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Stability of Pt/γ-Al_2O_3 Catalysts in Lignin and Lignin Model Compound Solutions under Liquid Phase Reforming Reaction Conditions

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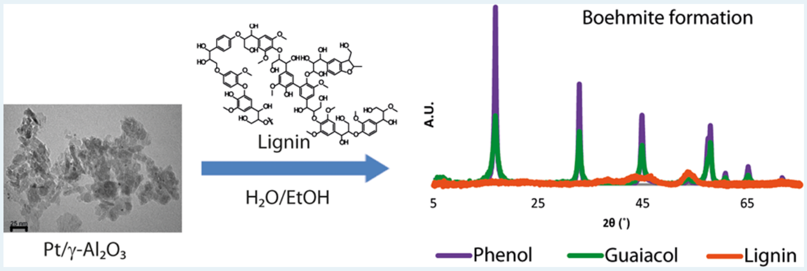
Supporting Information



ABSTRACT: The stability of a 1 wt % Pt/γ-Al_2O_3 catalyst was tested in an ethanol/water mixture at 225 °C and autogenic pressure, conditions at which it is possible to dissolve and depolymerize various kinds of lignin, and structural changes to the catalysts were studied by means of X-ray diffraction (XRD), ^{27}Al MAS NMR, N_2 physisorption, transmission electron microscopy (TEM), H_2 chemisorption, elemental analysis, thermogravimetric analysis-mass spectrometry (TGA-MS), and IR. In the absence of reactants the alumina support is found to transform into boehmite within 4 h, leading to a reduction in support surface area, sintering of the supported Pt nanoparticles, and a reduction of active metal surface area. Addition of aromatic oxygenates to mimic the compounds typically obtained by lignin depolymerization leads to a slower transformation of the support oxide. These compounds, however, were not able to slow down the decrease in dispersion of the Pt nanoparticles. Vanillin and guaiacol stabilize the aluminum oxide more than phenol, anisole, and benzaldehyde because of the larger number of oxygen functionalities that can interact with the alumina. Interestingly, catalyst samples treated in the presence of lignin showed almost no formation of boehmite, no reduction in support or active metal surface area, and no Pt nanoparticle sintering. Furthermore, in the absence of lignin-derived aromatic oxygenates, ethanol forms a coke-like layer on the catalyst, while oxygenates prevent this by adsorption on the support by coordination via the oxygen functionalities.

KEYWORDS: *alumina, boehmite, biomass, hydrothermal stability, hydration*

1. INTRODUCTION

With the declining availability of crude oil as a source for fuels, chemicals, and energy, the fraction of energy and chemicals supplied by renewable resources, such as biomass, can be expected to increase in the foreseeable future. This has led to an intensified interest in the development of technology and processes for the conversion of biomass.[1] Lignin is a natural, amorphous, three-dimensional polymer consisting of methoxylated phenylpropane structures that confers strength and rigidity to plants and protects the cellulose and hemicellulose from microbial attack.[2] A wide variety of bulk and fine chemicals, particularly aromatics, and fuels are potentially obtainable from lignin. Indeed, valorization of the lignin component of lignocellulosic biomass is attracting more attention, and processes for the conversion of lignin are being developed.[2−7] As is typical for biomass feedstock and renewable platform molecules, lignin and lignin-derived aromatic products have a low vapor pressure and high polarity. Therefore, processes for the conversion of lignin will most likely take place in the liquid phase. Consequently, catalyst materials originally developed for processing low oxygen content, nonpolar fossil fuel-derived streams will now be used in processes involving oxygen-rich biomass-derived molecules in a polar liquid phase. This change of reaction environment puts completely different requirements on the catalyst in terms of catalyst stability.

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A typical example of such a liquid-phase conversion process is the aqueous-phase reforming (APR) of biomass-derived oxygenates, which provides an interesting pathway for the production of hydrogen from various renewable oxygenates. APR reactions are run in aqueous solutions and have been reported at temperatures between 210 and 260 °C.[8] Most commonly, renewable oxygenates, such as glycerol and other polyols or sugars, are used,[9] but recently the first use of APR for the conversion of lignin was also reported, using a Pt/γ-Al_2O_3 catalyst at 225 °C and a pressure of 29 bar for the production of monomeric aromatic chemicals by cleavage and further conversion of some of the major linkages in lignin. The lignin APR system, however, suffers from extensive formation of solids caused by lignin recondensation, and relatively low yields of isolated monomeric products are obtained as a result.[10] It was shown that solvent optimization and in particular the addition of ethanol can improve APR processes.[11,12] The recently reported liquid-phase reforming (LPR) of lignin addresses the problem of lignin condensation by using water/ethanol as solvent to aid lignin solubilization leading to much improved monomer yields. The LPR process operates under conditions resembling those of APR with the exception that higher pressures are required (58 bar), because of the higher vapor pressure of ethanol.[13]

The stability of some common solid catalysts is limited under these harsh hydrothermal conditions. It is well established that γ-alumina supports, for instance, are thermodynamically unstable under these conditions and are easily hydrated in hot water. Some of us have previously reported on the stability of γ-alumina under APR conditions, showing that the conversion of γ-alumina into a hydrated boehmite takes place at 200 °C or above resulting in reduction in surface area and Lewis acid sites. γ-Alumina used as support for metal nanoparticles shows a lower rate of transformation compared to the bare support, but sintering of the metal nanoparticles is observed in this case.[14] In addition, the presence of 5 wt % oxygenates, such as glycerol and sorbitol, is found to greatly enhance the stability of the catalyst material compared to treatment in pure water. The conversion to boehmite is thought to be slowed down by blockage of the surface of the support, presumably by the formation of carbonaceous deposits on the alumina surface, thus preventing hydrolysis. The sintering of the supported Pt nanoparticles is reduced in runs with these oxygenates, but a large part of the metal surface area was blocked by the carbonaceous deposits.[15] There are to the best of our knowledge no investigations on the influence of ethanol, needed for lignin solubilization or phenolics, formed in lignin conversion processes, on the stability of γ-alumina and Pt/γ-Al_2O_3 catalyst materials.

In the present study, a commercial 1 wt % Pt/γ-Al_2O_3 catalyst material is treated in water/ethanol under LPR conditions at 225 °C and autogenic pressure. The influence of different aromatic oxygenates that can be derived from lignin on catalyst stability was studied by adding phenol, anisole, benzaldehyde, guaiacol, vanillin, as well as actual organosolv Alcell lignin, to the reaction mixture.[16] Various treatment times and guaiacol concentrations are used to gain insight in the stability of the catalyst under relevant LPR conditions. Treated catalyst samples were extensively characterized with different techniques, such as X-ray diffraction (XRD), ^{27}Al MAS NMR, N_2 physisorption, transmission electron microscopy (TEM), H_2 chemisorption, elemental analysis, thermogravimetric analysis-mass spectrometry (TGA-MS), and IR, to determine the extent of hydration, support and metal surface area, metal nanoparticle size, and extent of carbonaceous deposit formation.

