Microwave-initiated Catalytic Deconstruction of Plastic Waste into Hydrogen and High-Value Carbons

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Abstract:

The ubiquitous challenge of plastic waste has led to the modern descriptor 'plastisphere' to represent the human–made plastic environment and ecosystem. Here we report a straightforward, rapid method for the deconstruction of various plastic feedstocks into hydrogen and high-value carbons. We use microwaves together with abundant and inexpensive iron-based catalysts as microwave-susceptors to initiate the catalytic deconstruction process. The one-step process typically takes some 30–90 seconds to transform a sample of mechanically- pulverised commercial plastic into hydrogen and (predominantly) multi-walled carbon nanotubes. A high hydrogen yield of 55.6 mmol·$g_{plastic}^{-1}$ is achieved, with over 97 % of the theoretical mass of hydrogen being extracted from the deconstructed plastic. The approach is demonstrated on widely used, real-world plastic waste. This proof-of-concept advance highlights the potential of plastics waste itself as valuable energy feedstocks for the production of hydrogen and high-value carbon materials.

Introduction

Plastic materials are used extensively throughout the world, with their ever-rising proliferation being particularly marked during the past half century. Currently, of the 4.9 billion tonnes of plastics ever produced, the vast majority are accumulated into landfills or in the natural environment; this number is estimated to increase to around 12 billion tonnes by 2050[1,2].

Polyolefins such as polyethylene (PE), polypropylene (PP) and polystyrene (PS), are currently produced, used and discarded at the highest rate of all plastics, thereby accounting for over half of all plastic waste[2,3]. In order to overcome the problem of such large quantities of plastic waste, researchers have studied various ways to convert these waste polymers into value-added products such as hydrocarbon fuels and carbon nanotubes (CNTs) etc.[4-7].

Over the past decade there has been increasing interests and research into the conversion of plastic waste into synthetic oil mixtures[5,6,8,9] and great efforts have been made to improve the energy efficiency and to exert precise control over the resulting products[9]. Gasification of plastic waste[7,10,11] is one such approach to produce a stream of synthesis gas for energy or synthesis purposes[2,7]. More recently, researchers have focussed on producing hydrogen as the main product from plastic waste as an alternative renewable process since plastic materials represent hydrogen-rich energy feedstocks which contain between some 8 – 14 wt.% of hydrogen[12-17]. Czernik *et al.*[15] and others[12-16,18-22] have proposed an important two-step process to thermally decompose plastics to produce hydrogen-rich gases. In this two-step process (idealised in Fig. 1a), plastic polymers are first decomposed into a mixture of small hydrocarbons via pyrolysis at high temperature, followed by catalytic steam reforming

(> 750 °C) of the pyrolysis gases and vapours for syngas production (H_2 + CO)[15,18]. This represents an important advance but there is, inevitably, a significant energy input required for the two reaction steps and the problem of large volumes of CO_2 which are also produced (~12 kg CO_2 per 1 kg H_2 production)[17], Moreover, the pyrolysis-reforming two-step process, by its very nature, of course, is invariably complicated.

Here, we illustrate, a simple and rapid one-step process for the deconstruction of plastic waste (Fig. 1b). This involves the microwave-initiated, solid-solid reaction; whereby a mixture of mechanically pulverised plastics (1 mm – 5 mm) are mixed with an additive catalyst (microwave-susceptor) composite of iron oxide and aluminium oxide and subjected to microwave treatment. A schematic experimental configuration is given in Fig. 1c. Widely used plastic waste comprised milk containers (high density polyethylene, HDPE), food wraps (polypropylene, PP) and plastic foam (polystyrene, PS) used in this study were collected from commercial materials used by large supermarket chains. Following the microwave initiation, a large volume of H_2 gas is rapidly evolved arising from the deconstruction of mechanical mixture of plastics and microwave receptors (catalysts) (Fig. 1d and Movie 1). H_2 levels in the evolved gas stream can reach nearly 90 vol.% with a H_2 yield of 55.6 mmol$\cdot g_{plastic}^{-1}$ achieved (theoretically, the maximum is 71.4 mmol$\cdot g_{plastic}^{-1}$) leaving only a residue of carbonaceous materials, the bulk of which are identified as carbon nanotubes.

Results

The nomenclature FeAlOx refers in this paper to the catalyst that was prepared by a citric acid combustion method (see Methods for full details), with a molar ratio of Fe:Al:citric acid = 1:1:1, unless otherwise noted. We define as Selectivity, the

measured volume % of the product composition in the evolved gases obtained from GC analysis. The mass of each gas products was calculated according to the measured volume of gases obtained and the composition analysis from GC. The yield of gas, liquid and solid are therefore determined as their respective mass fractions in relation to the total weight of plastic. We describe the H_2 yield as the moles of H_2 obtained divided by the total weight of plastic. The Hydrogen Efficiency is determined as the total mass of hydrogen contained in all gas products as compared to the theoretical amount of hydrogen contained in the plastic (See Eq. 1-5 in the Methods section).

One-step microwave-initiated deconstruction of HDPE using FeAlO$_x$ catalysts

The data for a representative 'time-on-stream' experiment for the microwave-initiated dehydrogenation of mechanically- pulverised HDPE (in this case, waste milk containers) using the FeAlO$_x$ catalyst is illustrated in Fig. 2. Following mechanical pulverisation of the plastic, the individual pieces were physically mixed with FeAlO$_x$ catalyst particles in a weight ratio of 1:1. Upon exposure to microwaves, hydrogen was rapidly evolved (a dehydrogenation of hydrogen-stripping process) and solid carbon and other small fragments were formed over a period of ca. 90 seconds (Fig. 2a). The evolved hydrogen rapidly increased to ca. 80 vol.% of the evolved gases in 30 seconds from the onset of the microwave initiation process. And, as will be evidenced in our *in-situ* characterisation, the HDPE was almost decomposed or deconstructed in ca. 20s.

