

# Turning Polyethylene Waste to Hydrocarbons Using a Sustainable Acidic Carbocatalyst

Majd Al-Naji<sup>\*[a]</sup> and Markus Antonietti<sup>\*[a]</sup>

Careless release of plastic waste is a pressing problem for marine and other eco-environments, and materials recycling of this stream is an open problem. For this purpose, a new metalfree acidic carbocatalyst with 8 wt% sulfur is constructed from a side product of the paper industry namely Na-lignosulfonate. The catalyst shows an extraordinary performance for the fragmentation of polymer waste which smoothly occurs above the ceiling temperature of the polymers. The reaction is run without hydrogen and at ambient pressure with commercially available high-density polyethylene (HDPE) as well as a real polymer waste mixture of high and low-density polyethylene

## Introduction

In 2021 it was estimated the worldwide production and consumption of plastics (fossil-based plastic, post-consumer recycled plastics, and bio-based plastics) is 390.7 Mt, and in European Union is 57.2 Mt.<sup>[1-3]</sup>

In this context, plastic waste is a visible, pressing problem, and there is evidence that the oceanic and landfill garbage patches are still rapidly increasing in size.<sup>[3]</sup> This plastic is dirty and contaminated, and it is impossible to apply current conversion technologies to recover the material or its chemical value. Applying acid catalysts for the chemical recycling of polymers is a nearby thought, as (some) plastic waste is chemically very similar to crude oil. The potential of such a process would be visible and enormous. In Germany as our local model case, in 2020 (COVID-19 year) every citizen accounts for 78 kg of plastic waste from packaging per year (yellow trash bin).<sup>[4]</sup> It is fair to mention that recycling schemes are already operative but they focus on separable bigger pieces. More than half of the waste is made of polyethylene (PE) and polypropylene (PP). It is thereby the intention of chemical recycling schemes to break up such diverse, usually impure waste streams into light petrol or naphtha fractions, to be further processed in an oil refinery via steam cracking to olefins again.

[a]	Dr. M. Al-Naji, Prof. Dr. M. Antonietti					
	Department of Colloid Chemistry					
	Max Planck Institute of Colloids and Interfaces					
	Am Mühlenberg 1, 14476 Potsdam (Germany)					
	E-mail: majd.al-naji@mpikg.mpg.de					
	markus antonietti@mnika mna de					

Supporting information for this article is available on the WWW under https://doi.org/10.1002/cssc.202201991

© 2023 The Authors. ChemSusChem published by Wiley-VCH GmbH. This is an open access article under the terms of the Creative Commons Attribution License, which permits use, distribution and reproduction in any medium, provided the original work is properly cited. (HDPE, LDPE). In all cases, a homologous series of *n*-alkanes and *n*-alkenes are obtained. The unique sulfur-rich carbonaceous structure (transfer hydrogenation functionality) and the metal-free character of the acidic carbocatalyst makes it inert against many typical catalyst poisons, among them water, salt, polar functionalities, and sulfur species. The described performance in plastic recycling, as well as the low cost and large-scale availability of lignosulfonate from the pulp industry, makes this metal-free acidic carbocatalyst promising for real-life environmental applications.

Recently, several methods and solutions in the frame of chemocatalytic plastic waste recycling have been proposed in very important reviews.<sup>[5–8]</sup>

There is a number of publications along those lines out in the literature, but usually, they describe the use of partly very expensive noble metal catalysts on clean polymers, often even in excess to the substrate, and with externally supplied high H<sub>2</sub> pressure.<sup>[5-15]</sup> Ordinary catalysts are made up of transition metals, mainly noble metals, which enabled the many conversion schemes modern chemistry is built upon. In this context, Ru and Pt-based catalysts were used to convert PE and PP into hydrocarbons mainly in a liquid phase (C<sub>5</sub>-C<sub>21</sub>) in the presence of H<sub>2</sub> (20 bar and above).<sup>[16,17]</sup> Differently, using Cobased catalysts on zeolites for PP and PE hydrocracking leads to mainly gas-phase products with propane as a predominant product.<sup>[18]</sup>

Nevertheless, metals also bring many known downsides to the catalysts, such as sensitivity against water or polar organic molecules, sulfur and nitrogen compounds, and many more. These prohibit their application to dirty, salty, and wet plastic waste.

