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Product Scope and Reactivity in Hydrothermal Conversion of Polyethylene With Solid Catalysts

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ABSTRACT

Plastic waste can be converted into smaller hydrocarbons through hydrothermal conversion using supercritical water. It would be advantageous to introduce suitable catalyst materials under hydrothermal processing conditions to steer product selectivity. In this study, a series of commonly used solid catalysts were evaluated to identify those with the highest potential to tune the product portfolio and increase the overall performance of the hydrothermal conversion of polyethylene. Various metal oxides (i.e., TiO₂, ZrO₂, CeO₂, SiO₂ and γ -Al₂O₃) and aluminosilicates (i.e., zeolites H-Y and H-ZSM-5, as well as different amorphous aluminosilicates) improve the polyethylene conversion rate compared to non-catalytic hydrothermal reaction conditions. CeO₂ is a promising material because it produces a naphtha-like product stream, thereby achieving full conversion, high liquid yield, high alkane/alkene selectivity, and good hydrothermal stability. To steer the conversion toward aromatics, aluminosilicates were the most effective catalyst materials, with amorphous aluminosilicates outperforming their crystalline counterparts in terms of liquid yield (40 wt%), aromatic selectivity (16 wt%) as well as stability. Crystalline aluminosilicates, such as zeolites H-Y and H-ZSM-5, also enhanced activity, but lost their structural integrity under hydrothermal reaction conditions. However, despite significant structural changes, catalysts could be reused, as reactivity of spent materials only decreased slightly.

1 | Introduction

Plastics are embedded in our society, and a future without them seems rather unlikely. Over the last century, 9.2 billion tons of plastics have been produced, with production increasing by 460 million tons annually [1, 2]. Most of these materials are discarded as waste, making effective waste management important [3]. However, most plastic waste is currently landfilled or incinerated, emitting large amounts of CO₂, or released into the environment, thereby causing pollution [4]. Globally, only 9% of plastics are recycled by weight, meaning that plastic production still relies heavily on fossil-based resources [5].

Chemical recycling offers a pathway to reduce our dependency on fossil-based materials and to promote a transition toward a more sustainable and ultimately a circular economy [6]. This approach converts plastic materials into monomers or other valuable chemical components that can be used to manufacture new plastics or other (fine) chemicals. As target component, aromatics are of interest, which are valuable components for the production of polystyrene (PS), polyethylene terephthalate (PET), adhesives, dyes and resins [7]. Additionally, a naphtha-like mixture is desirable, as it can be used in established refinery processes to produce new plastics and other fine chemicals. Techniques for chemical recycling include pyrolysis, solvolysis,

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hydrocracking, (photo-)oxidation, and mechanochemical conversion [8–10].

Hydrothermal conversion is another promising method for producing reusable products from plastics [11–16]. This conversion technique utilizes supercritical water to break down the polymer. Previous work has shown that adjusting reaction parameters, such as reaction temperature and time, can increase conversion and alter product selectivity [17]. By introducing a catalyst, less harsh conditions can be used and the product stream can be modified. However, current literature on catalytic hydrothermal conversion either focuses on non-plastic feedstocks or different product streams, like methane, CO₂, and bio-oils. Therefore, this study explores the use of solid catalysts to convert polyethylene (PE), which accounts for a large fraction of global plastic production, into a higher-value, reusable product stream under milder conditions.

For example, Onwundili et al. reported using Ru/ γ -Al₂O₃ for the gasification of low-density polyethylene (LDPE), high-density polyethylene (HDPE), polypropylene (PP), and PS at 450°C and 300 bar, primarily producing CH₄ and CO₂ [18]. Mukundan et al. demonstrated that Nb₂O₅/ γ -Al₂O₃ improved oil yield during PP degradation, attributing this effect to the Lewis acid sites on γ -Al₂O₃, which can induce PP degradation via an ionic mechanism [19]. On the other hand, solid catalysts are more extensively studied in the hydrothermal conversion of biomass [20]. Supported Ni and Ru materials are used for the gasification of algae, lignin, glucose, cellulose, starch, and polyethylene glycol, thereby producing CH₄ as primary product [21–27]. Supported Pt- and Pd-based materials are used for liquefaction to generate bio-oil from algae and food waste [28, 29]. Zeolites have also been demonstrated to be effective for the conversion of fatty acids. Using zeolite ZSM-5, a high yield of mono-aromatics was obtained, and the material could be regenerated twice [30]. Additionally, zeolite ZSM-5 has been used in the study the cracking of dodecane in supercritical water [31, 32]. Materials that act as homogeneous catalysts, such as KOH and Na₂CO₃, have also been shown to positively affect the yield of bio-oil [26, 28, 33].

Polymer degradation can proceed through multiple mechanisms, depending on the chemical environment. The process generally follows either a radical pathway, typically initiated by thermal energy, or an ionic pathway, induced under acidic conditions. In the radical pathway, random scission of the polymer backbone generates hydrocarbon radicals, which, due to their high reactivity, can propagate further chain cleavage, but also many other side reactions. In contrast, ionic degradation is initiated by the presence of charged species, such as protons (H⁺), or by Lewis acid sites associated with catalytic materials. These species generate carbocationic hydrocarbon intermediates that can undergo β -scission, thereby facilitating cleavage of the polymer chain [34]. Cracking of dodecane under hydrothermal conditions showed that catalysts, like zeolites, can induce C–C bond cleavage by both the zeolitic Brønsted acid sites or by Lewis acid sites originating from extra-framework aluminium (EFAL) formed under hydrothermal conditions [35].

The stability of catalyst materials is critical for ensuring prolonged lifetime and use over several cycles. However, hydrothermal conditions can impose severe degradation of the solid catalysts used.

Jocz et al. employed thermodynamic calculations to evaluate the dissolution tendencies of various metals and metal oxides under supercritical conditions [36–38]. Their findings indicated that noble metal, such as Au, Pt, Pd, and Ru, along with metal oxides, including TiO₂, ZrO₂, CeO₂, and RuO₂, are hydrothermally stable, while Al₂O₃, SiO₂, WO₃, NiO, CuO, and Fe₂O₃ display poor hydrothermal stability. The interaction between catalyst material and polymer has proven to be challenging, as observed in pyrolysis reactions [39–41]. Hydrothermal conversion may help to overcome these limitations, since hydrocarbons can dissolve in supercritical water. While PE does not dissolve in supercritical water itself, the dissolution of hydrocarbon products might increase conversion of the polymer by driving the chemical equilibrium to the product side [42]. It is evident that catalyst materials can be used in supercritical water to enhance the yield toward CH₄ and CO₂ or toward (bio-)oil. However, the production of chemicals, such as a cracker feed or aromatics, could have a higher value for circularity.

