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Pore Blocking by Phenolates as Deactivation Path during the Cracking of 4-Propylphenol over ZSM-5

Michael J. Stellato ^{1,2}, Giada Innocenti ², Andreas S. Bommarius ^{1,2}  and Carsten Sievers ^{1,2,*} 

¹ Renewable Bioproducts Institute, Georgia Institute of Technology, 500 10th St. NW, Atlanta, GA 30332, USA; mstellato@gatech.edu (M.J.S.); andreas.bommarius@chbe.gatech.edu (A.S.B.)

² School of Chemical and Biomolecular Engineering, Georgia Institute of Technology, 311 Ferst Dr. NW, Atlanta, GA 30332, USA; giada.innocenti@chbe.gatech.edu

* Correspondence: carsten.sievers@chbe.gatech.edu

Abstract: Cracking of propyl side chains from 4-propylphenol, a model compound for lignin monomers, is studied for a commercial ZSM-5 zeolite catalyst. The decline of 4-propylphenol conversion with time on stream can be delayed by co-feeding water. FTIR spectroscopy shows the formation of chemisorbed phenolates during reactions and significant amounts of phenolics are detected by GC-MS of the extract from the spent catalysts. Thus, chemisorbed phenolates are identified as the main reason for deactivation in the absence of water. Regardless of the amount of co-fed water, substituted monoaromatics and polyaromatic species are formed. Comprehensive characterization of the spent catalysts including Raman and solid-state ²⁷Al NMR spectroscopy, and thermogravimetric analysis points to a combination of deactivation processes. First, phenolates bind to Lewis acid sites within the zeolite framework and hinder diffusion unless they are hydrolyzed by water. In addition, light olefins created during the cracking process react to form a polyaromatic coke that deactivates the catalyst more permanently.

Keywords: biomass; dealkylation; lignin; phenolate; zeolites



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1. Introduction

Bulk chemical production from biomass is one of the leading approaches to eliminating dependence on fossil carbon as feedstock for the chemical industry [1]. To improve the economics of biorefining, biomass utilization must take advantage of all available carbon [2,3]. Of the three major components of woody biomass (cellulose, hemicellulose, and lignin), the naturally aromatic structure of lignin makes it an attractive target for upgrading to chemicals [4]. To that end, research has focused on improving the extraction and conversion of lignin and its conversion into useful products for downstream upgrading [5–10]. The “lignin value prior to pulping” approach shows that limited modifications of industrial pulp and paper operations could advantageously generate a solvent-extracted lignin stream with sufficient quality for downstream processing [11]. Such a lignin could then be broken down by pyrolysis, acid digestion, or hydrogenolysis [4]. Alternatively, the lignin-first approach to second generation biorefinery operations uses reductive fractionation techniques to simultaneously extract and depolymerize the lignin from the native biomass [6,12]. These processes also generate a stream of cellulose and hemicellulose for further upgrading to ethanol or other sugar-based products [13].

Regardless of how lignin is extracted or broken down, lignin monomers are typically obtained as mixtures of similar aromatic oxygenates with a variety of different structures and functional groups. To convert such mixtures into useful replacements for petroleum-derived additives and polymers, the fractionated lignin must be separated and upgraded. In most cases, chemical upgrading will involve some combination of hydrodeoxygenation and carbon chain cracking [4]. Both of these processes have been performed over zeolites or metals on zeolite support independently in the literature [14–17]. Recent work by

Sels et al. has demonstrated the efficacy of cracking propylphenol over Brønsted acidic ZSM-5 with high selectivity to phenol and propylene (Figure 1). However, fast deactivation is observed unless water is introduced as a cofeed over all tested zeolites [17–19]. This has the potential to destabilize the zeolite framework and increase the mobility of the aluminum sites responsible for their Brønsted acidity, leading to a tradeoff between catalyst stability and activity [20,21]. Similar deactivation of catalysts by oxygenated aromatics has been observed by our group and others during reactions with aromatic oxygenates [14,22–24]. Chen et al. investigated the effect of desilication and mesopores on the cracking of 4-isopropylphenol and saw improvement, however they did not explore the mechanism of deactivation beyond attributing it to pore blockage by coke [25]. Understanding the nature of this deactivation and the interactions of these aromatic oxygenates will be critical in developing sustainable catalytic processes for lignin monomer upgrading.

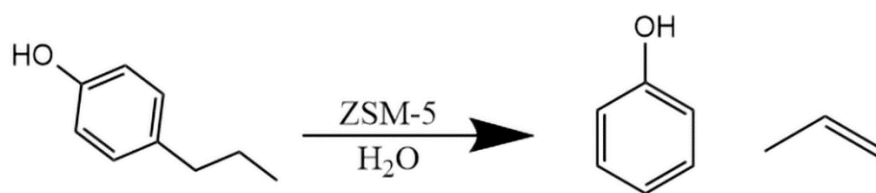


Figure 1. Reaction of 4-propylphenol to phenol and propylene over Brønsted acidic ZSM-5 zeolite in the presence of water vapor.

Despite the significant practical impact of the deactivation problem, few have attempted to study this issue in detail. Often deactivation is attributed to coke formation on the catalyst surface, which can block access to micropores and active sites [23]. In their study of benzene conversion to phenol by photocatalysis over TiO₂, Einaga et al. [26] hypothesized that the deactivation they observed was due to the formation of mono-oxygenate species on the surface which dimerize and eventually grow into deactivating polymers. Others have shown that some chemical structures, especially those involving phenolates, catecholates, and guaiacolates, can bind very strongly to surfaces [14,27–31]. Popov et al. [32] suggested several possible binding modes for these phenolates on Lewis acids on alumina surfaces. Although usually known for their Brønsted acidic character, zeolites can also have a significant density of Lewis acid sites from extra-framework aluminum species [20]. We hypothesized the same types of surface species form during the upgrading of aromatics from lignin depolymerization, forming a kind of chemical “roadblock” that contributes to the fast deactivation of upgrading catalysts, as previously suggested for hydrodeoxygenation reactions [14]. Alternative explanations for the fast deactivation during propylphenol cracking include polymerization of propylene to form polyaromatic coke [33], and the leaching of active sites due to dealumination [20,21].

In this work, we aim to understand the cause of the fast deactivation of ZSM-5 during the cracking of propylphenol. Several common paths of zeolite deactivation are examined using a variety of techniques including FTIR spectroscopy, ²⁷Al MAS NMR spectroscopy, and thermogravimetric analysis. By fully understanding the root cause of this deactivation, engineering efforts can be focused on prevention to improve the productivity of next gen biorefineries.

2. Results

2.1. Catalyst Characterization

The material properties of the ZSM-5 catalyst before the reaction were characterized by N₂ physisorption, X-ray diffraction, and pyridine chemisorption followed by IR spectroscopy. Nitrogen physisorption measurements showed a BJH adsorption micropore volume of 0.13 cm³/g (Figure S1, Supplementary Materials). X-ray diffraction measurements indicated that the crystal structure was consistent with the MFI structure both before and after reaction (Figure S2). SEM images of the catalyst post reaction clearly show pre-

served MFI crystallites (Figure S3). Pyridine adsorption followed by transmission FTIR spectroscopy showed that the untreated ZSM-5 had a Brønsted acid site concentration of 400 $\mu\text{mol/g}$ and a Lewis acid site concentration of 110 $\mu\text{mol/g}$. About a quarter of the pyridine on Lewis acid sites desorbed when the temperature was gradually raised to 450 $^{\circ}\text{C}$, while essentially all Brønsted acid sites were strong enough to retain pyridine at this temperature (Figure S4). These measurements are consistent with values found in the literature for this material [34].

2.2. Catalytic Cracking of 4-Propylphenol

The reactivity of 4-propylphenol over a commercial ZSM-5 catalyst in the presence of varying amounts of water matched well with previous reports in the literature (Figure 2) [17,18,35]. In the absence of water, the catalyst quickly deactivated, approaching a steady state conversion of approximately 5–10% and phenol selectivity of around 40%. Interestingly, with even a small amount of water present, the conversion and phenol selectivity increased to 50% and 65%, respectively. Increasing the water content of the reactant stream from 3% to 9% increased conversion and selectivity, but further increase to 12% resulted in no measurable increase in performance. In the case of 9–12% water content, both the initial conversion and phenol selectivity were close to 100%, while the steady state conversion was 65% and steady state selectivity to phenol was 75%. Steady state operation with slow deactivation was reached after approximately 120 min on stream. The first order deactivation rate constants for all water contents are given in Table 1. There is a dramatic decrease in the deactivation rate constant between 0% water and 3% water followed by a less drastic but still significant decrease from 3% water to 12%. The steady state turnover frequency also decreased from 100 min^{-1} at 12% water to 41 min^{-1} at 3% water and 3.6 min^{-1} at 0% water (Figure S5).