Another class of catalysts, the heterogeneous acids catalysts, are based on inorganic compounds and are the backbone of oil refineries and chemical plants. Crude oil is for instance refined in a catalytic cracking by zeolites process towards lower hydrocarbons. In 2022, the market for zeolites is correspondingly large and is estimated to be around 33.8 G $a^{-1}$ .<sup>[19]</sup> The weaknesses of zeolites restricting the current processes is their instability at elevated temperatures against water and other polar contaminants, and even in oil refineries, they deactivate quite rapidly so that the required catalyst streams are rather high.<sup>[11,20-22]</sup> For all applications facing water and biological functionality, zeolites are not very favored, and there are countless reported trials to replace them with highly acidic, polymeric ion exchange resins or sulfonated carbons for near-

ChemSusChem 2023, 16, e202201991 (1 of 7)

864564

3, 9, Downloaded from https://chemistry-europe.onlinelibary.wiley.com/doi/10.1002cssc.202201991 by Max-Planck-Institut Fir Koloi, Wiley Online Library on [23/05/2023], See the Terms and Conditions (https://onlinelibary.wiley.com/terms-and-conditions) on Wiley Online Library for rules of use; OA articles are governed by the applicable Creative Commons



Figure 1. Photograph of dried extruded pellets consisting of Na-lignosulfonate, ZnO, and a mixture of glucose/urea as binders (left); schematic illustration of carbonization procedure at 1223 K (right).

water catalytic purposes.<sup>[23-31]</sup> Such "biorefinery" applications for instance include transesterifications towards biodiesel or the dehydration of glucose to hydroxymethylfurfural (HMF).<sup>[29-33]</sup> Organic sulfonates are unstable at temperatures exceeding 403 K and can thereby not be used in the current context.

Many of the described problems could be resolved by moving from metal-based, inorganic catalysis to the new field of heterogeneous organocatalysis. In this context, our group has reported different types of carbon-based catalysis ("carbocatalysis") for a variety of catalytic reactions.<sup>[34-36]</sup> In most of these cases, the carbons are stable in a wider operating window and can be looped or recycled. Carbocatalysts are active catalysts as such. They are enzyme-inspired but by far more stable than enzymes, and the catalytic sites are carbonconnected organic functionalities, edge and surface terminations, or even just the conjugated pool of electrons of the carbons.<sup>[31-36]</sup> Porous carbons are already found in many environmental applications facing the real world as sorption materials to clean wastewater and air, as filters and fleeces, and they are known to handle environmental realities well.<sup>[23-25,37,38]</sup>

Here we present a highly acidic carbocatalyst with a new structure that resolves most of the above-discussed problems, as it is stable up to 773 K in air and 1073 K under N<sub>2</sub>, inert against water and polar impurities, and can even be thermally reactivated. This acidic carbocatalyst is synthesized using a side product of the paper industry available on the Mt a<sup>-1</sup> scale, Na-lignosulfonate (LS), and condensing it in the presence of a hard template (ZnO) to generate porosity. The resulting acidic carbocatalyst possesses a high surface area with an unexpectedly high amount of structural sulfur (8 wt%) when carbonized at 1223 K. This high amount of sulfur in the framework is linked to strong acidic sites. This catalyst is used for the depolymerization of high-density polyethylene (HDPE) and a real plastic waste mixture of low-density and high-density polyethylene (LDPE and HDPE).

#### **Results and Discussion**

The catalyst synthesis protocol is described briefly in the Experimental Section and in details in Supporting Information. The specific Na-lignosulfonate is a side stream product by

ChemSusChem 2023, 16, e202201991 (2 of 7)

Domsjö/Sweden. The Na-lignosulfonate was mixed with an aqueous mixture of glucose/urea as an additional carbon source and ZnO as a hard template to form an extrudable low-moisture mixture. Later this mixture was extruded and chopped into small uniform pellets (length = 1.5 mm and diameter = 1 mm), similar to our previous publication describing the extrusion of nitrogen-rich carbon source to generate catalyst beads (Figure 1).<sup>[37,38]</sup> The extruded brown pellets was dried at 333 K for 24 h and then carbonized under a nitrogen atmosphere at 1223 K for 2 h (see details at Supporting Information).

The catalyst was then structurally and functionally analyzed with a variety of techniques, i.e., elemental analysis, thermogravimetric analysis (TGA),  $N_2$  physisorption, X-ray diffraction (XRD), scanning electron microscopy (SEM) coupled with energy dispersive X-ray spectroscopy (EDX), temperature programmed desorption of ammonia (NH<sub>3</sub>-TPD), and X-ray photoelectron spectroscopy (XPS).

