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Upgrading of Lignin-Derived Compounds: Reactions of Eugenol Catalyzed by HY Zeolite and by Pt/γ-Al_2O_3

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Abstract The conversion of eugenol (4-allyl-2-methoxyphenol), a compound derived from the lignin in woody biomass, was catalyzed by HY zeolite at 573 K and atmospheric pressure. The main products were isoeugenol and guaiacol, formed by isomerization and by deallylation, respectively. Substituted guaiacols with saturated side-chains (4-methylguaiacol, 4-ethylguaiacol, and 4-propylguaiacol) were also formed, by hydrogen transfer and alkylation reactions. The pseudo-first-order rate constant for the overall disappearance of eugenol was found to be 12.4 L (g of catalyst)/h. When the catalyst was Pt/γ-Al_2O_3 used in the presence of H_2, significant hydrogenation of the propenyl side-chain took place, accompanied by isomerization, and hydrodeoxygenation. Under similar operating conditions, the reaction catalyzed by Pt/γ-Al_2O_3 in the presence of H_2 gave a higher eugenol conversion ($X = 0.70$) than the reaction catalyzed by HY zeolite ($X = 0.11$), primarily because of the dominant hydrogenation observed with the former catalyst. In the absence of H_2 as a co-reactant, the acidic γ-Al_2O_3 support in Pt/γ-Al_2O_3 evidently catalyzed all the classes of reactions catalyzed by HY zeolite.

Keywords Lignin upgrading · Eugenol · Zeolite Y · Isomerization · Dealkylation · Hydrogenation

1 Introduction

Because of its low cost and abundance, lignocellulosic biomass is a promising resource for the production of renewable fuels and chemicals [1, 2]. In contrast to the cellulosic components of biomass, lignin, which typically constitutes about 30 wt% of woody biomass, is challenging to convert, in part because of its highly complex structure, which consists of subunits derived from *p*-coumaryl, coniferyl, and sinapyl alcohols connected typically with ether linkages [3–5]. Lignin is currently used either as a low-grade fuel, mostly in the pulp and paper industry, or it is burned to produce steam for electricity generation [6]. But if efficient routes to lignin conversion could be found, this largely polyphenolic feedstock could potentially become a sustainable source of chemicals and fuels. The likely conversions would be expected to involve a combination of depolymerization and catalytic upgrading [3, 7].

Thermo–chemical lignin degradation processes (such as fast pyrolysis) yield complex mixtures of oxygen-containing compounds including phenolics, guaiacols, and syringols. For example, Telysheva et al. [8] obtained phenol, guaiacol (2-methoxyphenol), substituted guaiacols, 4-allyl-2-methoxyphenol (eugenol), 4-hydroxy-3-methoxybenzaldehyde (vanillin), and substituted vanillin from pyrolytic Kraft lignin. These compounds can be converted catalytically into useful fuel components and chemicals, as shown in several recent investigations [9–19].

Notwithstanding the recently increasing attention being paid to lignin, there is still only a limited understanding of the reaction networks and kinetics of the catalytic transformations of lignin-derived compounds. We now report an investigation of the catalytic conversion of eugenol, the alkenyl-substituted guaiacol that is commonly found in the products of lignin pyrolysis and in the volatile fraction of

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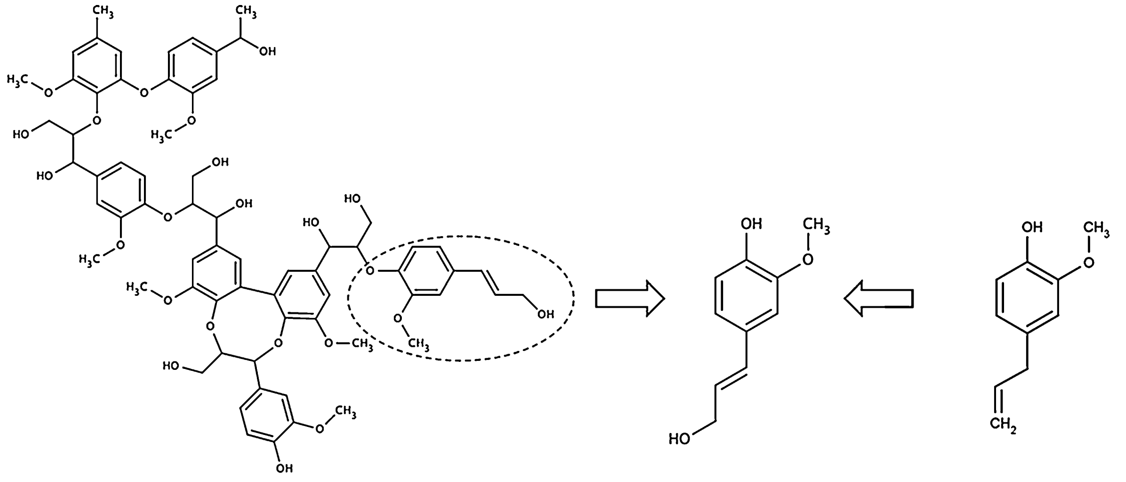