Unlike conventional thermal heating processes in which both catalytic particles and the feedstock (here plastic polyolefins) are necessarily heated, in this alternative approach, microwave electromagnetic energy is absorbed *directly and preferentially*

at, and in, the microwave - absorbing points of the catalyst particle. Thus, heat is instead generated initially and rapidly *solely* at the microwave absorbing $FeAlO_x$ catalyst particles, without initially heating the surrounding pieces of HDPE. In that sense, this approach is fundamentally different to conventional, thermally-initiated catalytic processes where the entire plastic bath must be heated externally and then - through diffusive heat transfer and thermal convection - the catalyst particle is ultimately heated and activated. Importantly, we find that this microwave approach significantly minimises the side reactions from the thermolysis of plastic and therefore achieves an excellent control and yield of hydrogen production.

As a preliminary comparison of the measured temperatures of HDPE and $FeAlO_x$ particles separately under the influence of microwave irradiation, an average temperature difference of over 400 °C was observed (Fig. 2b). The temperature of the sample ($FeAlO_x$ catalysts + HDPE) was measured by an optical pyrometer as ca. 300 °C during the microwave initiation; thus, heat then being provided for the necessary catalytic reactions, and leading to the deconstruction of HDPE. This plastic melts at about 120 -180 °C, so we clearly have a most complex heating process evolving in this heterogeneous mixture of rapidly heating solid $FeAlO_x$ catalyst particles, (locally) melting HPDE plastic (in the immediate vicinity of the catalyst) and a surrounding bath of colder, solid plastic as one moves away from the catalyst particles into the bulk of the plastic host.

The measured microwave absorption of the sample ($FeAlO_x$ + HDPE) surged in the initial time-on-stream of 10s to 20s and then dropped in the following 10 seconds (Fig. 2c); indicating, remarkably, that the catalytic chemical reactions occurred in this short period where HDPE was almost completely decomposed. This has been confirmed by our x-ray diffraction (XRD) studies (Fig. 2d) and ATR-FTIR spectrum (Fig. 2e) where

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no HDPE peak appears visible after 30s. The diffraction peaks of HDPE at 21.6° and 23.9°, corresponding to the typical orthorhombic unit cell structure of (110) and (200) reflection planes of HDPE[24], were found dramatically decreased from 10s to 20s and subsequently disappeared after 30s. In the ATR-FTIR spectrum, the three sets of peaks ascribed to the C-H and C-C absorption of HDPE[23] also disappeared after 30s treatment with the microwaves.

XRD studies on $FeAlO_x$ catalyst before and after the microwave treatment revealed that the initially -prepared $FeAlO_x$ catalyst particles contain primarily Fe_3O_4[25]. The absence of XRD peaks of Al_2O_3 is ascribed to the low calcination temperature (350 °C), which indicates the Al_2O_3 is amorphous under these conditions [26]. Importantly, the presence of metallic iron and also iron carbide was detected as the microwave initiation process progressed (Fig. 2d). The peaks for elemental iron particles were observed at 2 Theta = 44.79°, and the diffraction peaks of Fe_3C at the angles (2θ) of 37.84°, 42.92°, 43.82°, 44.72°, 45.04°, 45.9°, and 49.18° were observed[27] some 20s from the microwave initiation, corresponding to the degradation of plastic to yield elemental carbon and hence Fe_3C. The intensity of Fe_3O_4 peaks decreased after reaction and a broad peak observed at about $2\theta= 26°$, indicating the formation of MWCNTs.

Parametric studies of the microwave-initiated process

We have investigated different catalyst systems under microwave initiation using metals other than Fe (typically Ni and Co) and also experiments with $FeAlO_x$ of varying Fe content as well as Fe-based catalysts on different support materials. We find that different metal catalysts exhibited a marked variability in performance under their

exposure to microwaves, with noticeably different product distributions and H_2 yields (Fig. 3a-b).

The FeAlO$_x$ catalysts proved to be the most effective with a H_2 yield of over 55.6 mmol·$g_{plastic}^{-1}$ whilst other metals or metal oxides gave less than 35 mmol·$g_{plastic}^{-1}$. The theoretical H_2 yield is ca. 71.4 mmol· $g_{plastic}^{-1}$ for complete dehydrogenation (deconstruction) of the plastic if we consider that the HDPE is fully decomposed to only H_2 and carbonaceous materials. Moreover, the hydrogen efficiency obtained over FeAlO$_x$ catalyst is about 97% which indicates over 97% of hydrogen contained in plastic has been extracted as gases. In contrast to thermal catalytic processes, we find negligible volatile (liquid) produced (Fig. 3c) using FeAlO$_x$. And the mass balance, calculated on the sum of gas and solid carbon is close to 100%. In contrast, Ni and Co catalysts are found less effective under microwave initiation and various small hydrocarbons, and liquid and solid are produced (Supplementary Table 1).

Our investigation of Fe on different support materials and indeed carbon materials themselves (activated carbons, MWCNTs, graphite etc.) demonstrated the varying catalytic performance when different catalyst systems interact with microwaves in the catalytic initiation process (Fig. 3b). All these Fe supported catalysts and carbons - except MWCNTs- were able to drive the HDPE decomposition reactions upon microwave irradiation, but with markedly different product distributions and very low hydrogen yield and selectivity (Fig. 3b and Supplementary Table 2).

Although carbon materials have been widely acknowledged as excellent microwave -susceptors[28], in our experiments, such carbon materials gave a very low H_2 yield of less than 8.3 mmol·$g_{plastic}^{-1}$ and the hydrogen efficiency was typically below 40%. This again highlights the superior activity of FeAlO$_x$ catalysts under microwave initiation for

producing almost exclusively hydrogen and carbon nanotubes, as will be highlighted in our characterisation of carbonaceous products (Fig. 4).