The elemental composition analysis of the acidic carbocatalyst upon the carbonization procedure showed that the sulfur content remained on an unusually high level (7.9 wt%), which is similar to the initial amount in the parental Na-lignosulfonate, cf., Table 1. This already indicates to the carbon expert an unexpected chemistry, as ordinary coals desulfurize starting from 873 K, i.e., the ordinary carbon-sulfur bonds are thermally weak. The synthesized catalyst, born at high temperature, consequently shows high thermal stability, i.e., 773 K in air with ash content 12 wt% and 1073 K under N<sub>2</sub>, as confirmed via TGA analysis (Figure S1 in Supporting Information). The high content of (oxidized) sulfur in the sample, together with oxygen edge terminations, changes the electron density of the carbonized material and creates a "nobility" of this carbocatalyst.<sup>[34,35]</sup> Furthermore, within the carbonization process gaseous prod-

Table 1. Elemental         co           lignosulfonate (as receited)         co	mpos ved) a	ition, i. nd the	e., C, acidic c	S, H, arbocat	O, N, talyst.	and Na	for Na
Sample	Elem C	ental co S	omposit H	ion [wt O	:%] N	Na <sup>[a]</sup>	ash <sup>[b]</sup>
Na-lignosulfonate acidic carbocatalyst	40 64	8.0 7.9	4.0 1.3	36 25	1.4 1.4	10 0.4	27.3 12
[a] Obtained from eler TGA analysis.	menta	l analys	sis via l	CP-OES	6. [b] D	etermine	d from



ucts (mainly  $H_2O$  and  $CO_x$ ) are released, which leads to a lowered O content (25 wt%) with respect to starting Nalignosulfonate (Table 1).

The pore structure is one of a typical mesoporous sorption carbon, and N<sub>2</sub> physisorption (Figure S2 in Supporting Information) indicates the coexistence of micro- and mesopores with a specific surface area of 664 m<sup>2</sup>g<sup>-1</sup>, a specific pore volume of  $0.4 \text{ cm}^3 \text{g}^{-1}$  and a pore width between 2 and 6 nm (Figure S2 in Supporting Information). It is to be underlined that the mesoporosity is due to the ZnO template and was implemented by design to make a larger number of active sites accessible to the polymer chains to fragment. Polymers are usually larger species and hopefully match with the mid-nanometer pores. XRD pattern for acidic carbocatalyst showed typical broad graphitic peaks at  $2\theta$  of  $25^{\circ}$  and  $45^{\circ}$ , cf., Figure S3 in Supporting Information. In line with N<sub>2</sub> physisorption, SEM images (Figure 2) indicate the existence of a hierarchical pore structure which agrees with the higher end of the N<sub>2</sub>-physisorption isotherm, as well as an EDX sulfur content of 7.9 wt% in the structure of the acidic carbocatalyst. The uniformity of element distributions of C, O, and S is demonstrated and shown in Figure S4 in Supporting Information.

The density of acid sites (DAS) was quantified by thermal desorption of ammonia, NH<sub>3</sub>-TPD (Figure 3), which interestingly shows three different NH<sub>3</sub> desorption peaks corresponding to weak (423 K), medium (523 K) and strong (663 K) acid sites with a total density of acid sites of 1.6 mmol g<sup>-1</sup>.

A clue on the chemical nature of the acidic species is provided by XPS analysis (Figure S5 in Supporting Information),



Figure 2. SEM images of the acidic carbocatalyst. The images demonstrate the homogeneity of the product and the countless larger pores being big enough that allow polymers reaching the catalyst.



Figure 3. NH<sub>3</sub>-TPD profile of the acidic carbocatalyst.

which indicates the presence of an oxidized sulfur species, similar to electron-poor sulfones. In this context, sulfones are known to show a comparable high alpha-C acidity, while they are also thermally stable even as low molecular weight compounds or polymers.<sup>[39,40]</sup> Highly coordinated sulfone groups in the conjugated backbone of the carbon catalyst would explain the wanted medium-strong binding of NH<sub>3</sub> as a probe gas, which is significantly weaker than NH<sub>3</sub> binding by sulfuric acid or sulfonic acids. Besides the sulfone-like groups, we also find different carbon edge terminations with acidity, i.e., -COOH and phenolic C-OH, which explain the low and medium temperature peaks in the NH<sub>3</sub>-TPD profile (Figure 3). The proposed condensation scheme also goes well with the reactivity of the starting sulfonate groups of the Na-lignosulfonate, which readily undergo a second alkylation with activated aromatics at elevated temperatures. Based on these characterization results we can illustrate the chemical structure of this acidic carbocatalyst with its active acid species in Figure 4.

For polymer degradation, the catalyst was then contacted with commercially available high-density HDPE, as well as with a real waste plastic consisting of LDPE and HDPE from a sorting plant. As the first step, commercially available HDPE beads were used to simplify the product analysis. All catalytic experiments were performed in ordinary reflux-stirred glassware and performed under ambient pressure, here however under an oxygen-depleted nitrogen atmosphere to avoid explosive oxygen/alkane mixtures. More details of the catalytic experimental procedure and product analysis are described in Supporting Information.

The acidic carbocatalyst was used for the depolymerization of HDPE at three different temperatures, i.e., 653 K, 673 K, and 693 K, for 4 h of reaction time. These reaction temperatures were chosen in order to decouple the catalyst performance from the thermal degradation of HDPE (above 698 K). It is noteworthy that a blank experiment without a catalyst resulted only in a white solid phase (2% of conversion to mainly the evolved gas).