In this study, we have investigated metal oxides as well as amorphous and crystalline aluminosilicates that are less expensive than Ru, Pt, and Pd and are common catalysts capable of cleaving C–C bonds, and may therefore be promising under hydrothermal process conditions [43]. The metal oxides are chosen as they are proven to be hydrothermally stable. Zeolites, and other aluminosilicates, are chosen for their ability to induce aromatization, but are potentially not very hydrothermally stable. The extent to which this instability influences catalytic performance in the hydrothermal conversion of PE has yet to be determined and is the subject of this work. Performance metrics include catalyst activity, selectivity, hydrothermal stability, and reusability. Activity is evaluated by the decrease of the wax phase and the increase in gaseous and liquid products. Selectivity is assessed by the formation of aromatics or a naphtha-like mixture that can be used in new or existing refinery infrastructure. Structural stability is assessed by analysing the crystal and pore structures before and after reaction. Selected materials are recovered from the reaction mixture, regenerated and reused to assess whether hydrothermal instability also affects performance. All these criteria are considered when evaluating different catalyst materials.

2 | Results and Discussion

2.1 | Materials and Methods

Hydrothermal conversion of polyethylene (PE) was performed in a 50 mL high-temperature/high-pressure autoclave. For a typical experiment, the reactor was loaded with 15 mL ultrapure water, 2.5 g PE and 0.5 g of catalyst material. The reaction was conducted at 400°C for 1 h, following a heating period of 1 h 15 min to reach the target temperature. Commercially available catalyst materials were used to explore their potential for the hydrothermal conversion of PE: TiO₂, ZrO₂, CeO₂, SiO₂, γ -Al₂O₃, boehmite, zeolite H-Y (with a SiO₂/Al₂O₃ ratio of 30), zeolite H-ZSM-5 (with a SiO₂/Al₂O₃ ratio of 38), and amorphous aluminosilicates with a SiO₂/Al₂O₃ ratio of 0.2 (ASA-10), 0.4 (ASA-20) and 1.1 (ASA-40). After reaction, the gas phase was collected and the liquid and solid materials were extracted using dichloromethane (DCM) and filtered to separate the oil/DCM, water, wax, and

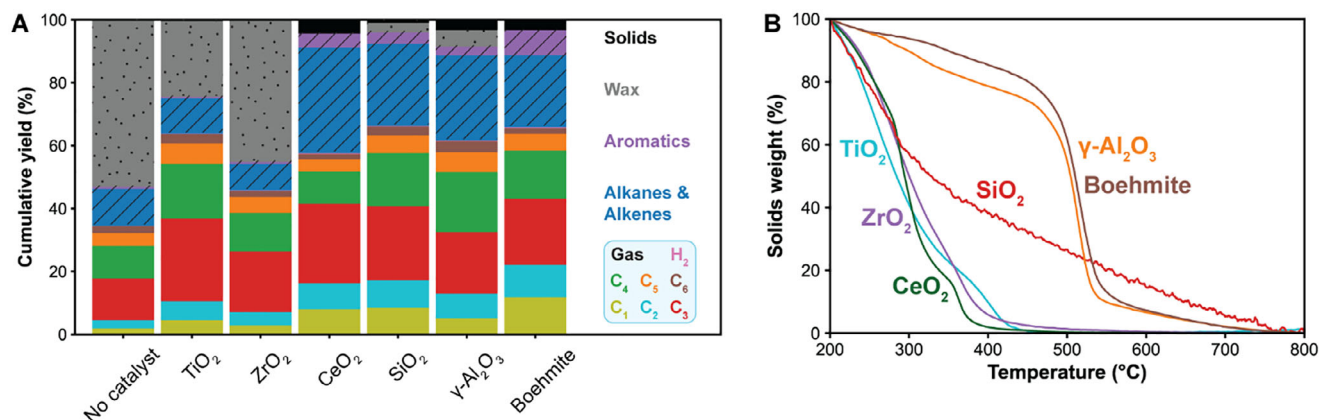


FIGURE 1 | (A) Overview of the product distribution after the hydrothermal conversion of polyethylene (PE) using different metal oxides as catalyst materials. Gaseous products are presented with full colored blocks, liquid products with stripes and waxes with dots. (B) Solid deposit removal in O₂ atmosphere by thermogravimetric analysis (TGA) of the spent catalyst materials.

spent catalyst. Butyl decanoate was added to the oil/DCM phase as internal standard. The gas phase was analysed using gas chromatography (GC) coupled with a flame ionization detector (FID) and a thermal conductivity detector (TCD). The oil phase was quantified using GC-FID and identified with two-dimensional GC (GCxGC). The carbonaceous material deposited on the spent catalyst material was analysed using thermogravimetric analysis (TGA).

2.2 | Metal Oxides

Metal oxides are commonly used as catalyst supports, however they can also act as active materials, as some materials exhibit Brønsted or Lewis acidity, enabling hydrocarbon conversion, or possess redox activity [19]. Therefore, different metal oxides with varying properties, such as porosity, surface area, and acidity, are investigated. All materials improve the process activity, with the wax phase decreasing from 53 wt% without a catalyst to 0 wt% for boehmite and ceria, and close to 0 wt% for γ-alumina and silica. However, TiO₂ and ZrO₂ show the lowest activity with 24 wt% and 44 wt% wax remaining, respectively (Figure 1A). The decrease in wax yield correlates with an increase in gas and liquid product yield, while liquid product yields increase proportionally much more than gas products. On some materials, a significant amount of solid deposits remains after the reaction. CeO₂, γ-Al₂O₃, and boehmite retain most solid deposits, with 3–4 wt% of PE being converted to solid residue. Based on the relatively low burn-off temperatures observed in TGA under air, the solid material deposited on the surfaces of TiO₂, ZrO₂, CeO₂ and SiO₂ is likely unreacted polymer or long-chain hydrocarbon wax (Figure 1B). In contrast, for γ-Al₂O₃ and boehmite, the solid deposits are of a different nature, as the burn-off temperature is ~ 500°C, indicative of graphitic-type hydrocarbon species.

TiO₂, ZrO₂, and CeO₂ are hydrothermally stable. Their crystal structures remain unchanged after reaction (Figures 2 and S7), and their surface areas and pore volumes remain similar. This aligns with thermodynamic calculations and experimental findings by Jocz et al., which show that these materials do not dissolve in supercritical water [36–38].

Silica and alumina are not very hydrothermally stable. Silica loses its porosity, with pore volume and surface area decreasing by 98% after the reaction. The pore volume of alumina decreases by 56%, while the surface area decreases by 83%. Scanning electron microscopy (SEM) images of alumina show that the overall round shape of the particles remains, while slight roughening of the particles is observed. The X-ray diffraction (XRD) pattern shows that alumina loses its crystal structure, as the diffractogram changes from one corresponding to γ-Al₂O₃ to one corresponding to boehmite (AlOOH). This indicates that the alumina converts back to its more stable hydroxide structure in the presence of supercritical water. When boehmite is used directly as a catalyst for the hydrothermal conversion, the XRD pattern after reaction indicates that the material retains the boehmite structure but becomes more crystalline. This suggests that the material may dissolve in the supercritical water and recrystallize. Boehmite shows a higher activity with no wax remaining after reaction and the gas yield increasing by 4 wt% compared to γ-Al₂O₃. The high activity of boehmite indicates that the structural transformation of γ-Al₂O₃ during the first cycle is not likely leading to a loss of activity, as the formed phase is inherently more active.

