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Lignin Depolymerization into Aromatic Monomers over Solid Acid Catalysts

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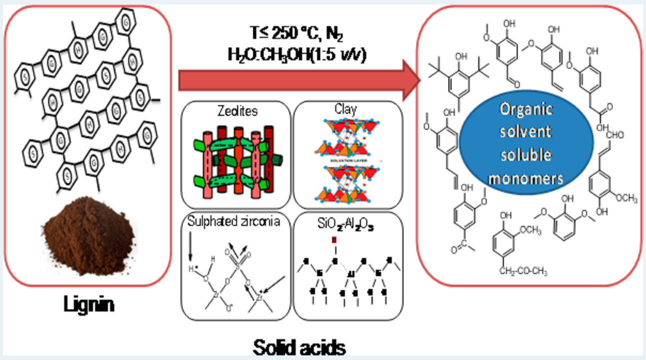
S Supporting Information



ABSTRACT: It is imperative to develop an efficient and environmentally benign pathway to valorize profusely available lignin, a component of nonedible lignocellulosic materials, into value-added aromatic monomers, which can be used as fuel additives and platform chemicals. To convert lignin, earlier studies used mineral bases (NaOH, CsOH) or supported metal catalysts (Pt, Ru, Pd, Ni on C, SiO_2, Al_2O_3, etc.) under a hydrogen atmosphere, but these methods face several drawbacks such as corrosion, difficulty in catalyst recovery, sintering of metals, loss of activity, etc. Here we show that under an inert atmosphere various solid acid catalysts can efficiently convert six different types of lignins into value-added aromatic monomers. In particular, the $SiO_2-Al_2O_3$ catalyst gave exceptionally high yields of ca. 60% for organic solvent soluble extracted products with 95 ± 10% mass balance in the depolymerization of dealkaline lignin, bagasse lignin, and ORG and EORG lignins at 250 °C within 30 min. GC, GC-MS, HPLC, LC-MS, and GPC analysis of organic solvent soluble extracted products confirmed the formation of aromatic monomers with ca. 90% selectivity. In the products, confirmation of retention of aromatic nature as present in lignin and the appearance of several functional groups has been carried out by FT-IR and ^1H and ^{13}C NMR studies. Further, isolation of major products by column chromatography was carried out to obtain aromatic monomers in pure form and their characterization by NMR is presented. A detailed characterization of six different types of lignins obtained from various sources helped in substantiating the catalytic results obtained in these reactions. A meticulous study on fresh and spent catalysts revealed that the amorphous catalysts are preferred to obtain reproducible catalytic results.

KEYWORDS: *biomass, lignin, solid acid catalysts, depolymerization, aromatic monomers, column chromatography*

1. INTRODUCTION

Plant-derived lignocellulosic biomass is considered as an important alternative source to fossil reserves for the production of fuels and chemicals.[1−4] Lignin, a common primary ingredient in biomass, is a natural amorphous three-dimensional polymer consisting mainly of methoxylated phenylpropane units, cross-linked with each other by C−C and C−O−C bonds. The lignocellulosic biomass typically contains 15−30% of lignin by weight and ca. 40% by energy.[5] The composition of lignin varies considerably from plant to plant, particularly with regard to the type and quantity of linkages in the polymer and the number of methoxy groups present on the aromatic rings. Due to its resistance to microbial attack, it helps in the protection of cellulose and hemicelluloses present in the cell wall. Lignin in large quantities is produced as a waste in many industrial processes, such as pulp production (isolation of cellulose to make paper) and the production of bioethanol from lignocelluloses, but it can be used for multiple functions, such as making lignosulfonates, burning for generation of heat, or even land filling. However, this readily available lignin is a rich source of aromatic monomers and hence, if depolymerized efficiently, it can produce value-added chemicals and fuels. Considering this, several research groups across the world are investigating its potential use in the synthesis of materials (adhesives, resins), plastics (as an additive or an ingredient), aromatic monomers, and biofuels.[6] Several reviews have discussed the possibility of converting lignin into chemicals to make the concept of biorefinery economically attractive, as these synthesized chemicals will add value to lignin.[7−14]

In the pyrolysis method, lignin is subjected to temperatures in the range of 300−1000 °C in the absence of air to obtain products such as gaseous hydrocarbons (methane, ethane), carbon monoxide, carbon dioxide, volatile liquids (e.g., acetone, methanol, water), and substituted aromatic monomers such as bio-oils (mixture of phenols, guaiacol, catechol, etc.).[15−17] In addition to these products, the formation of char and high-boiling complex phenols (below 15%) is also observed. Lignin can also be depolymerized under subcritical and supercritical conditions (>290 °C, 25−40 MPa) to yield aromatic monomers and gases.[18,19] The treatment of Kraft and organosolv lignin with

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soluble bases (KOH, NaOH, CsOH) under supercritical conditions of CH_3OH or C_2H_5OH to yield catechols and phenols is also known.[20] Supercritical water with *p*-cresol as a solvent is also used to treat organosolv lignin to yield phenols and gases.[21] A CO_2/acetone/water supercritical fluid system is used for the depolymerization of organosolv lignin at temperatures of 300−370 °C under 10 MPa pressure to obtain many aromatic products, syringol and guaiacol being among the major products.[22−24] Although these methods are capable of depolymerizing lignin, the major disadvantages of these methods are the use of high temperatures (290−400 °C) and high pressures (10−40 MPa) and the risk of corrosion and loss of selectivity to aromatic monomers, since these products at higher temperatures (>300 °C) generally undergo further reactions to yield gases, tar, and char. In addition to this, in the presence of hydrogen the use of supported metal catalysts such as, Pt, Ru, Pd, Ni, Co−Mo, and Ni−Mo supported on C, Al_2O_3, SiO_2, $SiO_2-Al_2O_3$, and zeolites is known. In these reactions, at 150−300 °C, lignin undergoes ca. 50% conversion to yield aromatic monomers and gases.[25−29] However, the use of H_2 and difficulty in catalyst recyclability due to sintering and leaching of metals are a few drawbacks of this method. A study has been done using Ni-based catalysts for native birchwood lignin conversion (50%), with very high selectivity (97%) to monomeric phenols such as propyl guaiacol and propyl syringol.[26] Recently, a NiAu bimetallic catalyst was developed for the efficient hydrogenolysis of organosolv lignin into aromatic monomers (14 wt %) under milder reaction conditions (170 °C) in water.[30] Another report has shown that NiRu, NiRh, and NiPd bimetallic catalysts were also evaluated in the hydrogenolysis of lignin C−O bonds into monomeric aromatic alcohols at 100 °C and 0.1 MPa H_2 pressure.[31] The production of phenols from alkaline lignin was reported using tungsten phosphide in hot compressed water−ethanol solvent at 280 °C and 2 MPa of H_2.[32] Conversion of Kraft lignin into C6−C10 esters, alcohols, arenes, phenols, and benzyl alcohols was also reported using a nanostructured α-MoC catalyst at 280 °C in pure ethanol.[33] A single-step process for the hydrogenolysis and depolymerization of organosolv lignin and subsequent aromatic ring hydrogenation was studied using Cu-doped porous metal oxide in supercritical methanol at 300 °C.[34] Recently, base-catalyzed depolymerization (BCD) of lignin into aromatic monomers has been claimed.[18,35,36] In this method, homogeneous bases such as NaOH/KOH/CsOH etc. are used at and above 260 °C in the presence of nitrogen to obtain aromatic monomers.[37,38] The main shortcomings of the BCD process are the use of harsh conditions, low selectivity toward desired products (aromatics) formation, necessity of a neutralization step, and corrosion of the reactor system. To overcome this, it has been reported that a Ni-supported layered double hydroxide, hydrotalcite (HTC, basic catalyst), could depolymerize lignin without the use of external hydrogen and reduced metal.[39] Another report has shown that Cu-doped hydrotalcite based porous metal oxides and supercritical MeOH can convert lignocellulose solids into liquid fuels (C2−C6 aliphatic alcohols).[40]

Lewis acids such as $NiCl_2$ and $FeCl_3$, are also known for the depolymerization of Alcell lignin to aromatic monomers such as catechols, guiacols, and syringols.[41] The highest lignin conversions of 30% and 26% from $NiCl_2$ and $FeCl_3$, respectively, were attained under the reaction conditions of 305 °C and 1 h reaction time. There have been few reports on the solid acid assisted depolymerization of lignins, typically carried out at very high temperatures (>340 °C) to obtain aromatics and gases. One of the reports claims the use of H-ZSM-5 zeolite at 340−410 °C in a fixed-bed microreactor for upgrading pyrolysis oil to yield hydrocarbons (C5−C10). The maximum organic distillate from upgrading of whole bio-oil was 19 wt % (of bio-oil), and the highest concentration of aromatic hydrocarbons in the distillate was 83 wt %.[42] Furthermore, pyrolysis of Kraft lignin in the presence of $NiCl_2$ and H-ZSM-5 zeolite as an additive has been examined at 700 °C.[43] The effects of acidity and variation in pore sizes have also been shown in the catalytic fast pyrolysis of alkaline lignin to aromatics and gases.[44] In these works, zeolites are helpful in cleaving ether bonds in lignin and also in improving the decomposition of aliphatic hydroxyl, carboxyl, and methoxy groups. A literature report has also discussed the pyrolysis of Kraft lignin at 500−764 °C using H-ZSM-5 catalyst with various Si/Al ratios (25/1 to 200/1), for the formation of 2−5.2 wt % of aromatic hydrocarbons.[45] The one-step thermal conversion of lignin to gasoline-range liquid products has also been accomplished by pyrolyzing softwood (SW) Kraft lignin at 600 °C, with zeolites such as MFI (Z), FAU (Y), BEA (B), FER (F), and MOR (M).[46] Deactivation and regeneration of H-USY zeolite during the pyrolysis of alkaline lignin has been studied at 550 and 650 °C.[47] In all of the previous reports on the depolymerization of lignin involving acid catalysts, the pyrolysis technique has mostly been used and a careful study of these reports reveals that, in all of these reactions, high temperatures (340−750 °C) are employed. Moreover, the involvement of high temperatures invariably shows the presence of coke and char along with the formation of gases and hence, a low yield for the aromatic monomeric products has been achieved.

In most of the works discussed above, model compounds such as dimers and trimers have been used and, therefore, it becomes difficult to replicate the catalytic results obtained in these reactions with the actual substrates, as those have highly complicated structures and contain other impurities in comparison to model compounds.[7,11,45−51]

In this study, the use of solid acid catalysts in the depolymerization of six different types of lignins derived from assorted sources is shown. The lignins have been well characterized in order to understand their differences in morphologies and properties from each other. These details were helpful in correlating the activities of the same catalysts with differences in the activities. The emphasis of this work is also on generalizing the catalytic system to give maximum yields for aromatic monomers.