Using the acidic carbocatalyst at 653 K, 673 K, and 693 K clearly resulted in a supernatant liquid with a soft waxy appearance (can be seen by the naked eye from the round bottom flask), cf., Figure S6A in Supporting Information. In all these cases three different phases were obtained (gas, oil, and wax), viz. Figure 5.

Furthermore, qualitative analysis via gas chromatography equipped with a mass spectrometer detector (GC–MS) nicely



**Figure 4.** Hypothetical structure of acidic carbocatalyst prepared by carbonization of Na-lignosulfonates at 1223 K with ZnO as a hard templating agent with its active species.

© 2023 The Authors. ChemSusChem published by Wiley-VCH GmbH



**Figure 5.** Influences of reaction temperatures (top) and reaction time (bottom) on the product fractions from HDPE fragmentation using acidic carbocatalyst. Reaction conditions:  $m_{\text{HDPE}}=5$  g,  $m_{\text{catalyst}}=0.5$  g, T=653 K, 673 K and 693 K, n=600 rpm,  $t_{\text{reaction}}=4$  h and 24 h, under N<sub>2</sub> atmosphere.

Time / h

4

24

0

characterizes the quality of the oil phase and gas phase (from the mass loss of the polymer after the reaction), indicating the formation of light hydrocarbons ( $C_1-C_4$ ) and hydrocarbons from  $C_5-C_{20}$  (see Figure S7 at Supporting Information). In addition, the wax fraction was found to be melting at 338 K, which indicates that the length of these wax chains is up to  $C_{30}$  (the melting point of  $C_{30}$  is 338 K).

As expected, increasing the reaction temperature from 653 K to 673 K and subsequently to 693 K coupled with increasing the oil fraction (directly processable via petrorefinery technology) from 15% to 35% and 65%, respectively. Also, with increasing the reaction temperature the wax content was found to be decreasing to 8% at 693 K.

Alternatively, the influence of the reaction time on the catalyst performance and products distribution was investigated. For this purpose 653 K as a reaction temperature was selected. By extending the reaction time from 4 h to 24 h, no significant change on the gas phase was observed (Figure 5). On contrary, the yield of oil fraction is increasing from 15% to 60%, whereas the wax fraction decreased from 85% to 30% (Figure 5). The low amount of the gas fraction by varying the reaction temperature and reaction time indicated the high activity and selectivity of our catalyst to obtain a liquid fraction from HDPE.

Surprisingly, the product distributions of the oil fraction obtained from the experiments performed at 653 K and 4 h and 24 h of reaction time under an  $N_2$  atmosphere, showed a regular repeat pattern of linear *n*-alkane and *n*-alkene fragments

 $(C_5-C_{21})$ . However,  $C_5$  and  $C_6$  were not quantified as they appeared before the solvent (cyclohexane) signal ( $t_{retention} =$ 4.79 min) in the GC with a flame ionization detector (GC-FID) (see Figure S7 in Supporting Information), where the intensity profiles run smoothly over odd and even alkyl lengths. This is proof that these species are made by cutting of HDPE chain, not by polymerization of formed ethene. It is noteworthy to be mentioned here that at 653 K and 4 h of reaction time, the total amount of n-alkene ( $C_7-C_{20}$ ) was 33.5 mg  $g_{HDPE}^{-1}$  and *n*-alkane ( $C_7-C_{20}$ ) was 54.3 mg  $g_{HDPE}^{-1}$  (Figure 6). Whereas at 653 K for 24 h of reaction time, the total amount of *n*-alkene ( $C_7-C_{20}$ ) was found to be 110.8 mg  $g_{HDPE}^{-1}$  and *n*-alkane is 348 mg  $g_{HDPE}^{-1}$ (Figure 6).

The formation of alkene and alkane as major products over this acidic carbocatalyst in the absence of externally supplied hydrogen gives an indication that the depolymerization mechanism of PE is different from the reported studies using noble metal-based catalysts with high pressure of H<sub>2</sub> in a pressurized batch reactor (autogenous pressure additional to H<sub>2</sub>).<sup>[9,10,41]</sup> The mechanism of the fragmentation of PE over this acidic carbocatalyst is in parts similar to the classical mechanism of Haag-Dessau for the protolytic cracking of alkanes over acidic zeolites.<sup>[42–44]</sup> This mechanism includes protonation of the alkanes (in our case the molten phase of PE) to a carbonium ion transition state which undergoes instantly fragmentation to give alkanes (or dihydrogen) and carbenium ions, which give back the protons to the catalyst to form alkenes. Deviating from zeolite-catalyzed hydrocarbon splitting we clearly observe an