2.3 | Effect of Surface Area

The selected metal oxides can be categorized into low and high surface area materials. Silica and alumina possess significantly higher surface areas and pore volumes than the other metal oxides. Both materials are catalytically active, as the wax yield decreases to 1–3 wt% and the gas and liquid yields increase to 65 wt% and 30 wt%, respectively (Figure 1A). This could indicate that a higher surface area leads to a higher hydrothermal activity. This would be supported by the low activity of TiO₂ and ZrO₂ with their low surface area (> 7 m²/g) and pore volume (< 0.02 cm³/g) (Table 1). However, CeO₂, which also has a low surface area and pore volume, demonstrates improved activity. This shows that low surface area and pore volume are not inherently detrimental to catalytic performance.

In pyrolysis, it has been shown that plastic struggles to infiltrate the pore system of the catalyst [39–41]. This is also a possibility for hydrothermal conversion and therefore a high surface area

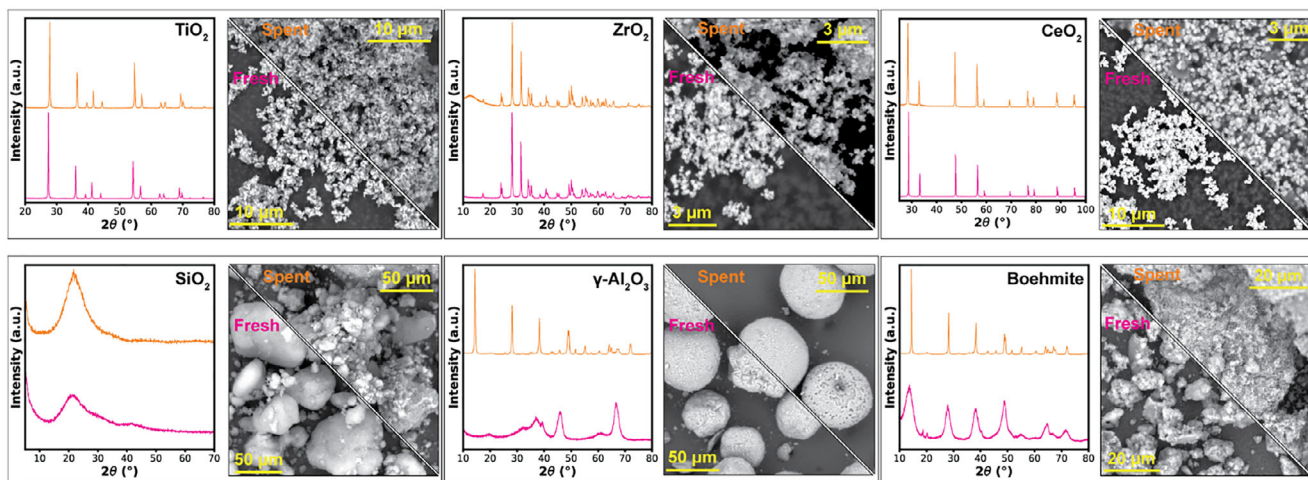


FIGURE 2 | Characterization of the fresh and spent metal oxides. Each panel contains the X-ray diffraction (XRD) patterns of the fresh (magenta) and spent (orange) catalyst material and the scanning electron microscopy (SEM) image of both materials.

TABLE 1 | Physicochemical properties of the different fresh and spent catalyst materials under study.

Catalyst material	Acidity (mmol/g) ^a	Fresh material		Spent material	
		BET surface area (m ² /g) ^b	Pore volume (cm ³ /g) ^b	BET surface area (m ² /g) ^b	Pore volume (cm ³ /g) ^b
TiO ₂	0.04	4.7	0.01	2.5	0.01
ZrO ₂	0.08	7.3	0.02	5.6	0.03
CeO ₂	0.06	4.0	0.01	2.4	0.01
SiO ₂	0.03	252	0.76	5	0.03
γ-Al ₂ O ₃	0.39	187	0.55	32	0.24
Boehmite	0.38	299	0.88	27	0.21
H-Y	0.44	788	0.51	10	0.07
H-ZSM-5	0.08	472	0.60	176	0.20
ASA-10	0.54	300	0.72	209	0.80
ASA-20	0.70	398	1.04	224	1.07
ASA-40	0.48	395	1.57	192	0.83

^aDetermined by NH₃ temperature programmed desorption (TPD).

^bDetermined by N₂ physisorption.

arising from micropores remains largely unused in polymer conversion. The high activity of the low porosity CeO₂ supports this interpretation while the high activity of silica and alumina does not [39, 41]. However, silica and alumina dissolve during reaction. Thus, a higher activity likely does not stem from better catalyst-polymer contact due to higher surface area, but rather due to interaction of polymer with dissolution products or smaller particles of the catalyst precursors. This is supported by the observation that starting with boehmite improved overall activity compared to that of γ-Al₂O₃.

The higher activity of ceria among the low surface area oxides cannot be explained by a higher stability, as all three materials are hydrothermally stable. Alternatively, the high activity of ceria could be due to its redox activity. CeO₂ is redox active and may contain Ce³⁺ species with free electrons that could catalyse C—C

bond cleavage. The phenomenon was previously observed for Zr³⁺ species in ZrO₂ [40, 44]. However, the low activity of ZrO₂ indicates that Zr³⁺ species are absent in the ZrO₂ material used here. This is consistent with the higher reduction potential of Zr⁴⁺ compared to Ce⁴⁺, making the formation of Zr³⁺ species under hydrothermal conditions less likely [45]. Electron paramagnetic resonance (EPR) spectroscopy of the spent TiO₂, ZrO₂ and CeO₂ materials shows a weak slightly isotropic signal ($g_{\text{eff}} \approx 2.004$), indicative of the presence of Ce³⁺ species, while no corresponding signals are observed for TiO₂ and ZrO₂ (Figure S9). Although the signal intensity is low, likely due to a limited concentration of Ce³⁺ species, these results provide an experimental indication of the redox activity of ceria.

