with the observation port to record the light emitted from the combustion zone. The starting pressure in the reactor was either 0.1 or 1.0 MPa. The combustion was terminated within ca 1 second and, after cooling period, the solid raw products were collected for the mass balance and the following analyses. The work-up of product mixtures was carried out by wet chemistry to remove non-converted starting reactants and unwanted side-products.

<table>
<thead>
<tr>
<th>Run No.</th>
<th>Starting reactants</th>
<th>Mass of starting reactants, g</th>
<th>Combustion atmosphere</th>
<th>Starting pressure, MPa</th>
<th>Peak pressure, MPa</th>
<th>Mass of raw products, g</th>
</tr>
</thead>
<tbody>
<tr>
<td>I-1</td>
<td>Si + CFx</td>
<td>4.71</td>
<td>Air</td>
<td>0.1</td>
<td>2.8</td>
<td>3.26</td>
</tr>
<tr>
<td>I-2</td>
<td>Si + CFx</td>
<td>6.63</td>
<td>Air</td>
<td>1.0</td>
<td>7.0</td>
<td>4.53</td>
</tr>
<tr>
<td>II-1</td>
<td>Mg + asbestos</td>
<td>6.70</td>
<td>Argon</td>
<td>0.1</td>
<td>0.4</td>
<td>6.34</td>
</tr>
<tr>
<td>II-2</td>
<td>Mg + asbestos</td>
<td>5.48</td>
<td>Argon</td>
<td>1.0</td>
<td>1.4</td>
<td>5.28</td>
</tr>
<tr>
<td>II-3</td>
<td>Mg + asbestos</td>
<td>5.35</td>
<td>Argon</td>
<td>0.1</td>
<td>1.2</td>
<td>5.32</td>
</tr>
<tr>
<td>II-4</td>
<td>Mg + asbestos</td>
<td>5.46</td>
<td>Argon</td>
<td>1.0</td>
<td>1.8</td>
<td>5.42</td>
</tr>
</tbody>
</table>
3. Results and Discussion

The exothermal combustion is accompanied by the strong emission of heat and light. The latter one can be a useful source of information about the nature of the reaction and its time. Thus, the Light Signal Diagnostics (LSD) protocol was developed, which enabled the on-line measurement of the reaction duration and characteristics, especially the detailed monitoring of the propagation of the combustion wave and its front. Fig. 1 presents few examples of such results for the selected combustions which confirm the short reaction duration (within ca 1 second) and its susceptibility to even the minor changes in initial operational parameters (such as the pressure and type of gaseous atmosphere). One may also follow the complex time signal trajectory with its oscillations and local combustion wave maxima. They correspond to the kinetics of the process. The light characteristics is reproducible within the same operational conditions. Thus, it can be treated as a reactions fingerprint.

Fig. 1. The in situ mapping of combustion synthesis for different run: A: run II-4; B: run II-3; C: run I-2; D: run II-1

As one can see, the combustion in the Si/CFₓ system is much more vigorous regarding the emission of a light and heat. Different mixtures of reactants may lead to the designed nanomaterials (Fig. 2). The versatility is a crucial advantage of the combustion synthesis. On the other hand, LSD enables its precise diagnostics and facilitates the optimization.

The morphology of raw products is quite different comparing to the starting mixture (Fig. 2). The raw product from combustions in the Si/CFₓ systems is amazingly voluminous due to the high amount of 1D SiC nanostructures.

3.1. Synthesis of silicon carbide nanowires (SiCNWs)

The silicon reduction of the fluorinated graphite CFₓ (x = 0.89) in air atmosphere follows the general equation:

\[ \text{Si} + \text{CF}_x = \text{SiC} + \text{C} + \text{Si} + \text{SiO}_2 + \uparrow\text{SiF}_x + \uparrow\text{C}_x\text{F}_y \]