**Figure 6.** Product distribution (yield of *n*-alkane and *n*-alkene) in the oil phase from HDPE fragmentation for 4 h (top) and 24 h (bottom) using acidic carbocatalyst. Reaction conditions:  $m_{\text{HDPE}} = 5$  g,  $m_{\text{catalyst}} = 0.5$  g, T = 653 K, n = 600 rpm, under N<sub>2</sub> atmosphere.

excess of alkanes to alkenes (usually alkene should occur twice as much in case of statistic fragmentation). This indicates that our acidic carbocatalyst is also active in transfer-hydrogenation due to its unique structure described above. This is confirmed due to the presence of dihydrogen in the gaseous stream. The sustainable, lignin-based, acidic carbocatalyst thereby possesses a dual functionality for fragmentation of polymers on the acid sites and hydrogenation of the formed unsaturated alkene via transfer-hydrogenation. Thus, it can be expected to be applicable also to other polymers and even in petrorefinery for heavy crudes.

For a proof of concept, real mixed waste of HDPE and LDPE from the consumer plastic recycling with adhered food leftovers, colorants, and contaminant water was shredded into smaller pieces (Figure S6B in Supporting Information) and treated under similar conditions (the experimental details are described in the Supporting Information). Again, practically complete decomposition of the polymer phase into a supernatant liquid with a soft waxy appearance was observed. GC-MS chromatograms of the depolymerized waste mixture exhibited again the formation of linear *n*-alkene and *n*-alkane from HDPE fraction, as well as branched *n*-alkene and *n*-alkane species with lower intensity (Figure S8 in Supporting Information). At this stage and due to the complexity of the liquid mixture, quantification of the linear and branched compounds was omitted. Finally, the pellet character of the shaped acidic carbocatalyst allows simple separation, and its high thermal stability regeneration by heating in air below 773 K for 5 h (characterization results of the regenerated catalyst are shown in Table S1 in Supporting Information), which enables to burn away any deposited organic species. Afterward, it was reused in HDPE cracking in an N2 atmosphere experiment. This experiment showed similar activity to the freshly used catalyst as it resulted in similar phase distributions (Figure S10 in Supporting Information).

For stronger evidence of the superior activity of the acidic carbocatalyst and the existence of the dual functionalities, an experiment with externally supplied molecular hydrogen (20 bar) was performed (see Supporting Information for the details of the experimental procedure).

The reaction was done in a pressurized autoclave at 613 K (the used parr autoclave is limited to a maximum operated temperature of 623 K) for 24 h.

The product distribution in the oil phase  $(C_7-C_{20})$  of the experiment is shown in Figure 7. The *n*-alkane yield was found to be 1302 mg g<sub>HDPE</sub><sup>-1</sup>, while the *n*-alkene yield was suppressed and corresponded to 188 mg g<sub>HDPE</sub><sup>-1</sup>. Furthermore, no solid was obtained at the end of the reaction, i.e., a 100% conversion to liquid and gas was obtained. Additionally, the presence of external hydrogen resulted in only oil fraction with product distribution rich with shorter *n*-alkane in the range of  $C_7-C_{14}$ , with respect to hydrogen-free experiments ( $C_{11}-C_{17}$ ). These results are in line with the findings of Wang et al.<sup>[45]</sup> for PE hydrocracking using H<sub>2</sub> pressure of 50 bar of external H<sub>2</sub> after 16 h of reaction time but using noble metal (ruthenium) supported catalyst, i.e., No wax was obtained, and the predominant fraction in the oil phase was  $C_8-C_{12}$ . Interestingly,



**Figure 7.** Product distributions (yield of *n*-alkane and *n*-alkene) from HDPE fragmentation over acidic carbocatalyst. Reaction conditions:  $m_{\text{HDPE}} = 5 \text{ g}$ ,  $m_{\text{catalyst}} = 0.5 \text{ g}$ , T = 613 K,  $p_{\text{H}_2} = 20 \text{ bar}$ , n = 600 rpm,  $t_{\text{reaction}} = 24 \text{ h}$ .

our findings are in an good agreement with the work of Rorrer et al.,<sup>[10]</sup> which has reported a comparable yield of *n*-alkanes of 1325 mg  $g_{PE}^{-1}$  at 22 bar of external H<sub>2</sub> after 16 h of reaction time, but using Ru based catalyst.

#### Conclusions

A carbocatalyst with high sulfur content and acidic character (dual-functionalities) was shown to be able to deconstruct diverse plastics into alkane and alkene fragments which is to realize chemical recycling of waste plastic. The fragments could be separated and refined, but could also directly be used as combustion fuel. Our vision is however the use of such ene-terminated ethylene oligomers in upcycling, i.e., generating telomeres for advanced polymer synthesis or novel surfactants. The economy of the new lignin-based catalyst is very favorable and more than competitive to zeolites, and so is the potential scale. Turning for instance the great pacific (macro)plastic patch with seawater into the estimated equivalent of diesel fuel (150 Mt) could propel 100 million cars for one year, a potentially even economically attractive alternative to remediate the environment.