2. EXPERIMENTAL SECTION

2.1. Materials. Dealkaline lignin (TCI Chemicals, Product No. L0045), alkali lignin (Aldrich, Product No. 370959), and organosolv lignin (Aldrich, Product No. 371017) were purchased and used without any pretreatment. ORG and EORG lignins were obtained from local industries. Bagasse lignin was isolated in the laboratory by the organosolv method. Zeolites, H-USY (Si/Al = 15), H-ZSM-5 (Si/Al= 11.5), H-MOR (Si/Al = 10), and H-BEA (Si/Al = 19) were obtained from Zeolyst International. Prior to use, zeolites were calcined at 550 °C for 16 h in an air flow. $SiO_2-Al_2O_3$ (Aldrich), K10 clay and Al pillared clay (Aldrich), and niobium pentoxide (Spectrochem) were also purchased. Various aromatic monomers were purchased from Aldrich, Alfa Aesar, and TCI Chemicals and used as received. Solvents such as methanol (99.9%, LOBA), ethanol (99.7%, LOBA), tetrahydrofuran (99.8%, LOBA), ethyl acetate (99.9%, LOBA), chloroform (99.8%, LOBA), diethyl ether (99.5%, LOBA), hexane (99%, LOBA), and dichloro-

Table 1. Summary of the Properties of Various Lignins Used in the Study

			elemental analysis, %					TGA-DTA residue, %			
lignin	source	mol wt, g mol^{-1}	C	H	S	ICP-OES, mg[a] Na	SEM-EDAX (elements)	N_2	air	H_2O (N_2)	monomer molecular formula[b]
dealkaline[c]	TCI[52]	60000	65	7	1	29	C, O, Na, S	36	17	11	$C_9H_{10.62}O_{2.89}S_{0.06}$
organosolv[d]	Aldrich	M_n = 2285, M_w = 4575, PD = 2	65	6	0	0	C, O	40	2	0	$C_9H_{10}O_3$
alkali[e]	Aldrich	M_n = 5000, M_w = 28000	61	6	1	70	C, O, Na	30	2	0	$C_{8.47}H_{10}O_{3.3}S_{0.05}$
ORG[d]	industry	M_n = 4177, M_w = 7059, PD = 1.68	57	8	0	0	C, O	34	0	0	$C_{8.5}H_{10}O_4$
EORG	industry	ND	59	5	0	1.1	C, O	36	3	0	$C_9H_{10}O_4$
bagasse	extraction	ND	51	7	0	0	C, O, K	30	0	0	$C_{7.9}H_{10.1}O_{4.5}$

[a]ICP-OES results for 1 g of lignin. [b]Calculated using elemental analysis. [c]Molecular weight determined by MALDI-TOF. [d]Molecular weight determined by GPC. [e]From Aldrich.

methane (99.8%, LOBA) were purchased and used as received. NaCl (Merck), H_2SO_4 (98.5−97%, Merck), HCl (37%, Merck), and HF (48%, Merck) were also obtained and used as received.

2.2. Lignin Extraction from Bagasse. Lignin was extracted from bagasse by the organosolv technique using methanol as solvent. A mixture of 10 g of crushed sugar cane bagasse in 180 mL of methanol was stirred at 120 °C for 24 h. The mixture was cooled, filtered, and washed with solvent (methanol). The methanol-soluble portion was concentrated, using a rotavap, and then dried overnight at 60 °C, followed by drying under high vacuum at 150 °C for 3 h.

2.3. Depolymerization of Lignin. All lignin depolymerization reactions were carried out in a 100 mL capacity batch reactor (high-temperature and high-pressure Parr autoclaves, USA). Lignin (0.5 g) dissolved in water + methanol (5 + 25 mL) solvent along with the catalyst (0.5 g) was charged in the reactor. The reactor was flushed with N_2 and was filled with 0.7 MPa of N_2 at room temperature. Initially the rpm was kept at 100 and after the desired reaction temperature was attained it was increased to 500/1000 rpm, and this time was considered as the starting time of the reaction. After the reaction, the reactor was cooled and gas was released. Initially, the reaction mixture (water + methanol) after filtration through a 0.22 μm filter was injected in GC-FID and GC-MS. The catalyst was recovered by centrifugation, and the solvent from the reaction mixture was removed by a rotavap. The recovered semisolid obtained contains unconverted lignin and depolymerized products. In order to separate the aromatic monomers from this mixture, various organic solvents such as tetrahydrofuran (THF), chloroform ($CHCl_3$), ethyl acetate (EtOAc), and diethyl ether (DEE) were used, depending on the type of lignin used. The percentage of aromatic monomer was calculated on the basis of the solid recovered after evaporating the respective solvents (see section II.2 in the Supporting Information).

2.4. Characterization of Lignin and Catalyst Synthesis and Characterization. Lignin was characterized by MALDI-TOF, GPC, CHNS elemental analysis, ICP-OES, FT-IR, ^{1}H and ^{13}C NMR, TGA-DTA, XRD, SEM-EDAX, and UV−vis analytical techniques, and details on the methods and sample preparation are described in section I of the Supporting Information.

MoO_3/SiO_2 (10 wt %) was synthesized by the sol−gel method, and the detailed procedure is discussed in section I.2.1 of the Supporting Information.

Solid acid catalysts were characterized by various physicochemical techniques such as XRD, ^{29}Si and ^{27}Al NMR, ICP-OES, NH_3 (ammonia)-TPD, IPA (isopropyl amine)-TPD, N_2 sorption, CHNS elemental analysis, and metal exchange studies, and details on the techniques can be found in section I.2.2 of the Supporting Information.

Reaction mixtures and organic solvent soluble products were analyzed using GC-FID, GC-TCD, GC-MS, HPLC, LC-MS, GPC (DMF and THF), NMR (^{1}H and ^{13}C), MALDI-TOF, ICP-OES, and CHNS elemental analysis (see section II of the Supporting Information).

3. RESULTS AND DISCUSSION

3.1. Characterization of Lignin. The lignins used in this study have been obtained from several sources, such as commercial samples purchased from TCI Chemicals (dealkaline) and Aldrich Chemicals (alkali, organosolv). We also obtained lignins isolated by the organosolv technique from local industries which produce it on a commercial scale (ORG and EORG), and the bagasse lignin was extracted in our laboratory using the organosolv method (section 2.2). It is well-known that the structures of lignin and linkages present between several aromatic units in lignin depend on the plant species, plant parts, and even the extraction technique used for the isolation of lignin from lignocellulosic biomass.[7,53−56] To understand the morphology and properties of various lignins, before depolymerization they were completely characterized using various techniques, and details of the characterization are summarized in Table 1. As observed, all lignins used in this study have high molecular weights (above M_n = 2000 g mol^{-1}), with dealkaline lignin having the highest value (M_n = 60000 g mol^{-1}) among all. As expected, the elemental analysis done using ICP-OES and SEM-EDAX characterizations revealed the presence of Na and S in dealkaline and alkali lignins, as those might have been isolated using the Kraft method, wherein Na_2S and NaOH are typically used as reagents.[53,54,57−59] The organosolv, ORG, EORG, and bagasse lignins do not contain any Na or S, as those are isolated by the organosolv method, wherein no Na- or S-containing reagents are used.[34,60] By ICP-OES and SEM-EDAX techniques we checked for the possibility of the presence of other metals (Mg, Ca, K, etc.) in lignin, which are required by plant during their growth as nutrients, but we could not detect their presence, as their concentration (if present) must be very low.

The CHNS elemental analysis revealed that the lignins are composed of 60−65% C and 5−8% H, except in the cases of ORG and bagasse lignin, which are made up of 57% and 51% C, respectively (Table 1).[34,60] On the basis of these results, the general (monomer) molecular formulas of lignins were determined and are given in Table 1. Typically, all of the lignins have the general formula $C_xH_yO_z$ (x, 7.9−9.0; y, 10−10.62; z, 2.89−4.5), which correlates well with the reported values.[7,61,62] Since lignin is an organic molecule, it is expected that, upon thermal degradation at high temperatures, it will completely disintegrate into CO, CO_2, or CH_4. The thermal degradation (TGA-DTA) studies of all of the lignins carried out at up to 1000 °C under a nitrogen atmosphere showed almost 35−40% of unburnt residues (Table 1). However, when a thermal degradation study was carried out in the presence of oxygen, a minimal quantity (0−3%) of unburnt residue was observed. The only exception is dealkaline lignin, where the quantity is almost 17%, which is in line with the manufacturer's (TCI Chemicals) specifications.[52] These studies suggest that, in the presence of nitrogen, not all of the carbon is burned off due to lack of oxidant (oxygen). However, almost 75% of carbon was burned, since the lignin molecule has O and H atoms that can help in forming CO and CH_4. A careful look at the molecular formula of lignin reveals that for 9 C atoms 10 H and 4 O atoms are present. It is possible that 4 C atoms will be consumed in the form of 4 CO molecules and another 2 C atoms will be consumed in the formation of 2 CH_4 (or 3 C atoms as 3 CH_4) molecules. However, after complete use of H and O atoms present in the lignin molecule in the presence of nitrogen, 3 or 4 C atoms will still remain unburned as coke or char. A quick calculation reveals that these remaining 3 or 4 C atoms among 9 C atoms will give rise to ca. 30−40% of residue. This percentage of unburned residue matches well with our experimental data (Table 1). However, in the presence of an oxygen atmosphere these entire C atoms are burned, and hence we saw almost no residue. In the case of dealkaline lignin, even in the presence of oxygen, 17% of ignition residue (ash) was observed, which represents some inorganic material, but not Na and S, since it covers ca. <4% of dealkaline lignin (calculated considering the milligram amounts of these metals present). From ICP-OES and SEM-EDAX analysis of the ash (after the lignin was calcined at 650 °C for 6 h) it was confirmed that this inorganic residue (ash) is composed of Na and S (see Figure S1a in the Supporting Information). However, we could not detect any other element. XRD analysis of the ash indicates the presence of Na_2SO_4 (see Figure S1b in the Supporting Information), which was confirmed by the JCPDS file (No. 360397). Therefore, we can conclude that the composition of the inorganic residue (ash) detected in dealkaline lignin is Na_2SO_4. Nevertheless, we are still unclear about the remaining composition of the ash, as from Table 1 it is very clear that the quantity of Na and S present is not sufficient give a total of 17% (29 mg in 1 g of lignin). The concentration of water in lignin was calculated on the basis of the loss of mass until 150 °C in the TGA-DTA study (Table 1). In addition to this study, FTIR and solid state NMR analysis of lignin were carried out (for details please refer to section 3.3.3). UV−vis analysis of various lignins has been carried out, and the results are summarized in Figure S2 in the Supporting Information. It is known that lignin and cellulose are linked together in the plant cell wall and there is a possibility of contamination of lignin with cellulose even after isolation of lignin. To confirm the absence of cellulose in the samples, XRD analysis of all the lignins was performed and no peaks for crystalline cellulose (2θ = 22.5°) and amorphous cellulose (2θ = 17.7−18.5°) were visible (Figure S3 in the Supporting Information).