2. EXPERIMENTAL SECTION

2.1. Stability Tests. The catalyst material stability tests were performed in a 40 mL Parr batch autoclave equipped with a thermocouple, a pressure transducer and gauge, and a magnetic driver (750 rpm). One gram of Pt/Al_2O_3 (Sigma Aldrich, 1 wt %) was suspended in 15 mL of deionized water (Milli-Q) and 15 mL of ethanol (Fisher, HPLC grade), and, if applicable, 4 mmol of the model compound or 0.5 g of lignin was added after which the mixture was heated to 225 °C. After the designated time, the autoclave was cooled in an ice bath and vented. The catalyst material was recovered by filtration and washed with water and ethanol. The model compounds phenol (Acros, 99%), anisole (Fluka, 99%), benzaldehyde (Fluka), guaiacol (Sigma), and vanillin (Sigma Aldrich, 99%) were all obtained commercially. The Alcell organosolv lignin (66.47% C, 5.96% H, 0.15% N, 27.43% O by difference), provided by Wageningen University, was obtained from hardwoods and isolated by an organosolv extraction method.[17]

2.2. X-ray Diffraction. X-ray powder diffraction (XRD) patterns were recorded on a Bruker-AXS D2 Phaser powder X-ray diffractometer using $Co_{K\alpha 1,2}$ with λ = 1.79026 Å. Measurements were carried out between 5−75° 2θ using a step size of 0.04° 2θ and a scan speed of 1 s.

2.3. Nitrogen Physisorption. N_2 physisorption isotherms were recorded with a Micromeritics Tristar 3000 at −196 °C. The samples were dried prior to performing the measurement for at least 16 h at 200 °C in a N_2 flow. The surface area was determined using the Brunauer−Emmett−Teller (BET) theory. The total pore volume was defined as the single-point pore volume at $p/p_0 = 0.95$.

2.4. Nuclear Magnetic Resonance. ^{27}Al magic angle spinning (MAS) nuclear magnetic resonance (NMR) experiments were performed using a Bruker DSX 400 Spectrometer. The catalyst samples were packed into a 4 mm zirconia rotor and spun at a frequency of 12 kHz. The resonance frequency of ^{27}Al was 104.2 MHz. A $\pi/12$ pulse was used for excitation with a recycling delay of 250 ms. Aqueous $Al(NO_3)_3$ was used as reference compound (δ = 0 ppm). The normalized ^{27}Al MAS NMR spectra were fitted as a linear combination of the spectra of pure boehmite and γ-alumina to calculate the fractional conversion to hydrated aluminum.[14,15]

2.5. Thermogravimetric-Mass Spectrometry Analysis. Thermogravimetric analysis (TGA) was performed with a Perkin−Elmer Pyris 1 apparatus. Typically, 15 mg of catalyst sample was dried at 150 °C for 2 h and heated with a ramp of 5 °C min^{-1} to 900 °C in a 10 mL min^{-1} flow of air. In parallel, evolved gas analysis was performed with a Pfeiffer Omnistar quadrupole mass spectrometer, which was connected to the outlet of the TGA apparatus. Ion currents were recorded for m/z values of 18 (H_2O) and 44 (CO_2).

2.6. Infrared Spectroscopy. For the infrared (IR) studies the catalyst sample was finely grained and pressed to form a self-supporting wafer with a weight of 10−15 mg and a diameter of 13 mm. The wafer was placed in an IR transmission cell with CaF_2 windows. The cell was evacuated to 10^{-6} bar and kept at 200 °C for at least 1 h after which it was cooled to 150 °C. IR spectra were obtained using a Perkin-Elmer 2000 FT-IR instrument with an optical resolution of 4 cm^{-1} and an accumulation of 25 scans from 4000 to 1000 cm^{-1}. Additional IR measurements were carried out on catalyst samples diluted

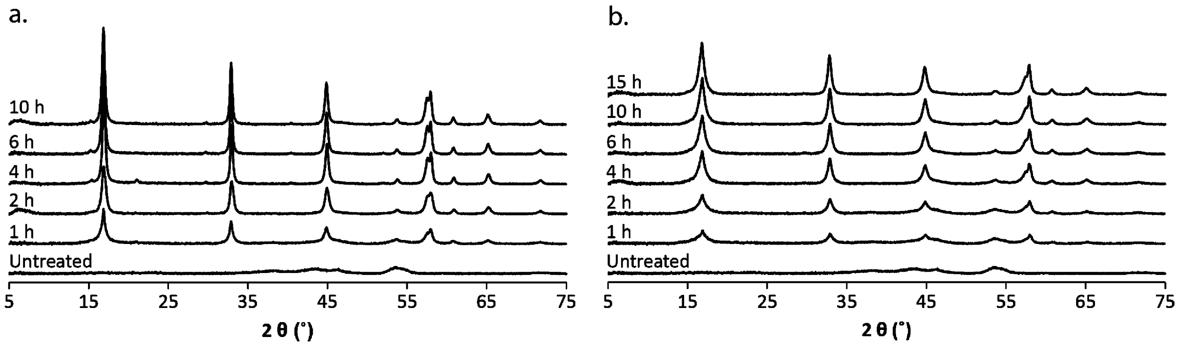

Figure 1. X-ray diffraction patterns of a 1 wt % Pt/Al_2O_3 catalyst treated at 225 °C for various treatment times in (a) ethanol/water and (b) ethanol/water with 4 mmol of guaiacol.

with KBr to reduce signal adsorption. IR spectra of the KBr wafers were obtained without drying at room temperature (RT) in air using a Perkin-Elmer 2000 FT-IR instrument with an optical resolution of 4 cm^{-1} and an accumulation of 10 scans from 4000 to 400 cm^{-1}. In situ DRIFTS measurements were performed with a Bruker Tensor 27 apparatus utilizing an HVC-DRP-3 diffuse reflectance reaction chamber with CaF_2 windows and an MCT detector. The bottom of the sample cup was filled with silicon carbide and covered by a grid to minimize temperature gradients, on which the sample mixed with KBr was placed. Nitrogen gas flowed through the sample from top to bottom at a flow rate of 10 mL min^{-1}, while the temperature was increased and kept at 200 °C for at least 1 h after which it was cooled to 50 °C. The sample was exposed to nitrogen flow that was led through D_2O for 30 min after which the sample was dried again in nitrogen overnight. IR scans were recorded from 4000 to 1000 cm^{-1} at a resolution of 4 cm^{-1}.

2.7. Transmission Electron Microscopy. Transmission electron microscopy (TEM) images were recorded with a JEOL 100CX microscope at a 100 kV acceleration voltage. The samples were prepared by applying three drops of a catalyst in ethanol slurry on a graphene-coated, 200 mesh copper grid. The slurry was homogenized via a sonication bath prior to applying to the sample grid.

2.8. Elemental Analysis. Samples were prepared by dissolving 125 mg of the catalyst sample in 6 mL of aqua regia at 90 °C overnight. After evaporation of the aqua regia at 160 °C the samples were dissolved in 20 mL of HCl at 90 °C. The Pt content was determined using a Spectro Arcos ICP-OES (Inductively Coupled Plasma−Optical Emission Spectroscopy) with a standard operating procedure.

2.9. Hydrogen Chemisorption. H_2 chemisorption measurements were performed using a Micromeritics ASAP 2020. Samples were dried at 100 °C for 60 min (ramp 10 °C min^{-1}) in vacuum. Subsequently, the samples were reduced at 200 °C (ramp 5 °C min^{-1}) for 2 h under H_2 flow. Hereafter, the samples were degassed for 30 min under vacuum at 200 °C. Adsorption isotherms were subsequently measured at 50 °C. Average particle sizes were calculated as described by Scholten et al.[18] using the linear part of the adsorption isotherm.