#### **Experimental Section**

#### **Catalyst preparation**

First, the glucose, urea, and water mixture with a molar ratio of 1:3:11 was prepared at 363 K for 2 h with continuous stirring. Then, a 1 kg mixture composed of Na-lignosulfonate (LS) (48 wt%), the previously prepared glucose, urea, and water mixture (8 wt%), and ZnO nanoparticles d=20 nm (24 wt%) were prepared. The latter mixture was extruded into 1 mm (diameter) and 1.5 mm (length) pellets. These pellets were dried at 333 K for 24 h and then carbonized at 950 °C for 2 h. Finally, the carbonized pellets were washed using 0.1 m HCl solution under continuous stirring for 10 h to remove the residual Zn from the pellet. The detailed synthesis is described in Supporting Information.



864564x

3, 9. Downloaded from https://chemistry-europe.onlinelibaray.wiley.com/doi/10.1002/csc.202201991 by Max-Planck-Institut Fur Kolloi, Wiley Online Library on [23:052023]. See the Terms and Conditions (https://anlinelibrary.wiley.com/terms-and-conditions) on Wiley Online Library for rules of use; OA articles are governed by the applicable Creative Commons License

## Catalyst characterization

The acidic carbocatalyst was characterized via elemental analysis, N<sub>2</sub> physisorption, powder XRD, TGA, SEM-EDX, and NH<sub>3</sub>-TPD. The measurement procedures for these characterization methods are described in detail in the Supporting Information.

### Catalytic fragmentation of PE under N<sub>2</sub> atmosphere

All catalytic experiments were performed in a 250 cm<sup>3</sup> round bottom flask connected to a condenser (Figure S6). Before the experiments, the air was purged from the system by a continuous flow of 1 bar of N<sub>2</sub> for 15 min Westfalen AG with purity of 99,998%. Afterward, the system was sealed with a balloon filled with N<sub>2</sub> to guarantee an inert environment in the reaction system (to avoid the formation of explosive oxygen/alkane mixtures).

In a typical experiment, 5 g of polymer HDPE with 0.5 g of acidic carbocatalyst was heated to the desired temperature by heating the mantle under an N<sub>2</sub> atmosphere with continuous stirring at 600 min<sup>-</sup> for 4 h. After completion of the reaction, the heating mantle was shut down and the mixture was cooled down to room temperature. For the product analysis, 10 cm<sup>3</sup> of cyclohexane was added to the supernatant liquid formed after the reaction, and 3.0 cm<sup>3</sup> was withdrawn and centrifuged at 9500 min<sup>-</sup> for 20 min to separate the liquid products from the solid residue. Then, 1.0 cm<sup>3</sup> was analyzed using GC–MS and GC–FID.

The product identification and quantification methods via GC-MS and GC-FID are described in detail in Supporting Information.

**Caution**: In the case of the real waste mixture of HDPE and LDPE, a shredder step of the polymer was performed using a hand blender Bosch MaxoMixx (750 W), cf. Figure S2.

### Catalytic fragmentation of PE with external $H_2$ supply

The fragmentation of HDPE in the presence of 20 bar of  $\rm H_{2}$  was conducted in a 300 cm<sup>3</sup> stainless-steel batch reactor from Parr Instrument Company (model 4561), equipped with heat and stirring controller, as well as pressure monitor model 4848 (Figure S11). In a typical experiment, commercial HDPE and acidic carbocatalyst (weight ratio of 0.1) were added to the reactor with a magnetic stirrer at room temperature. Afterward, the reactor was flushed 3 times with 10 bar of Ar Westfalen AG with purity of 99,999% to avoid the presence of oxygen in the system. Later the reactor was charged with 20 bar of cold H<sub>2</sub>. Then, the reactor was heated to 613  $\bar{K}$  with 10  $Kmin^{-1}$ , as soon as the reaction temperature (614 K) was reached the reactor was kept for 24 h. Finally, the reactor was cooled down to room temperature and degassed, and the content of the reaction was centrifuged to separate the catalyst from liquid products. The liquid samples were analyzed by GC-MS and FID as described above.

The product identification and quantification methods via GC–MS and GC–FID are described in detail in Supporting Information.

# Acknowledgements

The authors are grateful for the financial support of Max Planck Society. Thanks also extended to Irina Shekova, Bolortuya Badamdorj, Jose Chacon and Antje Völkel from Max Planck Institute of Colloids and Interfaces for Physisorption, SEM-EDX, elemental analysis, catalytic testing and TGA measurements, respectively. Dr. Iver Lauermann from Helmholtz Zentrum Berlin is greatly acknowledged for the access to X-ray photoelectron spectroscopy. Open Access funding enabled and organized by Projekt DEAL.