Before proceeding to the catalytic runs, we measured the solubility of lignins in different solvents and the results are tabulated in Table S1 in the Supporting Information. This study served two purposes, namely (1) selection of a suitable reaction medium for the lignin depolymerization reaction and (2) isolation of reaction products from the reaction mixture using a suitable solvent in which lignin is not soluble (Figure S4 in the Supporting Information). From the results it was found that a water/methanol (1/5 v/v) mixture would be the best solvent system for carrying out the reactions, since in this solvent system all six different types of lignins have complete solubility. Several other ratios of water/methanol such as 1/1 and 1/3 (v/v) were also observed to be suitable to carry out the reactions, but those were not used because the literature suggests that, in the presence of an excess amount of water; acid sites can get poisoned (solvation effect) and thus will not be available for reactions.[63,64] Considering this, a 1/5 (v/v) ratio of water−methanol was used to carry out all reactions.

A snapshot of lignin characterization indicates that lignins used in this study represent a wide range of properties and hence it would be challenging to develop a universal catalytic system which can convert this diverse set of lignin substrates into aromatic monomers.

3.2. Characterization of Solid Acid Catalysts.

A wide range of probe molecules (ammonia, isopropylamine, ethylamine, cyclooctylamine, *tert*-butylamine, etc.) have been developed for the characterization of acidity of solid acid catalysts.[61−63] We have attempted to do the TPD study with isopropylamine (IPA) as a probe molecule. It is known that above 275 °C, via a Hofmann elimination reaction, IPA undergoes conversions over Brønsted acid sites to produce propene and ammonia. When we subjected H-USY (Si/Al = 15) and SiO_2−Al_2O_3 catalysts for IPA-TPD studies, we could observe peaks in the temperature range of 350−500 °C corresponding to both propene and ammonia (Figure 1).

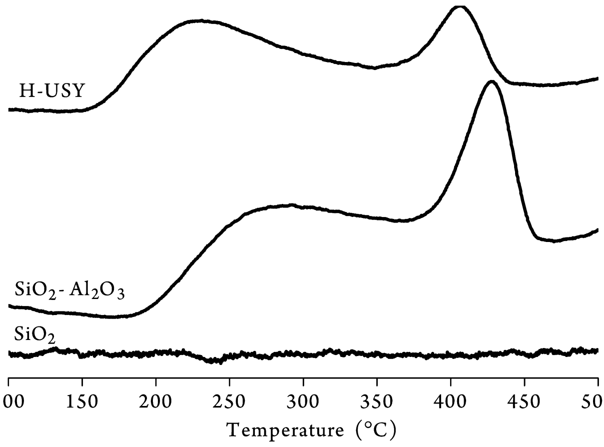


Figure 1. IPA-TPD of H-USY, SiO_2−Al_2O_3, and SiO_2.

On the basis of the number of IPA molecules decomposing at these temperatures, it is possible to measure the number of strong Brønsted acid sites in the sample.[65] The observance of peak in the temperature range of 175−350 °C corresponds to IPA which desorbs unreacted (at lower temperatures), after interacting with weak Brønsted acid sites and Lewis acid sites. The results obtained in this work are in good correlation with earlier reports.[65−67] However, quantification of the acid sites was not possible because of instrument limitations. To measure the acid amount in these catalysts, an NH_3-TPD study was also performed and the results reveal that, while H-USY (Si/Al = 15) has an acid amount of 0.55 mmol g^{-1}, SiO_2−Al_2O_3 has an acid amount of 0.63 mmol g^{-1} (Table S2a in the Supporting Information). Table S2b in the Supporting Information summarizes the properties (surface area, pore diameter, pore volume) of solid acid catalysts used in this study. It was purposefully decided to use a range of solid acid catalysts with different properties (surface area, pore structure, total acidity) to evaluate their activities in lignin conversions and to understand which properties play a role in achieving better activities.

3.3. Depolymerization of Dealkaline Lignin. *3.3.1. Evaluation of Catalytic Activity of Various Solid Acid Catalysts.* Typically, zeolites (H-USY (Si/Al = 15), H-MOR (Si/Al = 10), H-BEA (Si/Al = 19), H-ZSM-5 (Si/Al = 11.5)), clays (K10, montmorillonite; Al pillared), and metal oxides ($SiO_2-Al_2O_3$, Nb_2O_5, sulfated zirconia, MoO_3/SiO_2) were used as catalysts. The catalytic reactions were done in batch mode autoclaves with varying reaction parameters. The workup procedure, analysis of reaction mixtures by GC-FID, GC-TCD, GC-MS, HPLC, LC-MS, GPC, NMR, FTIR and calculations are described in section II (Figure S4) of the Supporting Information.

Initially the activity of solid acid catalysts was evaluated in the depolymerization of the dealkaline lignin, which has the highest molecular weight (60000 g mol^{-1}) among all six types of lignins and is also contaminated with Na and S (Table 1).

The depolymerization reactions of dealkaline lignin were carried out using various solid acid catalysts at 250 °C for 30 min, and the results are illustrated in Figure 2. After the reaction, the solvent (water + methanol) was evaporated and, from the obtained semisolid part containing aromatic monomers and unreacted lignin, aromatic products were selectively extracted using THF solvent (Figure S4 in the Supporting Information). For the extraction of aromatic monomers, THF was used, since dealkaline lignin is insoluble in this solvent. This precaution helped us to avoid contamination of lignin in the products. Under the reaction conditions without catalyst only 10% of aromatic monomers was formed, but when solid acid catalysts were used, the yield for aromatic monomers increased to 60% (THF-soluble products). Among the solid acid catalysts, the zeolites (H-USY, H-ZSM-5, H-MOR, H-BEA) having a definite structure (pore diameter, pore volume, channel structure) showed the highest activity for aromatic monomer formation (40–60% yield). Most of the other catalysts (clay, MoO_3/SiO_2, $SiO_2-Al_2O_3$) gave aromatic monomer yields of 25–40%. Efforts were taken to check the effect of total acid amount on the catalytic activity (Figure 2), but we could not draw an exact correlation. Similarly, efforts were made in drawing parallels between activities and other properties (surface area, pore volume, pore diameter; Table S2b in the Supporting Information) of catalysts but it was difficult to arrive at any definite conclusion because of the complexity of the reactions in terms of which bonds in lignin were interacting with catalytically active sites under the reaction conditions.

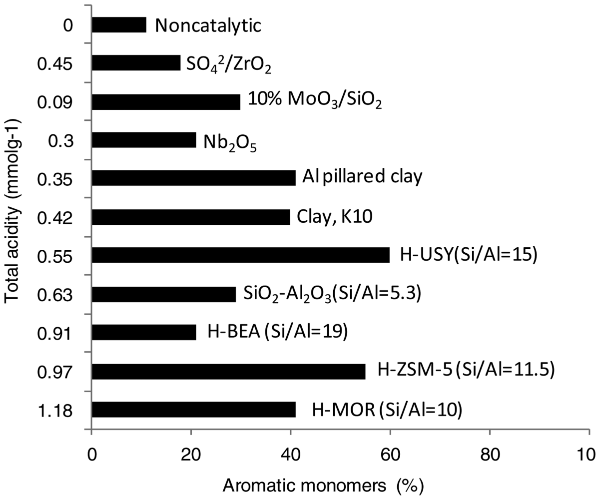


Figure 2. Catalyst evaluation study. Reaction conditions: dealkaline lignin (0.5 g), catalyst (0.5 g), H_2O/CH_3OH (1/5 v/v), 250 °C, 30 min, 500 rpm, 0.7 MPa of N_2, room temperature.

However, it can be suggested that, since no satisfactory correlations can be drawn, this implies that under the reaction conditions catalysts are probably undergoing changes that alter the catalyst properties. The THF-extracted products were identified using GC-FID and GC-MS (Figure S5 in the Supporting Information), and it was found that most of the products are aromatic monomers having molecular weights of 152–220 g mol^{-1}.

3.3.2. Confirmation of Aromatic Monomer Formation. The primary characterization of organic solvent soluble products (aromatic monomers) was done using GC-FID and GC-MS techniques. However, there might be a possibility of breaking down the lignin derived organic solvent (THF) and reaction solvent (water + methanol 5 + 25 mL) soluble oligomeric products during GC-FID and GC-MS analysis into aromatic monomers (as temperatures used for analysis are higher than the reaction temperature; see sections II.1.1 and II.1.3 in the Supporting Information for GC-FID and GC-MS).[68] To negate this effect, samples were analyzed by HPLC and LC-MS techniques (see sections II.1.4 and II.1.5 in the Supporting Information). A typical HPLC profile obtained for the reaction mixture is presented in Figure 3a. The products observed in HPLC analysis are similar to those identified using GC-FID and GC-MS techniques (Figure 3b). However, peaks due to a few products which can be observed in GC-FID analysis could not be seen in HPLC analysis because of overlapping of peaks for a few aromatic monomers (confirmed by injecting individual standards). Nevertheless, it is important to note here that from LC-MS analysis it can be suggested that no oligomeric products are formed (at least in large quantities) and the products observed are mainly aromatic monomers. Further, GC-FID analysis was also carried out at temperatures lower than the reaction temperature (250 °C), to see the effect of temperature on the decomposition of any oligomeric species. The oven program used was as follows: 100 °C (hold time, 4 min) → 5 °C min^{-1} ramp rate →150 °C (hold time, 2 min) → 5 °C min^{-1} ramp rate →200 °C (hold time, 10 min), injector temperature (200 °C), detector temperature (200 °C) were used. The temperatures used were lower than the reaction temperature of 250 °C. In this analysis, similar peaks were identified when GC-FID and GC-MS analyses were done under normal conditions was seen (see sections II.1.1 and II.1.3 in the Supporting Information). These results imply that the majority of the products formed under the reaction conditions are aromatic monomers and, under GC-FID and GC-MS conditions employed in this study, products do not undergo any structural changes.