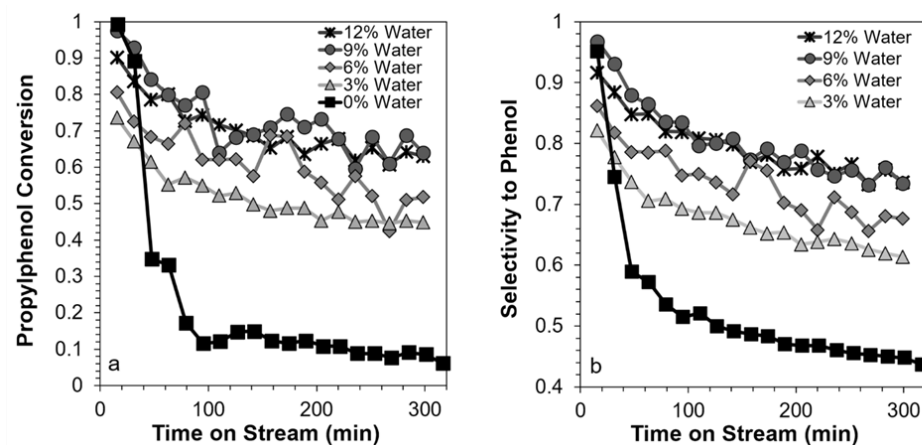


Figure 2. Cracking of 4-propylphenol over ZSM-5 in the presence of different amounts of water. Reaction conditions: 2% propylphenol in N_2 ; 0.2 g of calcined ZSM-5; 350 $^{\circ}\text{C}$; WHSV = 31.1 h^{-1} .

Table 1. Deactivation rate constants for the conversion of 4-propylphenol in the presence of different amounts of water.

Water Content	0%	3%	6%	9%	12%
Deactivation Constant k_d/h^{-1}	1.269	0.143	0.114	0.116	0.100

2.3. Characterization of the Deactivated ZSM-5

TGA of spent catalysts showed three significant peaks in the derivative (Figure 3). The first one below 150 $^{\circ}\text{C}$ is attributed to moisture loss from water adsorbed from the atmosphere during handling (not correlated with the water content of the reactant stream). A second small peak is observed around 250 $^{\circ}\text{C}$ and attributed to the desorption of bound surface species such as the chemisorbed molecules [36]. This peak is most prominent in the

case with 0% water in the reactant stream. This sample also exhibited additional mass loss between 375 and 450 °C compared to the other catalysts. This indicates that both water (in this case supplied by adsorption from the atmosphere between experiments) and heat are required to drive off these species and that they are most plentiful in the sample which did not have water in the reaction stream. The largest peak, observed between 400 and 640 °C, is attributed to strongly chemisorbed species or recalcitrant carbon deposits. It has been shown that recalcitrant types of coke typically burn in this region, shifting to higher temperatures as they become more graphitic [37]. The total mass loss attributed to this region on a dry, coke free catalyst was approximately 6% in all cases. Based on these results, it appears that water does not significantly reduce the formation of carbon deposits.

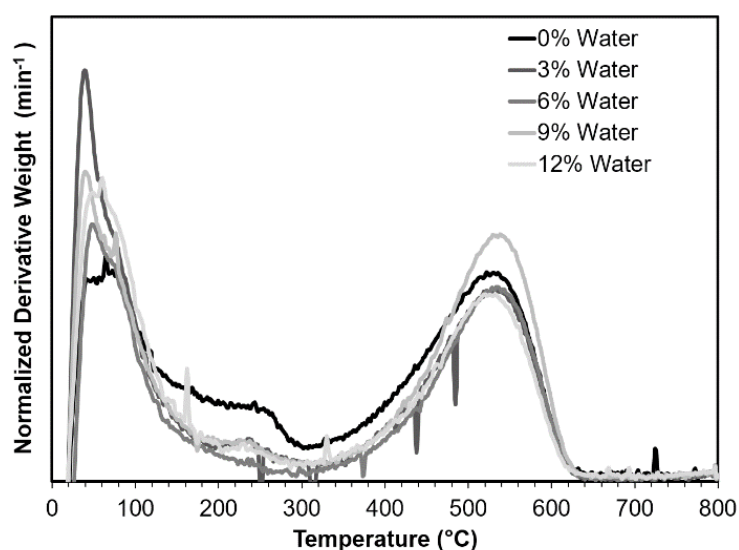


Figure 3. Normalized derivative weight curves with respect to temperature in 20 mL/min of air at a heating rate of 10 °C/min for all spent ZSM-5 catalysts.

To better understand the nature of these carbon species, Raman spectroscopy was performed on the most deactivated sample and compared to a deactivated ECat from a petroleum fluid catalytic cracking process (Figure S6), which contained the typical bands of polyaromatic coke deposits [38]. The amount of observable coke species was negligible compared to the FCC sample, indicating that our ZSM-5 catalyst was essentially free from ordered or graphitic coke species. From this observation, we conclude that the deactivating species in this system are not polyaromatic and deactivation in the absence of water should not be attributed to hard coke.

Hydrofluoric acid digestion followed by DCM extraction and GC-MS analysis was performed to identify specific species responsible for deactivation in both the 0% water case and 12% water case, representing the most deactivated and least deactivated catalyst, respectively (Figure 4). It is important to note that a negligible amount of DCM-insoluble coke was produced in both cases. Most of the DCM-soluble surface species were monocyclic aromatic compounds, primarily alkyl phenols and alkyl benzene, in both cases. In the case of 0% water, some bicyclic compounds, such as naphthalene and hydroxynaphthalene, were also observed. In a control experiment, diphenyl ether was subjected to the same treatment as the spent catalysts. After digestion and DCM extraction, only diphenyl ether was observed in the GC/MS analysis.

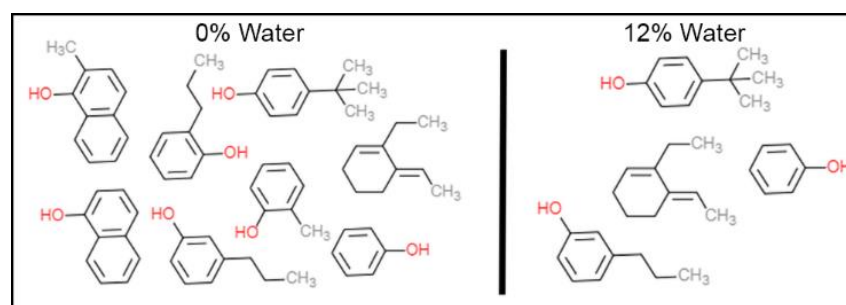


Figure 4. Suggested structures of products observed in the GC-MS analysis of extracts from spent catalysts digested in HF.

In addition to understanding the nature of the surface species, the integrity of the zeolite frameworks of spent catalyst was examined by ^{27}Al MAS NMR spectroscopy (Figure 5). The samples were calcined and rehydrated prior to analysis to avoid an influence of carbonaceous deposits on the quadrupolar induced shifts and associated line broadening [39,40]. All catalysts showed peaks at 60 and 0 ppm representing aluminum atoms in tetrahedral and octahedral coordination, respectively. A shoulder was also observed at 45 ppm which indicates aluminum nuclei in a distorted tetrahedral or pentahedral environment [41,42]. Most aluminum nuclei in crystalline zeolites are present as tetrahedrally coordinated framework species with a limited contribution from octahedrally coordinated extra-framework species [43]. However, such octahedral aluminum can be formed by dealumination, especially at elevated temperature and in the presence of steam [43]. The deconvolution of the NMR spectra indicated a slight increase in the contributions from distorted, tetrahedrally coordinated Al species at the expense of Al in undistorted framework positions, with no apparent change in the contribution of octahedrally coordinated Al (Figure 5b,c). This suggests that the zeolite framework was only damaged by the reaction conditions to a minor extent, causing a distortion of local environments without significant dealumination. This distortion could also be caused by small amounts of residues that were not efficiently removed during calcination. It also indicates that the majority of active sites for the reaction were still present in all samples.

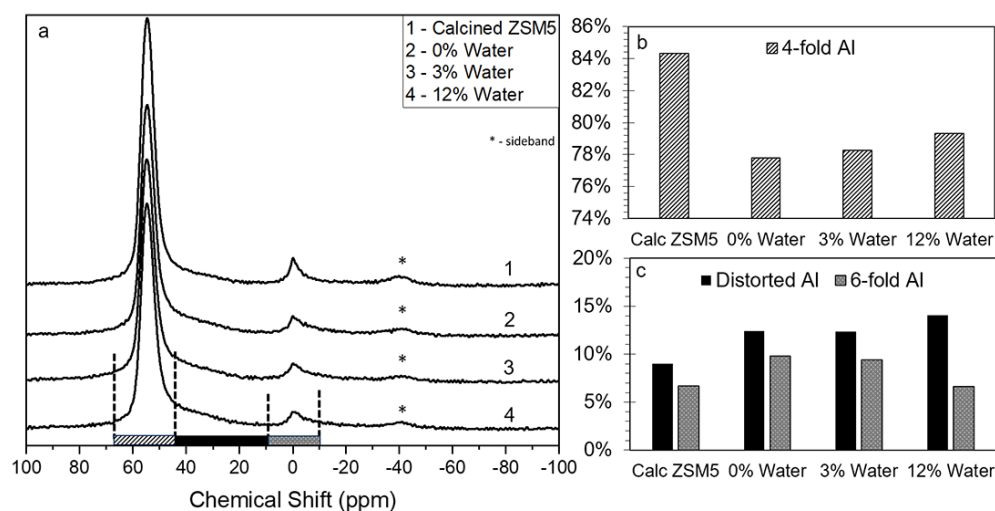


Figure 5. (a) ^{27}Al MAS NMR spectra of deactivated ZSM-5 zeolites; (b) deconvoluted integral of the peak at 60 ppm representing 4-fold coordinated aluminum sites; (c) deconvoluted integral of the peak at 0 ppm representing 6-fold coordinated aluminum sites and the deconvoluted integral of the intermittent region representing aluminum sites neither fully tetrahedrally nor octahedrally coordinated. * denotes a sideband echo of the 60 ppm peak generated by the spinning