We showed earlier [12] that the reaction of silicon with halogenated carbons (like TEFLON®) proceeds more efficiently under the presence of oxygen due to vigorous gas phase mass transport of silicon via gaseous SiO molecules. It was expected that the application of the fluorinated graphite as an oxidizer could enable not only the growth of SiCNWs but also the formation of layered graphene-like carbon nanostructures resulting from the silicon extraction of fluorine from layered graphite matrix. To isolate the SiCNWs, the un-reacted Si and silica were leached with boiled 30% KOH why the residual carbon was removed via air oxidation at 600 °C in the following step. The combustion was accompanied by a strong pressure increase (Table 1) due to the high temperature and formation of gaseous side products (SiFₓ + CₓF_y). The latter one is confirmed by a substantial mass decrease of solid reactants (Table 1). The content of un-reacted Si in a raw product (from wet chemistry analyses) for runs I-1 and I-2 was equal to 5.4 and 3.6 wt%, respectively. Thus, the total conversion of starting silicon was very high, 93.0% and 95.6% for runs I-1 and I-2, respectively.

Fig. 3 presents the SEM images of the starting mixture (runs I-1 and I-2) composed of several micron-sized Si crystallites (Fig. 3A) and layered CFₓ (Fig. 3B).

Fig. 3. SEM images of starting mixture (runs I-1 and I-2)

The morphology of the raw product (Fig. 4) does not depend on the starting pressure. The raw product is a non-homogeneous mixture of different nanosized species including SiCNWs, nanoballs (200-400 nm) of SiO₂, spherical (well below 100 nm) soot particles and microcrystallites of SiC.

Fig. 4. SEM images of raw product

The purified product (Fig. 5) is composed essentially of SiC nanowires (well below 100 nm) with some SiC cubic microcrystallites.

Fig. 5. SEM images of purified product
To confirm the purity of the product the EDS analysis was carried out (Fig. 6) which confirmed the stoichiometry of the formed SiC. The results (Table 2) confirm the content of SiC in a purified product above 90 at.%. 

![Fig. 6. EDS analysis of purified product](image)

<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Carbon</td>
<td>K-series</td>
<td>28.25</td>
<td>30.01</td>
<td>48.14 4.46</td>
</tr>
<tr>
<td>Oxygen</td>
<td>K-series</td>
<td>7.23</td>
<td>7.68</td>
<td>9.25 1.23</td>
</tr>
<tr>
<td>Silicon</td>
<td>K-series</td>
<td>56.47</td>
<td>59.99</td>
<td>41.15 2.37</td>
</tr>
<tr>
<td>Fluorine</td>
<td>K-series</td>
<td>0.16</td>
<td>0.17</td>
<td>0.17 0.10</td>
</tr>
<tr>
<td>Magnesium</td>
<td>K-series</td>
<td>1.16</td>
<td>1.24</td>
<td>0.98 0.09</td>
</tr>
<tr>
<td>Iron</td>
<td>K-series</td>
<td>0.85</td>
<td>0.90</td>
<td>0.31 0.08</td>
</tr>
</tbody>
</table>

Total: 94.12 100.00 100.00

TGA analysis (Fig. 7) confirmed that conclusion. The purified SiCNWs contain less that 5 wt% of carbon which removal from the final product occurs between 500 and 600 °C.

![Fig. 7. TGA analysis of purified SiCNWs product](image)

Fig. 8 presents XRD spectra of the reactants. The starting mixture (Fig. 8a) is composed of crystalline Si elemental (with some residual Ge presence)) while the CF$_x$ phase seems to be amorphous. The raw product (run I-2, Fig. 8b) contains mostly SiC with some un-reacted silicon while the carbon is evidently in an amorphous form. The purified product (Fig. 8c) is dominated by SiC reflexes.

The results showed that pure SiC nanowires can be efficiently produced via the silicon reduction of the fluorinated graphite. The observations of the product did not reveal, however, the presence of layered carbon nanostructures. Thus, it seems that the extremely strong thermal effect of combustion totally atomizes the carbon (forming the hexagonal network in starting CF$_x$) which later condenses as amorphous soot.

3.2. Magnesiothermic reduction of asbestos waste

The magnesiothermic processing of asbestos waste [13] with Mg as a reducing agent follows here the general scheme

\[
\text{Mg + MgO.SiO}_2.H_2.O = \text{MgO + Mg + Si + SiO}_2 + H_2.O
\]

Ma et al. [14] earlier produced porous silicon by magnesiothermic reduction of serpentine mineral. It was expected here that the final product, after chemical purification (acid leaching), would contain mostly fine silica (along with Si elemental) with some specific surface properties. As a matter of fact, silica-based amine-grafted sorbents exercised high amine efficiency for CO$_2$ capture, leading to a record-high CO$_2$ capacity of ~12 mmol g$^{-1}$ under simulated flue gas conditions [15].