## **Conflict of Interest**

The authors declare no conflict of interest.

## **Data Availability Statement**

The data that support the findings of this study are available from the corresponding author upon reasonable request.

**Keywords:** carbocatalysis • heteroatom-doped carbon • lignosulfonate • solid acid catalysts • waste polymer recycling

- Plastics the Facts 2022, Plastic Europe, October 2022, https:// plasticseurope.org/knowledge-hub/plastics-the-facts-2022/.
- [2] A. J. Martín, C. Mondelli, S. D. Jaydev, J. Pérez-Ramírez, Chem 2020, 7, 1487–1533.
- [3] L. Lebreton, B. Slat, F. Ferrari, B. Sainte-Rose, J. Aitken, R. Marthouse, S. Hajbane, S. Cunsolo, A. Schwarz, A. Levivier, K. Noble, P. Debeljak, H. Maral, R. Schoeneich-Argent, R. Brambini, J. Reisser, *Sci. Rep.* 2018, *8*, 4666.
- [4] Statistisches Bundesamt (Destatis), Press release No. 108, March 2022, https://www.destatis.de/EN/Press/2022/03/PE22 108 321.html.
- [5] J. C. Worch, A. P. Dove, ACS Macro Lett. 2020, 9, 1494–1506.
- [6] G. Xu, Q. Wang, Green Chem. 2022, 24, 2321–2346.
- [7] J. Payne, M. D. Jones, ChemSusChem 2021, 14, 4041–4070.
- [8] L. Houqian, H. A. Aguirre-Villegas, R. D. Allen, X. Bai, C. H. Benson, G. T. Beckham, S. L. Bradshaw, J. L. Brown, R. C. Brown, V. S. Cecon, J. B. Curley, G. W. Curtzwiler, S. Dong, S. Gaddameedi, J. E. García, I. Hermans, M. S. Kim, J. Ma, L. O. Mark, M. Mavrikakis, O. O. Olafasakin, T. A. Osswald, K. G. Papanikolaou, H. Radhakrishnan, M. A. S. Castillo, K. L. Sánchez-Rivera, K. N. Tumu, R. C. Van Lehn, K. L. Vorst, M. M. Wright, J. Wu, V. M. Zavala, P. Zhou, G. W. Huber, *Green Chem.* **2022**, *24*, 8899–9002.
- [9] L. D. Ellis, S. V. Orski, G. A. Kenlaw, A. G. Norman, K. L. Beers, Y. Román-Leshkov, G. T. Beckham, ACS Sustainable Chem. Eng. 2021, 9, 623–628.
- [10] J. E. Rorrer, G. T. Beckham, Y. Román-Leshkov, JACS Au 2020, 1, 8–12.
- [11] F. Meirer, S. Kalirai, D. Morris, S. Soparawalla, Y. Liu, G. Mesu, J. C. Andrews, B. M. Weckhuysen, *Sci. Adv.* 2015, *1*, e1400199.
- [12] Plastic upcycling, Nat. Catal. 2019, 2, 945–946.
- [13] X. Jie, W. Li, D. Slocombe, Y. Gao, J. Banerjee, I. Gonzalez-Cortes, B. Yao, H. AlMegren, S. Alshihri, J. Dilworth, J. Thomas, T. Xiao, P. Edwards, *Nat. Catal.* 2020, 3, 902–912.
- [14] F. Zhang, M. Zeng, R. D Yappert, J. Sun, Y.-H. Lee, A. M. LaPointe, B. Peters, M. M. Abu-Omar, S. L Scott, *Science* 2020, 370, 437–441.
- [15] X. Jia, C. Qin, T. Friedberger, Z. Guan, Z. Huang, Sci. Adv. 2016, 2, e15015.
- [16] P. A. Kots, S. Liu, B. C. Vance, C. Wang, J. D. Sheehan, D. G. Vlachos, ACS Catal. 2021, 11, 8104–8115.
- [17] S. Liu, P. A. Kots, B. C. Vance, A. Danielson, D. G. Vlachos, *Sci. Adv.* 2021, 7, eabf8283.
- [18] G. Zichittella, A. M. Ebrahim, J. Zhu, A. E. Brenner, G. Drake, G. T. Beckham, S. R. Bare, J. E. Rorrer, Y. Román-Leshkov, JACS Au 2022, 2, 2259–2268.
- [19] https://www.grandviewresearch.com/press-release/global-zeolite-market (accessed 18.10.2022).
- [20] T. Ennaert, J. Van Aelst, J. Dijkmans, R. De Clercq, W. Schutyser, M. Dusselier, D. Verboekend, B. F. Sels, *Chem. Soc. Rev.* 2016, 45, 584–611.
- [21] E. T. Vogt, B. M. Weckhuysen, Chem. Soc. Rev. 2015, 44, 7342–7370.
  [22] F. Brandi, I. Khalil, M. Antonietti, M. Al-Naji, ACS Sustainable Chem. Eng.
- 2020, 9, 927–935. [23] L. J. Konwar, P. Maki-Arvela, J. P. Mikkola, *Chem. Rev.* 2019, *119*, 11576–11630.