2.4. FTIR Spectroscopic Analysis of Adsorbed Phenol and Spent Catalysts

Infrared spectroscopy was used to understand which surface species play a key role in the deactivation pathway. As a reference, phenol was dosed onto a self-supported ZSM-5 catalyst at 50 °C in the gas phase and allowed to equilibrate before being heated to 350 °C (Figure 5 and Figure S7). A band was observed at 1597 cm⁻¹ corresponding to the quadrant vibration of the aromatic ring [44]. Bands at 1495 and 1474 cm⁻¹ can be assigned to semicircle vibrations of the aromatic ring with additional contribution from OH deformation in the band at 1474 cm⁻¹ [44,45]. The band at 1353 cm⁻¹ can be attributed to C–O–H bending together with ring vibration [45,46]. All band areas decreased when the temperature increased because phenol desorbed. A relative decrease in the intensity of the band at 1474 cm⁻¹ was observed along with an almost complete reduction of the band at 1353 cm⁻¹ to the baseline.

Because both bands contain contributions from the C–O–H bond system, the reduction of the relative band area at higher temperatures suggests either dehydroxylation or deprotonation of the phenol group. As these bands are known to increase with increasing hydrogen bonding of the phenol group to other surface species or surface silanols [45], their decrease at higher temperatures could also be attributed to increasing isolation of the phenols from zeolitic hydroxyl groups. However, because the bands of both terminal silanols and bridging Brønsted acidic OH groups were clearly visible in the IR spectrum (Figure 6b), the former static at 3744 cm⁻¹ and the later shifting from a perturbed position at 3500 cm⁻¹ to unperturbed at 3611 cm⁻¹ as phenol concentration decreases, reduced hydrogen bonding due to a lack of binding partners seems unlikely. Thus, the most plausible explanation is the dissociation of the phenolic OH bond and chemisorption of the resulting phenolate at elevated temperature.

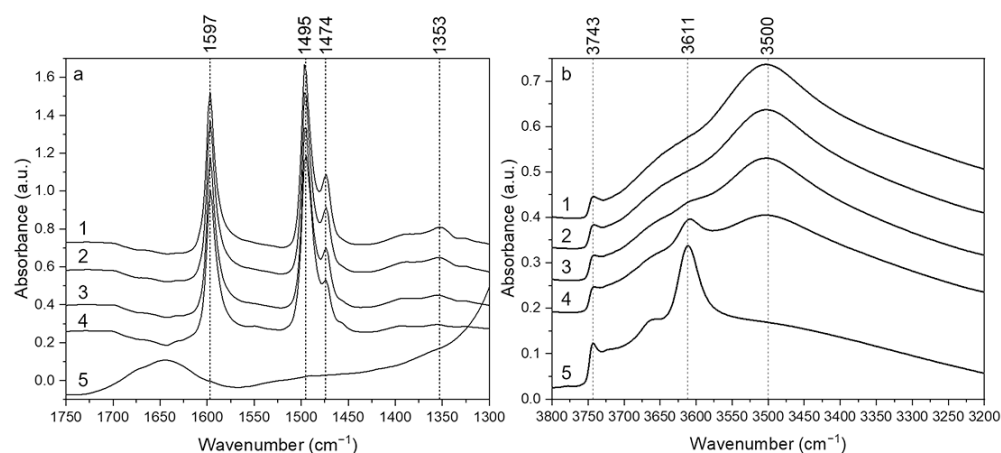


Figure 6. (a) Aromatic region of the infrared spectra of adsorbed phenol with ZSM-5 support subtracted and normalized to the 1495-band maximum; (b) hydroxyl region of the infrared spectra of ZSM-5 before and after exposure to phenol. Traces taken after being heated to the following temperatures: 50 °C (1), 150 °C (2), 250 °C (3) and 350 °C (4) with calcined ZSM-5 prior to dosing included for comparison (5).

This hypothesis was further corroborated by reintroducing water vapor after treatment at high temperatures (Figure S8). Adding water vapor to the system regenerated the relative intensities of the bands at 1474 and 1353 cm⁻¹. These bands then reduced in intensity again upon secondary heating to 300 °C, suggesting a reversible process which restores the phenol groups of the surface species. The reversible nature of this phenomenon in the presence of water may explain the fast and reversible deactivation observed during reaction.

It is also useful to directly compare the spectra of adsorbed model compounds to the deactivated catalysts to see if any patterns can be discerned in the surface species (Figure 7). The sharp band at 3744 cm⁻¹ is attributed to $\bar{\nu}(\text{OH})$ of non-acidic surface silanols at the external surface or defects of the zeolite [47]. The slight decrease in intensity of this band

after reaction indicates that some of these surface silanols are interacting with adsorbed species. The reduction of this band was less pronounced at high water content, which is consistent with hydrolysis of more accessible surface species on the external surface of the zeolite.

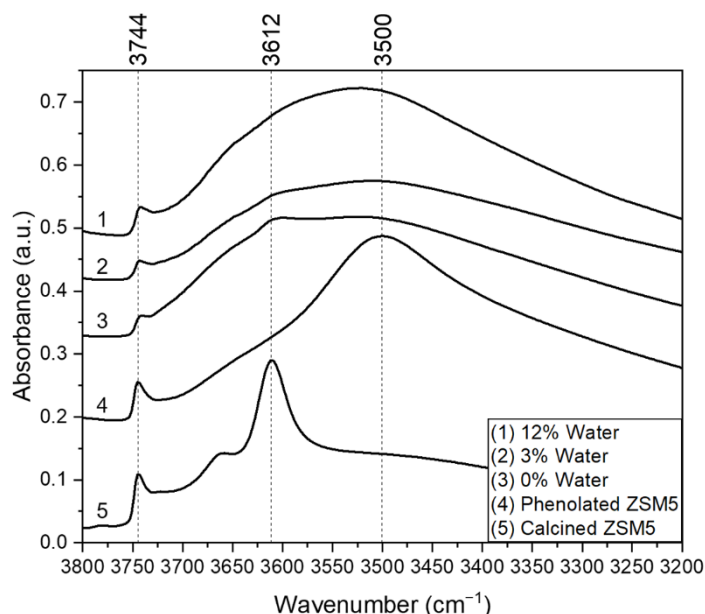


Figure 7. Infrared spectra in the hydroxyl region of ZSM-5 after reaction with various water content (1–3), with gaseous phenol adsorbed (4) and post calcination (5) spectra included for reference.

In contrast, the band at 3612 cm^{-1} is attributed to free $\bar{\nu}(\text{OH})$ of Brønsted acidic groups that are predominantly within the micropores [47]. This group shifted to a lower wavenumber both after the addition of phenol and after the reaction, indicating that the acidic bridging hydroxides are no longer free but instead interacting with nearby organics. After six hours on stream, the deactivated catalysts exhibited different proportions of acidic hydroxides in the free and interacting state. In the case of the high water content reaction, all of the Brønsted acid sites are in the interacting state even after heating and evacuation, while in the absence of water more acid sites remain free. One possible explanation for this phenomenon is that, in the absence of water, diffusive barriers quickly form in the outer shells of the zeolite, preventing access to the inner acid sites and allowing them to remain in the free state.

In the C–H stretching region, pronounced aliphatic $\bar{\nu}(\text{CH}_2)$ and $\bar{\nu}(\text{CH}_3)$ stretching bands were observed between 2800 and 3000 cm^{-1} , with relatively smaller contributions from the $\bar{\nu}(\text{CH})$ vibrations of aromatic moieties at 3000 – 3100 cm^{-1} (Figure S9). The ratio of $\bar{\nu}(\text{CH}_3)$ asymmetric stretching at 2964 cm^{-1} to $\bar{\nu}(\text{CH}_2)$ asymmetric stretching at 2932 cm^{-1} was approximately constant between all samples. Although not strictly quantifiable due to the different molar extinction coefficients of these vibrations, the consistency of this ratio indicated that the same proportions of alkyl groups are present in each sample. In other words, water does not appear to have an effect on the intrinsic rates of side chain cracking or propylene polymerization.