Fig. 9 presents the micrograph of starting asbestos waste which reveals its particle size well below 5 µm and heterogeneous morphology.
The combustions were carried out with a two-fold excess of Mg (runs II-1 and II-2) and with a stoichiometric amount of a reducer (runs II-3 and II-4) – Table 1. The mass of the collected raw product did not differ substantially from the starting mass and the pressure increase was quite moderate this all showing that we dealt entirely with the solid-phase reaction. Fig. 10 presents the SEM images of the starting reactants (runs II-3 and II-4), composed of heterogeneous mixture of Mg particles and waste microcrystallites with some residual asbestos fibers.

The raw product (Fig. 11) has a quite different morphology. There are only very few of asbestos fibers and the material is dominated by cubic nanocrystallites of MgO.

The purified product (Fig. 12) has a heterogeneous morphology; MgO nanocrystallites are essentially gone while some interesting platelet-like porous nanostructures are easily spotted.

To identify its identity the EDS analysis was carried out (Fig. 13).

### Table 3. EDS analysis of the purified product

<table>
<thead>
<tr>
<th>Element</th>
<th>Series</th>
<th>unn. C norm.</th>
<th>Atom. C Error (1 Sigma)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>[wt.%]</td>
<td>[wt.%] [at.%] [wt.%]</td>
</tr>
<tr>
<td>Oxygen</td>
<td>K-series</td>
<td>16.59</td>
<td>17.84 27.83 2.43</td>
</tr>
<tr>
<td>Silicon</td>
<td>K-series</td>
<td>74.18</td>
<td>79.74 70.89 3.11</td>
</tr>
<tr>
<td>Iron</td>
<td>K-series</td>
<td>1.87</td>
<td>2.01 0.90 0.13</td>
</tr>
<tr>
<td>Aluminium</td>
<td>K-series</td>
<td>0.38</td>
<td>0.41 0.38 0.05</td>
</tr>
</tbody>
</table>

Total: 93.03 100.00 100.00

The porous material (in a purified product) is mostly composed of the elemental Si with some residual silica – Table 3.

The XRD spectra of reactants are shown in Fig. 14. The starting mixture (run II-4, Fig. 14a) is dominated by Mg elemental with the waste mineral phase (here denoted as a serpentine). The raw product (run II-4, Fig. 14b) contains mostly MgO with some un-reacted magnesium and serpentine, along with other side products. Surprisingly, the purified product (Fig. 14c) is dominated by the elemental silicon (instead of the expected silica) with some iron silicide and silicon carbide (formed from a residual carbon). That result proves that the sought reaction proceeded much deeply and resulted in a magnesiothermic reduction of silica.
The adsorption performance of both raw and purified products was analyzed in the process of 4-chlorophenol removal from aqueous solution. The adsorption of raw product (runs II-3 and II-4) was negligible due to the basicity of the surface. However, the surface of the purified products (after leaching with HCl) does not exhibit basic properties. In these cases the adsorption of 4-chlorophenol was detectable and measurable. However, the highest obtained values of the adsorption capacity were not high, namely 12 mg/g and 18 mg/g for run II-3 and II-4, respectively. The obtained adsorption isotherms (Fig. 15) are typical for S1 isotherms in Giles’ classification [16] or for the III type in the IUPAC classification [17]. Both correspond to the weak attraction between solute molecules and the surface of the adsorbent.

4. Conclusions

Combustion synthesis was used to produce SiC nanowires and to reduce the asbestos waste. The silicon defluorination of fluorinated graphite yields 95% pure SiCNWs. However, the residual carbon did not form 2D nanostructures, as expected, but condensed as a soot. The asbestos waste, containing mostly silicon-related compounds, was deeply reduced with Mg elemental, but contrary to expectations, the purified product contained almost 50% of elemental Si along with some residual fine silica.

5. References