In contrast, experiments using traditional thermal pyrolysis and catalytic cracking using the same FeAlO$_x$ catalyst showed a very low H$_2$ yield of only 4.3 mmol$\cdot g^{-1}_{plastic}$ and also produced oil products with a yield of 66% (Fig. 3c). We attribute this to the fundamental differences between conventional and microwave heating processes with the microwave electromagnetic energy being selectively, effectively and preferentially absorbed by FeAlO$_x$ particles without (initially) heating the bulk of plastic. This leads to a significant narrowing of the products distribution and the preferential extraction of hydrogen from plastic polymers through the microwave-initiated catalytic scission of C-H chemical bonds.

We have also tested different starting weight ratios of HDPE and FeAlO$_x$ catalyst particles, from 0.3 to 10 (Fig. 3d). The preferred mixing ratio is found to be 1 - 2 where the very high H$_2$ yield (over 50.3 mmol$\cdot g^{-1}_{plastic}$) was obtained. Negligible amounts of liquid were produced when the mixing ratio is less than 2. At higher mixing ratios, both the oil and solid yields increased, and with the mixing ratio over 10 there was no visible reactions take place.

Importantly, at the optimal mixing ratio, the catalyst system can continue to function efficiently in the degradation of plastic for several catalytic cycles through successive additions of the plastic substrate.

Data for successive cycles of deconstruction of different kinds of plastic waste (HDPE, PP and PS) are illustrated in Fig. 3e-f. Successive additions of plastic pieces were added, importantly, with no further FeAlO$_x$ additions, between every test cycle. The highest H$_2$ yield obtained from the deconstruction of HDPE, PP and PS are 55.6,

51.4 and 26.9 mmol$\cdot g_{plastic}^{-1}$, respectively (Fig. 3e). The H$_2$ yield of HDPE and PP are typically between 35 – 55.6 mmol$\cdot g_{plastic}^{-1}$ (theoretically, the maximum is 71.4 mmol$\cdot g_{plastic}^{-1}$) and was found gradually decreased throughout the cyclic tests; whilst the H$_2$ yield of PS remained constant at around 24 mmol$\cdot g_{plastic}^{-1}$ (theoretically, the maximum is 38.4 mmol$\cdot g_{plastic}^{-1}$). Moreover, over 80 - 97 % of the (theoretical) mass of hydrogen contained in these plastics was rapidly extracted through this process leaving only MWCNTs. This corresponds to a carbon yield of around 70, 60 and 80 wt.%/g-plastic from the HDPE, PP and PS, respectively.

The H$_2$ selectivity in the evolved gases remained steady at ca. 76 – 90 vol.% and interestingly the highest H$_2$ selectivity was achieved at the 2nd or 3rd cycle (Fig. 3f) due to the inevitable extraneous oxygen contained in the FeAlO$_x$ that produced CO$_x$ in the initial cycle of experiment. For all test cycles, the mass balance which is determined as the sum of gas and solid yield, ranged from 93.6 to 100.4 % (Supplementary Tables 3-5). These values reflect the almost complete degradation of these plastics through this microwave-initiated solid-solid reaction to only gases and carbons. It is worth noting also that the process can be used to degrade mixtures of HDPE, PP and PS with different mixing ratio which showed similar results (Supplementary Table 6).

Since the polymeric molecules that constitute the plastics are of high Molecular Weight (typically 5,000 – 5,000,000 g/mol), in conventional pyrolysis or pyrolysis – catalysis processes, plastic polymers are invariably decomposed to a myriad of small molecules via side reactions, and these can result in even thousands of products [5,8,29]. The state-of-the-art catalysts and processes designed for plastic thermal pyrolysis are now primarily aimed, understandably, to narrow down the products in a desired diesel range[9]. For this reason, it is more difficult to selectively produce only H$_2$ and carbon

by these routes. Thus, important previous work[12-16,18-22] on hydrogen production from plastic always involves a two-step processes where plastics are first thermally decomposed to small molecules before the instigation of catalytic cracking or reforming reactions for ultimate hydrogen production.

The approach used in this work significantly simplifies the process; it achieves, selectively - in a one-step reaction - high purity hydrogen and high-value carbon materials (The results have been compared with literature in Supplementary Table 7).

The characterisation of carbonaceous products

Carbon nanotubes are almost the sole solid product from these processes. These product materials continue to attract attention due to their high commercial value and multiple applications[13,14,19,30], including the aerospace, automotive and civil engineering industries [30,31]. Thus, this work illustrates a process making use of an inexpensive and abundant catalyst, iron, in an oxide form to produce hydrogen fuel whilst also producing multi-walled carbon nanotubes (MWCNTs) as a valuable by-product.

In Fig. 4a, we show a 10-cycle test on HDPE@ FeAlO$_x$. The plastic pieces were physically mixed with FeAlO$_x$ catalyst particles in a weight ratio of 1:1, and the resulting residues at each cycle were additional mixed (only) with the same amount of fresh plastic pieces between every cycles of test. The H$_2$ yield was found to gradually decrease throughout the successive degradation of added HDPE. We attribute this gradual diminution to the substantial amount of ever- growing carbon deposition. As demonstrated in our temperature programmed oxidation (TPO), x-ray photoelectron spectroscopy (XPS) and electron microscopy studies (Fig 4c -f) the produced carbon

materials consisted primarily of MWCNTs.

The carbon yield at each cycle of test – except cycle 1 – was nearly constant ranging from 57.6 to 73.1 wt.% (Fig 4a); and the low carbon yield obtained in cycle 1 is ascribed to the formation of CO_x during the reactions. After 10 successive cycles of test, around 1.9 g of carbons were ultimately accumulated on the catalyst, thus the overall carbon (MWCNTs) yield in the process is ca. 620 mg· $g_{plastic}^{-1}$. As also shown in our thermogravimetric analysis (Fig. 4b), the spent sample after 7 cycles contained nearly 88.6 wt.% of MWCNTs and subsequently the resulting residue after 10 cycles is composed of ca. 92 wt.% of MWCNTs.