Significant changes between phenolated and deactivated catalysts were observed in the lower wavenumber part of the spectrum (Figure 8). New bands were observed at 1618 , 1607 , 1573 , and 1512 cm^{-1} in the region typically attributed to aromatic ring vibrations [14]. The bands at 1618 and 1607 cm^{-1} were likely due to quadrant stretching of the 4- and 2-substituted alkylphenols [44]. Interestingly, the phenol (monosubstituted) quadrant stretch was most visible after the reaction with 0% water. This finding is tentatively attributed to entrapment of products by fast pore plugging that would also lead to deactivation. The vibrations at 1573 and 1512 cm^{-1} were most prominent in the case of high water and

decrease with increasing water content. The band at 1573 cm^{-1} is attributed to polyaromatic coke species, which formed to a larger extent when more water in the feed preserved the cracking activity for an extended time [14]. The band at 1512 cm^{-1} is assigned to the semicircle stretching mode of 4-propylphenol [44].

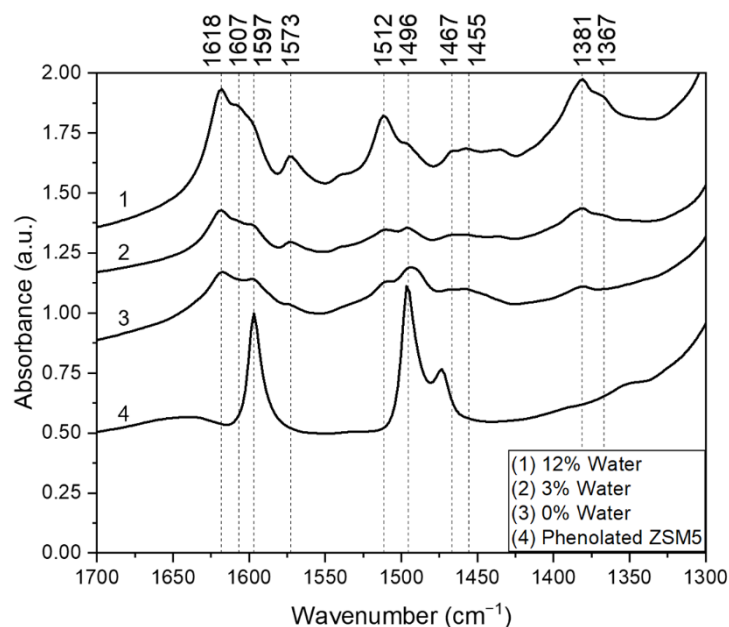


Figure 8. Infrared spectra in the aromatic region of post reaction ZSM-5 (1–3) and phenolated ZSM-5 (4).

Bands observed at 1467 and 1455 cm^{-1} are attributed to $\bar{\nu}(\text{CH}_3)$ asymmetric and symmetric deformations, respectively. The appearance of these bands in deactivated samples is consistent with the aliphatic nature of the side chain in propylphenol and the propylene product. The large band at 1381 cm^{-1} is attributable to $\bar{\nu}(\text{CH})$ of geminal methyl groups possibly formed by the reaction of propene with an aromatic ring to form an isopropyl side chain [48,49]. We also observe a decrease in the band associated with $\delta(\text{OH})$ at 1350 cm^{-1} in all the samples, although due to interference from neighboring bands this may not be shown definitively.

3. Discussion

3.1. Routes to Deactivation

Deactivation of zeolite catalysts is a well-known and studied phenomenon [38,50–54]. In many processes for oil and gas conversion, the formation of carbonaceous deposits, such as polyaromatic coke species, is responsible for deactivation. These carbon deposits come in many forms and can deactivate the catalyst through several different routes including the covering of individual active sites, formation of transport barriers, and distortion of the zeolite framework [53]. In particular, at high temperatures and with highly unsaturated feedstocks, this coking can deactivate zeolites extremely quickly. Commercial FCC catalysts are fully deactivated by coke deposition after only a few seconds on stream at $500\text{--}550\text{ }^{\circ}\text{C}$ and require a high temperature calcination step to regenerate [54]. Often the activity level after regeneration is not the same as the activity before the initial deactivation because the combination of heat and steam during the calcination steps can lead to structural changes and dealumination of the zeolite [38]. During the conversion of oxygenates, which are common in biomass derived feedstocks, the formation of strongly chemisorbed deposits also needs to be considered [14,55,56].

In the present study, polyaromatic deposits were not observed in Raman spectra (Figure S6) or extraction of deposits by HF digestion (Figure 4) and only a small amount

of polyaromatic vibration was observed in the infrared spectra of spent ZSM-5 (Figure 8). Therefore, a deactivation path similar to the oligomerization and aromatization of carbocations to coke during the FCC process can be ruled out as the primary source of deactivation over the course of 6 h on stream. However, this type of deactivation still appears to contribute to slower deactivation observed when the presence of water increases the turnover number per acid site of the catalyst. As water limits the fast deactivation, a larger number of reactive species form and polymerize into polyaromatic coking species that, eventually, deactivate the catalyst.

Polyaromatic coke is not the only way that zeolites can lose activity. In the presence of water, Si–O–Al bonds can be hydrolyzed leading to dealumination, loss of Brønsted acid sites and, consequently, deactivation of the catalyst [20,57]. It is plausible that this process could happen when water is co-fed during a reaction at elevated temperature as in the present study. However, based on ^{27}Al MAS NMR spectra (Figure 5), this process does not occur to a dramatic extent during 6 h on stream at 350 °C. While framework distortion was observed to a limited extent, the change in intensity of tetrahedrally coordinated aluminum species was not significant enough to explain the observed change in reactivity. However, dealumination may cause slow deactivation if the catalyst is used for much longer times on stream.

Because dealumination and coking are shown to not be the main reasons for the observed deactivation, the most plausible remaining theory is the formation of strongly chemisorbed or bulky molecules with moderate size that poison active sites and/or create diffusional barriers within the micropores of the catalyst. Considering that the maximum sphere diameter within the ZSM-5 structure (6.36 Å) [58] is only slightly larger than the kinetic diameter of a benzene ring (5.85 Å) [59], it is to be expected that rigidly chemisorbed species, such as phenolates, dimers or even other propylphenol isomers can create diffusional barriers that prevent reactants from reaching active sites that are located deeper in the pores. This mode of deactivation is supported by the observation of the OH stretching band of Brønsted acid sites that are not hydrogen bonding to any molecular species after the reaction in the absence of water (Figure 7, trace 3). Thus, the diffusional barriers form rapidly in the absence of water and prevent some active sites from ever interacting with the reactant. Given the possibilities of molecular species to create diffusional barriers in microporous systems, understanding the nature of possible pore blocking species is critical (vide infra).

3.2. Nature of Species Causing Pore Blockage

The formation of diffusional barriers in the present study (Figure 2) and previous publications [17,18,35,55,60] can be explained by the formation of rigidly chemisorbed species or molecules that are too large to diffuse through the windows of the ZSM-5 structure. Given the sizes of these cages (6.36 Å compared to the kinetic diameter of p-xylene at 5.85 Å and o/m-xylene at 6.8 Å) [58,59] even an isomerization of 4-propylphenol to 2-propylphenol or 3-propylphenol would create species that occupy a significant part of a cage that they cannot leave. However, the ability of water to remove the diffusional barriers allows for ruling out a major impact of isomerization products.

Liao et al. recently suggested that the formation of diphenyl ethers as the main cause for deactivation [35]. It is plausible that co-fed water would be able to hydrolyze these species forming products that are capable of diffusing out of the zeolite framework. At first sight the presence of diphenyl ether seems to be consistent with their observation of IR bands at 1580 and 1497 cm^{-1} . However, similar bands are also observed in the spectra of phenol and other monosubstituted aromatics. In the present study, the spectra of most spent catalysts contained a band at 1573 cm^{-1} , which is red shifted with respect to reference diphenyl ether, which typically shows a band between 1595 and 1580 cm^{-1} [61]. After reaction with a high water content, the band at 1573 cm^{-1} did appear, but this is equally well explained by hydrolysis of other surface species. Additionally, if this band was caused by diphenyl ether, one would expect lower band intensity on catalysts deactivated with

more water in the reactant stream, which is opposite the observed trend. More importantly, diphenyl ethers were not detected in the DCM extracts of the spent catalyst after HF digestion, while a reference experiment indicated that diphenyl ether was not degraded during the workup of the sample. Thus, a significant impact of diphenyl ethers on the deactivation of the catalysts is unlikely.

Based on the IR spectra of spent catalysts and adsorbed phenol (Figure 8), it is concluded that significant amounts of phenolates form during reaction in the absence of water. These species strongly chemisorb and thus deactivate the catalyst. Interestingly, water had a minimal effect on the types of surface species observed after reaction (Figure 4), but it is capable of removing them. The most logical explanation for this is that phenolate species are readily hydrolyzed, so that the resulting phenols can be removed. It has been shown in the literature that phenols can strongly bind onto Lewis acid sites, such as extra framework aluminum species and defect sites of zeolites [14,45,60]. Brønsted acid sites are less likely to be affected by these species because the acidic proton should readily restore the phenol group instead of forming a surface ether.