Interestingly, the addition of ceria to the reaction produces 5 wt% aromatics in the liquid phase. Aromatics are usually associated

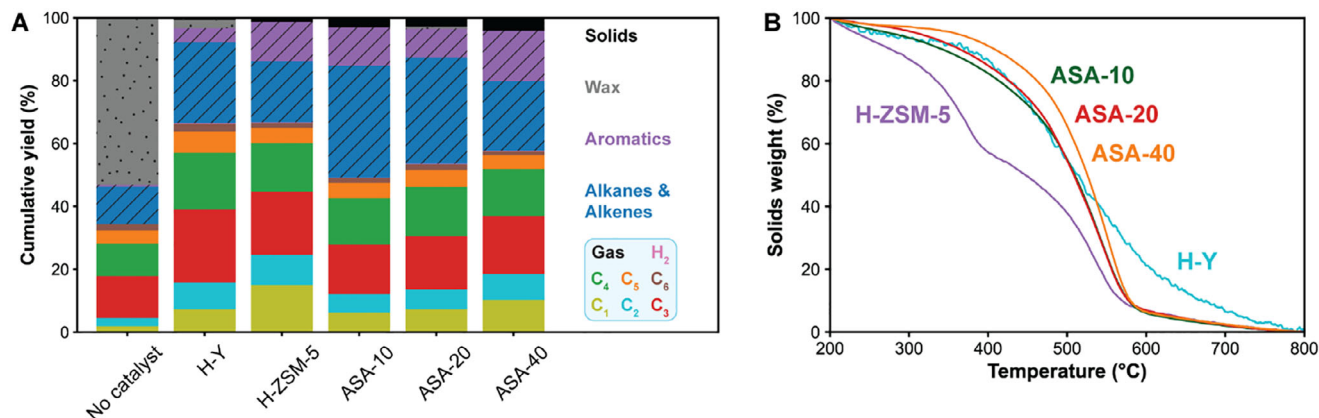


FIGURE 3 | (A) Overview of the product distribution after the hydrothermal conversion of polyethylene (PE) using different crystalline and amorphous aluminosilicates as catalyst materials. Gaseous products are presented with full coloured blocks, liquid products with stripes and waxes with dots. (B) Solid deposits removal in O₂ atmosphere by thermogravimetric analysis (TGA) of the spent catalyst materials.

with dehydrogenation reactions catalysed by Brønsted acid sites and not known to form via radical mechanisms. However, under hydrothermal conditions above the critical point, the radical pathway dominates. For the (slightly) acidic materials SiO₂, γ -Al₂O₃ and boehmite, aromatics are also observed, which is consistent with the ability of acidic sites and surface hydroxyl groups to catalyse their formation, however, it is unclear whether these pathways are still viable above the critical point [46].

2.4 | Amorphous and Crystalline Aluminosilicates

The fact that slightly acidic silica and alumina showed relatively high activity under hydrothermal conditions, although the reaction conditions favour a radical pathway over an ionic one, encouraged us to test highly acidic zeolite materials. Zeolites are often used for activating C–C bond cleavage via cationic intermediates [47]. Two common materials are investigated, namely zeolite H-Y, which has a FAU structure, and zeolite H-ZSM-5, which has an MFI structure and possesses slightly smaller pores than H-Y. Both zeolite materials are catalytically active in the hydrothermal process, with the wax yield decreasing to 0 and 3 wt% for H-ZSM-5 and H-Y, respectively (Figure 3A). Zeolite H-ZSM-5 produces a similar amount of gas as zeolite H-Y, but the selectivity shifts toward smaller hydrocarbons, with 15 wt% yield towards CH₄. Additionally, the aromatic yield is 14 wt% higher compared to zeolite H-Y. These results indicate that zeolite H-ZSM-5 accelerates C–C bond cleavage and subsequent reactions. The amounts of solid deposits on these catalyst materials are very similar (~1 wt%). However, their nature differs. More specifically, for zeolite H-Y, the deposits consist mostly of coke, whereas those on zeolite H-ZSM-5 comprise a mixture of long-chain hydrocarbon waxes and coke-type hydrocarbons, as evidenced by the two degradation temperature regimes in the TGA profile (Figure 3B).

Despite the improved performance, both zeolite materials do not exhibit hydrothermal stability. Zeolite H-Y shows a complete loss of crystallinity in XRD, with the pore volume decreasing with 86% and surface area with 99% (Figures 4 and S8). On the other hand, zeolite H-ZSM-5 retains its crystallinity, as the XRD patterns of

the fresh and spent material are very similar. However, its pore volume and surface area both decrease by 65%.

The loss of crystallinity and the destruction of the porous structure can be attributed to several phenomena. In literature, various zeolite materials have been reported to be used in supercritical water [30–32, 35, 48–58]. An overview of these studies is provided in Table S1. All of them report a similar outcome: the crystalline framework of zeolites X and Y (with framework type FAU), β (with framework type BEA) and SAPOs (with e.g., framework type CHA in the case of SAPO-34) are completely destroyed, while zeolite ZSM-5 retains part of its crystallinity and structure. The destruction of the zeolite-based materials is proposed to take place via dealumination and desilication. Hydrolysis of the Al–O and Si–O bonds can lead to the migration of aluminium and silicon, thereby degrading the zeolite framework [52]. The migration of aluminium species to the surface can result in the formation of extra-framework aluminium (EFAL), which can exhibit Lewis acidity. The differences in stability between the zeolite-type materials remain elusive and can possibly be attributed to their framework structures, as the MFI framework material show higher stability compared to the FAU framework material [48]. Additionally, it is important to mention here that zeolite ZSM-5 can also be synthesised in supercritical water at similar reaction conditions, providing another explanation for its ability to remain crystalline in the reaction conditions explored in this work [59–61].

With crystallinity disappearing in zeolite H-Y and a partial crystallinity loss in zeolite H-ZSM-5, one could question whether a complex crystalline structure is necessary for activity. Therefore, an amorphous aluminosilicate, more specifically ASA-40, is tested. It is remarkable that this material performs even better, with no waxy components remaining, an increase in liquid yield (38 wt%) and the highest selectivity toward aromatics (16 wt%) of all materials tested. It also retains the highest solid content (4 wt%) on the spent material, which is present in the form of coke-type hydrocarbon species (Figure 3B). ASA-40 remains mostly amorphous after reaction, however, small crystalline domains are visible in the XRD pattern, resembling the mullite phase (Figures 4 and S8). Both pore volume and surface area