Scanning electron microscopy / Energy-dispersive x-ray spectroscopy (SEM / EDS) images of resulting carbon nano-materials confirmed the growth of a substantial amount of filamentous carbon (Fig. 4d). The MWCNTs observed in TEM images (Fig. 4e-f) showed outer diameters of ca. 10 - 20 nm, with inner diameters ca. 6 nm, and spacing values of the produced MWCNTs are ca. 0.32 – 0.34 nm.

The TPO analysis supported the proposal of the formation of MWCNTs on the $FeAlO_x$ catalyst (Fig. 4c), whereby the spent samples in cycle 1 gave two peaks at around 450 °C and 560 °C, associated with amorphous carbons and CNTs, respectively[20,32]. These peaks shifted to the higher temperatures throughout the successive cycles of reaction and in addition, the peak observed at lower temperature tended to merge into the peak at higher temperature. Consequently, only one peak at about 610 °C was detected in the spent samples after 10 cycles of test, which indicates that high purity MWCNTs can indeed be manufactured from plastic waste via this process. Furthermore, the XPS spectrum (Supplementary Fig. 1) and Raman spectrum (Supplementary Fig. 2) of carbon also suggests the resulting carbon

materials are primarily MWCNTs[33,34].

Proposed reaction scheme

Despite the acknowledged – and continually rising- interest in the application of microwaves in many areas of chemistry, there is still controversy about the fundamental nature of the interaction of microwaves with chemicals and materials. This is particular the case for microwave-initiated heterogeneous catalysis[35,36].

What we have in this present system is the initiation or activation of the heterogeneous catalysts by microwaves; the starting objects are obviously non-uniform, multi-phase systems that undergo catalysis under the action of the incident electromagnetic radiation.

Notwithstanding the controversy concerning the relative importance of thermal effects and non-thermal effects in microwave chemistry[35,36], we propose here a tentative mechanistic model of the microwave-initiated solid-solid reaction using Fe-based catalysts for hydrogen and carbon nanotubes production from plastic waste (Fig. 5).

The fundamental difference and advance of using microwaves is due to the fact that $FeAlO_x$ catalyst particles play two roles simultaneously in this process; First, there is efficient energy transfer from the incoming microwave electromagnetic radiation to initiate the physical heating process (driving force) of the catalyst particle. Secondly, the ensuing catalytic reaction at the particle surface occurs when the particle reaches the necessary temperature. When microwaves interact with $FeAlO_x$ catalyst particles, heat is rapidly generated throughout the catalyst particles themselves (these particles have physical dimensions below the characteristic microwave skin depth at these

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operating frequencies). Moreover, since the microwave heating is itself a function of the electrodynamic properties of the catalyst (i.e. the charge dynamics associated with the susceptibility of the catalyst material), electromagnetic heating is closely connected to the material properties which dictates the heating rate – thereby influencing the catalytic processes.

In contrast, plastics are essentially fully transparent to incoming microwaves and the plastic substrate will initially remain cold (Fig. 5b). As have been shown in Fig. 2bthe temperature gap between the catalyst and substance can be over 400 °C.

Therefore, heat is generated selectively at the catalyst and subsequently transferred to the plastic (reactant). This is an important fundamental distinction in that the heat flux (flow) is obviously directed from the surface of the catalyst particle and mass transfer will obviously occur in the same direction. This will help facilitate the desorption of neutral hydrogen (either atoms or molecules) from the active sites on the catalyst surface. This is fundamentally different from a conventional heating catalytic process, usually limited by the mass transfer rate of molecular desorption.

We believe that this advantageous effect is fundamentally important for narrowing the possible chemical product distribution by avoiding the many side reactions from the (usual) self-decomposition of plastic polymers. Thus, we propose that the overriding catalytic mechanism here is the microwave-initiated catalytic scission of chemical C-H bonds.

Given that the plastic is surely melted in the vicinity of the (constantly) heating catalyst particle, the polymer molecules have large kinetic energy in order to create a high frequency of collisions on the catalyst active sites. That will clearly lead to an increase in the key factors in the Arrhenius reaction equation ($k = A \exp(-E_a /kT)$), most

notably the pre-exponential factor, A, which represents the collision frequency between the (incoming) reactant (polymer) molecules and the active sites, while the exponential factor represents the quantity of species that can overcome the activation energy barrier.

In addition, important interfacial polarisation at the surface of the microwave – absorbing $FeAlO_x$ catalyst particles causes a major, local increase in the electric field strength[37] and hence dramatic differences in heating rates[38] exist between the two constituents - the catalyst particles and the plastic pieces and at their interface.

Most significant, therefore, we believe that microwave electromagnetic radiation enhances the desorption of product H_2 molecules from the catalyst surface. This does raise also the fundamental issue of the comparison of traditional conditions (thermal heating) with this microwave-initiated regime. As noted elsewhere[39], direct comparison is not always possible because of the intrinsic difficulties relating to the true localprocess temperature at the catalyst in the latter case. If indeed, this local temperature is much higher than our pyrometer –measured temperatures, the kinetic energy of our gaseous product, H_2 will also assist rapid diffusion away from the catalyst.

In Fig. 5f we show a representative finite element simulation model mapping of the E-field strength and the heating rate at the interface of a spherical Fe particle with plastic, based upon a quasi-static solution of the electromagnetic fields[38] (see Method for details). From these simulations, we find both the E-field strength and the heating rate at the interface increased significantly due to the interfacial polarisation. The E-field strength at the interface of catalyst and plastic is about 3 times larger than in the bulk plastic. Due to the fact that microwave electric fields will be screened from the deep interior of the Fe particle, localised high E-field and heating will occur at the

particle surface[37]. Recent advances in the field-assisted catalysis have shown electric fields can affect catalytic activity and selectivity with a focus on heterogeneous catalysts in much the same way as temperature and pressure[40]. The computational and experimental studies by Che et al.[41,42] for the methane steam reforming reaction (MSR) have shown an electric field can improve the efficiency of MSR processes and lower the overall temperature requirements.