3.3. Effect of Propylene Polymerization

The formation of polyaromatic coke is a common path of catalysts deactivation during processes involving light olefins [51]. The formation of these species involves acid catalyzed oligomerization and aromatization reactions. Their presence is indicated by a characteristic IR band around 1575 cm^{-1} [62,63]. Based on the IR spectra of deactivated catalysts (Figure 8), the band attributed to polyaromatic coke is most significant after the reaction in the presence of a high amount of water. It is suggested that water continuously removes diffusional barriers in the zeolite micropores to increase the turnover numbers of sites inside of catalyst particles. As these sites keep producing propylene, there is a certain probability for oligomerization and aromatization reactions to occur resulting in coke precursors and polyaromatic coke. These coke species will accumulate and eventually fully deactivate the catalyst in a similar way to FCC catalysts. It has been shown in the literature that these kinds of deposits significantly hinder diffusion through the micropores of the catalyst [64]. This blocks access to active sites and significantly increases the length of the diffusive path, decreasing overall activity [65,66].

3.4. Implications for Catalyst Design of Biorefining Processes

Catalyst deactivation is a serious threat to the profitability of future biorefining processes. As the present study shows, oxygen-containing aromatics are prone to deactivating zeolite catalysts by chemisorbing as phenolates or similar species (e.g., catecholates) that quickly prevent reactants from reaching active sites within the micropores. It has been shown that these phenolate species form primarily on Lewis acid sites [14,45]. Thus, limiting the Lewis acid content of zeolites, either through careful manufacturing or framework healing, can prevent this kind of adsorption [57]. In addition, the impact of phenolates and diffusional barriers in general is reduced in mesoporous or hierarchical zeolites. The wider channels in the hierarchical structure allow for fast transport into and out of the core of zeolite crystals so that each diffusional barrier blocks a smaller fraction of the micropore volume [19,67,68]. The impact of barriers such as phenolates will also be reduced in large pore zeolites, but these frameworks are less effective at imposing shape selectivity and will stabilize adsorbed reactants and transition states in a different manner. Moreover, such zeolites will also provide additional space for polyaromatic coke species to form in the cages, potentially decreasing the time between regenerations. In the present study, thermogravimetric analysis (Figure 3) showed that harsh calcination conditions are not required to regenerate ZSM-5 zeolites, provided that the concentration of coke precursors remains limited.

The need to dry bio-oil streams before further upgrading has also been discussed in the literature [69,70]. However, this work shows the critical role water plays in preventing the adsorption of pore blocking species. In their study, Xu et al. claim that water affects

the alkylation of phenol over HBEA in two ways, through the creation of additional Brønsted acid sites and through interaction with reactive intermediates [60]. NMR spectra collected in this study corroborate their conclusion that dilute water vapor does not have a profound impact on zeolite dealumination under reaction conditions (Figure 5). This means that bio-oil does not need to be fully dried before reaction, as a small amount of water “contaminants” would prove beneficial as a cofeed. This insight points to opportunities for decreasing separation costs while simultaneously reducing the frequency of catalyst regeneration cycles.

4. Materials and Methods

4.1. Materials

Reactivity studies were performed using a commercial ZSM-5 from Zeolyst (CBV 3024E, Si/Al = 15) without further modification. Silicon carbide (200–450 mesh), 4-propylphenol (>97% purity), phenol (>99.5%), hydrofluoric acid (40–45%), and pyridine (>99.8%) were purchased from Sigma Aldrich. Diphenyl ether (99%) was purchased from Alfa Aesar. Dichloromethane (99.5%) was purchased from VWR. Deionized water was produced in house by a Barnstead NANOpure water system to a resistivity > 17 MΩ. Ultra-high purity (grade 5) nitrogen and ultra-zero grade air were purchased from AirGas.

4.2. Catalyst Characterization

Nitrogen physisorption data was collected on a Micromeritics ASAP2020 physisorption/chemisorption analyzer. Catalysts were degassed at 250 °C at a pressure of <2 μm Hg pressure for 6 h prior to analysis. The micropore volume was calculated based on the adsorption branch of the isotherm using the BJH method [71]. X-ray diffraction of calcined ZSM-5 was performed on a PANalytical Alpha-1 using a Cu K_α source and an X'Celerator detector between 4 and 40 °2θ. SEM imaging was performed on a Hitachi SU8010 ultra-high resolution scanning electron microscope at 3.0 kV. Acid site concentrations were determined by pyridine adsorption followed by FTIR spectroscopy. Pyridine was introduced to the sample at 0.1 mbar and allowed to equilibrate for 30 min at 150 °C. The pressure was then reduced below 10^{−3} mbar for one hour to desorb physisorbed and weakly chemisorbed pyridine. The temperature was then increased first to 250 °C, then to 350 °C, and finally 450 °C under vacuum for one hour to desorb pyridine. Samples were then returned to 150 °C, and IR spectra were collected after each desorption step. The characteristic bands of pyridine adsorbed on Brønsted acid sites (1540 cm^{−1}) and Lewis acid sites (1440 cm^{−1}) were integrated, and these band areas were then converted to surface site concentration based on the Lambert–Beer equation, as is common in the literature [34,72]:

$$C_{BAS} = \frac{A_{BAS}}{S * \epsilon_{BAS}} \quad (1)$$

where A_{BAS} is the integrated absorbance of the band corresponding to pyridine bound to Brønsted acid sites in units cm^{−1}, S is the area density of the pressed catalyst wafer in units of g·cm^{−2}, and ϵ_{BAS} is the molar extinction coefficient of pyridine bound to Brønsted acid sites. The molar extinction coefficients used in this study were 1.23 cm/μmol for the pyridinium ion bound to Brønsted acid sites and 1.73 cm/μmol for pyridine adsorbed on Lewis acid sites as reported by Tamura et al. [34].

4.3. Catalytic Cracking Reactions

Reactivity studies were performed in a custom packed bed reactor setup with online GC sampling. A 0.25 in. outer diameter stainless steel tube was used as the reactor. The temperature was controlled by using a Eurotherm 2416 temperature controller. The reactor was packed with quartz wool followed by 0.2 g of pressed ZSM-5 positioned in the center of the reactor. The catalyst particle size was 90–212 μm. An inert layer of 0.2 g silicon carbide (35–75 μm) was then added directly on top of the ZSM-5 to promote the evaporation of the liquid reactants and gas mixing.

Liquid 4-propylphenol was fed through 1/16 in. tube by a 500D Teledyne ISCO syringe pump directly onto the heated silicon carbide. Water was supplied upstream of the reactor by an 8 mL KDSscientific Legato 100 syringe pump and vaporized over inert quartz wool.

Experiments were performed at 350 °C under a constant flow rate of 80 mL/min of nitrogen. The catalyst was heated at ~10 °C/min and pretreated at the reaction temperature under inert flow of nitrogen for at least 30 min before liquid injection began. Effluent lines were heated to 300 °C to prevent condensation of products that were analyzed on stream by an Agilent 7890A gas chromatograph equipped with an HP-5 column and a flame ionization detector. Conversion and selectivity were calculated as:

$$\text{Conversion} = \frac{C_{0,pph} - C_{f,pph}}{C_{0,pph}} \quad (2)$$

$$\text{Selectivity to } x = \frac{C_x}{\sum_i C_i} \quad (3)$$

where, $C_{0,pph}$ is the concentration of 4-propylphenol in the inlet, $C_{f,pph}$ is the concentration of 4-propylphenol in the outlet, C_x is the concentration of the product of interest and C_i is the concentration of each of the products containing aromatic rings. Deactivation rate constants were calculated assuming a first order decay model:

$$X = X_0 \exp(-k_d t) \quad (4)$$

where X is the conversion of 4-propylphenol at time t , X_0 is the initial conversion, and k_d is the first order decay constant. More complex deactivation models were excluded so as to not overfit the data.

After the reaction, the flows of all liquid streams were stopped to desorb loosely bound surface species, reactants, and products from the catalyst in the same carrier gas stream of 80 mL/min of N₂ for 30 min. The reactor was then cooled to room temperature overnight in static atmosphere, and the catalyst was collected the following morning for further analysis. ZSM-5 catalyst pellets were separated from SiC using a 90 µm sieve before being further characterized.

4.4. FTIR Spectroscopy of Adsorbed Phenol and Carbonaceous Deposits

Fourier transform infrared spectroscopy (FTIR) was performed using a Thermo Nicolet 8700 spectrometer with an MCT/A detector in transmission mode through a custom high vacuum cell. Catalysts were pressed into wafers (5–20 mg) and held in the beam path by a temperature-controlled heating coil and aluminum cups inside a high vacuum cell with ZnSe windows. Fresh ZSM-5 samples were pretreated at 450 °C high vacuum to drive off water and physisorbed species and cooled to 50 °C for data collection. Post-reaction catalysts were activated at 350 °C (i.e., reaction temperature) before collecting spectra at 50 °C. Spectra were collected as the sum of 64 scans at 4 cm^{−1} resolution. Phenol was introduced to untreated ZSM-5 in the gas phase at 0.2 mbar and 50 °C. After equilibration, the sample was evacuated before being heated to 350 °C to observe changes of adsorbed species. Water was then introduced at 50 °C, and the sample was heated to 300 °C.