3. RESULTS AND DISCUSSION

3.1. Structural Changes in the Aluminum Oxide Support. The use of γ-Al_2O_3 as a support oxide has found widespread use in the field of heterogeneous catalysis. Under the hydrothermal conditions that are often used for liquid-phase biomass conversion processes, γ-Al_2O_3, which is prepared via dehydration of gibbsite, will be rehydrated. Indeed, it was shown before that alumina is hydrated to boehmite in hot liquid water at conditions typically used in APR reactions and that this process is slowed down by the presence of metal particles on the support.[14,19,20] Furthermore, the presence of oxygenates, such as glycerol or sorbitol (5 wt %), in solution stabilizes the catalyst material by slowing down boehmite formation. This effect was shown to be stronger with increasing number of hydroxyl functionalities.[15] The influence of ethanol and lignin-derived aromatic oxygenates on the stability of Pt/γ-Al_2O_3 under conditions that are used to dissolve and convert lignin has not been investigated before. In a first set of experiments a fresh 1 wt % Pt/γ-Al_2O_3 catalyst material was treated at 225 °C in ethanol/water and ethanol/water containing 4 mmol of different lignin-derived aromatic molecules. The catalyst was treated for various durations in ethanol/water and ethanol/water/guaiacol. XRD, nitrogen physisorption, and ^{27}Al NMR spectroscopy were used to observe and identify structural changes in the support.

Figure 1 shows the XRD patterns of 1 wt % Pt/γ-Al_2O_3 after various treatment times in ethanol/water and ethanol/water with 4 mmol of guaiacol. The XRD pattern of the fresh Pt/γ-Al_2O_3 catalyst material shows the small, broad peaks of the γ-alumina support. Diffraction peaks corresponding to a crystalline phase were observed after treatment of the catalyst, and the intensity of these diffraction peaks increased with increasing treatment time. This phase was identified as boehmite with the main peaks located at 2θ = 16.8°, 32.9°, 44.9°, 57.5°, and 57.9° corresponding to the (020), (120), (031), (051), and (200) lattice planes, respectively (Figure 1a).[21] The peak intensity leveled off after 4 h for the samples treated with only ethanol/water (Figure 3a). The rehydration to boehmite was much slower in the presence of 4 mmol (0.5 g) of guaiacol, as the diffraction peaks associated with boehmite were much less intense and still increasing in intensity after 15 h (Figures 1b and 3a). The influence of ethanol itself on the transformation of γ-alumina can be deduced from a comparison with a sample treated in water alone. After 4 h in water at 225 °C, the boehmite peaks were 1/3 more intense than for the sample treated in ethanol/water, indicating that ethanol also slowed down the formation of (larger) boehmite crystals, but only to a limited extent (Supporting Information, Figure S1).

The transformation of the support causes changes in the pore volume and surface area. The untreated Pt/γ-Al_2O_3 catalyst has a BET surface area of 156 m^2/g, which dropped below 40 m^2/g within 4 h after treatment in ethanol/water and then leveled off. In line with the changes in BET surface area, the total pore volume decreased and the average pore size increased

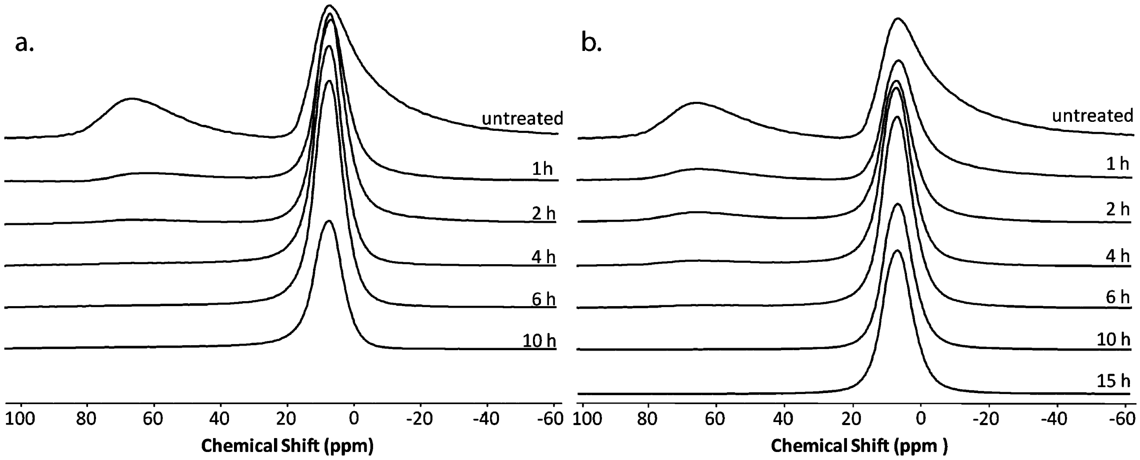

Figure 2. ^{27}Al MAS NMR spectra of a 1 wt % Pt/γ-Al_2O_3 catalyst treated at 225 °C for various durations in (a) ethanol/water and (b) ethanol/water and 4 mmol of guaiacol.

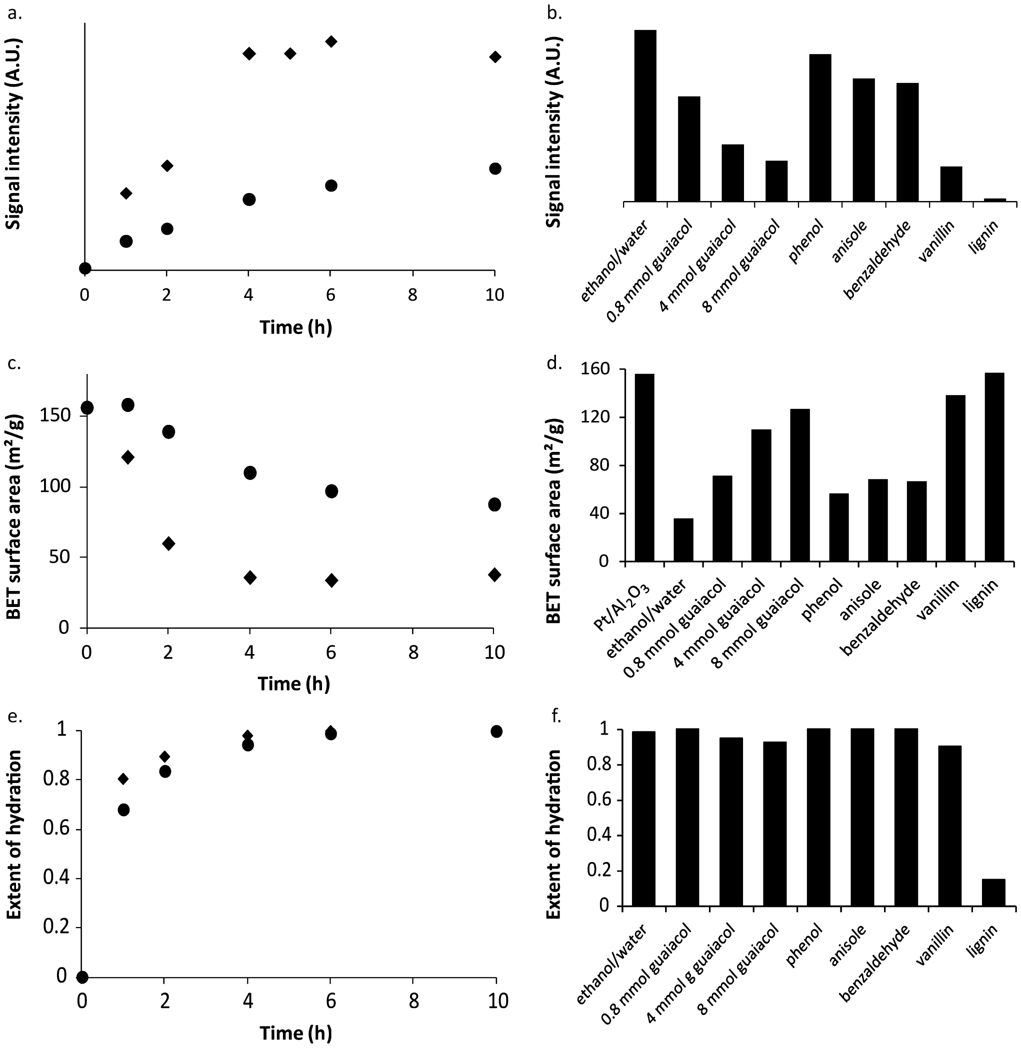

Figure 3. X-ray diffraction peak intensity at $2\theta = 16.8°$ (a and b), BET surface area (c and d) and boehmite formation based on ^{27}Al MAS NMR (e and f) of a 1 wt % Pt/Al_2O_3 catalyst after treatment with and without guaiacol at 225 °C. (a,c,e ◆) Samples treated in ethanol/water and (a,c,e ●) samples treated in ethanol/water with 4 mmol of guaiacol. (b,d,f) Catalyst treated in ethanol/water at 225 °C with 4 mmol of various aromatic oxygenates for 4 h.