In this microwave-initiated solid-solid reactions, typically, the microwave heating rate per unit volume $\langle P_E \rangle$ in Joules per second is given by $\langle P_E \rangle = \frac{1}{2}\omega\varepsilon_0\varepsilon_2 E_0^2$, where ω is the angular frequency, ε_0 is the permittivity of free space, ε_2 is the local imaginary permittivity and E_0 is the applied microwave electric field strength. Since the heating rate is proportional to the square of the electric field strength, a three-fold local increase in field strength at the particle-plastic interface due to interfacial polarisation – typical for high permittivity materials of spherical shape - leads to a nine-fold increase in the interfacial heating rate. In addition, as the deposition of highly microwave absorbing carbon takes place, the microwave heating rate will increase still further[38]. Importantly, the growth of high aspect ratio carbons will also increase this effect by orders of magnitude due to the high depolarisation factor of the growing carbon nanostructures. As shown in the simulations (Fig. 5f), the heating rate at the interface increased due to the polarisation field and with a 500nm layer of carbon that becomes deposited, the heating rate will be over three orders of magnitude greater than in the bulk plastic.

Furthermore, the close contact/ proximity of catalyst particles and plastic pieces in the interaction with the incoming microwave irradiation could potentially generate non-equilibrium plasma in their interface and thus enhance the catalytic reactions. In

several studies[43-45] the combination of plasma and catalysts has been found to have synergistic effects. Combining plasma with a solid catalyst whose dielectric properties and morphology are suitable, enhancement of the average electric field strength can occur, resulting in an enhanced efficiency of the chemical reactions taking place on the dual system. Surface adsorption within a plasma volume can make a significant contribution to improved reaction performance. When reactant molecules (here plastic polymers) are adsorbed onto the catalyst surface, the retention time and concentration of those species in the plasma can be enhanced. This could lead to an increased probability of reactive collisions with active species in the plasma volume.

In summary, for the present process, we believe that the very nature of microwave initiation of these catalytic chemical reactions significantly minimises the (potentially numerous) chemical side reactions. Hence the catalytic process takes place only at the interface between the hot (and almost certainly constantly heating) catalyst particle and the (initially) cold plastic (substrate or "bath") and the cleavage of C-H bonds is dominant.

As the catalytic process must always be preceded by incoming reactant adsorption[46], it suggest that the plastic polymer in the vicinity of the catalyst particle may well be molten. The polymer is then absorbed on the catalyst particle with rapid activation-decomposition occurring on the Fe catalyst surface (Fig. 5c). Thus, H_2 and carbon are subsequently produced via a (proposed) consecutive reaction pathway as given in Fig. 5 (eqn. 1).

Our TGA analysis (Supplementary Fig. 3) has confirmed the presence of intermediate compounds (i.e. alkenes/aromatics) as several peaks other than plastic were detected in samples collected in the first 10s to 20s. This suggests plastic could

initially be catalytically decomposed to small alkene/aromatics through a dehydrogenation step, and then these intermediates quickly and completely decomposed to produce further H_2 and MWCNTs. We note again that this interlude with the presence of intermediates is limited and importantly the $FeAlO_x$ catalyst can efficiently convert these species in a very high turnover rate under microwave irradiation.

Following carbon production, we propose that carbon species then diffuse into the Fe catalyst to form Fe_3C (Fig. 5d). Our XRD study (Fig 3c) showed that the diffraction peaks of Fe_3C were detected after 20s turned on the microwave. Previous work by Zhou et al.[47,48] reported the mechanism models of catalytic methane decomposition (CMD) over Fe-Al catalyst, and they claimed the important role of Fe_3C in terms of CNTs formation. Thus, we assume the formation of Fe_3C to be vital for the subsequent –and selective - formation of MWCNTs.

With continuing carbon formation and precipitation, carbon then crystallizes in the form of a cylindrical network on the surface of the catalyst particle and finally grows into tubular structures (Fig. 5e). In addition, the surrounding "sink" of cold (not yet heated) plastic pieces may also produce thermal cooling of the Hot spot catalyst particle to the surrounding lattice or bath as well as the catalytic process itself. This is clearly an extremely unusual and complex heating / catalytic process and further studies are underway to ascertain more details of the precise mechanisms at the heating surface.

Conclusions

We have described a simple one-step microwave-initiated process for rapidly deconstructing pulverized samples of common bulk plastics into hydrogen and high value carbon materials. The combination of the highly effective FeAlO$_x$ catalyst / microwave-susceptor through its interaction with incident microwaves can rapidly extract almost 97% of the hydrogen from plastic waste in about 20 seconds. A high H$_2$ yield of 55.6 mmol$\cdot g_{plastic}^{-1}$ was achieved with the H$_2$ concentration in the evolved gases reaching ca. 90 vol.%. Through the successive additions of plastics, the FeAlO$_x$ catalyst produced 85.7 mmol-H$_2$ /$g_{plastic} \cdot g_{catalyst}$, accompanying with a carbon production of 1560 mg-C/$g_{plastic} \cdot g_{catalyst}$ which the resulting sample is composed of > 92 wt.% MWCNTs.

Such a rapid and selective production of H$_2$ and carbon nanomaterials from the deconstruction of plastics reveals a potential route for helping tackle the burgeoning issue of plastics waste. The applicability and sustainability credentials (including energy minimisation) of this approach for scale- up must obviously be the next steps for any practical utilisation. However, we feel that these findings are important in representing an attractive potential solution for plastic waste; thus, now and in the future, plastics waste can be utilised as a valuable, anthropogenically-sourced feedstock for producing clean H$_2$ fuel and value-added carbon products.