Part of simplified lignin structure

Lignin Monomer "Coniferyl alcohol"

Prototypical compound "Eugenol"

Fig. 1 Illustration of part of simplified lignin containing coniferyl alcohol subunit. Eugenol was chosen as a prototypical compound

lignocellulosic bio-oils. [20]. We chose eugenol because, as shown in Fig. 1, it is an aromatic compound that incorporates several key functional groups that link it to lignin and to coniferyl alcohol, the predominant lignin monomer in softwood [21, 22]. These functional groups are methoxy, hydroxy, and alkenyl. Thus, we regard eugenol as a prototypical compound representing lignin-derived products and have chosen it for an investigation designed to identify the important reaction classes in its catalytic conversion.

The following is a report of the conversion of eugenol in the presence of catalysts representing solid acids (zeolite HY) and supported metals (platinum on γ-Al_2O_3, Pt/γ-Al_2O_3). The experiments with the latter were carried out in the presence of H_2 to allow reactions such as hydrogenation and hydrogenolysis [including hydrodeoxygenation (HDO)].

2 Experimental

Commercial zeolite HY (Zeolyst CBV 720, Si:Al ratio = 15, atomic) and Pt/γ-Al_2O_3 (1 wt% Pt, Sigma–Aldrich) were pretreated in flowing streams of N_2 and H_2/N_2, respectively, at 573 K. Before the beginning of each catalytic reaction experiment, the HY zeolite catalyst was usually treated in flowing N_2 [100 mL (NTP)/min]. The Pt/γ-Al_2O_3 catalyst was treated in a 90/10 N_2/H_2 mixture flowing at 100 mL (NTP)/min. In these treatments, the catalyst in the flowing gas was heated at a rate of 5 K/min to the desired reaction temperature and held at this temperature for 30 min prior to the start of reactant flow. Catalytic reactions were carried out in a once-through continuous flow reactor under the following conditions, with liquid eugenol (99 wt%, Aldrich) vaporized into a flowing gas stream (N_2 in experiments with HY zeolite and H_2/N_2 in experiments with Pt/γ-Al_2O_3): temperature, 573 K; pressure, 140 kPa; liquid reactant feed rate, 0.015 mL/min; gas feed flow rate, 100 mL (NTP)/min, and catalyst mass, 0.010–0.120 g (the catalyst particles were diluted with particles of inert, non-porous α-Al_2O_3). The product gas stream was condensed at 282–286 K.

Condensed samples collected periodically and the uncondensed gas stream were analyzed by gas chromatography and by gas chromatography/mass spectrometry. Peaks in the chromatograms were identified on the basis of the mass spectra by matching to a library of NIST spectra. A ten-point calibration (5–20,000 ppm) was performed by using the following compounds individually mixed with eugenol: guaiacol, 4-ethylguaiacol, 4-propylguaiacol, and isoeugenol. Concentrations of other compounds were estimated by using semi-quantitative values of response factors based on data obtained with similar components having the same numbers of carbon atoms [23]. Analysis of isoeugenol enantiomers was carried out by gas chromatography/mass spectrometry and comparisons of the retention times and mass spectra with those characterizing authentic standards. Alkane-based Kovats indices were calculated for both a non-polar and a polar column (DB-5 and DB-Wax, respectively; Agilent Technologies, Little Falls, DE) by use of standard procedures [24]; the experimental values were compared with published values for confirmation of compound identities [25]. Details of the reactor system and analytical instrumentation are reported elsewhere [13].

3 Results

Control experiments carried out with 5 g of inert α-Al_2O_3 instead of catalyst in the reactor at 573 K showed that the conversion (X) of eugenol was minimal ($X < 0.001$), indicating negligible non-catalytic reactions under our operating conditions.

The typical overall mass balance closure was approximately 95%. The conversion of eugenol in the presence of each catalyst yielded dozens of products. The structures of some of the major products are illustrated in Fig. 2. Predominant products of the reactions catalyzed by HY zeolite were 2-methoxy-4-(1-propenyl)phenol (*cis*- and *trans*-isoeugenol) and guaiacol; less abundant products were 2-methoxy-4-methylphenol (4-methylguaiacol), 2-methoxy-4-ethylphenol (4-ethylguaiacol), and 2-methoxy-4-propylphenol (4-propylguaiacol). Numerous minor and trace products were also detected, including 2-methoxy-4-vinylphenol (*p*-vinylguaiacol), 3-methylguaiacol, 5-methylguaiacol, 6-methylguaiacol, 1,2-benzenediol (catechol), 3-methylcatechol, and 1,2-dimethoxybenzene (veratrole) (Fig. 2). Propane and propene were detected in the product gas stream.

