

Polyethylene waste, such as grocery bags, is of low value for recycling. “Upcycling” to more valuable products could save it from landfills.



PERSPECTIVES

POLYMER CHEMISTRY

Creating value from plastic waste

Polyethylene can be upcycled into alkylaromatic compounds for the production of detergents

By Bert M. Weckhuysen

Plastic waste presents a number of environmental problems (1–3). Although only a small fraction of it enters rivers, lakes, and oceans, it can be transformed there into micro- and nanoplastics that are harmful to aquatic organisms. When plastic waste is buried in landfills or incinerated, it generates heat and carbon dioxide. However, plastic waste also offers great opportunities if its economic value can be increased substantially through upcycling processes that convert it into more valuable chemical products. On page 437 of this issue, Zhang *et al.* (4) report on an upcycling process that converts polyethylene

(often used for packaging and grocery bags) into long-chain alkylaromatics that can be sulfonated to make biodegradable surfactants. This process operates at a moderate reaction temperature, does not need any solvent or added hydrogen, and produces only a small amount of light-gas by-products such as methane.

Chemical recycling has emerged as a promising technology to valorize waste plastics (5, 6). Plastics can be gasified into hydrogen and carbon monoxide (synthesis gas) as a feedstock for fuel production. Pyrolysis and solvolytic routes can convert polymers back into monomers and oligomers that, after purification, can be repolymerized. Unfortunately, the low cost of virgin monomer from fossil carbon-based feedstocks and the lack of regulatory incentives often make chemical recycling commercially unattractive.

One way to overcome this economic hurdle is to convert waste plastics into value-added materials or chemicals. Several approaches have been explored, which include the use of waste plastic to make battery electrodes or photovoltaics films (7, 8). With regard to the upcycling of polyethylene, Bäckström *et al.* recently reported on the selective conversion of high-density polyethylene (HDPE) waste into succinic, glutaric, and adipic acid, which could be converted into plasticizers for polylactic acid (PLA) processing (9).

Zhang *et al.* present an innovative catalytic process in which two chemical reactions, hydrogenolysis and aromatization, are combined. They produce long-chain alkylaromatics from a low-molecular-weight polyethylene model compound for plastic waste with a commonly used heterogeneous catalyst, platinum (Pt) nanoparticles dis-

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persed on an alumina (Al_2O_3) support (see the figure). An essential step is the in situ synthesis of hydrogen through the dehydroaromatization reaction of shorter hydrocarbon chains, which leads to the formation of aromatic compounds. These chains can be made from longer hydrocarbon chains through a hydrogenolysis reaction that requires hydrogen as reactant.

A delicate balance between these two catalytic reactions must be maintained to avoid the unnecessary production of less valuable gases, such as methane, ethane, and propane, as well as carbon (coke) deposits that may lead to catalyst deactivation. Fine-tuning was realized by opting for a moderate reaction temperature (280°C), because higher reaction temperatures (e.g., 330°C) led to production of gases and volatile hydro-

plete mechanism, including proper reaction kinetics, of this upcycling process. For example, they noted that a higher amount of hydrogen formed than was anticipated, and also observed a wider range of aromatics. Notwithstanding, the authors noted a competition between adsorbed polyethylene chains and alkylaromatics on the platinum surfaces, in that alkylaromatics adsorb more strongly than polyethylene. The higher temperatures needed to desorb these products also enhanced hydrogenolysis activity and led to a larger fraction of light gases in the outlet stream.

