Recovering waste plastics using shape-selective nano-scale reactors as catalysts

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Waste plastic composed of low-density polyethylene can be converted into a potential new fuel source. This research describes a new nano-scale catalyst with well-defined and uniform surface openings. This material, called Al-SBA-15, is shape-selective, so it uses only one step to generate a gasoline-type product that requires less additional processing compared to that produced by previous catalysts.

Waste plastic disposal is widely recognized as a major environmental problem, with more than 8 million tonnes of plastic entering the ocean each year¹. Waste plastics are generally handled by land-filling, incineration or mechanical recycling, the latter being the most environmentally attractive option². A number of approaches can be applied to convert plastic residues into chemical commodities or fuel precursors³. Recently, chemical recycling has gained more impact based on novel studies by IBM^{4,5}. Additionally, catalytic pyrolysis can be easily applied. Pyrolysis consists of rapidly heating plastics in a gas stream in the absence of oxygen. After rapid cooling, a liquid product is isolated. In addition to the liquid, a gas fraction and a solid residue are obtained. In this study, we propose a much simpler concept than previous methods, which use a complex multistep approach of treating plastics at high temperatures under controlled conditions to convert them into a mixture of gases, a mixture known as synthesis gas; then, a well-known chemical process called Fischer–Tropsch synthesis is used to convert that gas mixture into a liquid fuel.

Initial studies on the catalytic pyrolysis of polyethylene plastics focused on conventional cracking of zeolites, such as ZSM-5^{6,7} and USY⁷. These studies showed that these porous structures produced a large fraction of aromatic compounds and gases. Then, Mobile Oil⁸ developed a new family of ordered mesoporous materials, known as MCM-41, with remarkable features, such as high surface area and well-defined pores, larger than those found in zeolites. The increased pore size made these materials more attractive to process bulky feedstocks, such as polyethylene plastics. However, they lacked shape selectivity. Serrano et al.⁹ reported that, when processing low-density polyethylene (LDPE), the aluminium-substituted mesoporous silicon Al-MCM-41 did not show shape selectivity but yielded a wide range of hydrocarbons, up to C₂₀. Better aromatic yields were achieved when a second metal was added to Al-MCM-41¹⁰. Ratnasari et al.¹¹ recently reported that a combination of Al-MCM-41 and ZSM-5 in a two-stage pyrolysis-catalysis of

high-density polyethylene produced a C₈–C₁₂ gasoline-type hydrocarbon oil. Therefore, two separate catalysts were required. In this study, we show that comparable gasoline-type hydrocarbons can be obtained with only a single and low-cost porous catalyst.

The main aspects missing from the state-of-the-art technology are the lack of a thorough understanding of the effect of the acidity of mesoporous materials, and the practical yet important manufacturing cost of the catalyst. In particular, Al-MCM-41 is not an inexpensive material because special organic structural directing agents are used in its synthesis; typically, these are tetraalkyl quaternary ammonium compounds ranging from C₁₂ to C₂₀-trimethylammonium bromide¹².

Another family of mesoporous materials, SBA-15¹³, are relatively cheaper to synthesize. Since their organic template is a block copolymer, they can be synthesized rapidly¹⁴, the template can be removed at mild conditions^{15,16} and low-cost silicon precursors can be used in the synthesis¹⁷. Based on these promising features, we investigated the effect of well-defined aluminium-incorporated SBA-15 materials on the pyrolysis of LDPE.

A series of Al-SBA-15 materials with varying aluminium content were prepared using the pH adjustment method reported by Ungureanu et al.¹⁸ Elemental analysis using inductively coupled plasma (ICP) mass spectrometry showed that aluminium is fully incorporated, with a silicon/aluminium ratio approaching the nominal composition (silicon/aluminium ratio = 5–100; see Table 1). Small-angle X-ray scattering (SAXS) in Fig. 1a illustrates the material with the highest aluminium content, Al-SBA-15(5), compared to its all-silicon counterpart; the pattern reveals a hexagonally packed cylindrical morphology characterized by a very regular distance between the cylinders. In all cases, well-defined secondary reflections (110 and 200) with a p6mm space group were found, having hexagonal lattice parameters ranging from 11.2 to 11.9 nm (Table 1). This is particularly remarkable for the prominent level of aluminium in the Al-SBA-15 materials. In general, previous studies found that aluminium incorporation distorts ordered mesoporous structures. The Brunauer–Emmett–Teller (BET) surface areas range between 415 and 510 m² g^{−1} (Table 1); this is in agreement with the well-defined hexagonal structure evidenced by SAXS. The geometrical pore size ranged from 6.9 to 12.1 nm (Table 1), which is well within the mesoporous range (2–50 nm). The acidity of the materials was evaluated by pyridine-adsorbed Fourier-transform infrared

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Table 1 | Summary of structural, acidic and textural properties of SbA-15 materials