Methods

Preparation of FeAlO$_x$ catalyst

The FeAlO$_x$ particles were prepared using the so-called citric acid combustion method. Analytical grade iron nitrate (Fe(NO$_3$)$_3$·9H$_2$O, Iron (III) nitrate nonahydrate, Sigma-Aldrich), aluminum nitrate (Al(NO$_3$)$_3$·9H$_2$O, aluminum nitrate nonahydrate, Sigma-Aldrich) and citric acid (Sigma-Aldrich) were used as starting materials. Appropriate amount of Fe(NO$_3$)$_3$·9H$_2$O, Al(NO$_3$)$_3$·9H$_2$O and citric acid were mixed in a desirable molar ratio. A minimum amount of distilled water was then added into the mixture to produce a viscous orange gel. The gel was burnt and calcined in air at 350 °C for 3 hours. The gel burnt in a self-propagating combustion manner and formed a loose powder. Finally, the powders were ground into fine particles.

For comparison purpose, same method and procedure is used to prepare Ni and Co alumina catalyst. Nickel nitrate (Ni(NO$_3$)$_2$·6H$_2$O, Nickel (II) nitrate hexahydrate, Sigma-Aldrich) and cobalt nitrate (Co(NO$_3$)$_2$·6H$_2$O, Cobalt (II) nitrate hexahydrate, Sigma-Aldrich) are used as precursors.

For studies on the effect of different support materials, the catalyst was prepared using incipient wetness impregnation method. Iron nitrate, Fe(NO$_3$)$_3$·9H$_2$O (Iron (III) nitrate nonahydrate, Sigma-Aldrich) was used as iron precursor. We synthesised a series of Fe catalysts supported by SiC (silicon carbide, Fisher Scientific), AC (activated carbon, Sigma-Aldrich), Al$_2$O$_3$ (aluminium oxide, Sigma-Aldrich) and ZSM-5 (Sigma-Aldrich) with Fe loading of 20 wt.%. The details of catalyst preparation have been described whereas[49].

All the carbon materials were used as purchased without further purification. Activated carbon (AC), carbon nanoplatelets (GNPs), Graphite and carbon nanotubes (multi-walled) were purchased from Sigama Aldrich.

Experimental setup and microwave reactor

The microwave reactor setup is given in Fig. 1d. The system consists of a microwave generator, a purpose-built microwave cavity and a controller [50,51].

The microwave heating system chain prior to the applicator consisted of a power generator, microwave head, microwave circulator, dummy load, microwave power meters and tuneable waveguide sections (Sairem Ltd.). The system was computer controlled using Labview software. The applicator section was fabricated in the Inorganic Chemistry Laboratory at the University of Oxford. The operating frequency was 2450 MHz ($\pm$ 25 MHz) from 10% to 100% of nominal power. The maximum output power was 2000 W with 1% stability from 10% to 100% of maximum power after thirty minutes on. The microwave source is a magnetron with a ripple rate of < 1% RMS from 10% to 100%. The power rise time is about 100 μs. The power generator is a resonant switching converter with frequencies of 30 kHz up to 80 kHz and an efficiency of 93% at nominal power. The power supply and microwave head are both water and air cooled. The microwave output is via WR 340 waveguides. The generator is controlled remotely via an RS232 MODBUS gateway using Labview software. The reflected power R, was measured by a crystal detector mounted onto the isolator load, from which we determine the power absorbed by the sample, P. If the power transmitted to the applicator is W, then $P = W - R - X$, where X is the microwave power lost in the cavity walls and through minor applicator leakages. The applicator

used was a TM010 resonant cavity to enable a well-characterized field distribution and high nominal field strength. Thus, in this work we investigate electric field driven processes, with a high electric energy density in the sample region [50,51].

The sample temperature was measured using an infrared (IR) pyrometer, which was also used to control the power to the generator. The pyrometer was positioned horizontally to face a side hole in the microwave cavity. The IR thermometer can only measure the external surface temperature of the sample. During the microwave experiment a temperature (T) versus time (t) of reaction profile was recorded [50,51].

Experimental procedure

The real-world plastic waste of milk containers (high density polyethylene, HDPE), food wraps (polypropylene, PP) and plastic foam (polystyrene, PS) used in this study were collected from waste materials used by large supermarket chains. The plastics were pre-treated by crushing/pulverising into small pieces (< 5mm) using a household blender. These pieces of plastic were then physically mixed with catalyst particles in a typical weight ratio of 1:1 unless otherwise noted. Typically, 0.3-0.4g of plastic is used for single cycle of test.

The sample of mixture (catalyst + plastic) was placed in a quartz tube (inner diameter 6mm, outer diameter 9mm), with typically volumes of about 1.13 cm^3 and the height of about 3.5-4cm. This is to ensure the sample is fully exposed to the axially polarised (TM$_{010}$) uniform electric fields (4 cm long). Then, the filled tube was placed axially in the centre of the TM$_{010}$ microwave cavity in order to minimise depolarisation effects under microwave radiation. Before starting microwave irradiation, the samples were purged with an Ar flow at a rate of 100 mL/min for a period of 15 minutes. Then,

the sample was irradiated under 1000 W microwave power (unless stated otherwise) for 3-5 min. The generated gases are collected and analysed by Gas Chromatography (GC) using a Perkin-Elmer, Clarus 580 GC. A ''Cold trap'' was set up for collecting liquid products.

For comparison purpose, the conventional thermal experiments on deconstruction of HDPE using same FeAlO$_x$ catalysts were carried out in an electric furnace. The experimental setup is shown in Supplementary Fig. 4. The temperature set for the thermal cracking of plastic in the electric furnace is 550 °C with the heating rate of 20 °C/min. The thermal experiments follows the same procedure as microwave experiments which has been described above.