(Supporting Information, Table S1). In comparison, in the presence of guaiacol the decrease was less pronounced as after 15 h the BET surface area was 76 m^2/g and still decreasing (Figure 3c). This increased stability was also observed for samples treated in water with glycerol and sorbitol present, for which no significant change in alumina surface area was observed in solutions of 5 wt % of the oxygenates.[15] The surface area of Pt/Al_2O_3 in hot water at 200 °C was previously reported to increase during the first 6 h of treatment after which it decreased again.[14]

The hydration of γ-Al_2O_3 causes the conversion of tetrahedral aluminum sites to octahedral ones, which can be quantitatively monitored with ^{27}Al MAS NMR spectroscopy. The ^{27}Al MAS NMR spectrum of an untreated 1 wt % Pt/Al_2O_3 catalyst shows resonances at 66 and 7 ppm, which correspond to the tetrahedrally and octahedrally coordinated aluminum species, respectively (Figure 2).[22,23] Linear combination of the ^{27}Al MAS NMR spectra of γ-Al_2O_3 and boehmite allows the fraction of fully hydrated Al to be calculated. The untreated sample contained 26% tetrahedrally coordinated aluminum, comparable with previously reported results, whereas in pure boehmite all aluminum species are octahedrally coordinated.[24] The ^{27}Al MAS NMR spectra show that γ-Al_2O_3 is gradually converted into boehmite when treated in ethanol/water with and without guaiacol (Figure 2a and 2b). This was indicated by the continuous decrease in intensity of the peak corresponding to tetrahedrally coordinated Al with time. In the presence of 4 mmol of guaiacol, the rate of the hydration is slower compared to treatment without guaiacol (Figure 3e). However, complete conversion was reached after 6 h in both cases. This was much faster than the phase transformation of 1 wt % Pt/Al_2O_3 treated in water at 200 °C, in which case a boehmite fraction of 0.6 was reported after 10 h.[14]

All techniques show changes in the structure of the support that proceed over time. For samples that were treated in ethanol/water without guaiacol these changes appear to be complete after 4h, while for the guaiacol-treated samples the changes take place more slowly and continue for a longer time. The XRD and physisorption data show that for the guaiacol-treated samples even after 15 h recrystallization is still in progress, while the ^{27}Al MAS NMR data show the conversion to octahedral aluminum to be complete after 10 h. This difference between XRD and NMR data was also observed before.[14] The initial hydration of the tetrahedral aluminum species to octahedral aluminum species is detected by NMR, but does not immediately result in the formation of a boehmite crystal lattice of sufficiently long-range order to be detected by XRD. After complete transformation to octahedral aluminum, the first small domains of boehmite crystals will still grow and as a result the physical properties of the support material continue to change.

Comparison of samples treated for 4 h in the presence of different concentrations of guaiacol shows that higher concentrations slowed down the loss of BET surface area and formation of a crystalline boehmite phase more (Figure 3b, 3d, and Supporting Information, Figure S2). Furthermore, the XRD patterns and BET surface area of samples treated with 4 mmol of different aromatic lignin model compounds show that the addition of guaiacol and vanillin, with two and three oxygen functionalities, respectively, resulted in less intense boehmite peaks and smaller loss of surface area than did mono-oxygenated, phenol, anisole, and benzaldehyde. Only small differences are observed between the methoxy, phenolic, and aldehyde functional groups (Figure 3b, 3d, Supporting Information, Figure S3), indicating that the type of oxygen functionality does not influence the stabilization of the support much. This comparable reactivity suggests that the different molecules eventually form the same surface oxygen species. Demethylation of anisole would thus, for instance, give the same chemisorbed phenolate species on the support as phenol would. ^{27}Al MAS NMR shows that the influence of the oxygenates on the rate of hydration of alumina is relatively small. The differences in extent of hydration observed are small compared to the variation observed in XRD peak intensity (Figure 3f). For phenol, anisole, benzaldehyde, and 0.8 mmol of guaiacol, conversion was complete after 4 h. Only vanillin and 8 mmol guaiacol treated samples still have tetrahedrally coordinated aluminum left after 4 h with conversions of 0.90 and 0.92, respectively.

The increased stability of the support in the presence of guaiacol and other aromatic oxygenates indicates that these molecules prevent hydrolysis of the alumina. Most likely the oxygen functionalities coordinate to unsaturated aluminum sites on the support thereby preventing water molecules to access these sites. Previously, the polyols glycerol and sorbitol were also shown to inhibit the transformation from γ-alumina to boehmite. Boehmite fractions of only 15% and 2% for 5 wt % glycerol and sorbitol were calculated from ^{27}Al MAS NMR after 10 h reaction, which is less than for the samples treated in 4 mmol solutions of guaiacol after 4 h.[15] The increasingly strong inhibitory effect of polyols with growing carbon chain length is attributed to the increasing number of hydroxyl groups present in longer polyols, allowing stronger adsorption via the formation of multidentate surface species.[25] Moreover, a spatial separation between the different functional groups allows for the formation of more stable surface species.[26] We here observe a similar correlation with the aromatic oxygenates where mono-oxygenated species show only limited stabilization of the support compared to compounds that are able to form bidentate or multidentate surface species.

Remarkably, when the stability of the catalyst was tested in the presence of 0.5 g of Alcell organosolv lignin, no significant change in the diffraction pattern and surface area of the original catalyst material was observed (Supporting Information, Figure S3). The total pore volume and the average pore diameter both were reduced by half. The fraction of hydrated aluminum as observed by ^{27}Al NMR was only 0.15. This together with the XRD results indicates that the hydration only took place to a very small extent and that the transformation to boehmite was completely blocked. The inherently multidentate mode of adsorption of the highly functionalized and relatively hydrophobic lignin macromolecule leads to a strong interaction with the support and ultimately prevents water from hydrating the surface.

3.2. Reactivity of Ethanol and Aromatic Oxygenates on the Alumina Support.

As was suggested before, the adsorption of oxygen-containing molecules on the alumina support, both by coordination of the molecule to specific sites on the alumina and by the formation of coke, may block the access of water molecules to these positions, thereby preventing hydration of the support.[15] The type of organic deposits will depend on the oxygenate(s) they are derived from, and quantity and nature can be determined with thermogravimetric analysis (TGA) and IR spectroscopy, respectively.

Upon heating to 900 °C, untreated Pt/γ-Al_2O_3 catalyst showed a gradual weight loss of up to 3%. All ethanol/water-treated samples as well as the samples treated in the presence of guaiacol and other model compounds showed a total weight decrease between 14 and 17% with a sharp decrease around 450 °C. The total loss of weight was similar for all samples regardless of the treatment time and guaiacol concentration with exception of the lignin-treated sample which showed a total weight loss of 22% over a temperature range between 250 and 500 °C. Weight loss started at lower temperatures for samples treated with higher guaiacol concentrations as well as samples treated with vanillin, resulting in a more gradual decrease in weight over a longer temperature range. In comparison, samples treated with only ethanol/water always lost most of their weight in a narrow temperature range around 500 °C (Figure 4 and Supporting Information, Figure S4).