Material	Silicon/aluminium (molar ratio) ICP	$d_{0\text{SAXS}}$ (nm) ^a	S_{DeT} (m ² g ⁻¹)	Φ (nm) ^b	Strength of acid sites ^c
Al-SBA-15(5)	5	11.2	417	8.8	0.63
Al-SBA-15(15)	16	11.8	415	8.3	0.72
Al-SBA-15(35)	37	11.9	435	9.1	0.98
Al-SBA-15(100)	98	11.7	510	12.1	1.00
SBA-15 (aluminium-free)	>10,000	11.3	720	6.9	–

^aHexagonal lattice parameter determined as $a_0 = \sqrt{\frac{4}{3}} \frac{d_{100}}{100}$ where d_{100} is the lattice spacing for the (1 0 0) reflection. ^bGeometrical mesopore size determined as: $\Phi(\text{nm}) = 4 \times 10^3 \frac{V_{\text{meso}}}{S_{\text{BET}} - S_{\text{micro}}}$ where V_{meso} is the mesoporous volume ($\text{cm}^3 \text{g}^{-1}$) as determined by the Barrett-Joyner-Halenda (BJH) model, S is the specific surface area ($\text{m}^2 \text{g}^{-1}$) as determined by the BET model. S is the S_{BET} and S_{micro} is the microporous surface area ($\text{m}^2 \text{g}^{-1}$) as determined by the t -plot model. ^cStrength of acid (Brønsted) sites as determined by the pyridine₃₃₀/pyridine₇₇₀ ratio, where pyridine₃₃₀ and pyridine₇₇₀ are the intensities of the PyH⁺ ion bands (pyridines interacting with Brønsted sites) on desorption at 330 and 770 °C, respectively. It expresses the ratio of pyridine molecules to neutralizing protonic sites that survived desorption at 330 °C.

Fig. 1 | Physico-chemical characterization of Al-SbA-15 materials tested for the pyrolysis of LDPe. a, Low-angle SAXS patterns for the all-silicon SBA-15 and Al-SBA-15(5) materials. The hexagonal lattice parameters (a_0) of the complete series can be found in Table 1. b, Correlation between the Brønsted sites ($\mu\text{mol g}^{-1}$) with the bulk aluminium molar concentration (mmol g^{-1}) as determined by chemical analysis. Inset: pyridine-adsorbed FTIR spectra of the pyridines interacting with the Lewis (PyL) and Brønsted (PyH⁺) acid sites. Labelling of spectra in the inset: SBA-15 (a); Al-SBA-15(100) (b); Al-SBA-15(35) (c); Al-SBA-15(15) (d); Al-SBA-15(5) (e). c, High-resolution HAADF-STEM image of an Al-SBA-15(5) domain. Inset: magnified image, scale bar, 50 nm. d, Energy-dispersive X-ray spectra of Al-SBA-15(5) for the elements oxygen, silicon and aluminium.

(FTIR) spectroscopy (Fig. 1b). The inset in Fig. 1b shows the FTIR spectra, which display the characteristic Lewis and Brønsted acid sites. Conventionally, the activity of this reaction, LDPE cracking, has been ascribed to Si–OH–Al Brønsted sites. The FTIR results reveal a linear correlation between the bulk aluminium oxide concentration and the available Brønsted sites (Fig. 1b), confirming that the aluminium incorporation method is effective in quantitative terms. The strength of the acid sites was evaluated by pyridine thermal desorption (Table 1). Acid strength decreased with the

silicon/aluminium ratio from 1 to 0.63. This trend indicates that the acid sites behave like those in zeolites, whose strength also decreases with the silicon/aluminium ratio. Based on the same rationale used for zeolitic-type acidity, the acid strength of Al-SBA-15 agrees with a ZSM-5 benchmark at comparable silicon/aluminium ratios of 0.72 and 0.75, respectively, using a similar acid strength methodology (that is, a pyridine₃₃₀/pyridine₁₇₀ ratio). The ordering of the material was confirmed with high-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM) (see Fig. 1c), and

Fig. 2 | Catalytic performance as the outcome of cracking LDPE. **a**, Cracking conversion curves for the Al-SBA-15 series. X_{LDPE} is the conversion of LDPE given as: $X_{LDPE} = (W_0 - W_T) / W_0 \times 100$ where W_0 is the initial LDPE weight and W_T is the weight of LDPE at a given temperature T . **b**, Temperature at the 50% conversion (T_{50}) for the aluminium-based SBA-15 series compared to the reference materials ZSM-5, Al-MCM-41, mesoporous ZSM-5 and SDUSY (FAU-30). **c**, Pyrolysis–gas chromatography–mass spectrometry results for the ZSM-5 catalyst. B, benzene; T, toluene; o-X, ortho-xylene; m-X, meta-xylene; p-X, para-xylene; EB, ethylbenzene; ET, ethyltoluene; N, naphthalene; 2-MN, 2-methylnaphthalene; MCP, methylcyclopentane. **d**, Pyrolysis–gas chromatography–mass spectrometry results for the Al-SBA-15(5) catalysts. The C values refer to the carbon number for alkenes/alkanes (alkanes are very minor in Al-SBA-15(5) and ZSM-5).

exemplified by the material containing the highest aluminium content, that is, Al-SBA-15(5). Straight channels along the Al-SBA-15 particle are visible with a highly regular distance between the walls. The correlation between linear acidity and bulk composition was verified by chemical mapping with HAADF-STEM (Fig. 1d); elemental mapping for oxygen, silicon and aluminium was carried out for a $0.5 \times 0.5 \mu\text{m}^2$ section. From the images, it is evident that all elements, in particular aluminium, are evenly distributed across the particle. Therefore, this corroborates the good distribution of Brønsted sites observed using pyridine-adsorbed FTIR.