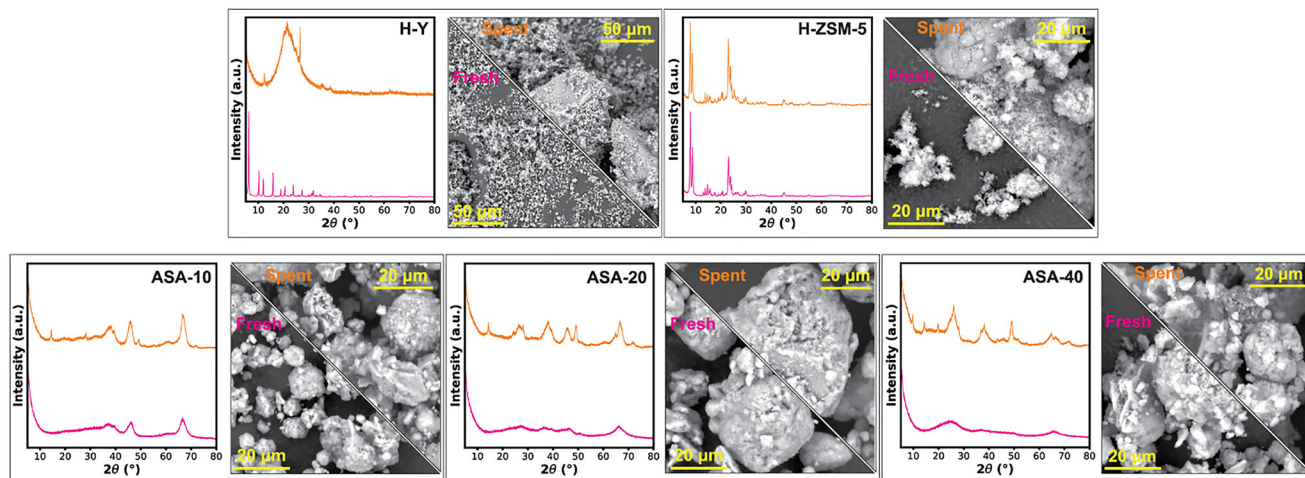


FIGURE 4 | Characterization of the fresh and spent crystalline and amorphous aluminosilicates. Each panel contains the X-ray diffraction (XRD) patterns of the fresh (magenta) and spent (orange) catalyst material and the scanning electron microscopy (SEM) image of both materials.

decrease by 50% after the reaction, indicating that the material is not fully hydrothermally stable.

The alumina-to-silica ratio could affect the performance of the aluminosilicates. Therefore, two other materials with higher alumina content and thus higher acidity, ASA-10 and ASA-20, are compared to ASA-40 (Figure 3A). The gas yield increases with increasing alumina content, from 49 wt% for ASA-10 to 57 wt% for ASA-40. ASA-10 thus shows the highest liquid yield, but ASA-40 still exhibits the highest selectivity toward aromatics (16 wt%). Aromatization appears to be inversely correlated with the acidity of the materials, as the least acidic ASA-40 exhibits the highest production. This observation is counterintuitive, since higher acidity is typically associated with increased activity and aromatization in hydrocarbon conversion. In this case, however, acidity does not appear to directly govern product selectivity. It is imaginable that these materials could also catalyse radical-based pathways.

The solid content is similar for all materials in the amount (3–4 wt%) and also in nature (Figure 3B). Both ASA-10 and ASA-20 remain amorphous, with small crystalline domains observed in the XRD patterns of the spent materials (Figures 4 and S8). The surface area decreases by 30%–50% with increasing alumina content, indicating that lower alumina loading is more beneficial for the hydrothermal stability of aluminosilicates, which is in line with literature [62]. The pore volumes of the ASA-10 and ASA-20 materials are not affected by the hydrothermal conditions, whereas it decreases with 47% for the ASA-40 material, which could suggest that the reaction is partially catalysed by dissolved species.

2.5 | Effect of Catalyst Loading

Catalyst loading can significantly influence both the reactivity and selectivity of the hydrothermal conversion process. An increased catalyst concentration provides more active sites,

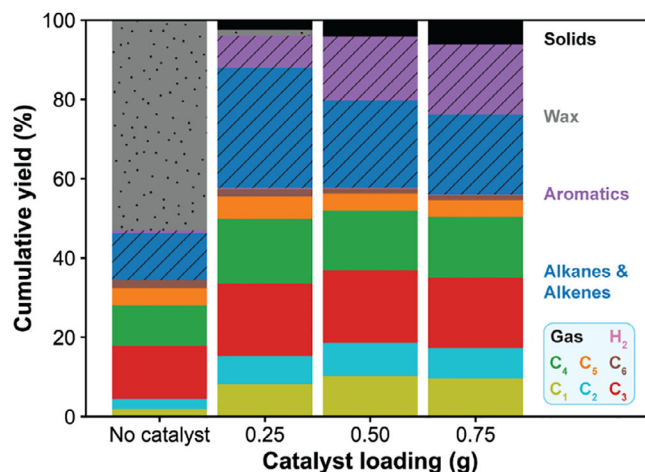


FIGURE 5 | Overview of the product distribution after the hydrothermal conversion of polyethylene (PE) using ASA-40 with different catalyst loadings. Gaseous products are presented with full coloured blocks, liquid products with stripes and waxes with dots.

thereby enhancing the likelihood of hydrocarbon interaction and enabling a higher extent of transformation. To investigate the effect of this, the ASA-40 material is used at different amounts, namely 0.25, 0.5, and 0.75 g. As the amount of ASA-40 increases, the reactivity increases (Figure 5). With 0.25 g of catalyst material, 1.5 wt% of wax remains, indicating that the starting material does not fully convert to smaller hydrocarbons. When the catalyst loading is increased, no wax is present. The gas yield is similar for all loadings. The oil yield does not change with catalyst loading. However, the selectivity shifts toward more aromatics, increasing from 8 wt% to 18 wt% with higher catalyst loadings. The highest catalyst loading also shows the highest solid content on the spent catalyst (6 wt%). As more catalyst material is present in the system, more surface is available for deposition. Additionally, increasing the amount of material enhances overall activity, which can lead the reaction to progress toward coke formation.