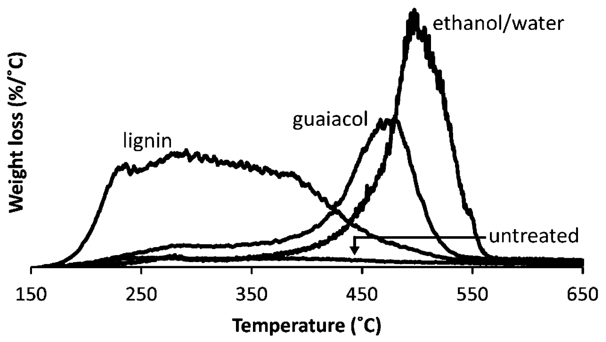

Figure 4. Thermogravimetric analysis of a 1 wt % Pt/γ-Al_2O_3 catalyst after treatment at 225 °C with ethanol/water, 0.5 g (4 mmol) of guaiacol and 0.5 g of lignin.

These results are comparable to those previously observed with polyols.[15] The nature of these deposits, which given the multiple peaks in TGA were shown to be heterogeneous in nature in the case of the polyols, seems to be more homogeneous in the case of the guaiacol-treated sample.

Mass spectrometric analysis of the gases released during heating showed the formation of CO_2 with maxima between 225 and 450 °C and an evolution of water resulting from dehydration of the boehmite around 500 °C (Figure 5a, b, Supporting Information, Figures S5, S6). As the samples were dried at 150 °C for 2 h before the TGA measurements, any remaining volatile aromatic molecules would have already been desorbed during this preheating stage and should not contribute to any detected weight loss in the TGA measurements. Samples treated in ethanol/water without model compound showed additional CO_2 release at 520 °C. In the presence of lignin and lignin model compounds, these deposits, which apparently do not contribute to the stabilization of alumina toward boehmite formation, are not formed. This release of CO_2 at this relatively high temperature points to the formation of more stable carbonaceous deposits (Figure 5b).[27] This has also been observed after steam reforming reactions of ethanol over alumina-supported catalysts.[28] Samples that were shown to contain a higher amount of boehmite by XRD also released more water during TGA analysis, and samples treated with guaiacol and vanillin released water at a lower temperature (485 °C). As the samples treated with lignin model compound solutions released most of the CO_2 at temperatures lower than 410 °C and most water at a higher temperature, it is possible to compare the amount of weight loss due to CO_2 and water release between the different samples (Supporting Information, Table S2). With the exception of the sample treated with lignin, the majority of the weight loss was caused by release of water at temperatures above 410 °C. Increasing the amount of a model compound in solution also resulted in an increased amount of CO_2 release during TGA (3, 4, and 6 wt % for the samples treated with 0.8, 4, and 8 mmol guaiacol, respectively). Samples treated in ethanol/water with phenol, anisole, and benzaldehyde released only a small amount of CO_2, which indicates that compared to guaiacol less of these molecules were strongly adsorbed on the support at the same molar concentration. This again points at the relatively weak monodentate adsorption of these molecules.

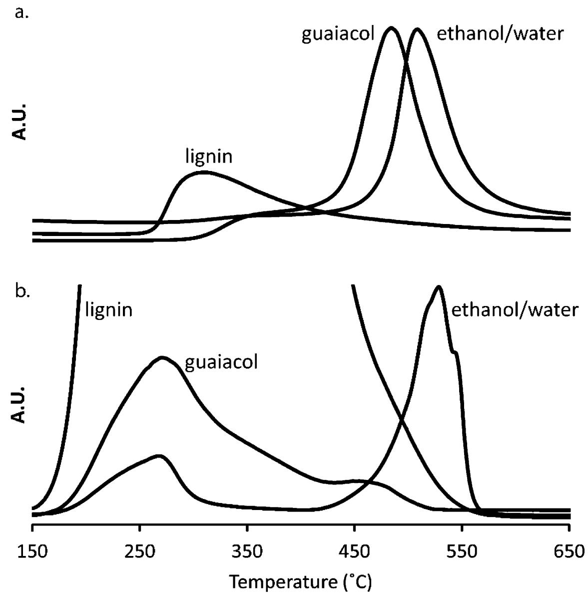

Figure 5. (a) H_2O and (b) CO_2 released during thermogravimetric analysis of a 1 wt % Pt/γ-Al_2O_3 catalyst after treatment at 225 °C with ethanol/water, 0.5 g (4 mmol) of guaiacol and 0.5 g of lignin.

Longer treatment times did not lead to an increased amount of CO_2 formation, but for both the ethanol/water and ethanol/water/guaiacol samples longer reaction times did lead to more release of water. The continued uptake of water is consistent with the growth of the boehmite phase over time as is corroborated by the XRD and physisorption data.

IR spectra of the treated samples were recorded to determine the nature of the carbonaceous deposits on the catalyst material. The original Pt/γ-Al_2O_3 catalyst shows a broad band in the region 3700−3000 cm^{-1} corresponding to the O−H stretching vibrations of surface hydroxyl groups and small peaks at 1537, 1458, and 1259 cm^{-1} originating from carbonate-like species coordinated to the surface OH groups.[29] After treatment in ethanol/water the spectrum showed an increased absorption in the O−H stretch area because of the formation of a hydrated boehmite phase. The spectrum of the sample diluted with KBr shows two major bands at 3299 and 3085 cm^{-1}, which are characteristic for the OH stretching bands of boehmite.[30] New, broad bands appeared at 2096 and 1973 cm^{-1} as a result of both combination bands and overtones of Al−O resonances, and a sharp peak at 1071 cm^{-1} is assigned to OH bending vibrations of boehmite (Figure 6).[30] In-situ DRIFT analysis of the guaiacol-treated sample in a nitrogen flow with D_2O showed a decrease in the OH bands at 3670, 3325, and 1072 cm^{-1} and formation of new bands at 2707 and 2390 cm^{-1}. No changes were observed in the vibrations around 2000 cm^{-1} confirming that these do not belong to OH vibrations (Supporting Information, Figure S7).[31] No peaks characteristic for ethanol are observed, which could have been expected since ethanol is present in large quantities. Any ethanol deposits could be masked though by the strong boehmite bands in the CH stretch and CO stretching regions. Ethanol is known to form acetates on alumina above 200 °C,

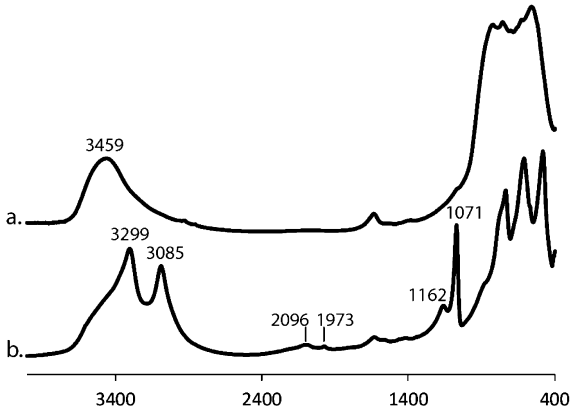

Figure 6. IR spectra of a 1 wt % Pt/γ-Al_2O_3 catalyst pressed into a KBr wafer (a) before and (b) after treatment at 225 °C in ethanol/water with 4 mmol of guaiacol.