GPC analysis was performed for three samples, namely dealkaline lignin, methanol-soluble reaction mixture (dealkaline lignin reaction), and THF-soluble products (dealkaline lignin reaction) (see section II.1.6 in the Supporting Information). Dealkaline lignin dissolved in DMF was analyzed on DMF-GPC (Figure 4), and data resemble those from MALDI-TOF analysis (Table 1). In the case of the methanol-soluble reaction mixture (Figure 4), a peak was observed almost overlapping with the

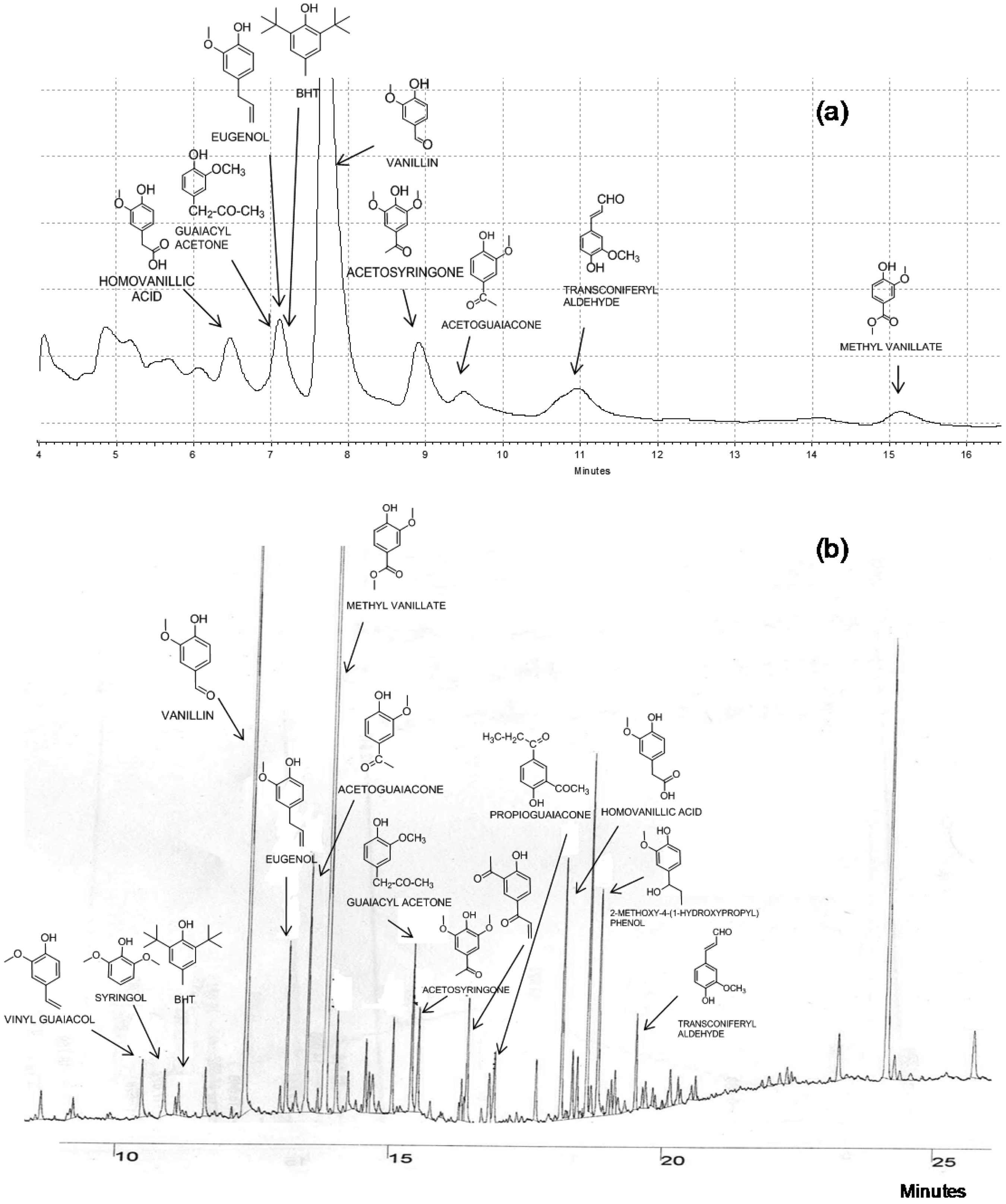


Figure 3. Analysis of dealkaline lignin reaction mixture: (a) HPLC analysis; (b) GC analysis. Reaction conditions: dealkaline lignin (0.5 g), $SiO_2-Al_2O_3$ (0.5 g), H_2O/CH_3OH (1/5 v/v), 250 °C, 30 min, 500 rpm, 0.7 MPa of N_2, room temperature.

eluting solvent (DMF) peak and thus it is suggested that this peak must be arising due to the presence of low-molecular-weight (M_n ca. <500 g mol^{-1}) products. The absence of a peak for high-molecular-weight products implies that the lignin is converted into products with low molecular weight. These data imply that in our reaction almost complete conversion of lignin is possible. However, the conversion may not be completely into aromatic monomers. The GPC study performed for THF-

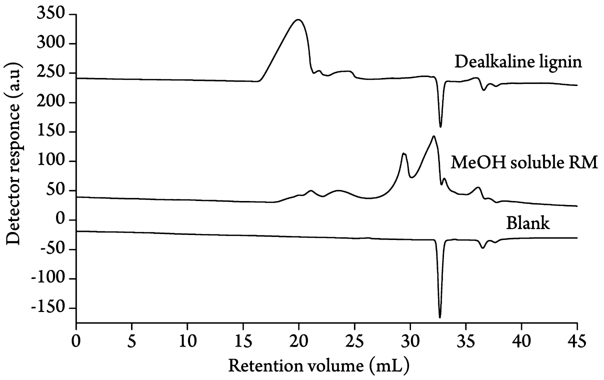


Figure 4. GPC (DMF) analysis of dealkaline lignin, MeOH-soluble reaction mixture, and blank (only DMF).

soluble products also confirmed that there is no contribution from high-molecular-weight products (oligomeric species) in the THF-soluble fraction (Figure 5). Since in this sample the compounds were also eluting along with the solvent (THF), this indicates that the products have lower molecular weights (M_n <500 g mol^{-1}). These results are in line with earlier characterizations such as those by GC-FID, GC-MS, HPLC, and LC-MS. However, it is important to note here that, though high-molecular-weight products were not observed in GPC analysis, some unknown peaks seen in GC-MS reveal that at least a few products with higher molecular weight (M_n = 300−600 g mol^{-1}) are formed during the reaction.

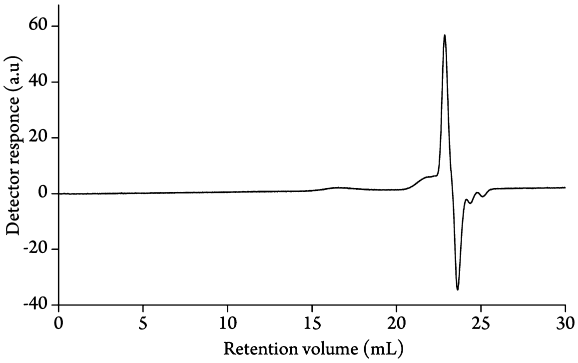
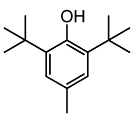
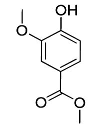
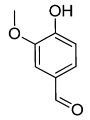
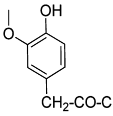
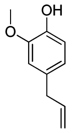
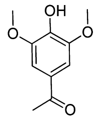
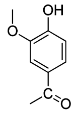
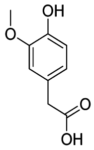
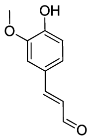
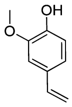


Figure 5. GPC (THF) for THF-soluble products.

To further confirm that the products formed are aromatic monomers, THF-soluble products were also analyzed by the MALDI-TOF technique to verify that no high-molecular-weight fragments (1000−10000 g mol^{-1}) are formed. The products obtained with all of the catalysts remained almost the same; however, the quantities obtained were altered. To quantify the formation of aromatic monomers, GC-MS identified aromatic compounds were commercially procured and were injected on GC-FID and GC-MS columns to draw calibration curves. From the calibration curve drawn we could quantify ca. 90% (out of 60%) of THF-soluble products obtained in the depolymerization of dealkaline lignin using H-USY catalyst as aromatic monomers (Table 2). This information corroborates the fact that the oligomeric products formed (see the paragraph above) do not contribute >10% to the total yield. Moreover, in addition to matching the retention times (of standards and THF-soluble products obtained in the reaction) on GC-FID and GC-MS (Figure S5 in the Supporting Information), the fragmentation patterns obtained in GC-MS for THF-soluble products also matched those of the commercially procured samples. Considering the fact that most of the (ca. 90%) THF-soluble products are aromatic monomers, the same term is used to describe the depolymerization products obtained in our work.

Table 2. Quantification of Monomeric Products in Dealkaline Lignin Reaction[a]

Compounds identified	Quantity (%)	Compounds identified	Quantity (%)
 BHT	2%	 Methyl vanillate	8%
 Vanillin	30%	 Guaiacyl acetone	24%
 Eugenol	1%	 Acetosyringone	2%
 Acetoguaiacone	3%	 Homovanillic acid	10%
 Trans-coniferyl aldehyde	6%	 Vinyl guaiacol	3%

[a]Reaction conditions: dealkaline lignin (0.5 g), SiO_2−Al_2O_3 (0.5 g), H_2O/CH_3OH (1/5 v/v), 250 °C, 30 min, 500 rpm, 0.7 MPa of N_2, room temperature.

The functional groups (−OCH_3, OH, −CHO, −CH_3) present in lignin as evidenced by IR and NMR characterizations (see section 3.3.3) were also found in aromatic monomeric products obtained after solid acid catalyzed depolymerization of dealkaline lignin.