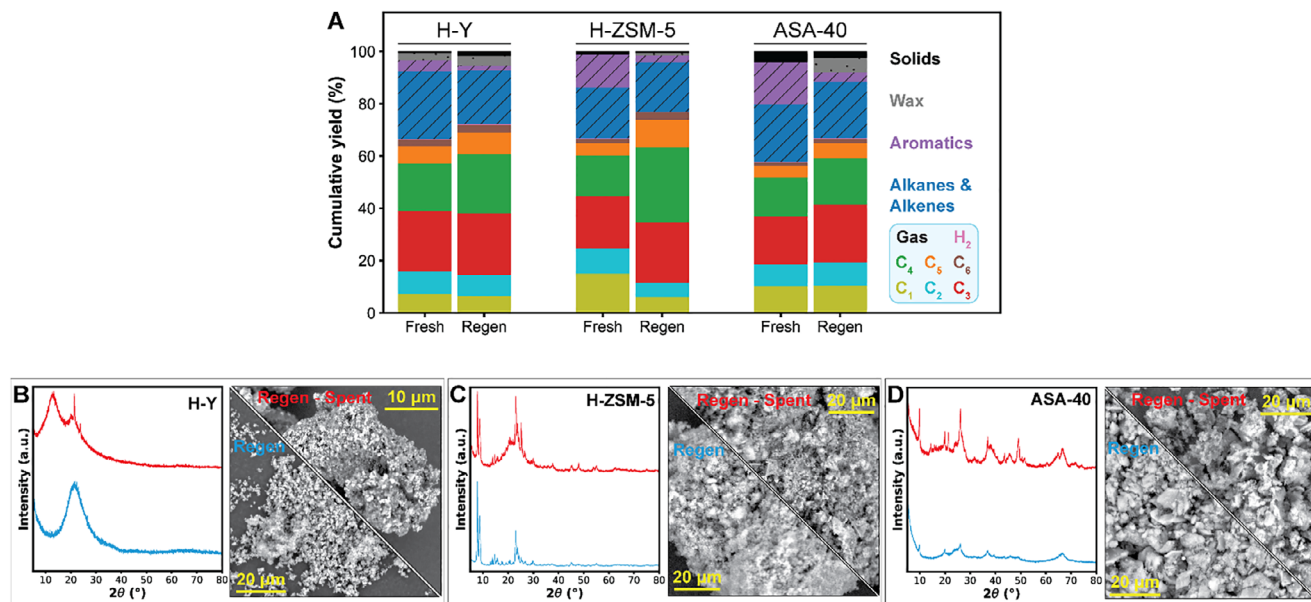


FIGURE 6 | (A) Product distributions of the hydrothermal conversion of polyethylene (PE) using fresh and regenerated zeolite H-Y, zeolite H-ZSM-5, and ASA-40 material. Gaseous products are presented with full coloured blocks, liquid products with stripes and waxes with dots. Catalyst characterization with X-ray diffraction (XRD) and scanning electron microscopy (SEM) of the regenerated (B) H-Y, (C) H-ZSM-5, and (D) ASA-40 catalyst material after regeneration (blue) and after the second reaction (red).

2.6 | Catalyst Reusability

Reusability is another important feature to consider when choosing a suitable catalyst material for a particular conversion process. Previous sections show that the catalyst materials undergo structural changes under hydrothermal conditions, but the question arises whether this affects their reuse. To investigate this aspect, spent ASA-40, zeolite H-Y, and zeolite H-ZSM-5 are regenerated at 600°C in air to remove the solids from the catalyst surface. The catalyst loading for the second reaction is 0.25 g for all materials compared to 0.5 g in the initial experiments, as some material is lost during the work up steps or is possibly partially dissolved in the water phase. The regeneration step does not severely affect the structure, as all materials show similar XRD patterns before and after regeneration (Figure 6B-D). With the regenerated catalyst materials, the activity decreases, as more wax is present, and the oil yield is lower (Figure 6A). The selectivity for aromatics decreases with 2 wt%, 10 wt%, and 12 wt% for zeolite H-Y, zeolite H-ZSM-5, and ASA-40, respectively. This drop in performance can be partially attributed to the lower catalyst loading. As described in the previous section, a lower catalyst loading decreases the conversion of PE, resulting in more wax formation and lower aromatic selectivity. However, at the same 0.25 g loading, regenerated ASA-40 exhibits lower activity than fresh ASA-40 and produces more wax and fewer aromatics. This indicates that the catalyst materials lose some performance after their initial use. The regenerated materials still enhance the hydrothermal conversion process, as the PE conversion is higher than in the non-catalytic process, but their performance does not match that of the fresh catalyst materials.

The structure of all catalyst materials further changes after the second reaction. Zeolite H-Y remains amorphous, but the

amorphous peak shifts toward lower values of 2θ in XRD, and SEM shows agglomeration of the zeolite particles, forming large clusters of smaller crystals. The crystalline structure of zeolite H-ZSM-5 further degrades after the second reaction. The crystalline domains in the diffractogram decrease in intensity, indicating a further loss of crystallinity. SEM reveals agglomerates of zeolitic particles similar in size as before. Interestingly, the ASA-40 material shows more crystalline domains in XRD, while SEM indicates a similar particle morphology.

These results show that the catalysts can be reused up to a certain extent, which is in correspondence with literature of other aluminosilicate catalysts in supercritical water [30]. In the initial reaction, the zeolite materials undergo dealumination, resulting in the migration of aluminium species to the surface and the formation of EFAL. These species are known to act as LAS and therefore are considered to be catalytically active.⁶³ Secondly, although it has been shown that zeolite ZSM-5 loses more than 90% of its BAS, the remaining sites can still be sufficient to catalyse the reaction [31]. For the cracking of dodecane, it was demonstrated that although zeolite ZSM-5 lost most of its BAS, it still retained 50% of its original activity. Diffusion of the hydrocarbons to the active site was rate determining, and thus most of the original active sites were never utilized.

2.7 | Catalyst Material Consideration

Different classes of catalyst materials are evaluated in this work, and their effectiveness depends on multiple criteria. Multiple performance metrics are known to compare catalyst materials, including activity, selectivity, stability, and reusability. An overview of the catalysts' performance and their relative ranking is provided in Figure 7.

Conversion	10	11	1	8	9	1	7	1	1	6	1
Gas	5	11	8	3	6	4	2	1	10	9	7
Liquid	10	11	4	9	8	6	7	5	1	2	3
Alkanes Alkenes	10	11	3	5	4	7	6	9	1	2	8
Aromatics	11	10	6	8	9	5	7	2	3	4	1
Solids	10	11	1	8	3	4	9	7	5	6	2
	TiO ₂	ZrO ₂	CeO ₂	SiO ₂	γ-Al ₂ O ₃	Boehmite	H-Y	H-ZSM-5	ASA-10	ASA-20	ASA-40

FIGURE 7 | Ranking of the catalyst materials based on the formation of different product fractions, from the highest producer (rank 1) to the lowest (rank 11) for each fraction.

A key aspect of a catalyst's performance is its ability to enhance process activity, which is assessed in this research by the absence of wax. Several catalyst materials achieve full conversion (i.e., there is no wax formation), with the ranking from lowest to highest conversion as follows: $\text{ZrO}_2 < \text{TiO}_2 < \gamma\text{-Al}_2\text{O}_3 < \text{SiO}_2 \leq \text{H-Y} < \text{ASA-20} < \text{CeO}_2 \approx \text{AlOOH} \approx \text{H-ZSM-5} \approx \text{ASA-10} \approx \text{ASA-40}$. Among the materials that achieve full conversion, specific candidates show promise for different applications. Selectivity toward liquid products is of particular importance, as this fraction is the desired one for further usage in existing refinery facilities. The materials rank from lowest to highest liquid yield as: $\text{ZrO}_2 < \text{TiO}_2 < \text{SiO}_2 \approx \gamma\text{-Al}_2\text{O}_3 \approx \text{H-Y} \approx \text{AlOOH} < \text{H-ZSM-5} < \text{CeO}_2 \approx \text{ASA-40} < \text{ASA-20} < \text{ASA-10}$. Within the liquid fraction, the relative selectivity toward alkanes/alkenes versus aromatics determines the possible applications. The ranking for alkane/alkene selectivity is: $\text{ZrO}_2 < \text{TiO}_2 < \text{H-ZSM-5} < \text{ASA-40} \approx \text{AlOOH} < \text{H-Y} \approx \text{SiO}_2 < \gamma\text{-Al}_2\text{O}_3 < \text{CeO}_2 \approx \text{ASA-20} < \text{ASA-10}$. In contrast, aromatic selectivity ranks as: $\text{TiO}_2 < \text{ZrO}_2 < \gamma\text{-Al}_2\text{O}_3 < \text{SiO}_2 < \text{H-Y} \approx \text{CeO}_2 < \text{AlOOH} < \text{ASA-20} < \text{ASA-10} \approx \text{H-ZSM-5} < \text{ASA-40}$. Solid formation is an undesirable outcome of catalytic processing. The materials rank from least to most solid production as: $\text{ZrO}_2 < \text{TiO}_2 < \text{H-Y} < \text{SiO}_2 < \text{H-ZSM-5} < \text{ASA-20} < \text{ASA-10} < \gamma\text{-Al}_2\text{O}_3 \approx \text{AlOOH} < \text{ASA-40} < \text{CeO}_2$.