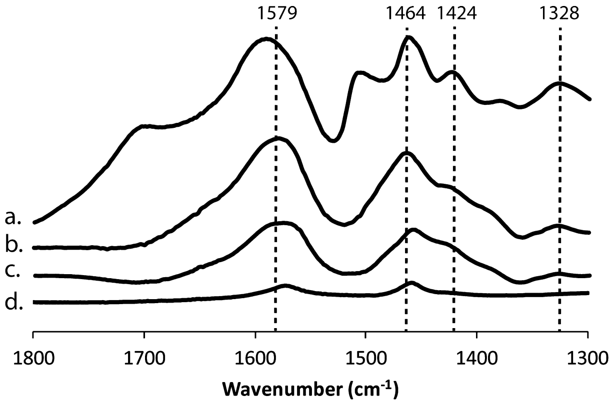

Figure 7. IR spectra of a 1 wt % Pt/γ-Al_2O_3 catalyst (a) after treatment at 225 °C with 0.5 g of lignin, (b) after treatment at 225 °C with 4 mmol of guaiacol, and (c) after treatment at 225 °C with 4 mmol of phenol, (d) fresh catalyst.

but no clear OCO stretching modes at 1585 cm^{-1} for organic acetates are found.[32] The limited amount of hard coke formed in ethanol/water-treated samples that was observed in the TGA measurements is not visible in the IR spectrum. The vibrations associated with the newly formed boehmite phase can also be seen in spectra of the catalyst treated in guaiacol and phenol solutions, now with additional new peaks at 1579 and 1464 cm^{-1} (Figure 7), which can be assigned to aromatic ring vibrations.[31] This indicates that the molecules are adsorbed with intact aromatic rings, most likely via the oxygen groups. The absence of a guaiacolic OH group in the 1366 cm^{-1} region points toward the formation of a guaiacolate species that is directly bound to the alumina. Also, no peaks corresponding to the CH stretching modes of a methyl group were observed in the 2900 cm^{-1} region, indicating that demethylation has taken place for the most strongly adsorbed guaiacol-derived species, which remain after isolation of the spent catalyst to give bidentately bound catecholate species. While it has been shown for vicinal diols such as 1,2-ethyleneglycol or 1,2-propanediol that such bidentate coordination modes are not very favorable because of geometric constraints,[26] they have indeed been reported before for guaiacol on alumina. It was shown that the methoxy group of guaiacol can react with alumina at temperatures between 150 and 200 °C resulting in the formation of guaiacol molecules strongly anchored on the support as bidentate catecholates.[31] Although it is likely that, under the relatively mild conditions applied here, many guaiacol molecules interact weakly with the support and coordinate to the alumina mostly with both the OH and the methoxy group still intact. Such species would be washed off the catalyst rather easily at the end, leaving only the more firmly anchored molecules for which deprotonation or deprotonation/demethylation has taken place. It should be noted in this respect that previous results under conditions where pure guaiacol is introduced to alumina show much higher surface coverages than were observed here for the ethanol/water/guaiacol-treated samples. This clearly indicates that guaiacol adsorption is reversible and that the adsorption of water and ethanol is still highly competitive with the adsorption of the aromatic oxygenates. Therefore, the stabilization of the support by these molecules will be limited and, as was shown in the previous section, will only slow down and not stop the transformation to boehmite.[31]

Large amounts of CO_2 (17 wt % of the total sample weight of the original sample) were released during TGA analysis from the sample treated with lignin, consistent with the larger weight loss observed for this sample. Possibly, stronger adsorption due to multidentate interactions of the molecule increases the stability of lignin on the alumina surface and prevents it from being washed away after the treatment. Formation of water occurred in the same temperature region as the CO_2 release, indicating that the lignin adsorbed on the support still has a high oxygen content. This is also seen in the IR spectra where a broad OH stretch band with a maximum at 3530 cm^{-1} was observed for the catalyst treated in the lignin solution which can be attributed to the alcohol functionalities in the lignin macromolecule. A vibration corresponding to aliphatic CH stretching modes at 2935 cm^{-1} and bands at 1713 cm^{-1} and 1506 cm^{-1} corresponding to C=O stretch and aromatic ring vibrations were also observed, in addition to phenolic vibrations at 1579, 1464, 1424, and 1328 cm^{-1}. Peaks corresponding to the hydrated boehmite phase were not observed in the OH stretch region, nor were the broad bands at 2085 and 1963 cm^{-1} or the OH bending vibration at 1072 cm^{-1}. A comparison of the spectrum of pure lignin with the lignin adsorbed on the catalyst (Figure 8) shows that some major peaks were still present after adsorption, although large changes in peak ratios and small shifts did occur in the fingerprint region. The major differences are a relative decrease of the C=O stretching vibrations at 1704 cm^{-1}, the symmetric aryl stretching vibrations at 1607 cm^{-1}, and the aromatic C−H in plane deformations at 1120 cm^{-1} and an increase of the asymmetric aryl stretching vibrations at 1516 cm^{-1}.[33] Remarkably, a pure lignin sample loses weight at higher temperatures during TGA than the lignin adsorbed on the alumina (Supporting Information, Figure S8), indicating that the support is able to lower the lignin decomposition temperature.

3.3. Stability of the Supported Metal Nanoparticles.

The transformation of the γ-alumina support to boehmite affects the stability of the metal nanoparticles on the surface. The mobility of the metal nanoparticles increases when the support surface changes, which in turn leads to sintering or encapsulation of the metal nanoparticles. In addition, added organics can lead to coke formation resulting in blockage of the particles. In both cases the accessibility of Pt during the reaction is drastically reduced. It is important to gain more insight in the

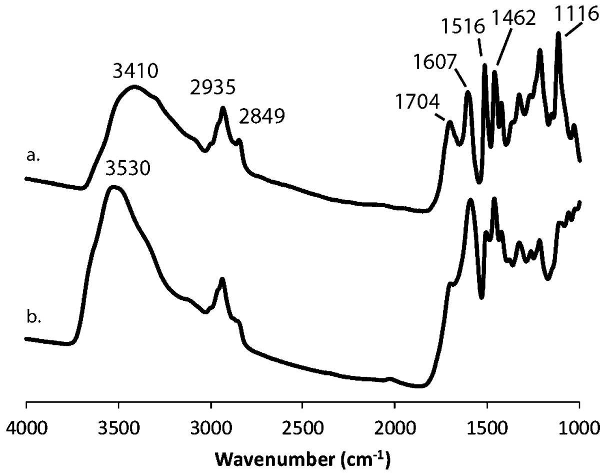

Figure 8. (a) IR spectrum of a lignin KBr pellet, (b) IR spectrum of a self-supporting wafer of a 1 wt % Pt/γ-Al_2O_3 catalyst treated in a lignin solution.

stability of the supported metal nanoparticles as a decrease in dispersion will lead to loss of catalyst activity.

The platinum loading of the Pt/γ-Al_2O_3 catalyst and all samples treated in ethanol/water with and without model compounds were determined by ICP-OES. The untreated catalyst was found to have a platinum content of 0.95 wt %, whereas loadings between 0.8% and 0.85% were found for the ethanol/water treated samples with and without guaiacol and other model compounds. The sample treated in ethanol/water with lignin contained 0.79% Pt. Taking into account the uptake of water and deposition of carbonaceous deposits during the run, shown to be between 14 and 17% by TGA, it can be concluded that no significant amount of platinum was leached into solution during the treatment.