Elemental analysis of methanol + water soluble products showed the presence of C (67%) and H (6%). This matches well with the elemental analysis of lignin (Table 1; C 65% and H 7%, dealkaline lignin), indicating that almost no loss of any functional groups in the product is possible. However, a slight increase in C content and reduction in H content implies that addition of carbon in the structure might be possible (see section 3.3.3). The molecular formula thus calculated for products, $C_{9.5}H_{11}O_3$, almost matches that for dealkaline lignin, $C_9H_{10.62}O_{2.89}S_{0.06}$. The absence of S-containing functional groups in the product (dealkaline lignin has a 1% presence of S; Table 1) can be due to either adsorption of it on catalyst or its insolubility (S-containing product) in the THF solvent in which products are extracted. UV−vis spectroscopic analysis of the THF-soluble products was carried out, but since it is a complex mixture of similar types of aromatic monomers, this technique was not quite suitable for the identification of exact product formation.[69]

3.3.3. Correlation between Lignin and Aromatic Monomer Structures and Functional Groups. In order to establish a correlation between the structure of the starting material (lignin) and aromatic monomers formed, it was decided to perform IR analysis of dealkaline lignin and THF-soluble products. As observed from Figure 6, the dealkaline lignin shows an intense peak at 1118 cm^{-1} for C−O stretching assigned to alcohols, esters, and ethers. Considering the structure of lignin, we tend to assign this peak mainly to ether and alcohol groups. In the range of 700−850 cm^{-1} peaks due to aromatic C−H (oop) are expected. The peaks at 1022 and 1265 cm^{-1} can be assigned to C−O stretching in the alkoxy functional group. The peaks for −OH in phenol can also appear in the range of 1150−1250 cm^{-1}. Typically, from 1450 to 1600 cm^{-1} multiple peaks for C=C stretching in aromatics (in the ring) are observed and in the spectrum for dealkaline lignin we could see peaks at 1455 and 1595 cm^{-1} along with several other weak peaks. The observance of a peak at 1690 cm^{-1} is due to C=O stretching in an *α*,*β*-unsaturated aldehyde or ketone.

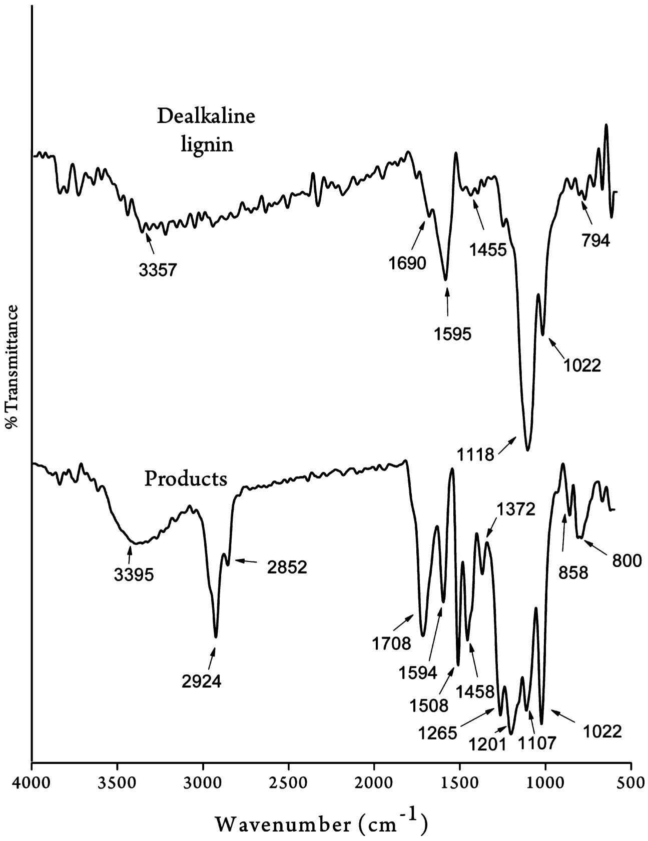


Figure 6. FTIR spectra of dealkaline lignin and products.

A glance at the IR spectrum for THF-soluble products (Figure 6) shows peaks due to C−H bending (oop) in the range of 700−850 cm^{-1}. A careful look indicates that the intensity of peaks at 1022 and 1265 cm^{-1} due to alkoxy groups has increased, indicating that the presence of $-OCH_3$ has increased after depolymerization. The retention of the peak at 1107 cm^{-1}, though with lower intensity, indicates that few of the products still have ether bonds or alcohol groups. On the basis of the results obtained in our work, we suggest that this peak is mainly due to alcoholic groups. The appearance of a peak at 1372 cm^{-1} due to sp^3 C−H bending/rocking implies the presence of alkyl groups. The intensities of the peaks from 1450 to 1600 cm^{-1} again emphasize that the aromaticity is intact in the products. A very intense peak at 1708 cm^{-1} can be assigned to C=O stretching in *α*,*β*-unsaturated aldehydes (or ketones). The new peak appearing at 2852 cm^{-1} is attributed to the presence of C−H stretching in the aldehyde group. Moreover, another peak at 2924 cm^{-1} can be assigned to C−H stretching in alkanes/alkyl groups. To confirm the cleavage of the Ar(C)−O−Ar bond to form the Ar(C)−OH bond, a broad peak appearing at 3395 cm^{-1} is helpful. Overall, it can be clearly seen that the appearance and increase in the intensities of peaks of $-OCH_3$, −CHO, and $-CH_3$ groups and the decrease in the intensity for signals for the ether bond (1118−1107 cm^{-1}) demonstrate that lignin undergoes a depolymerization reaction and gives rise to monomers which have functional groups as mentioned above.[70] A glance at Table 2, where we have summarized the products formed in our reaction (from GC-MS, LC-MS) with different functional groups, correlates well with the IR data.

To learn more about the presence of functional groups in dealkaline lignin and products obtained after depolymerization, we have performed a ^{1}H and ^{13}C NMR study (700 MHz; see section II.1.7 in the Supporting Information). ^{1}H NMR spectra for both dealkaline lignin and products are presented in Figure 7. As can be seen, most of the peaks present in lignin are retained in the products; however, there is a difference in the intensities. Typically, peaks for primary, secondary, and tertiary alkyl groups are observed around 0.8−1.70 ppm ($Ar-C(CH_3)_3$ proton at 1.4 ppm) in both samples. The appearance of peaks at 2.06, 2.16 ppm and at 2.56, 2.61 ppm can be assigned to the proton *α* to the carbonyl group ($Ar-CO-CH_3$) or benzylic proton ($Ar-CH_3$) or ester ($Ar/R-CH_2-COOR/Ar$) groups.

The appearance of a peak at 3.9 ppm is due to the presence of an ester group ($Ar/R-COOCH_2R/Ar$). A new peak present in products at 3.71 ppm is due to the substitution of $-OCH_3$ in the aromatic ring. Peaks due to aromatic protons appear between 6.5 and 8.5 ppm. A careful look at the spectra shows that peaks due to the aldehyde (−CHO) group (9.67 and 9.74 ppm) show an increase in intensity in products in comparison to those of lignin. The ^{1}H NMR data thus bring us to the conclusion that an increase in methoxy groups and aldehyde groups is in line with the IR data and eventually corroborates our efforts to claim that depolymerization of lignin gives the products shown in Table 2. ^{13}C NMR spectra recorded for both dealkaline lignin and products are presented in Figure 8. As can be observed, all of the peaks appearing in the lignin sample are also retained in the products, indicating that the overall structure of lignin (and substituents) is retained after depolymerization. Peaks in the range of 20−50 ppm are typically assigned to CH_3CO- species or R_3CH species. The observance of peaks at 55−90 ppm is assigned to the sp^3 carbon appearing next to oxygen ($Ar/R-CH_2-O-$; $Ar_2/R_2-CH-O-$; Ar_3/R_3-C-O-).

It is also seen that between 30 and 60 ppm there are peaks due to $-C(CH_3)_3$. In the case of products, the appearance of a new peak at 54.02 ppm similar to the new peak appearing at 3.71 ppm in ^{1}H NMR indicates the formation of $-O-CH_3$ groups. Peaks due to sp^2 carbons (C=C, 110−150 ppm) in aromatics (125−150 ppm) and alkenes (110−140 ppm) are clearly visible in both spectra. The peaks between 175 and 180 ppm are assigned to carbon in ester groups ($Ar/R-CO-R/Ar$), and interestingly it can be seen that in products the peak intensity is decreased, implying that during depolymerization of lignin these bonds are cleaved. At the same time, the peak intensity for 192−193 ppm

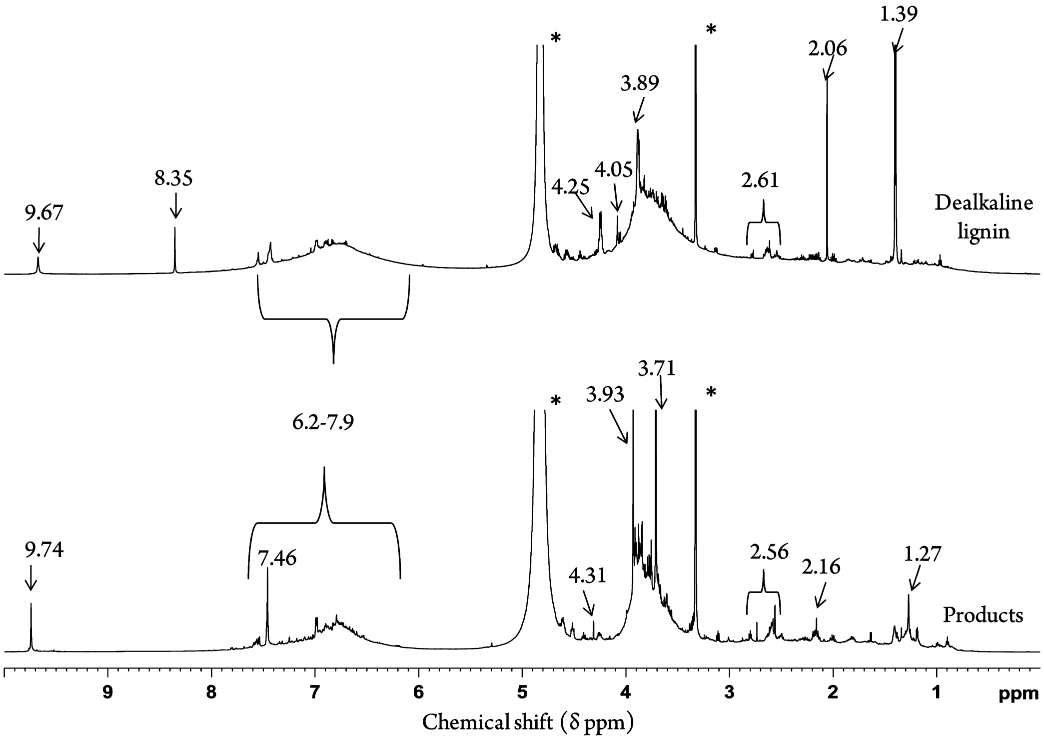


Figure 7. ^{1}H NMR spectra of dealkaline lignin and products (asterisks denote peaks due to solvent).