4.5. Thermogravimetric Analysis

Thermogravimetric analysis was performed in a TA Instruments simultaneous DSC-TGA Q series 600 instrument. Samples between 5 and 10 mg were loaded into alumina cups and allowed to equilibrate in 20 mL/min of flowing dry air until the mass was stable, typically 10–20 min. The temperature was then ramped at 10 °C/min to 800 °C under the same flowrate of air and held at 800 °C for 30 min. Weight loss below 200 °C is attributed to moisture loss.

4.6. Raman Spectroscopy

Raman spectra were collected on a Renishaw Qontor inVia Raman spectrometer using a blue 488 nm excitation laser source with 0.3–3 mW of power. Samples were prepared by placing the spent catalyst onto a glass microscope slide and manually focusing the optical microscope. Spectra were acquired at 5 $\times$ magnification in the range of 105–3200 cm^{-1} . Deconvolution was done as suggested by Sadezky et al. with D1-D4 bands at 1350, 1600, 1500, and 1200 cm^{-1} , respectively, and a G band at 1585 cm^{-1} [73].

4.7. Hydrofluoric Acid Digestion

HF digestion of deactivated ZSM-5 catalysts, followed by liquid–liquid extraction was performed following the procedure proposed by Guisnet and coworkers [74]. Deactivated catalyst (100 mg) was mixed with 10 mL of HF acid (40 wt% in water) and stirred at room temperature for 12 h in a polypropylene vessel to fully dissolve the zeolite. Liquid–liquid extraction was performed by adding 3 mL of dichloromethane (DCM) to the HF solution and thoroughly mixing. After settling, this mixture separated into a water phase and an organic phase. The soluble fraction of the surface deposits entered the lower DCM phase, while any insoluble deposits floated on top of the water phase. Both phases were then passed through a 0.2 μm nylon filter tipped syringe to collect any solid deposits. The DCM phase was then separated by pipetting, concentrated to 1 mL, and analyzed on a Shimadzu QP2010 GC-MS using an Agilent HP-5 column to identify soluble species. Filter tips were removed and allowed to dry before collecting any solid insoluble species, if present.

4.8. Solid State ^{27}Al NMR Spectroscopy

Samples were prepared for NMR spectroscopy by calcining at 550 $^{\circ}\text{C}$ for 6 h in dry air. Then, the samples were left in a closed vessel with a flask of water overnight to hydrate fully. ^{27}Al MAS NMR spectroscopy was performed on a 400 MHz Bruker Avance III instrument with a 9.4 T magnetic field. Approximately 0.1 g of catalyst was packed into 4 mm zirconia rotors and spun at 10 kHz before sampling. Scans were taken by 0.6 ms pulse followed by a 1 s decay time. The total number of scans for each sample was 2048. Integration was performed with DMfit2015 using the Q 1/2 mas peak model (Figure S10).

5. Conclusions

In this work, we examine the mechanism of fast, reversible deactivation of ZSM-5 during the cracking of 4-propylphenol. We propose a two-step deactivation mechanism: First, phenols quickly bind to Lewis acid sites creating diffusional barriers to parts of the zeolite framework. Reactivity studies combined with the analysis of deposits on the catalyst showed that a sufficient amount of water in the feed stream allows for removing the phenolates by hydrolysis, which eliminates their negative impact on catalytic activity. If the impact of phenolates is sufficiently reduced, slow deposition of polyaromatic species derived from polypropylene eventually causes deactivation.

FTIR spectroscopic analysis of deactivated catalysts showed significant contributions from mono substituted aromatics as well as 2- and 4- disubstituted rings. This result is consistent with the proposed theory of strongly bound phenolates as the primary cause of deactivation. Secondary deactivation due to coke formation was most apparent when the cracking activity remained high over an extended time on stream. Further characterization of spent catalysts showed little structural degradation despite the fact that steam is known to harm zeolite frameworks. This suggests that future biorefineries need not include energy intensive pre-drying steps before further upgrading lignin oils.

Supplementary Materials: The following are available online at <https://www.mdpi.com/article/10.3390/catal11060721/s1>, Figure S1: N₂ physisorption, Figure S2: XRD, Figure S3: SEM, Figure S4: Pyridine adsorption followed by FTIR spectroscopy, Figure S5: TOF, Figure S6: Raman spectroscopy, Figure S7: FTIR spectra of Phenol on ZSM-5, Figure S8: FTIR spectra of water regenerated phenol bands, Figure S9: FTIR spectra of aliphatic bands in deactivated ZSM-5, Figure S10: Deconvoluted ²⁷Al MAS NMR spectra of calcined ZSM-5.

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References

- Katelhon, A.; Meys, R.; Deutz, S.; Suh, S.; Bardow, A. Climate change mitigation potential of carbon capture and utilization in the chemical industry. *Proc. Natl. Acad. Sci. USA* **2019**, *116*, 11187–11194. [CrossRef] [PubMed]
- Alonso, D.M.; Hakim, S.H.; Zhou, S.; Won, W.; Hosseinaei, O.; Tao, J.; Garcia-Negron, V.; Motagamwala, A.H.; Mellmer, M.A.; Huang, K.; et al. Increasing the revenue from lignocellulosic biomass: Maximizing feedstock utilization. *Sci. Adv.* **2017**, *3*, e1603301. [CrossRef]
- Brodin, M.; Vallejos, M.; Opedal, M.T.; Area, M.C.; Chinga-Carrasco, G. Lignocellulosics as sustainable resources for production of bioplastics—A review. *J. Clean. Prod.* **2017**, *162*, 646–664. [CrossRef]
- Zakzeski, J.; Bruijninx, P.C.; Jongerius, A.L.; Weckhuysen, B.M. The catalytic valorization of lignin for the production of renewable chemicals. *Chem. Rev.* **2010**, *110*, 3552–3599. [CrossRef]
- Ragauskas, A.J.; Beckham, G.T.; Biddy, M.J.; Chandra, R.; Chen, F.; Davis, M.F.; Davison, B.H.; Dixon, R.A.; Gilna, P.; Keller, M.; et al. Lignin valorization: Improving lignin processing in the biorefinery. *Science* **2014**, *344*, 1246843. [CrossRef]
- Renders, T.; Van den Bosch, S.; Koelewijn, S.F.; Schutyser, W.; Sels, B.F. Lignin-first biomass fractionation: The advent of active stabilisation strategies. *Energy Environ. Sci.* **2017**, *10*, 1551–1557. [CrossRef]
- Arato, C.; Pye, E.K.; Gjennestad, G. The lignol approach to biorefining of woody biomass to produce ethanol and chemicals. *Appl. Biochem. Biotechnol.* **2005**, *123*, 871–882. [CrossRef]
- Gillet, S.; Aguedo, M.; Petitjean, L.; Morais, A.R.C.; Lopes, A.M.D.; Lukasik, R.M.; Anastas, P.T. Lignin transformations for high value applications: Towards targeted modifications using green chemistry. *Green Chem.* **2017**, *19*, 4200–4233. [CrossRef]
- Scown, C.D.; Gokhale, A.A.; Willems, P.A.; Horvath, A.; McKone, T.E. Role of lignin in reducing life-cycle carbon emissions, water use, and cost for United States cellulosic biofuels. *Environ. Sci. Technol.* **2014**, *48*, 8446–8455. [CrossRef]
- Tricker, A.W.; Stellato, M.J.; Kwok, T.T.; Kruyer, N.S.; Wang, Z.; Nair, S.; Thomas, V.M.; Realff, M.J.; Bommarius, A.S.; Sievers, C. Similarities in recalcitrant structures of industrial non-kraft and kraft lignin. *ChemSusChem* **2020**, *13*, 4624–4632. [CrossRef]
- Kwok, T.T.; Luetgen, C.O.; Realff, M.J.; Bommarius, A.S. Lignin value prior to pulping (LVPP): An advanced pulping concept. *Tappi J.* **2017**, *16*, 553–555.
- Anderson, E.M.; Stone, M.L.; Katahira, R.; Reed, M.; Beckham, G.T.; Roman-Leshkov, Y. Flowthrough reductive catalytic fractionation of biomass. *Joule* **2017**, *1*, 613–622. [CrossRef]
- Van den Bosch, S.; Schutyser, W.; Vanholme, R.; Driessen, T.; Koelewijn, S.F.; Renders, T.; De Meester, B.; Huijgen, W.J.J.; Dehaen, W.; Courtin, C.M.; et al. Reductive lignocellulose fractionation into soluble lignin-derived phenolic monomers and dimers and processable carbohydrate pulps. *Energy Environ. Sci.* **2015**, *8*, 1748–1763. [CrossRef]
- Foo, G.S.; Rogers, A.K.; Yung, M.M.; Sievers, C. Steric effect and evolution of surface species in the hydrodeoxygenation of bio-oil model compounds over Pt/HBEA. *ACS Catal.* **2016**, *6*, 1292–1307. [CrossRef]
- Luo, Z.; Zheng, Z.; Li, L.; Cui, Y.-T.; Zhao, C. Bimetallic Ru–Ni catalyzed aqueous-phase guaiacol hydrogenolysis at low H₂ pressures. *ACS Catal.* **2017**, *7*, 8304–8313. [CrossRef]