The TEM micrograph of the untreated catalyst shows well-dispersed Pt nanoparticles on the amorphous γ-Al_2O_3 support (Figure 9a). TEM micrographs of the catalyst treated for 4 h in ethanol/water and ethanol/water containing benzaldehyde show that the support changed to a uniform density with sharp edges, indicative of crystallinity. The Pt particles on the fresh catalyst have an average size of 2.0 nm with 16% of the particles having a diameter of less than 1 nm. Most particles (48%) have a diameter between 2.0 and 3.0 nm. The average Pt particle size increased when the catalyst was treated for 4 h in ethanol/water and ethanol/water with phenol, anisole, benzaldehyde, 0.8 mmol of guaiacol, 8 mmol of guaiacol, and vanillin (Figure 10). The degree of sintering is again not influenced much by the particular monoaromatic compound used, even though it did influence the relative change in surface area and boehmite formation. This increase in average particle size was also observed for a Pt/Al_2O_3 catalyst hydrothermally treated in aqueous glycerol and sorbitol solutions. However, for these hydrothermal treatments, sintering was found to be less severe when the polyols were present.[15] In contrast, with the aromatic oxygenates, larger increases in average particle size are seen compared to ethanol/water alone. The Pt particles sintered significantly during these treatments (Figure 9b and c). The untreated catalyst, and the catalyst treated with guaiacol (4 mmol) and lignin were the only samples that contained Pt particles with diameters less than 1 nm. In hydrogen chemisorption measurements, the untreated Pt/γ-Al_2O_3 catalyst showed a hydrogen uptake of 16 μmol/g, corresponding to an average particle diameter of 1.7 nm, which is consistent with the TEM measurements (average particle size of 2 nm). The hydrogen uptakes of samples treated in ethanol/water with and

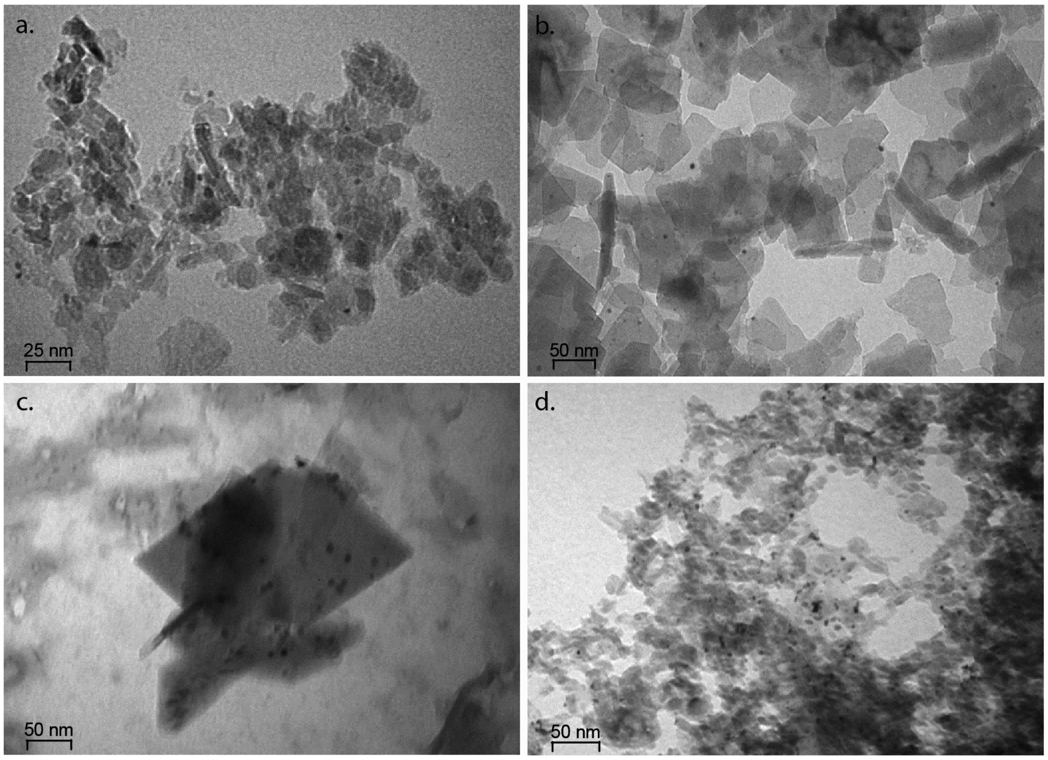

Figure 9. (a) TEM micrographs of an untreated 1 wt % Pt/Al_2O_3 catalyst, (b) treated at 225 °C in ethanol/water for 4 h, (c) treated at 225 °C in a benzaldehyde solution, and (d) treated at 225 °C in a lignin solution for 4 h.

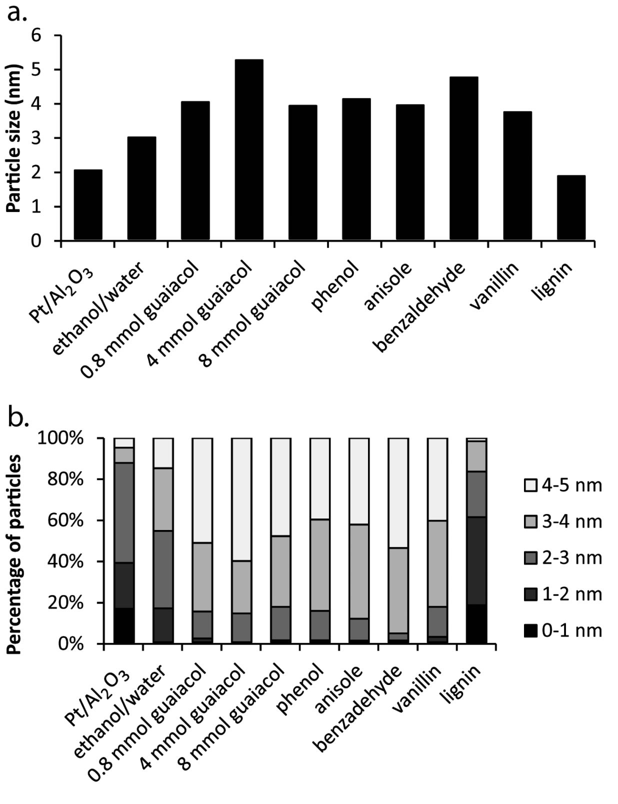

Figure 10. (a) Average diameter of Pt nanoparticles, (b) particle size distributions of an untreated 1 wt % Pt/Al_2O_3 catalyst and of a 1 wt % Pt/Al_2O_3 catalyst after 4 h treatment at 225 °C in various aromatic oxygenate solutions.

without guaiacol were 3 and 4 μmol/g, which are, however, much lower than expected based on the TEM results. After calcination at 400 °C the guaiacol treated sample still showed a hydrogen uptake of 4 μmol/g. According to TGA measurements, a treatment at this temperature should have removed any carbonaceous deposits that cover the Pt particles. This indicates that some particles were encapsulated in the boehmite crystals and are not accessible anymore. The XRD and physisorption data show that samples treated in ethanol/water without any aromatic model compound show a faster transformation of the Pt/γ-Al_2O_3 to boehmite. It can be expected that this faster change of the support also leads to faster encapsulation of the Pt particles, thereby decreasing the time they are prone to sintering. With the exception of the lignin-treated sample, all samples that showed a slow conversion to boehmite in XRD therefore show a larger average particle size by TEM.