We define the volume % of the product composition in the evolved gases from GC analysis as selectivity. And the mass of each gas products was calculated according to the volume of gases obtained and the composition analysis from GC. We therefore describe the H$_2$ yield as the mole of H$_2$ obtained divided by the total weight of plastic (Eq. 1). The Hydrogen Efficiency is determined as the total mass of hydrogen contained in all gas products divided by the theoretical mass of H contained in the plastic (Eq. 2). The gas yield is calculated by the mass obtained in relation to the total weight of plastic which is given by Eq. 3. The solid (carbon) yield was then determined as the mass difference between fresh and spent sample in relation to the total weight of feedstock (Eq. 4). The mass balance is obtained based on the sum of gas and solid yields because a negligible amount of volatile (liquid) is produced in these processes and undetectable. But for comparison purpose, we estimated the oil yield (liquid yield) as, 100% - gas yield – carbon yield (Eq. 5).

$$H_2 \ yield = \frac{Mole \ of \ H_2 \ produced}{Mass \ of \ plastic} \ (mmol \cdot g_{plastic}^{-1}) \tag{1}$$

$$Hydrogen \ Efficiency = \frac{Total \ mass \ of \ H \ contained \ in \ all \ gas \ products \ (g)}{Theoretical \ mass \ of \ H \ in \ plastic \ (g)} \ (\%) \quad \text{Eq. 2}$$

$$Gas \ yield = \frac{Mass \ of \ Gas}{Mass \ of \ Plastic} \times 100\% \ (wt.\%) \quad \text{Eq. 3}$$

$$Solid \ yield \ (Carbon \ yield) = \frac{Mass \ of \ spent \ catalyst - Mass \ of \ fresh \ catalyst}{Mass \ of \ Plastic} \times 100\% \ (wt.\%) \quad \text{Eq. 4}$$

$$Oil \ yield \ (Liquid \ yield) = 100\% - Gas \ yield - Soild \ yield \quad \text{Eq. 5}$$

Characterisation and analysis of samples

The samples were carefully characterised before and after experiments by powder X-ray diffraction (XRD, BRUKER D8 ADVANCE), Thermogravimetric analysis (TGA, TA Instrument, SDT Q-600), X-ray photoelectron spectroscopy (XPS, ESCALAB 250XI), ATR-FTIR analysis, Laser-Raman spectroscopy (PerkinElmer RamanStationTM 400F spectrometer), Scanning electron microscope and Energy-dispersive X-ray spectroscopy (SEM-EDS, ZEISS EVO).

The powder X-ray diffraction (XRD) used a Cu Kα X-ray source (45 kV, 40 mA) on a BRUKER D8 ADVANCE diffractometer. The scanning range (in 2θ) in this study was 10° to 90°. Thermogravimetric analysis (TGA) was used to characterise the resulting

carbons in spent samples. A temperature-programmed oxidation (TPO) was carried out to determine the thermal stability of the produced carbons. The sample was heated from room temperature to 1000 °C at a heating rate of 10 °C/min under an air atmosphere with a flow rate of 100 ml/min. The resulting carbon was also investigated via Laser-Raman spectroscopy, with laser excitation at 785nm. The scanning electron microscope (SEM, ZEISS EVO) was used to characterise the surface morphology of the samples before and after microwave initiation. The surface elemental was analysed by Energy-dispersive X-ray spectroscopy (EDS, ZEISS EVO).

The morphologies of produced multi-walled carbon nanotubes (MWCNTs) were also examined by transmission electron microscopy (TEM) using JEM-3000F microscope (300 kV). The sample powder was dispersed in ethanol in an ultra-sonic bath for 15 min. The solution was then drop cast onto a 300-mesh copper TEM holey carbon grid on a filter paper and allowed to evaporate. Scale bars of all the TEM images were calibrated using an oriented gold crystal grid.

Modelling of the electromagnetic fields and heating rates

Finite element modelling of microwave receptors and plastic was carried out using COMSOL v4.4 software. A representative, spherical particle of radius 2μm was used to provide a baseline for field distributions around particles. Changes in aspect ratio can lead to an increased depolarisation factor and a dramatic increase in the field strength at the extremities of the structure.

In the simulation model, a representative spherical catalyst particle is embedded in the surface of the plastic. In the quasi-static regime, we apply a uniform quasi-

microwave *E*-field and solve for the field strengths with frequency appropriate complex permittivities assigned to the model domains. The microwave heating rate per unit volume $\langle P_E \rangle$ in Joules per second is then calculated by $\langle P_E \rangle = \frac{1}{2}\omega\varepsilon_0\varepsilon_2 E_0^2$, where ω is the angular frequency, ε_0 is the permittivity of free space, ε_2 is the local imaginary permittivity and E_0 is the applied microwave electric field strength. The complex permittivity used for plastic in this work is $\varepsilon = 2.35 - j2 \times 10^{-4}$ [52] and for the representative receptor particle, we use conducting, metallic Fe, with permittivity approximated by $\varepsilon \approx 1 - j1 \times 10^7$. The carbon is modelled as a 500nm thick continuous layer, with permittivity $\varepsilon \approx 25 - j15$ [53].

The quasi-static model and applied electric fields

The heating mechanism in this work is via the microwave-electric field at a frequency of 2.45GHz, thus the model is in the long-wavelength regime and uniform fields may be applied in a quasi-static analysis. In addition, the skin depth of iron at 2.45GHz is hundreds of microns, accounting for its increased permeability, and does not affect our simulation. The applied field strength used in the simulation is 10 kV/m, which corresponds to around 30W of absorbed power in our cavity under normal operation:

The peak field strength in a cavity at resonance is given by

$$\langle U \rangle = 2\langle U_e \rangle = 2 \cdot \int_{vol.} \frac{1}{4}\varepsilon_0 E^2 dV = \frac{1}{2}\varepsilon_0 \int_{vol.} E^2 dV$$

where *<U>* is the time averaged, stored electromagnetic energy, *<U*e*>* is the time averaged, stored electric energy and *E* is the peak electric field strength.