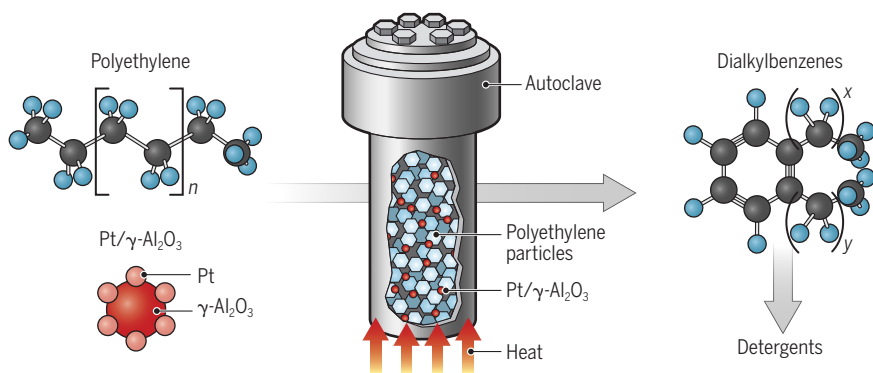
The acid sites of the Al_2O_3 support also play a role in these reactions. This acidity may promote competing processes, such as β -scission reactions, but very little of the expected light olefin products was detected.

(10, 11). The catalyst performance could be largely maintained, and the observed decreases in activity could be correlated with a lower Pt surface area. Although these metals, such as chromium, titanium, and zirconium, are present in only small amounts in plastic waste, they can influence both the activity and selectivity of the Pt catalyst. The chosen $\text{Pt}/\text{Al}_2\text{O}_3$ catalyst can be further optimized and made more resistant to coking and metal deactivation. Cheaper alternatives based on non-noble metals, as well as other support oxides with different acid-base properties, should also be explored.

Zhang *et al.* have developed a promising tandem catalysis route to convert plastic waste into valuable chemical building blocks, from which daily life products can be manufactured (4). Several other tandem combinations are possible, although some of them may require solvents to separate the product ionic or oxygenated compounds from the plastic waste mixture. These new plastic-solvent-process combinations will unlock potential methods for dealing with real-world plastic waste that may contain plasticizers, inks, and dyes, or are mixed with other polymers. Most likely each type of plastic will require a specific chemical conversion process to be upcycled (5). When this can be realized, non-fossil-based plastics may become more economically attractive as carbon atoms can be recycled and chemical functionality can be reintroduced in a high-value product. These developments will pave the way toward a circular plastics economy, in which plastic is not considered waste but rather a valuable raw material (12). ■

From plastic waste to detergents

Zhang *et al.* upconverted polyethylene waste into aromatic compounds that could be used to make more valuable products such as detergents.



Reactants and catalyst

Polyethylene, $\text{CH}_3(\text{CH}_2)_n\text{CH}_3$, reacts with a platinum on γ -alumina ($\text{Pt}/\gamma\text{-Al}_2\text{O}_3$) catalyst.

Reaction conditions

The reaction of polyethylene particles under pressure for 24 hours at 280°C generates in situ oxygen.

Products

Dialkylbenzenes with different side chain lengths can be sulfonated to make detergents.

carbons. The partial pressure of hydrogen was high enough to realize hydrogenolysis but low enough to avoid hydrogenation of the valuable alkylaromatics formed.

The authors also used a low-density polyethylene (LDPE) plastic bag as well as a HDPE water-bottle cap to explore their upcycling process for treating actual plastic waste. Although the catalytic yields were somewhat lower than for the conversion of the low-molecular-weight polyethylene model compound, these experiments indicated that polymer density and degree of branching did not largely influence the developed tandem hydrogenolysis-aromatization process. The authors' upcycling process produced long-chain alkylaromatics and alkylphenathenates with an average number of ~ 30 carbon atoms and in a yield of $\sim 80\%$ by weight.

Despite their experimental efforts, Zhang *et al.* were not yet able to develop a com-

Shorter or longer contact times between feedstock and catalyst material will affect the carbon and hydrogen transfer reactions taking place on the Pt surface. More characterization studies, including labeling experiments in combination with advanced product analysis, are needed to elucidate the different reaction pathways, which can be taken by various catalyst systems. This knowledge should lead to the selective production of aromatics (benzene, toluene, and xylene) to make polymers (such as polystyrene, polyurethane, and polyester), cyclohexanes (a component of jet and gasoline fuels), or alkylaromatics (used to make detergents and lubricants).

Zhang *et al.* also performed catalyst stability tests by performing three consecutive runs with the $\text{Pt}/\text{Al}_2\text{O}_3$ catalyst. This experiment sought to clarify the long-term effect of trapped metal polymerization catalysts

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