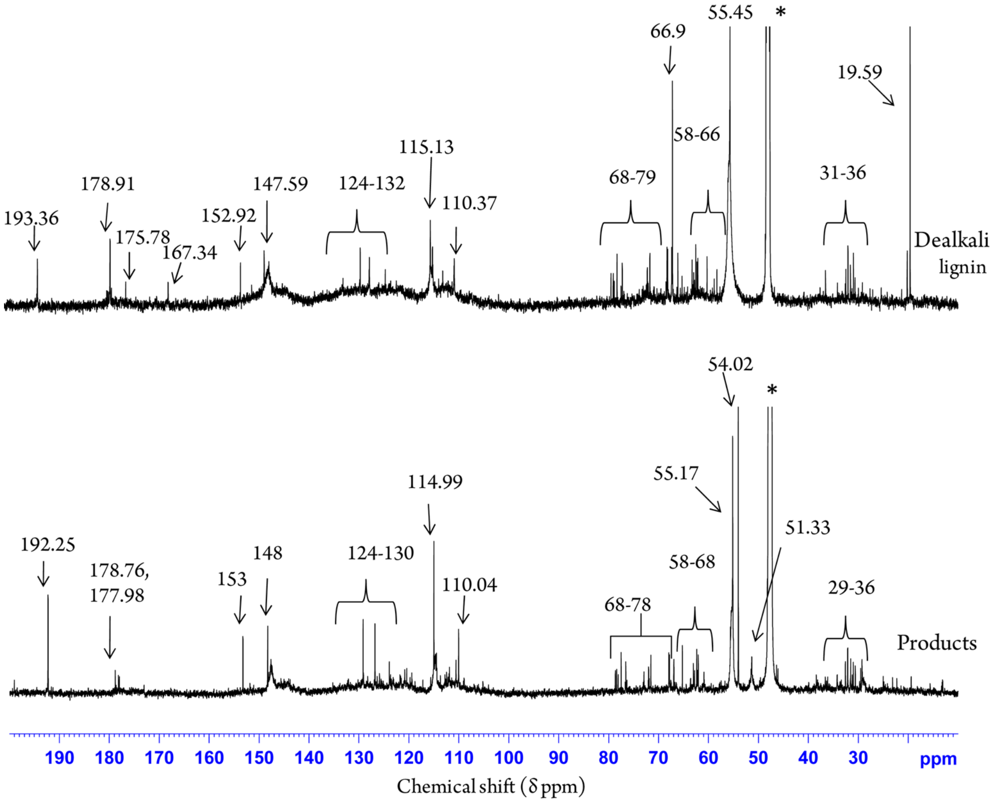


Figure 8. ^{13}C NMR spectra of dealkaline lignin and products (asterisks denote peaks due to solvent).

due to aldehyde (Ar/R−CO−H) is increasing in products in comparison to those of lignin. These observations also align well with the ^{1}H NMR and IR data. The absence of a peak at 167.34 ppm in products corresponding to ester groups indicates that under the reaction conditions breaking of the C−O bond is feasible. It is important to call attention to the fact that in HPLC (Figure 3a) and GC (Figure 3b) analysis we could detect similar compounds (Table 2). A few small peaks present in NMR spectra must be arising from various substitutions on aromatic rings (lignin and products), but due to the complex structure of lignin it would be very difficult to assign all of the peaks (due to varying environments, chemical shifts will vary). All of these analyses help us to establish the fact that the few functional groups and aromaticity present in lignin are retained in products and identification of products can be achieved with the help of IR and NMR spectroscopic techniques along with GC, GC-MS, HPLC, and LC-MS characterizations. Additionally, it is confirmed that due to the cleavage of several linkages in lignin (ether, C−C) the products have higher numbers of hydroxyl (−OH) and methoxy ($-OCH_3$) groups. It is also important to note here that insertion of these groups is possible, since solid acid catalysts are known to catalyze hydrolysis and methanolysis reactions.

Under the reaction conditions (250 °C, 30 min, 500 rpm, 0.7 MPa N_2, room temperature) formation of BHT (butylated hydroxytoluene; Table 2), an aromatic monomer having tertiary butyl groups, was observed. The IR (1372, 2924 cm^{-1}), ^{1}H NMR (1.39 ppm), and ^{13}C NMR (30−60 ppm) data suggest formation of this compound in the products. The mechanism behind the formation of BHT from lignins is not clear at the moment, but earlier reports also suggest the formation of this product from lignin and show that this product is stable.[71−74] In our studies also, we checked the stability of BHT at 250 °C (30 min, 500 rpm, $SiO_2-Al_2O_3$), and it was observed that only <5% BHT undergoes conversion to yield unknown products (not detected on GC-FID), indicating that the product is stable under our reaction conditions.

Thus, we could conclude here that, in the methodology described here for lignin depolymerization using solid acid catalysts, the depolymerization products retain the characteristics of the substrate molecule. However, it should be noted here that, though most of the products are identified as aromatic monomers from various techniques employed in this work, it is still difficult to assess the exact structure, since most of the products have two or more substituents on the aromatic ring and hence there is a possibility of the formation of isomers (which are difficult to separate on GC-FID or GC-MS or HPLC or LC-MS and identify from fragmentation profiles and spectroscopic techniques).

3.3.4. Analysis of Gases and Reproducibility of Catalytic Activities.

To check whether under the reaction conditions any gaseous products are formed, the gas released from the reactor was analyzed (online sampling was done) using GC-TCD (see section II.1.2 in the Supporting Information). However, we could not detect the formation of gaseous products such as CO, CO_2, CH_4, H_2, and C_2-C_4. These observations indicate that the lignin conversion reactions are selective toward the formation of aromatic monomers. Interestingly, in all of the reactions 90 ± 10% (weight basis) mass balance (see section II.3 in the Supporting Information) was obtained. To check the reproducibility of our results, care was taken to carry out all the reactions two or three times.

An error of ±3% was observed in obtaining the THF-soluble products (weight basis), and the peak intensities and areas under the peak were also within the analysis limits of ±4%. These results prove that under the reaction conditions employed (250 °C; 30 min; water/methanol, 1/5 v/v) to depolymerize dealkaline lignin having 60000 g mol^{-1} molecular weight, solid acid catalysts can give aromatic monomers in 25−60% yields.

3.3.5. Comparison of Catalytic Activities between Solid Acids and Homogeneous Acids.

The activity of solid acid catalysts in the depolymerization of lignin was compared with that of homogeneous acids such as HCl and H_2SO_4 under similar reaction conditions (with an initial pH of 2; 250 °C; 30 min; water/methanol 1/5 v/v), and we observed ca. 29% and 39% of THF-soluble products, respectively. However, the THF-soluble products obtained in the homogeneous acid catalyzed reactions were not all aromatic monomers, which was confirmed by GC-FID and GC-MS analysis (Figure S6 in the Supporting Information). A few products with *m*/*z* values of 152 and 166, corresponding to aromatic monomers, were also observed in the noncatalytic reaction. Along with this, *m*/*z* values of 220, 252, 234, and 270 which correspond to higher molecular weight fragments were also observed. Thus, it can be concluded that the homogeneous acids HCl and H_2SO_4 depolymerize dealkaline lignin to give mainly dimers or oligomers as products, instead of giving aromatic monomers as the major products under the above reaction conditions.

3.4. Study of the Reuse, Stability, and Characterization of H-USY Catalyst.

Since among all the catalysts evaluated in the depolymerization of dealkaline lignin reaction the H-USY catalyst showed (Figure 2) the highest aromatic monomer formation (60%), we undertook further studies with this catalyst. To test the stability of H-USY catalyst, recycle studies were done after washing the catalyst recovered from earlier run with water/methanol (1/5 v/v, 60 mL) and then drying it (at 60 °C, overnight in a drying oven) and further calcining it at 550 °C for 600 min in air. In the first run the THF-soluble product yield was 60%, which decreased to 36% in the second run; in the third run the catalyst gave only 22% yield, thereby showing a drastic decrease in the activity of the catalyst (Figure S7 in the Supporting Information). This decrease in the catalytic activity can be expected, since dealkaline lignin contains ca. 29 mg of Na (per 1 g of lignin) which can possibly poison the Brønsted acid sites present in the H-USY catalyst. In this way the activity of the solid acid catalyst in each successive run was prone to decrease. To check this hypothesis, we first subjected fresh and spent H-USY catalysts to an NH_3-TPD study. The results indicated that, in comparison to the 0.55 mmol g^{-1} acid amount present in the fresh catalyst, the spent catalyst showed 0.05 mmol g^{-1} of amount of acid. Moreover, the complete loss of strong acid sites was observed in spent catalysts (Figure S8 in the Supporting Information). This result is in line with the consideration that Na may poison the catalytically active site (Figure S9 in the Supporting Information). For an investigation on whether this loss of acid sites is due to Na contamination, we subjected fresh and spent catalysts to ICP-OES characterization. The results indicate (Table S3 in the Supporting Information) that in the spent catalyst (19 mg) a greater amount of Na is present in comparison to that in fresh catalyst (0.46 mg). A quick calculation suggests that an increase in Na content by 18.54 mg (0.8060 mmol) in the spent catalyst is capable of killing all the acid sites. Again, this information helps in suggesting that the possible contamination of acid sites by Na might be the reason behind the loss in activity. To investigate further, we carried out a metal-exchange study for H-USY (Si/Al = 15) at 60 °C using an Na concentration of 240 ppm. It should be noted here that in 1 g of lignin 29 mg of Na is present, which amounts to 480 ppm; on considering, this we charged 0.5 g of lignin in 60 mL of solvent for the reaction (i.e., in the reaction 480 ppm of Na is charged). In view of this in our study on metal exchange, we used a 240 ppm solution (50% of actual). The fresh and metal-exchanged catalysts were characterized with XRD, ICP-OES, and NH_3-TPD. The XRD patterns of fresh and metal-exchanged catalysts showed no detectable change in the peak positions, which emphasizes the fact that just on stirring of the catalyst in water at

60 °C and after the metal exchange treatment, the morphology of the zeolites is retained (Figure S10 in the Supporting Information). ICP-OES and NH_3-TPD data for fresh and metal-exchanged catalysts are presented in Table S4 in the Supporting Information. The presence of Na can be clearly seen in the catalyst after the metal exchange treatment; however, its concentration was too low (0.218 g). This might lead to a decrease in the acid amount for treated catalysts. The NH_3-TPD study revealed that, in the case of H-USY catalysts, the acid amount decreased to 0.46 mmol g^{-1} (0.06 mmol g^{-1} of weak acid sites and 0.40 mmol g^{-1} of strong acid sites) from 0.55 mmol g^{-1} (fresh) after 240 ppm treatment. Thus, the strong acid sites were reduced during the metal-exchange study. From this study it can be stated that the presence of Na in lignin has an effect on reduction of the catalyst activity. In contrast with these results, however, in lignin reaction work we observed a very large decrease in the number of acid sites, which points to the fact that under lignin reaction conditions (250 °C) some other changes are also happening in the catalyst which cause it to lose acid sites.