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For TM$_{010}$ fields in a cylindrical resonant cavity of radius 4.6cm and height 4cm, we have,

$$\langle U \rangle = \frac{1}{2}\varepsilon_0 \int_{vol.} E^2 dV = \frac{1}{2}\varepsilon_0 E_0^2 (0.266)V_{cav}$$

Where V_{cav} is the volume of the cavity, giving,

$$\langle U \rangle = \frac{Q_U \langle P_{in} \rangle}{\omega_0} \quad \rightarrow \quad E_0 \approx \sqrt{\frac{2Q_U \langle P_{in} \rangle}{\varepsilon_0 \omega_0 (0.266)V_{cav}}}, \quad \text{i.e. } E_0 \propto \sqrt{Q_U P_{in}}$$

Q_u is the unloaded quality factor of the resonant cavity and $<P_{in}>$ is the input power.

For a cavity of the dimensions used in this work, with Q_U = 400 and P_{in} = 30W, we have an applied peak electric field strength of

$$E_0 \approx \sqrt{\frac{2 \times 400 \times 30}{8.854 \times 10^{-12} \times 2\pi \times 2.45 \times 10^9 \times 0.266 \times 0.0002659044}} = 49.9 \text{ kV/m}$$

An applied peak electric field of at least 49kV/m is expected, though 10kV/m is used in this model.

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Figure legends

Fig. 1: Schematic diagram of **(a)** The two-step pyrolysis and gasification process and, **(b)** The present one-step microwave-initiated catalytic process for deconstruction of plastic waste to produce hydrogen and carbon multiwalled nanotubes. **(c)** Experimental setup and reaction system configuration. **(c1)** The purpose built TM010 mode aluminium cavity. 1) The central hole where samples are inserted along the axis of the microwave electric field. 2) The viewing port for temperature measurement by IR pyrometer. **(d)** A typical configuration of gas collection for determining volumes of H_2 evolved when the microwave is switched on. 0.3g of HDPE and 0.3 g $FeAlO_x$ catalysts were physically mixed before exposure to microwaves. The H_2 is rapidly evolved and was collected over water (as indicated by the red arrows with the produced bubbles were circled in blue) and a movie illustrating the system in action can be found in the supplementary movie 1.

Fig. 2. Representative single cycle experiment of the microwave-initiated decomposition of 0.4g HDPE using 0.4g of FeAlO$_x$ catalysts**. (a)** "Time on stream" analysis showing gas evolution as a function of time. **(b)** Bed temperature and **(c)** microwave absorbed power of FeAlO$_x$ catalyst particles (red), HDPE (black) and a mixed sample of FeAlO$_x$ catalysts and HDPE (blue). **(d)** and **(e):** Mimicking an *'in-situ'* characterisation of HDPE@ FeAlO$_x$ under microwaves. Samples were exposed to microwave irradiation for different time of 10s, 15s, 18s, 20s, 30s, 60s and 90s, respectively. **(d)** XRD patterns, illustrating the evolved changes of HDPE and FeAlO$_x$ catalyst; **(e)** ATR-FTIR spectrum. The strong bands appeared at 2916 and 2849 cm^{-1} are assigned to CH$_2$ asymmetric stretching. Absorption band observed at 1474 and 1464 cm^{-1} indicates the bending deformation of the CH$_2$ groups in the molecules. Another set of peaks at 719 and 729 are due to the rocking deformation[23].

Fig. 3: Microwave-initiated decomposition of HDPE. (a) Investigation on different metal catalysts and **(b)** various supported Fe catalysts and carbons. **(c)** Comparison of microwave and conventional thermal processes. The temperature used for thermal experiments were 550 °C and the highest temperature recorded under microwave was ca. 350 °C. **(d)** Experiments with a different starting weight ratio of HDPE and FeAlO$_x$ catalysts. **(e)** and **(f)** Successive cycles of the deconstruction of HDPE, PP and PS on FeAlO$_x$ catalysts. The resulting residues were additional mixed (only) with fresh plastic pieces with a weight ratio of 1:1 between every cycles of test. The mixture was exposed to 1000W microwave irradiation for 5 min, and the generated gases were collected and analysed by GC. **(e)** H$_2$ yield and solid (carbon) yield. **(f)** Hydrogen efficiency and Evolved gas composition (vol.%).

Fig. 4: 10 cycles of successive deconstruction of HDPE over FeAlO$_x$ catalysts under microwave irradiation. (a) H$_2$ yield and solid (carbon) yield; cumulative carbon production as a function of cycles. **(b)** Yield of carbon quantified by thermogravimetric analysis (TGA); **(c)** Derivative plots of temperature programmed oxidation (TPO) of representative spent samples throughout the successive tests; **(d)** Scanning electron microscope (SEM) images, showing the production of primarily carbon nanotubes. **(e)** Transmission electron microscopy (TEM) image of produced carbon nanotubes, inset (1) illustrates the enlarged tube wall with the spacing value ca. 0.34 nm. **(f)** Lattice fringe images of the tube wall. The distance between adjacent graphene layers is ca. 0.32 nm.

Fig. 5: Suggested mechanism of microwave-initiated decomposition of plastic over a FeAlO$_x$ catalyst.

Author Contributions

P. P. Edwards, T. Xiao and J. M. Thomas supervised the project. P. P. Edwards, T. Xiao, H. AlMegren and S. Alshihri contributed to the funding acquisition. X. Jie, T. Xiao

and P. P. Edwards, conceived and then designed the project. X. Jie designed and developed the experiments and evaluated and analysed the performance data. X. Jie and W. Li designed and carried out the EM measurements, and analysis of the data. D. R. Slocombe and X. Jie designed and carried out the modelling and analysis of the data. X. Jie drafted the original manuscript. All authors, including J. R. Dilworth, Y. Gao, I. Banerjee, S. Gonzalez-Cortes and B. Yao contributed to the analysis, interpretation and discussion of results and the writing and revisions of the manuscript.

Conflicts of interest

The authors declare no conflict of interest.