Overall, acidic catalysts consistently rank among the best performers across all categories, highlighting acidity as an important feature for effective hydrothermal conversion of PE. However, most of this acidity is lost under hydrothermal conditions, and it remains unclear how an ionic pathway can dominate above the critical point of water [31]. Based on their performance, possible applications can be assigned to the best performing catalyst materials. For instance, CeO_2 achieves full PE conversion, a high liquid yield with a high selectivity toward alkanes/alkenes, and good stability. These characteristics make CeO_2 attractive for producing a naphtha-like mixture suitable for further processing

in existing refinery infrastructure. However, its high solid content represents significant drawbacks. Another promising class of catalyst materials is aluminosilicates, particularly for the production of aromatics. This was already shown for the conversion of fatty acids in supercritical water using different zeolites [30]. Zeolite H-ZSM-5 achieves full conversion, high aromatic selectivity, and relatively low solid deposit formation. However, its stability remains a concern, as hydrothermal conditions reduce its surface area and pore volume by 65% upon the first use and even more upon further reaction cycles. Amorphous aluminosilicates show better stability in this regard. Both ASA-10 and ASA-40 materials achieve full PE conversion, with ASA-10 offering the highest liquid yield and ASA-40 the highest aromatic selectivity. Nevertheless, ASA-40 retains the highest solid content and the largest loss of surface area and pore volume. ASA-10, despite a slightly lower aromatic selectivity (4 wt% lower than ASA-40), combines higher stability with lower solid formation, marking the best candidate of the tested catalyst materials. Furthermore, the already high liquid yield can be further tuned by optimizing reaction parameters (e.g., reaction temperature, time, and catalyst loading), to improve the selectivity toward liquid products, especially aromatics.

2.8 | Implications for Product Distribution and Deactivation

Catalytic hydrothermal conversion shares several similarities with catalytic pyrolysis in terms of reaction temperature, product formation, and catalyst selection. However, there are also significant differences between the two chemical conversion processes. To illustrate this, the outcomes of this study are compared with the results of previous studies on catalytic pyrolysis and hydrothermal conversion [17, 40]. A comparison of the two reaction systems, namely the batch reactor used for hydrothermal

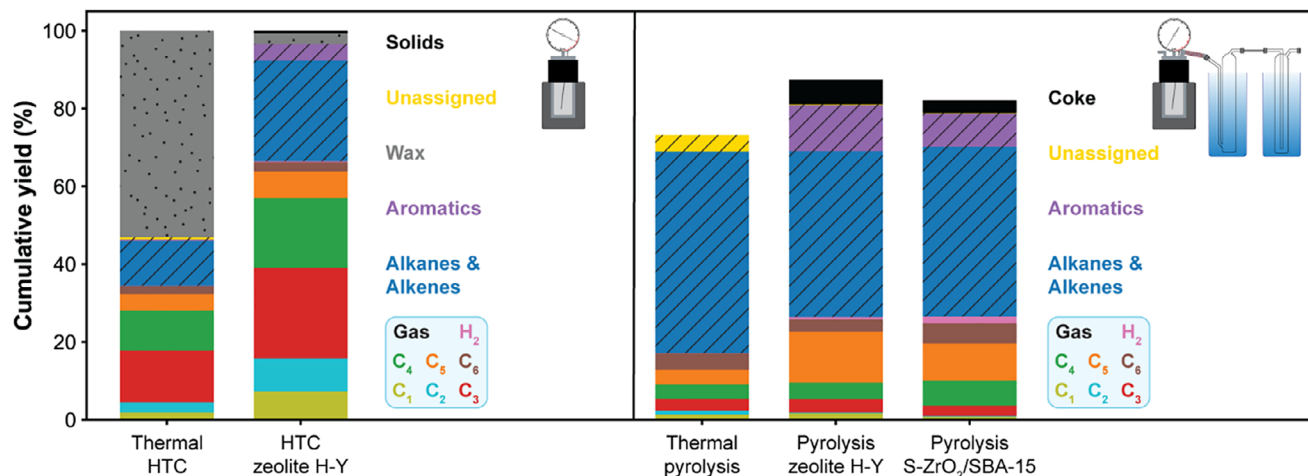


FIGURE 8 | Product distributions of the conversion of polyethylene (PE) by (catalytic) hydrothermal conversion (HTC) using a batch reactor at 400°C for 1 h with 2.5 g of PE and 0.5 g of catalyst (left) and by (catalytic) pyrolysis using a semi-batch reactor at 400°C for 1 h with 1 g of PE and 0.5 g of catalyst (right) [17, 40]. Gaseous products are presented with full coloured blocks, liquid products with stripes and waxes with dots.