The series of Al-SBA-15 materials were tested for the pyrolysis of LDPE. The results in Fig. 2a show an S-type behaviour for polymer conversion with a light-off temperature ranging from 250 to 350 °C. Thermal cracking was evaluated for reference. For silicon/aluminium ratios smaller than 100, the catalytic effect of aluminium is noticeable, with a shift of the conversion curves towards lower temperatures. A quantitative comparison is given on Fig. 2b where the temperature at 50% conversion (T_{50}) for the Al-SBA-15 series was plotted, as well as other reference materials, such as all-silicon SBA-15 (that is, without aluminium), commercial ZSM-5, Al-MCM-41¹⁹, mesoporous ZSM-5²⁰ and a commercial SDUSY zeolite. From the comparison, it is evident that the Al-SBA-15 materials are active, showing conversions in the same temperature window as the reference materials. An expected decay exists for the T_{50} parameter of the Al-SBA-15 series because of the higher concentration of aluminium

sites. From an activity point of view, these Al-SBA-15 materials are attractive. However, selectivity is a key factor in evaluating their technical feasibility. Pyrolysis-coupled gas chromatographic separation and mass spectrometry detection was used to evaluate product distribution. Fig. 2c shows the product distribution for ZSM-5. This includes the typically low-weight hydrocarbons as well as benzene, toluene, ethylbenzene and xylenes, and other heavier aromatics, such as ethyltoluene, naphthalene and 2-methylnaphthalene, and shows well-defined shape selectivity, as expected. The results for Al-SBA-15(5) (silicon/aluminium=5) are remarkable. It gives rise to a well-defined gasoline-type product with a distribution between C4 and up to C10, although small traces of heavier hydrocarbons were observed up to C13; Supplementary Fig. 1 displays the wide-range plot, including thermal cracking of LDPE for comparison purposes. For both ZSM-5 and Al-SBA-15(5), mostly alkenes were found. However, these can be easily saturated in a simultaneous or in situ step with the aid of hydrogen. Supplementary Figure 2 shows a duplicate catalytic test for the Al-SBA-15(5) material, evidencing the reproducibility of the results. The promising results of this catalyst (Al-SBA-15(5)) can be preliminary attributed to several notable features, such as: (1) the large pore size, which enables penetration of the LDPE chains and limits secondary re-cracking reactions; (2) it contains fully accessible Brønsted sites and those sites possess a modulated strength (0.63, which is weaker than the ZSM-5 benchmark). This allows for moderate cracking rather than the

formation of gases, which is undesirable if a liquid fuel is the target end product; (3) an additional feature of the wide-pore system is that it facilitates the easy diffusion of gasoline-like hydrocarbons, preventing them from undergoing re-adsorption and secondary re-cracking reactions, leading to gases. To put these results into a broader perspective, the lack of hazardous metals in the catalyst and the outstanding selectivity of a single product, compared to previously reported state-of-the-art catalysts²¹, are significant improvements from a sustainability point of view; they minimize the impact on the environment and avoid energy-intensive separation. In conclusion, our results show the promise of Al-SBA-15 as a potentially attractive shape-selective, nano-scale catalyst, which, as a value-added gasoline-type product, could be used to revert waste plastics back into the supply chain.

Methods

The materials used and the synthesis, characterization and cracking methods are discussed in detail in the Supplementary Information.

Data availability

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

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Author contributions

I.M.C. was the originator of the concept, and planned and supervised the experiments. Z.Z. synthesized the SBA-15-type materials, and carried out the preliminary characterization and catalytic testing, particularly ensuring the good quality of the materials. K.G.M. undertook the characterization of materials with the FTIR of probe molecules and interpreted the trends. J.S.W. carried out the pyrolysis-coupled gas chromatographic separation and mass spectrometry detection experiments and interpreted the product distribution. J.T. carried out the HAADF-STEM measurements and chemical mapping interpretation. M.R.R. assisted in the interpretation of the results and preparing the manuscript. K.A.T. prepared the mesoporous ZSM-5 material and assisted in the interpretation of the acidity and textural results. L.L.P. prepared the Al-MCM-41 material and assisted in the interpretation of the textural results. J.M.T. carried out the analysis of the elements and interpreted it. I.M.C. wrote the manuscript.

Competing interests

The authors declare no competing interests.

Additional information

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