Subsequently, to check the theory of Na contaminating the acid sites, H-USY catalyzed depolymerization of organosolv lignin was attempted. As observed from ICP-OES and SEM-EDAX analysis (Table 1), organosolv lignin is free of Na and S contaminants and, hence, it was expected that H-USY used in these reactions would show repeated activity in recycle runs (as there would be no poisoning of acidic sites by Na). Nevertheless, also in these reactions the H-USY catalyst (recycled in a similar fashion as was done in case of dealkaline substrate) showed a decrease of ca. 70% in the catalytic activity in repeated runs (Figure S11 in the Supporting Information). This result was unexpected, since we believed that the loss of activity was due to poisoning of Brønsted acid sites by Na and in the case of organosolv lignin Na is not present in the substrate. Again we performed the ICP-OES analysis of the spent catalyst and we did not find any increase in Na content in the spent catalyst (0.46 mg or 15 ppm) in comparison to the fresh catalyst (0.46 mg or 15 ppm). However, when spent catalyst from the organosolv reaction was analyzed by the NH_3-TPD technique, a decrease in the acid amount was observed. To understand then the real cause behind the decrease in the activity, the H-USY catalyst was characterized in detail using various techniques (XRD, ^{29}Si and ^{27}Al NMR, and N_2 sorption study). The XRD analysis of spent H-USY (Figure S12 in the Supporting Information) catalyst showed a slight decrease in the intensity of the peaks, which implies that the crystallinity of the material has decreased slightly. The ^{29}Si and ^{27}Al NMR spectra obtained for fresh and spent catalysts (Figures S13 and S14 in the Supporting Information) reveal that the environment around Si and Al has changed, thus indicating that the catalyst has undergone some deformation during the course of the reaction. However, from an ICP-OES analysis of fresh and spent catalysts, we found that the Si/Al ratio remains constant in both samples (14.7 for fresh and 14.2 for spent catalyst). This implies that the catalyst H-USY is undergoing some structural changes without losing any element. The N_2 sorption studies (Table S5 in the Supporting Information) of the spent H-USY catalyst showed a reduction in the surface area of the catalyst from 873 m^2 g^{-1} (fresh) to 303 m^2 g^{-1} (spent), a decrease in pore volume from 0.45 cm^3 g^{-1} (fresh) to 0.14 cm^3 g^{-1} (spent), and an increase in pore diameter from 0.75 nm (fresh) to 1.51 nm (spent). All of these studies support the fact that structured catalysts (having a definite pore and channel structure) such as H-USY, even though capable of giving a very high yield for aromatic monomers (ca. 60%), are not stable under the reaction conditions.

3.5. Study on Amorphous $SiO_2-Al_2O_3$ Catalysts.

3.5.1. Effect of Lignin Substrates and Other Reaction Parameters. As mentioned above, since structured catalysts were not stable under the reaction conditions, we continued our studies using an amorphous solid acid catalyst such as $SiO_2-Al_2O_3$. From earlier experience, first the stability of the catalyst in the depolymerization of organosolv and ORG lignin was checked by subjecting the catalyst to recycle studies (before the next run, the catalyst recovered from the earlier run was washed with water/methanol (60 mL), dried in an oven at 60 °C overnight, and calcined in air at 550 °C for 600 min). As is known from Table 1, both of these substrates do not contain any Na or S and, hence, if there would be any decrease in the activity it would be only because of morphological changes happening in the catalyst. The catalytic results for these substrates are illustrated in Table 3, and as can be seen, the $SiO_2-Al_2O_3$ catalyst showed a similar activity in a minimum of three recycle runs.

Table 3. Catalyst Recycle Study for Organosolv and ORG Lignin[a]

	catalyst run		
lignin	first	second	third
organosolv	35	33	32
ORG	60	60	59

[a] Reaction conditions: organosolv/ORG lignin (0.5 g), $SiO_2-Al_2O_3$ (0.5 g), CH_3OH/H_2O (5/1 v/v), 250 °C, 30 min, 1000 rpm, 0.7 MPa of N_2.

In these reactions, DEE and chloroform were used to extract the products obtained in organosolv lignin and ORG lignin reactions, respectively (Figure S4 in the Supporting Information), since both of these substrates are soluble in THF solvent (Table S1 in the Supporting Information), which is used for extracting products in dealkaline lignin reactions. Interestingly, $SiO_2-Al_2O_3$ gave a 60% yield for aromatic monomers in a minimum of three runs when ORG lignin with M_n = 4177 g mol^{-1} (Table 1) was used as a substrate. These results are contradictory to earlier studies with H-USY, where a decrease in activity in the reactions with organosolv was observed. Therefore, the results obtained with $SiO_2-Al_2O_3$ encouraged us to work on this catalyst.

As shown in Figure 2, $SiO_2-Al_2O_3$ catalyst is capable of converting dealkaline lignin to yield 29% of aromatic monomers at 250 °C within 30 min when stirring was maintained at 500 rpm. To improve the yields of aromatic monomers obtained from dealkaline lignin with $SiO_2-Al_2O_3$ as a catalyst, the reaction temperatures were altered. When the reaction temperature was increased from 250 to 270 °C, a decrease in the product yield (15%) was observed which was due to the formation of degradation products such as char (visible by a black THF-insoluble solid). Further, the reaction temperatures were reduced to 230 and 215 °C and again lower yields were obtained (25% and 1%), which confirmed that 250 °C is the optimum temperature for this reaction.

Further, the role of pressure was investigated by charging 0.1 and 0.7 MPa pressures of N_2 in the autoclave at room temperature and the reactions were performed at 250 °C for 30 min in water/methanol (1/5 v/v). With an initial N_2 pressure of 0.7 MPa, a 29% yield was possible; it decreased to 24% when 0.1 MPa of N_2 was charged. This indicates the possible dependence of activity on overall final pressures, which were found to be 7.5 MPa with 0.7 MPa of N_2 charged at room temperature in comparison to 6.5 MPa in the case when 0.1 MPa of N_2 was charged at room temperature.

Now, to find milder reaction conditions, the reactions were performed at lower temperature and pressure. When SiO_2–Al_2O_3 catalyzed depolymerization of dealkaline lignin was carried out at 215 °C with 0.7 MPa N_2 at room temperature, only a 1% yield was achievable. However, under these conditions a final pressure of only 4.0 MPa was observed. To investigate whether boosting the final pressure from 4.0 to 7.0 MPa would help us achieve higher yields at 215 °C, we charged 2.5 MPa of N_2 (at room temperature) instead of 0.7 MPa N_2 (at room temperature) and conducted the reaction at 215 °C for 30 min. In this reaction, the final pressure reached 7.0 MPa; however no increase in yield was achieved (1%). This emphasizes that both temperature and pressure are important parameters in these reactions and that 250 °C and 7.5 MPa of final pressure are required to achieve the maximum yields.

The effect of solvent on the conversion of lignins was also explored, and it was found that reactions conducted with pure water did not proceed, possibly due to a lower final pressure (5.0 MPa at 250 °C). From our earlier discussions it is evident that final pressures of at least 6.5 MPa are required to achieve respectable yields. Moreover, as observed from Table S1 in the Supporting Information, dealkaline lignin is not completely soluble in water, which may hamper the reaction rate. With water/methanol and water/ethanol solvent systems similar product yields (29%) are obtained. Subsequently water to methanol ratios (v/v) were varied from 1/5 (29% yields) to 1/1 (22% yield) to 5/1 (1% yield), but the best result was obtained only with a 1/5 ratio (29%). This is due to the fact that when the water concentration was increased the final pressures were decreased (7.5 MPa at 1/5 v/v, 6.0 MPa at 1/1 v/v, and 5.2 MPa at 5/1 v/v water to methanol ratios).

In addition to these studies on the water/methanol solvent system, other solvents such as phenol, acetone, THF, and dioxane were used in the reaction, as the literature reports the use of these solvents in the depolymerization of lignin.[24,28,75] It is also mentioned in the literature that phenol can act as a capping agent to avoid the repolymerization of aromatic products and thus improve the product selectivity.[76,77] In our reaction we do not expect repolymerization products, since we use conditions milder than those reported where phenol was used.[78] We checked the solubility of dealkaline lignins in these solvents and found that it is almost completely soluble in all solvents. Before using these solvents in the reaction, we checked the stability of these solvents at 250 °C for 60 min in the presence of SiO_2–Al_2O_3 catalyst and found out that all of these solvents undergo self-decomposition reactions and form various products detected in GC-FID. Considering this, we did not carry out lignin depolymerization reactions with these solvents. Since the final pressures would be very high (>8.0 MPa), reactions were not done using only methanol as solvent, as our reactor system had a limitation of working up to only 10 MPa pressures. Moreover, from a safety point of view it was not advisible to mix methanol and solid acid catalysts at high temperatures, since methanol can give rise to the highly volatile dimethyl ether as a product[79−81] that would increase the pressures beyond our reactor limits. Also, the formation of dimethyl ether (DME) may trigger some other reactions with lignin and aromatic monomers. The reaction of the water/methanol (1/5 v/v) system with solid acid catalysts (H-USY) was performed at 250 °C for 30 min in the presence of 0.7 MPa of N_2, to check the formation of dimethyl ether. The gas phase (N_2) was analyzed using GC-TCD, and the reaction mixture was analyzed using GC-FID, but no trace of DME was observed during the analysis. Thus in our work, with the addition of water along with methanol even in the presence of solid acid catalysts we believe that DME formation can be suppressed.

After the reaction conditions for the depolymerization of dealkaline lignin with SiO_2–Al_2O_3 as catalyst were narrowed down to obtain higher product yields at 250 °C and 0.7 MPa of N_2 pressure (room temperature) using water/methanol (1/5 v/v), all further reactions were carried out under similar conditions. To improve the yields and to make the amorphous SiO_2–Al_2O_3 catalyst as efficient as zeolites in yielding aromatic monomers, the reaction was carried out for 90 min instead of the usual 30 min. In this reaction, a very high yield of 56% was achieved for aromatic monomers. A further increase in time duration (120 min) did not improve the yields (54%), but the formation of char was observed in a minor amount (visible as a black solid). The effect of mass transfer limitations was explored by varying the stirring speed to improve the catalyst–substrate interactions. A stirring rate of 500 rpm gave a yield of 29% (30 min), which could be enhanced to 59% (30 min.) by increasing the stirring rate to 1000 rpm. However, a further increase in stirring rate (1200 rpm) did not yield any better results.