16. Rezaei, P.S.; Shafaghat, H.; Daud, W.M.A.W. Production of green aromatics and olefins by catalytic cracking of oxygenate compounds derived from biomass pyrolysis: A review. *Appl. Catal. A Gen.* **2014**, *469*, 490–511. [\[CrossRef\]](#)
17. Verboekend, D.; Liao, Y.H.; Schutyser, W.; Sels, B.F. Alkylphenols to phenol and olefins by zeolite catalysis: A pathway to valorize raw and fossilized lignocellulose. *Green Chem.* **2016**, *18*, 297–306. [\[CrossRef\]](#)
18. Liao, Y.H.; d'Halluin, M.; Makshina, E.; Verboekend, D.; Sels, B.F. Shape selectivity vapor-phase conversion of lignin-derived 4-ethylphenol to phenol and ethylene over acidic aluminosilicates: Impact of acid properties and pore constraint. *Appl. Catal. B Environ.* **2018**, *234*, 117–129. [\[CrossRef\]](#)
19. Liao, Y.H.; Zhong, R.Y.; d'Halluin, M.; Verboekend, D.; Sels, B.F. Aromatics production from lignocellulosic biomass: Shape selective dealkylation of lignin-derived phenolics over hierarchical ZSM-5. *ACS Sustain. Chem. Eng.* **2020**, *8*, 8713–8722. [\[CrossRef\]](#)
20. De Lucas, A.; Canizares, P.; Durán, A.; Carrero, A. Dealumination of HZSM-5 zeolites: Effect of steaming on acidity and aromatization activity. *Appl. Catal. A Gen.* **1997**, *154*, 221–240. [\[CrossRef\]](#)
21. Triantafillidis, C.S.; Vlessidis, A.G.; Nalbandian, L.; Evmiridis, N.P. Effect of the degree and type of the dealumination method on the structural, compositional and acidic characteristics of H-ZSM-5 zeolites. *Microporous Mesoporous Mater.* **2001**, *47*, 369–388. [\[CrossRef\]](#)
22. Anderson, E.; Crisci, A.; Murugappan, K.; Roman-Leshkov, Y. Bifunctional Molybdenum polyoxometalates for the combined hydrodeoxygenation and alkylation of lignin-derived model phenolics. *ChemSusChem* **2017**, *10*, 2226–2234. [\[CrossRef\]](#)
23. Ardizzi, M.; Ballarini, N.; Cavani, F.; Chiappini, E.; Dal Pozzo, L.; Maselli, L.; Monti, T. Environmentally friendly, heterogeneous acid and base catalysis for the methylation of catechol: Chances for the control of chemo-selectivity. *Appl. Catal. B Environ.* **2007**, *70*, 597–605. [\[CrossRef\]](#)
24. Yung, M.M.; Foo, G.S.; Sievers, C. Role of Pt during hydrodeoxygenation of biomass pyrolysis vapors over Pt/HBEA. *Catal. Today* **2018**, *302*, 151–160. [\[CrossRef\]](#)
25. Chen, T.-S.; Yang, W.-Y.; Du, Z.-Y.; Feng, J.; Li, W.-Y. Effects of mesopore introduction on the stability of zeolites for 4-isopropylphenol dealkylation. *Catal. Today* **2021**, *371*, 40–49. [\[CrossRef\]](#)
26. Einaga, H.; Futamura, S.; Ibusuki, T. Heterogeneous photocatalytic oxidation of benzene, toluene, cyclohexene and cyclohexane in humidified air: Comparison of decomposition behavior on photoirradiated TiO₂ catalyst. *Appl. Catal. B Environ.* **2002**, *38*, 215–225. [\[CrossRef\]](#)
27. Pujari, S.P.; Scheres, L.; Marcelis, A.T.; Zuilhof, H. Covalent surface modification of oxide surfaces. *Angew. Chem. Int. Ed. Engl.* **2014**, *53*, 6322–6356. [\[CrossRef\]](#) [\[PubMed\]](#)
28. Sedo, J.; Saiz-Poseu, J.; Busque, F.; Ruiz-Molina, D. Catechol-based biomimetic functional materials. *Adv. Mater.* **2013**, *25*, 653–701. [\[CrossRef\]](#)
29. Ye, Q.; Zhou, F.; Liu, W. Bioinspired catecholic chemistry for surface modification. *Chem. Soc. Rev.* **2011**, *40*, 4244–4258. [\[CrossRef\]](#)
30. Yuen, A.K.; Hutton, G.A.; Masters, A.F.; Maschmeyer, T. The interplay of catechol ligands with nanoparticulate iron oxides. *Dalton Trans.* **2012**, *41*, 2545–2559. [\[CrossRef\]](#)
31. Yang, Y.; Yan, W.; Jing, C. Dynamic adsorption of catechol at the goethite/aqueous solution interface: A molecular-scale study. *Langmuir* **2012**, *28*, 14588–14597. [\[CrossRef\]](#)
32. Popov, A.; Kondratieva, E.; Goupil, J.M.; Mariey, L.; Bazin, P.; Gilson, J.P.; Travert, A.; Mauge, F. Bio-oils hydrodeoxygenation: Adsorption of phenolic molecules on oxidic catalyst supports. *J. Phys. Chem. C* **2010**, *114*, 15661–15670. [\[CrossRef\]](#)
33. Jiang, F.; Zeng, L.; Li, S.; Liu, G.; Wang, S.; Gong, J. Propane dehydrogenation over Pt/TiO₂–Al₂O₃ catalysts. *ACS Catal.* **2014**, *5*, 438–447. [\[CrossRef\]](#)
34. Tamura, M.; Shimizu, K.; Satsuma, A. Comprehensive IR study on acid/base properties of metal oxides. *Appl. Catal. A Gen.* **2012**, *433*, 135–145. [\[CrossRef\]](#)
35. Liao, Y.H.; Zhong, R.Y.; Makshina, E.; d'Halluin, M.; van Limbergen, Y.; Verboekend, D.; Sels, B.F. Propylphenol to phenol and propylene over acidic zeolites: Role of shape selectivity and presence of steam. *ACS Catal.* **2018**, *8*, 7861–7878. [\[CrossRef\]](#)
36. Cheng, Y.T.; Huber, G.W. Chemistry of furan conversion into aromatics and olefins over HZSM-5: A Model biomass conversion reaction. *ACS Catal.* **2011**, *1*, 611–628. [\[CrossRef\]](#)
37. Zhang, H.; Shao, S.; Xiao, R.; Shen, D.; Zeng, J. Characterization of coke deposition in the catalytic fast pyrolysis of biomass derivatives. *Energy Fuels* **2013**, *28*, 52–57. [\[CrossRef\]](#)
38. Almas, Q.; Naeem, M.A.; Baldanza, M.A.S.; Solomon, J.; Kenvin, J.C.; Muller, C.R.; da Silva, V.T.; Jones, C.W.; Sievers, C. Transformations of FCC catalysts and carbonaceous deposits during repeated reaction-regeneration cycles. *Catal. Sci. Technol.* **2019**, *9*, 6977–6992. [\[CrossRef\]](#)
39. Jiao, J.; Kanellopoulos, J.; Behera, B.; Jiang, Y.; Huang, J.; Reddy Marthala, V.R.; Ray, S.S.; Wang, W.; Hunger, M. Effects of adsorbate molecules on the quadrupolar interaction of framework aluminum atoms in dehydrated zeolite H,Na-Y. *J. Phys. Chem. B* **2006**, *110*, 13812–13818. [\[CrossRef\]](#)
40. Wang, W.; Buchholz, A.; Arnold, A.; Xu, M.; Hunger, M. Effect of surface methoxy groups on the ²⁷Al quadrupole parameters of framework aluminum atoms in calcined zeolite H-Y. *Chem. Phys. Lett.* **2003**, *370*, 88–93. [\[CrossRef\]](#)
41. Chen, T.-H.; Houthoofd, K.; Grobet, P.J. Toward the aluminum coordination in dealuminated mordenite and amorphous silica-alumina: A high resolution ²⁷Al MAS and MQ MAS NMR study. *Microporous Mesoporous Mater.* **2005**, *86*, 31–37. [\[CrossRef\]](#)
42. Isobe, T.; Watanabe, T.; d'Espinose de la Caillerie, J.B.; Legrand, A.P.; Massiot, D. Solid-state ¹H and ²⁷Al NMR studies of amorphous aluminum hydroxides. *J. Colloid Interface Sci.* **2003**, *261*, 320–324. [\[CrossRef\]](#)