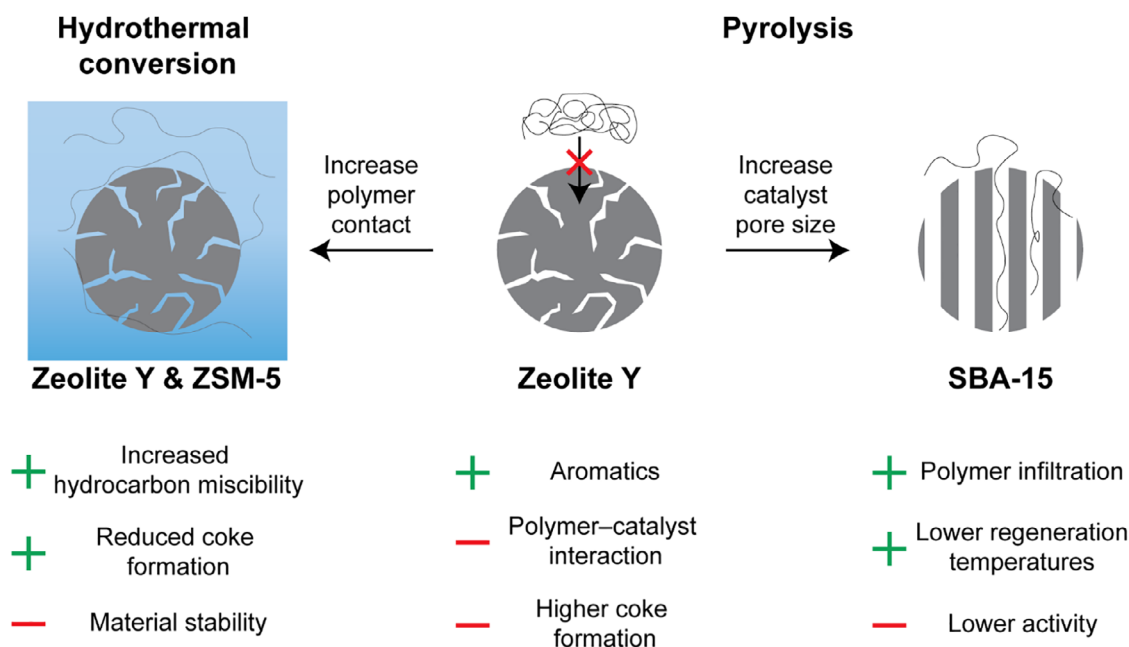


FIGURE 9 | Strategies for improving polymer-catalyst interactions using supercritical water in the hydrothermal conversion thereby enhancing catalyst-polymer contact, or by increasing the catalyst pore size during pyrolysis.

conversion and the semi-batch used for pyrolysis, reveals that the most pronounced difference is the gas yield (Figure 8). Due to the longer residence time in the batch reactor, hydrocarbons are cracked into smaller compounds (C₁–C₅).

More interestingly, however, is the comparison of the two catalytic systems. In both cases, zeolite H-Y has been used as catalyst material. Aside from the differences in gas and liquid yields, similarities are observed in the liquid products, as under both reaction conditions zeolite H-Y is found to promote the formation of aromatic compounds. A difference, however, is found in the formation of coke-type hydrocarbons. During the process of

hydrothermal conversion, zeolite H-Y produces only ~ 0.6 wt%, whereas in pyrolysis it forms roughly 10 times more.

The lower coke formation under supercritical water conditions can be attributed to coke suppression mechanisms, both direct and indirect. Guerra et al. demonstrated through dodecane cracking that supercritical water inhibits coke formation via two pathways [32]. It can directly suppress the formation by passivating the active sites, thereby preventing oligomerization reactions. Additionally, it can indirectly influence coke formation by modifying the catalyst through framework amorphization and acid site removal. These structural changes increase mesoporosity

and reduce acidity and activity, all of which are associated with decreased coke formation. Furthermore, the presence of supercritical water affects the type of coke that is formed. Under hydrothermal reaction conditions, mainly soft coke consisting of aliphatic and single-ring aromatic compounds is produced, whereas in pyrolysis, hard coke composed of polyaromatics dominates.

Both suppression mechanisms play a crucial role in catalytic hydrothermal conversion and consequently influence hydrocarbon production and catalyst lifetime.

2.9 | Strategies to Improve Polymer–Catalyst Interaction

In this and previous studies, different approaches were explored to improve the interaction between polymers and catalyst materials. Inherently, the interaction is hindered by the size mismatch between the catalyst pores and the large polymer chains, as well as, by the limited contact resulting from the high viscosity of polymers [39, 41]. In the catalytic pyrolysis, we previously examined the use of a catalyst material with a larger pore size compared to the microporous zeolite Y, enabling the polymer to infiltrate the porous structure. This allowed the polymer to access the active sites and react with them. However, compared to the microporous zeolite Y, this material exhibited lower activity.

In this study, another approach was investigated by using supercritical water in the hydrothermal conversion process. Supercritical water may improve the contact between the polymer and the catalyst. One hypothesis is that in supercritical water, the polymer untangles more easily, freeing the chain ends [64]. This could facilitate chains to enter the catalytic pores, thereby improving catalyst accessibility, an issue known to limit the performance of microporous materials during pyrolysis. Secondly, because the hydrocarbon products dissolve in supercritical water, their local concentration at the catalyst surface is reduced, shifting the reaction equilibrium toward the product side. Finally, the presence of supercritical water has a beneficial effect on coke formation, as it inhibits coke deposition and can therefore prolong catalyst lifetime. However, the hydrothermal conditions can negatively affect the catalyst structure by inducing dealumination and desilication, which may ultimately lead to the collapse of the crystalline framework.

Both chemical conversion approaches, increasing the pore size and employing supercritical water, have their respective advantages and disadvantages and must therefore be carefully considered when selecting a method to improve polymer–catalyst interactions (Figure 9).

3 | Conclusions

A wide range of solid catalysts, namely TiO_2 , ZrO_2 , CeO_2 , SiO_2 , $\gamma\text{-Al}_2\text{O}_3$, boehmite, zeolite H-Y, zeolite H-ZSM-5, and various amorphous aluminosilicates, were tested in the hydrothermal conversion of polyethylene (PE) using supercritical water to improve the overall process performance. All catalysts under study showed improved conversion compared to the non-catalytic

process. Metal oxides, such as SiO_2 , $\gamma\text{-Al}_2\text{O}_3$, and boehmite, achieve (almost) full conversion with 0–5 wt% wax remaining, and increase the selectivity toward liquid products and aromatics. On the other hand, TiO_2 and ZrO_2 showed a decreased catalytic performance, with lower PE conversion as 24–44 wt% wax remained. Among the tested metal oxides, CeO_2 proved to perform the best, as it achieved full PE conversion, high selectivity toward liquid products, and good stability. This suggests that CeO_2 could particularly be suitable for producing a naphthalene-like product stream that can be implemented in new or existing refinery infrastructure.

To produce aromatics as main end product, aluminosilicates were identified as the most effective solid catalyst materials, especially their amorphous variants. Zeolites H-Y and H-ZSM-5 enhanced process activity, but underwent structural changes during hydrothermal reaction conditions. In contrast, amorphous aluminosilicates achieved the highest selectivity toward aromatics, with high liquid yields, and showed better stability than their crystalline counterparts. An amorphous aluminosilicate with a $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratio of 1.1 proved to perform the best of the tested catalyst materials.

Catalyst reuse was also demonstrated. In the case of zeolites H-Y and H-ZSM-5, as well as an amorphous aluminosilicate, the spent materials retained their catalytic activity, although at a lower level than the fresh catalyst material. This finding suggests that structural changes are not necessarily detrimental to catalyst lifetime. Nevertheless, the definitive property that governs catalyst activity remains unclear and requires further studies. Surface area and acidity appeared to influence catalyst performance, but no single parameter could be identified as the determining factor for optimal performance in the hydrothermal conversion of PE and questions remain regarding the reaction mechanism of hydrocarbon activation using solid acids at supercritical conditions that favour radical-based pathways.

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Data Availability Statement

All data and python scripts utilized in the manuscript have been uploaded to the Yoda repository and are available under <https://doi.org/10.24416/UU01-NSSBBB>.

Conflicts of Interest

The authors declare no conflicts of interest.

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