3.5.2. Isolation of Aromatic Monomers by Column Chromatography. Once the optimization of reaction conditions with SiO_2–Al_2O_3 catalyst for the depolymerization of dealkaline lignin was achieved, we undertook the task of identifying and isolating the products obtained in our work (see section II.4 in the Supporting Information). As shown in Figure 3a and given in Table 2 (for quantification of products), we could already identify most of the products as aromatic monomers. Next, the fact that it is a difficult task to isolate those products in pure form from the product mixture, especially in the case of lignin conversions, hardly needs emphasizing. However, we undertook this work of separating products using column chromatography and we could successfully isolate three products in pure form: namely, vanillin (*m*/*z* 152), methyl vanillate (*m*/*z* 182), and butylated hydroxytoluene (BHT) (*m*/*z* 220) (Table 2; see also section II.4, Figure S15, and Table S6 in the Supporting Information).

3.5.3. Depolymerization of Various Lignin Substrates. After the optimization of the reaction conditions for the depolymerization of dealkaline lignin (250 °C, water/methanol 1/5 v/v, SiO_2–Al_2O_3, 30 min, 1000 rpm, nitrogen 0.7 MPa, room temperature) various other lignin substrates such as alkali lignin, bagasse lignin, and ORG and EORG lignins were evaluated under similar conditions. Figure 9 shows that, except for organosolv lignin, all other lignins gave aromatic monomers with 52−60% yield. It is important to note here that these results clearly prove that our catalytic system is able to convert lignin from various sources with diverse physical and chemical properties, as mentioned in Table 1. In addition, it is important to state here that for different lignins we used different solvents for the extraction of products formed (see Table S1 and Figure S4 in the Supporting Information), taking into account the solubility of lignins in solvents. This was done to avoid any contamination from lignin getting dissolved in the solvent (if the same solvent is used for workup in all of the reactions with different lignins, then there is a possibility of lignin also becoming soluble in the solvent).

We believe that, when solid acid catalyzed depolymerization studies are performed in this work, it is possible to typically cleave

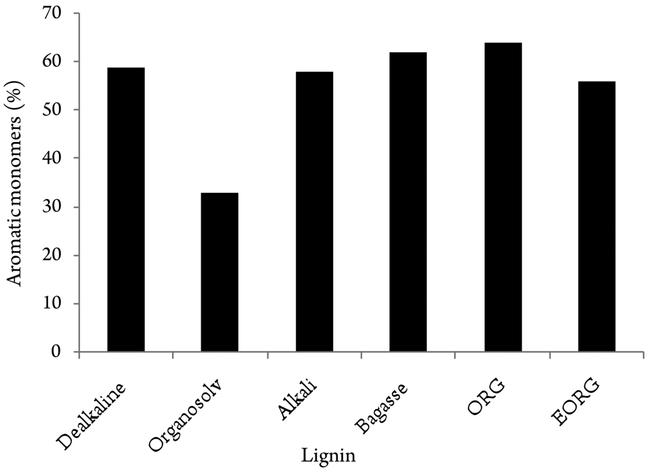


Figure 9. Effect of various lignin substrates. Reaction conditions: lignin (0.5 g), $SiO_2-Al_2O_3$ (0.5 g), H_2O/CH_3OH (1/5 v/v), 250 °C, 30 min, 1000 rpm, 0.7 MPa of N_2, room temperature.

β-O-4 and α-O-4 ether linkages present in lignin while C−C bonds remain intact. From our results it was observed that, even after the optimization of reaction conditions (temperature, pressure, time, and rpm) we could not attain a monomer yield of above 60%. From several literature reports, it was observed that in lignin (softwood or hardwood) the percentage of various types of ether linkages in lignin is ca. 65−70%.[48,82−86] Hence, it is proposed that under our reaction conditions only these ether linkages are broken down by way of hydrolysis, thereby giving an aromatic monomer yield only up to 60%.

3.5.4. Study on Reuse, Stability, and Characterization of $SiO_2-Al_2O_3$ Catalyst. In the catalyst recyclability study, $SiO_2-Al_2O_3$ was recovered from the reaction mixture, washed (with water/methanol, 60 mL), dried overnight in an oven, calcined in air (550 °C, 600 min), and then subjected to the next reaction. It was found that with organosolv and ORG (Table 3) lignin we could obtain similar yields (ca. 60%) in a minimum of up to three runs. However, with dealkaline lignin the activity decreased. In the first run the product yield was almost 57%, and in the second run the yield decreased to 33%; after the third run, the catalyst became inactive (Figure S16 in the Supporting Information). This showed that for dealkaline lignin substrate even the amorphous catalyst could not be recycled. This happened since dealkaline lignin contains Na and S as impurities (Table 1) which may poison the catalytically active sites and there may also be morphological changes happening in the catalyst.

To study the reason behind the deactivation of spent $SiO_2-Al_2O_3$ catalyst in dealkaline lignin reactions, several characterizations were done. Spent $SiO_2-Al_2O_3$ was calcined in air (550 °C, 600 min) and then characterized. From XRD analysis (Figure S17 in the Supporting Information) it was found that there was a minor shift in the broad peak (23°) toward a lower 2θ value, which represents an increase in the pore diameter of the of the spent catalyst. This was further supported by N_2 sorption studies (Table S7 in the Supporting Information); there also we could observe an increase in the pore diameter of the spent catalyst from 4.90 to 9.6 nm. A significant decrease in surface area from 532 to 221 $m^2\ g^{-1}$and decrease in pore volume from 0.83 to 0.65 $cm^3\ g^{-1}$ was observed in the case of spent $SiO_2-Al_2O_3$. These observations show that even the amorphous catalyst was undergoing several morphological changes during the lignin depolymerization reaction.

From ammonia-TPD (Table S7 and Figure S18 in the Supporting Information) analysis it was observed that the total acidity of the spent $SiO_2-Al_2O_3$ was decreased (0.29 mmol g^{-1}) in comparison to that of the fresh catalyst (0.63 mmol g^{-1}). From TPD profiles it was clear that both strong (510−790 °C) and weak acid (100−450 °C) sites were reduced during the reaction, unlike the case for H-USY, where strong acid sites completely vanished (Figure S8 in the Supporting Information). This reduction in acidity corresponds to 26.5 mg of Na present in the spent catalyst, since Na has killed the Brønsted acidic sites present in the $SiO_2-Al_2O_3$ by exchanging with them. However, it was found from ICP-OES analysis that only a part of Na present in the spent $SiO_2-Al_2O_3$ is exchanged with Brønsted acid sites, as 0.79 mmol of Na (18.2 mg of Na) (1.58 mmol g^{-1}) is capable of killing all of the acidic sites present in the catalyst (Table S7). As a result, we can explain why the spent catalyst could lose ca. 15% activity in the dealkaline lignin reaction. On the other hand, when other lignins (ORG, EORG, organosolv) were used as substrates, spent $SiO_2-Al_2O_3$ catalyst did not show any Na contamination and it gave similar activities in recycle runs. However, the loss of a few acid sites is observed with these substrates, due to the fact that during the reaction the catalyst morphology is slightly changing and thus a few of the acid sites might be buried or are inaccessible. To probe further, solid-state ^{29}Si and ^{27}Al NMR spectra (Figure S19 in the Supporting Information) of the fresh and spent catalysts were measured. The spent catalyst showed a broad peak for Q^4 species (Si(0Al)) at −108.2 ppm, while peaks due to Q^3 (Si(1Al)) and Q^2 species (Si(2Al)) at −93.7 and −87.6 ppm that were present in the fresh catalyst were missing. The ^{27}Al NMR showed broadening of the tetrahedral (T_d) Al peak in the spent catalyst in comparison with the peak in the fresh catalyst. This indicates that a few Al atoms change their coordination by undergoing extraction from the framework to form extra framework species. NMR studies reveal that, after the Al extraction, the environment around Si will change and it may form more Si−O−Si bonds. This will give rise to Q^4 species at the expense of Q^2 and Q^3 species. Characterizations revealed that the catalyst undergoes morphological changes; however, it is important to note that still the catalyst is active in recycle runs.

In summary, we have demonstrated that various actual lignin substrates can be converted below 250 °C to aromatic monomers using only solid acid catalysts with a very high yield of ca. 60%. Even a lignin having a molecular weight of 60000 g mol^{-1} was successfully depolymerized into value-added aromatic monomers with exceptionally high yields (60%) using solid acid catalysts under an inert atmosphere. All of the lignins were completely characterized using various physicochemical techniques. Confirmation of aromatic monomer formation and retention of functional groups and the formation of new groups on the products was examined by FTIR and NMR (^1H, ^{13}C) studies. The aromatic monomers obtained were isolated in pure form from the complex mixture using column chromatography and were well characterized. Various types of solid acid catalysts were evaluated in our study, ranging from crystalline to amorphous; however, it was difficult to establish the exact correlation between catalyst property and activity. Catalyst characterization showed the deformation happening in the case of crystalline solid acids. However, it has been shown that $SiO_2-Al_2O_3$, which is an amorphous catalyst, can be effectively recycled, although with a slight decrease in the activity after each catalytic run. An optimization of reaction conditions was done in order to improve the aromatic monomer yield. Poisoning of the solid acid catalyst was observed due to the presence of metal ions present in the dealkaline lignin substrate which are kill the acid sites present in the catalyst. It is envisaged that future advancements in this field will benefit from this study on the complete profile of lignin characterization, catalytic results, product isolation and characterization, and catalyst characterization.[69]

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

The following file is available free of charge on the ACS Publications website at DOI: 10.1021/cs501371q.

> Characterization of various types of lignins using techniques such as FT-IR, NMR, XRD, and UV analysis, information on the solubility of lignins in different organic solvents, calculations on the yield, mass balance, and substrate to catalyst ratio for lignin reactions, analysis of products by GC-FID, GC-MS, GC-TCD, HPLC, LCMS, GPC, NMR, and FTIR, product isolation by column chromatography and their further characterization, characterization of fresh and spent catalysts and their recycle study, and a discussion on the metal exchange study on solid acid catalyst (PDF)

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Author Contributions

All authors contributed equally to this work. All authors discussed the results and implications and commented on the manuscript at all stages.

Notes

The authors declare no competing financial interest.

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■ ABBREVIATIONS

GC-FID, gas chromatography-flame ionization detector; GC-TCD, gas chromatography-thermal conductivity detector; GC-MS, gas chromatography mass spectrometry; HPLC, high performance liquid chromatography; LC-MS, liquid chromatography mass spectrometry; MALDI-TOF, matrix assisted laser desorption ionization-time of flight; GPC, gel permeation chromatography; ICP-OES, inductively coupled plasma-optical emission spectroscopy; FT-IR, Fourier transform infrared spectroscopy; NMR, nuclear magnetic resonance spectroscopy; TGA-DTA, thermogravimetric analysis-differential thermal analysis; XRD, X-ray diffraction; SEM-EDAX, scanning electron microscopy-energy dispersive X-ray spectroscopy; UV−vis, ultraviolet−visible; TPD, temperature-programmed desorption

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