43. Silaghi, M.C.; Chizallet, C.; Raybaud, P. Challenges on molecular aspects of dealumination and desilication of zeolites. *Microporous Mesoporous Mater.* **2014**, *191*, 82–96. [CrossRef]
44. Colthup, N.B.; Daly, L.H.; Wiberley, S.E. Aromatic and Heteroaromatic Rings. In *Introduction to Infrared and Raman Spectroscopy*; Colthup, N.B., Daly, L.H., Wiberley, S.E., Eds.; Academic Press: San Diego, CA, USA, 1990; pp. 261–288.
45. Popov, A.; Kondratieva, E.; Gilson, J.P.; Mariey, L.; Traver, A.; Mauge, F. IR study of the interaction of phenol with oxides and sulfided CoMo catalysts for bio-fuel hydrodeoxygenation. *Catal. Today* **2011**, *172*, 132–135. [CrossRef]
46. Roth, W.; Imhof, P.; Gerhards, M.; Schumm, S.; Kleiner, K. Reassignment of ground and first excited state vibrations in phenol. *Chem. Phys.* **2000**, *252*, 247–256. [CrossRef]
47. Karge, H.G. Characterization by IR spectroscopy. In *Verified Syntheses of Zeolitic Materials*; Robson, H., Lillerud, K.P., Eds.; Elsevier Science: Amsterdam, The Netherlands, 2001; pp. 69–71.
48. Colthup, N.B.; Daly, L.H.; Wiberley, S.E. Methyl and Methylene Groups. In *Introduction to Infrared and Raman Spectroscopy*; Colthup, N.B., Daly, L.H., Wiberley, S.E., Eds.; Academic Press: San Diego, CA, USA, 1990; pp. 215–233.
49. Jo, C.; Ryoo, R.; Zilkova, N.; Vitvarova, D.; Cejka, J. The effect of MFI zeolite lamellar and related mesostructures on toluene disproportionation and alkylation. *Catal. Sci. Technol.* **2013**, *3*, 2119–2129. [CrossRef]
50. Bhatia, S.; Beltramini, J.; Do, D.D. Deactivation of zeolite catalysts. *Catal. Rev. Sci. Eng.* **1989**, *31*, 431–480. [CrossRef]
51. Guisnet, M.; Costa, L.; Ribeiro, F.R. Prevention of zeolite deactivation by coking. *J. Mol. Catal. A Chem.* **2009**, *305*, 69–83. [CrossRef]
52. Argyle, M.D.; Bartholomew, C.H. Heterogeneous catalyst deactivation and regeneration: A Review. *Catalysts* **2015**, *5*, 145–269. [CrossRef]
53. Cerqueira, H.S.; Caeiro, G.; Costa, L.; Ramôa Ribeiro, F. Deactivation of FCC catalysts. *J. Mol. Catal. A Chem.* **2008**, *292*, 1–13. [CrossRef]
54. Vogt, E.T.; Weckhuysen, B.M. Fluid catalytic cracking: Recent developments on the grand old lady of zeolite catalysis. *Chem. Soc. Rev.* **2015**, *44*, 7342–7370. [CrossRef]
55. Luo, W.H.; Cao, W.X.; Bruijninx, P.C.A.; Lin, L.; Wang, A.Q.; Zhang, T. Zeolite-supported metal catalysts for selective hydrodeoxygenation of biomass-derived platform molecules. *Green Chem.* **2019**, *21*, 3744–3768. [CrossRef]
56. Shi, Y.C.; Xing, E.H.; Wu, K.J.; Wang, J.L.; Yang, M.D.; Wu, Y.L. Recent progress on upgrading of bio-oil to hydrocarbons over metal/zeolite bifunctional catalysts. *Catal. Sci. Technol.* **2017**, *7*, 2385–2415. [CrossRef]
57. Maier, S.M.; Jentys, A.; Lercher, J.A. Steaming of zeolite BEA and its effect on acidity: A comparative NMR and IR spectroscopic study. *J. Phys. Chem. C* **2011**, *115*, 8005–8013. [CrossRef]
58. Baerlocher, C.; McCusker, L.B.; Treacy, M.M.J. Database of Zeolite Structures. Available online: <http://www.iza-structure.org/databases/> (accessed on 19 December 2020).
59. Baertsch, C.D.; Funke, H.H.; Falconer, J.L.; Noble, R.D. Permeation of aromatic hydrocarbon vapors through silicalite-zeolite membranes. *J. Phys. Chem.* **1996**, *100*, 7676–7679. [CrossRef]
60. Xu, W.; Miller, S.J.; Agrawal, P.K.; Jones, C.W. Positive effect of water on zeolite BEA Catalyzed alkylation of phenol with propylene. *Catal. Lett.* **2013**, *144*, 434–438. [CrossRef]
61. NIST Mass Spectrometry Data Center; Wallace, W.E. (Director). Infrared Spectra. In *NIST Chemistry WebBook, NIST Standard Reference Database Number 69*; Linstrom, P.J., Mallard, W.G., Eds.; National Institute of Standards and Technology: Gaithersburg, MD, USA, 2018. [CrossRef]
62. Rozwadowski, M.; Lezanska, M.; Wloch, J.; Erdmann, K.; Golembiewski, R.; Kornatowski, J. Investigation of coke deposits on Al-MCM-41. *Chem. Mater.* **2001**, *13*, 1609–1616. [CrossRef]
63. Palumbo, L.; Bonino, F.; Beato, P.; Bjorgen, M.; Zecchina, A.; Bordiga, S. Conversion of methanol to hydrocarbons: Spectroscopic characterization of Carbonaceous species formed over H-ZSM-5. *J. Phys. Chem. C* **2008**, *112*, 9710–9716. [CrossRef]
64. Haider, M.H.; D’Agostino, C.; Dummer, N.F.; Mantle, M.D.; Gladden, L.F.; Knight, D.W.; Willock, D.J.; Morgan, D.J.; Taylor, S.H.; Hutchings, G.J. The effect of grafting zirconia and ceria onto alumina as a support for silicotungstic acid for the catalytic dehydration of glycerol to acrolein. *Chem. Eur. J.* **2014**, *20*, 1743–1752. [CrossRef]
65. Kortunov, P.; Vasenkov, S.; Kärger, J.; Fé Elía, M.; Perez, M.; Stöcker, M.; Papadopoulos, G.; Theodorou, D.; Drescher, B.; McElhiney, G. Diffusion in fluid catalytic cracking catalysts on various displacement scales and its role in catalytic performance. *Chem. Mater.* **2005**, *17*, 2466–2474. [CrossRef]
66. D’Agostino, C.; Ryabenkova, Y.; Miedziak, P.J.; Taylor, S.H.; Hutchings, G.J.; Gladden, L.F.; Mantle, M.D. Deactivation studies of a carbon supported AuPt nanoparticulate catalyst in the liquid-phase aerobic oxidation of 1,2-propanediol. *Catal. Sci. Technol.* **2014**, *4*, 1313–1322. [CrossRef]
67. Possato, L.G.; Diniz, R.N.; Garetto, T.; Pulcinelli, S.H.; Santilli, C.V.; Martins, L. A comparative study of glycerol dehydration catalyzed by micro/mesoporous MFI zeolites. *J. Catal.* **2013**, *300*, 102–112. [CrossRef]
68. Rodrigues, M.V.; Vignatti, C.; Garetto, T.; Pulcinelli, S.H.; Santilli, C.V.; Martins, L. Glycerol dehydration catalyzed by MWW zeolites and the changes in the catalyst deactivation caused by porosity modification. *Appl. Catal. A Gen.* **2015**, *495*, 84–91. [CrossRef]
69. de Miguel Mercader, F.; Groeneveld, M.J.; Kersten, S.R.A.; Way, N.W.J.; Schaverien, C.J.; Hogendoorn, J.A. Production of advanced biofuels: Co-processing of upgraded pyrolysis oil in standard refinery units. *Appl. Catal. B Environ.* **2010**, *96*, 57–66. [CrossRef]
70. Demirbas, A. Competitive liquid biofuels from biomass. *Appl. Energy* **2011**, *88*, 17–28. [CrossRef]

-
71. Barrett, E.P.; Joyner, L.G.; Halenda, P.P. The determination of pore volume and area distributions in porous substances. I. Computations from nitrogen isotherms. *J. Am. Chem. Soc.* **2002**, *73*, 373–380. [[CrossRef](#)]
 72. Emeis, C.A. Determination of integrated molar extinction coefficients for infrared-absorption bands of pyridine adsorbed on solid acid catalysts. *J. Catal.* **1993**, *141*, 347–354. [[CrossRef](#)]
 73. Sadezky, A.; Muckenhuber, H.; Grothe, H.; Niessner, R.; Pöschl, U. Raman microspectroscopy of soot and related carbonaceous materials: Spectral analysis and structural information. *Carbon* **2005**, *43*, 1731–1742. [[CrossRef](#)]
 74. Magnoux, P.; Roger, P.; Canaff, C.; Fouche, V.; Gnep, N.S.; Guisnet, M. New Technique for the Characterization of Carbonaceous Compounds Responsible for Zeolite Deactivation. In *Studies in Surface Science and Catalysis*; Delmon, B., Froment, G.F., Eds.; Elsevier: Amsterdam, The Netherlands, 1987; Volume 34, pp. 317–330. [[CrossRef](#)]
 75. Momma, K.; Izumi, F. VESTA 3 for three-dimensional visualization of crystal, volumetric and morphology data. *J. Appl. Crystallogr.* **2011**, *44*, 1272–1276. [[CrossRef](#)]