Notably, the sample treated in lignin solutions exhibited only marginal changes in average Pt particle size and particle size distribution. The TEM micrograph of the catalyst treated for 4 h with lignin furthermore shows that the support retains an amorphous appearance (Figure 9d), similar to that of the untreated catalyst (Figure 9a) and in line with the XRD data. With 6 μmol/g the hydrogen uptake of the lignin-treated sample was also lower than for the untreated catalyst. As a result, the average particle size of 4.0 nm calculated from the hydrogen chemisorption results was higher than the particle size of 1.9 nm obtained by TEM. These results indicate that the Pt surface on the lignin-treated sample is less accessible for molecular hydrogen as it is partially covered by the support or, more likely, a layer of adsorbed lignin. Formation of a layer of lignin can explain the increased stability of the catalyst in the presence of lignin, both by occupying the positions that would otherwise be hydrated but probably also by increasing the hydrophobicity of the surface. Glycerol and sorbitol were also shown to prevent part of the loss of active sites, but a 60% drop in accessible metal surface area was still observed, which was explained by the formation of coke.[15]

4. CONCLUSIONS

Under liquid phase reforming conditions, the γ-alumina support of a 1 wt % Pt/Al_2O_3 catalyst material is converted into boehmite, which causes the formation of a crystalline phase and loss of surface area. These severe changes in the support also cause sintering and encapsulation of the Pt nanoparticles leading to loss of active surface area and catalytic activity. This transformation is slowed down in the presence of lignin-derived molecules, such as guaiacol, which are believed to adsorb on the alumina via its oxygen functionalities. The ability of each of these molecules to stabilize the support is proportional to the number of oxygen functionalities it contains. Higher concentrations of guaiacol increase the stability of the catalyst. Lignin itself shows an increased affinity for the alumina support resulting in adsorption of a large amount of lignin. The multidentate interactions between lignin and the support in that way completely prevent the formation of a boehmite phase and sintering of the supported Pt nanoparticles, while retaining the metal surface area. The Pt/Al_2O_3 catalyst material is not stable at the conditions required to dissolve lignin; however, high lignin concentrations could be used to partially overcome this problem. It is important to note that other supports (e.g., titania and carbon) might be more stable, but detailed studies need to be performed to assess potential transformations of these materials under reaction conditions.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Further details are given in Figures S1−S8 and Tables S1 and S2. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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REFERENCES

(1) Corma, A.; Iborra, S.; Velty, A. *Chem. Rev.* **2007**, *107*, 2411−2502.

(2) Zakzeski, J.; Bruijnincx, P. C. A.; Jongerius, A. L.; Weckhuysen, B. M. *Chem. Rev.* **2010**, *110*, 3552−3599.

(3) Werhan, H.; Mir, J. M.; Voitl, T.; van Rohr, P. P. *Holzforschung* **2011**, *65*, 703−709.

(4) Patwardhan, P. R.; Brown, R. C.; Shanks, B. H. *ChemSusChem* **2011**, *4*, 1629−1636.

(5) Schinski, W. L.; Kuperman, A. E.; Han, J.; Naae, D. G. Process for Generating a Hydrocarbon Feedstock from Lignin. U.S. Patent 2009/0218061 A1, 2009.

(6) Dorrestijn, E.; Laarhoven, L. J. J.; Arends, I. W. C. E.; Mulder, P. *J. Anal. Appl. Pyrol.* **2000**, *54*, 153−192.

(7) Nagy, M.; David, K.; Britovsek, G. J. P.; Ragauskas, A. J. *Holzforschung* **2009**, *63*, 513−520.

(8) Cortright, R. D.; Davda, R. R.; Dumesic, J. A. *Nature* **2002**, *418*, 964−967.

(9) Tanksale, A.; Beltramini, J. N.; Lu, G. M. *Renewable Sustainable Energy Rev.* **2010**, *14*, 166−182.

(10) Zakzeski, J.; Weckhuysen, B. M. *ChemSusChem* **2011**, *4*, 369−378.

(11) Chheda, J. N.; Powell, J. B. Direct Aqueous Phase Reforming of Bio-Based Feedstocks. International Patent 2011/082000A1, 2011.

(12) Tokarev, A. V.; Kirilin, A. V.; Murzina, E. V.; Ernen, K.; Kustov, L. M.; Yu, D.; Murzin; Mikkola, J.-P. *Int. J. Hydrogen Energy* **2010**, *35*, 12642−13649.

(13) Zakzeski, J.; Jongerius, A. L.; Bruijnincx, P. C. A.; Weckhuysen, B. M. *ChemSusChem* **2012**, *5*, 1602−1609.

(14) Ravenelle, R. M.; Copeland, J. R.; Kim, W. G.; Crittenden, J. C.; Sievers, C. *ACS Catal.* **2011**, *1*, 552−561.

(15) Ravenelle, R. M.; Copeland, J. R.; Van Pelt, A. H.; Crittenden, J. C.; Sievers, C. *Top. Catal.* **2012**, *55*, 162−174.

(16) Pye, E. K.; Lora, J. H. *Tappi J.* **1991**, *74*, 113−115.

(17) Kleinert, T. N. Organosolv pulping and recovery process. , U.S. Patent 3585104, 1971.

(18) Scholten, J. J. F.; Pijpers, A. P.; Hustings, M. L. *Catal. Rev. Sci. Eng.* **1985**, *27*, 151−206.

(19) Ravenelle, R. M.; Diallo, F. Z.; Crittenden, J. C.; Sievers, C. *ChemCatChem* **2012**, *4*, 492−494.

(20) Ketchie, W. C.; Maris, E. P.; Davis, R. J. *Chem. Mater.* **2007**, *19*, 3406−3411.

(21) Christoph, G. G.; Corbató, C. E.; Hofmann, D. A.; Tettenhorst, R. T. *Clays Clay Miner.* **1979**, *27*, 81−86.

(22) Pecharroman, C.; Sobrados, I.; Iglesias, J. E.; Gonzalez-Carreno, T.; Sanz, J. *J. Phys. Chem. B* **1999**, *103*, 6160−6170.

(23) Urretavizcaya, G.; Cavalieri, A. L.; Lopez, J. M. P.; Sobrados, I.; Sanz, J. *J. Mater. Synth. Process.* **1998**, *6*, 1−7.

(24) Zhou, R. S.; Snyder, R. L. *Acta Crystallogr., Sect. B* **1991**, *47*, 617−630.

(25) van Bronswijk, W.; Watling, H. R.; Yu, Z. *Colloid Surf. A* **1999**, *157*, 85−94.

(26) Copeland, J.R.; Shi, X.-R.; Sholl, D.S.; Sievers, C. *Langmuir* **2012**, *29*, 581−593.

(27) Henry, M.; Bulut, M.; Vermandel, W.; Sels, B.; Jacobs, P.; Minoux, D.; Nesterenko, N.; Van Donk, S.; Dath, J. P. *Appl. Catal., A* **2012**, *413*, 62−77.

(28) Sánchez-Sánchez, M. C.; Navarro, R. M.; Fierro, J. L. G. *Int. J. Hydrogen Energy* **2007**, *32*, 1462−1471.

(29) Morterra, C.; Magnacca, G. *Catal. Today* **1996**, *27*, 497−532.

(30) Ryskin, Y. I. The infrared spectroscopy of minerals. *Mineral. Soc.* Monograph 4, **1974**.

(31) Popov, A.; Kondratieva, E.; Gouil, J. M.; Mariey, L.; Bazin, P.; Gilson, J. P.; Travert, A.; Maugé, F. *J. Phys. Chem. C* **2010**, *114*, 15661−15670.

(32) Evans, H. E.; Weinberg, W. H. *J. Chem. Phys.* **1979**, *71*, 1537−1542.

(33) Heitner, C.; Dimmel, D.; Schmidt, J. A., Eds.; *Lignin and Lignans: Advances in Chemistry*; CRC Press, Taylor & Francis group: Boca Raton, FL, 2010.