© 2023 The Authors. ChemSusChem published by Wiley-VCH GmbH



864564x

- [24] J. Yao, K. Odelius, M. Hakkarainen, Funct. Compos. Mater. 2020, 1, 5.
- [25] S. Liu, A. P. van Muyden, L. Bai, X. Cui, Z. Fei, X. Li, X. Hu, P. J. Dyson,
- ChemSusChem 2019, 12, 3271–3277. [26] Q. Deng, S. C. Abbas, Z. Li, J. Lv, X. Ma, S. Cao, Y. Ni, W. Zhao, J. Colloid
- Interface Sci. 2020, 574, 33–42. [27] M. Demir, A. A. Farghaly, M. J. Decuir, M. M. Collinson, R. B. Gupta, *Mater*.
- Chem. Phys. **2018**, *216*, 508–516. [28] Q. Guan, Y. Li, Y. Chen, Y. Shi, J. Gu, B. Li, R. Miao, Q. Chen, P. Ning, RSC Adv. **2017**, 7, 7250–7258.
- [29] C. E. Bounoukta, C. Megías-Sayago, F. Ammari, S. Ivanova, A. Monzon, M. A. Centeno, J. A. Odriozola, *Appl. Catal. B* 2021, *286*, 119938.
- [30] M. Al-Naji, B. Puertolas, B. Kumru, D. Cruz, M. Baumel, B. Schmidt, N. V. Tarakina, J. Perez-Ramirez, *ChemSusChem* 2019, 12, 2628–2636.
- [31] M. Al-Naji, F. Brandi, B. Kumru, M. Antonietti, *ChemCatChem* **2022**, e202201095.
- [32] E. O. Eren, E. Senokos, Z. Song, E. Begum, I. Shekova, B. Badamdorj, I. Lauermann, N. V. Tarakina, M. Al-Naji, M. Antonietti, P. Giusto, J. Mater. Chem. A 2023, 11, 1439–1446.
- [33] Q. Qin, F. Brandi, B. Badamdorj, M. Oschatz, M. Al-Naji, J. Mol. Catal. 2021, 515, 111935–11940.
- [34] M. Antonietti, N. Lopez-Salas, A. Primo, Adv. Mater. 2019, 31, e1805719.
- [35] M. Antonietti, M. Oschatz, Adv. Mater. 2018, 30, e1706836.
  [36] S. Navalon, A. Dhakshinamoorthy, M. Alvaro, M. Antonietti, H. Garcia,
- Chem. Soc. Rev. 2017, 46, 4501–4529. [37] F. Brandi, M. Bäumel, V. Molinari, I. Shekova, I. Lauermann, T. Heil, M. Antonietti, M. Al-Naji, *Green Chem.* 2020, 22, 2755–2766.

- [38] F. Brandi, M. Bäumel, I. Shekova, V. Molinari, M. Al-Naji, Sustain. Chem. 2020, 1, 106–115.
- [39] S. S. Chourasiya, D. R. Patel, C. M. Nagaraja, A. Chakraborti, P. V. Bharatam, *New J. Chem.* 2017, *41*, 8118–8129.
- [40] E. D. Glendening, A. Shrout, J. Phys. Chem. A 2005, 109, 4966-4972.
- [41] I. Vollmer, M. J. F. Jenks, R. Mayorga Gonzalez, F. Meirer, B. M. Weckhuysen, Angew. Chem. Int. Ed. 2021, 60, 16101–16108; Angew. Chem. 2021, 133, 16237–16244.
- [42] W. O. Haag, R. M. Dessau, Congress on Catalysis, Berlin, DECHEMA, Frankfurt am Main: Berlin, **1984**, p 305.
- [43] S. Kotrel, H. Knönzinger, B. C. Gates, Microporous Mesoporous Mater. 2000, 35, 11–20.
- [44] J. Weitkamp, ChemCatChem 2012, 4, 292–306.
- [45] C. Wang, T. Xie, P. A. Kots, B. C. Vance, K. Yu, P. Kumar, J. Fu, S. Liu, G. Tsilomelekis, E. A. Stach, W. Zheng, D. G. Vlachos, *JACS Au* 2021, *1*, 1422–1434.

Manuscript received: October 27, 2022 Revised manuscript received: January 12, 2023 Accepted manuscript online: January 13, 2023 Version of record online: March 17, 2023