The most abundant product observed in the conversion catalyzed by Pt/γ-Al_2O_3 in the presence of the co-reactant H_2 was 4-propylguaiacol; less abundant products were *cis*-isoeugenol, *trans*-isoeugenol, 4-prop-2-enylphenol (*p*-allylphenol), and 4-propylphenol. Methanol and water were also formed (but these were not quantified). Trace products included phenol, 4-propylbenzene, cresols, guaiacol, catechol, methylguaiacols, 3-methylcatechol,

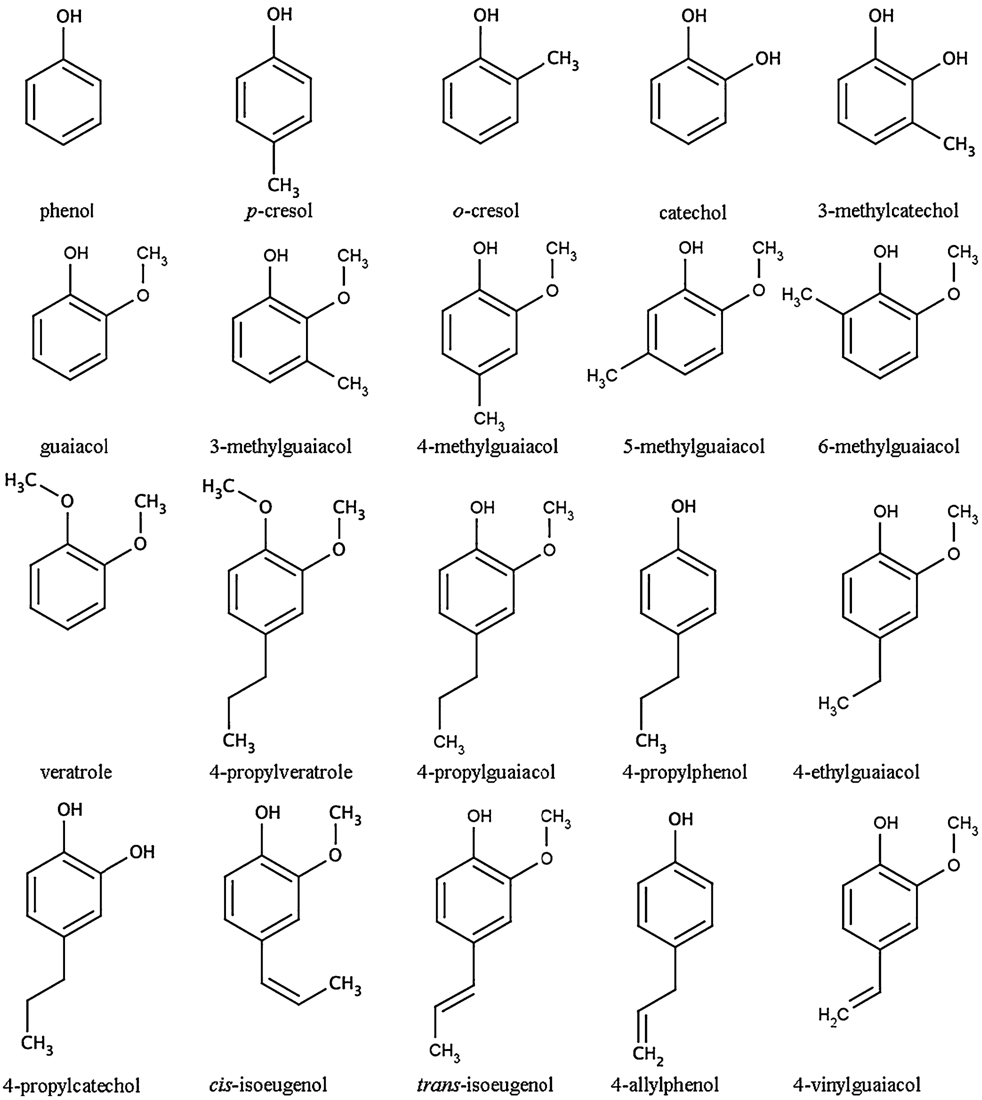


Fig. 2 Structures of products formed in the catalytic reactions of eugenol

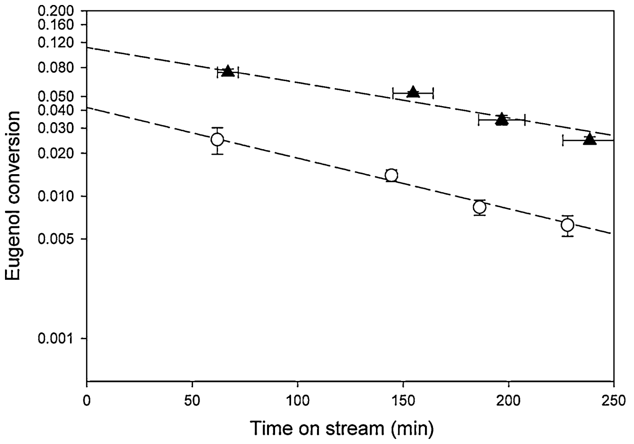


Fig. 3 Conversion of eugenol catalyzed by HY zeolite (*filled triangle*) and by Pt/γ-Al_2O_3 (*circle*) at 573 K, 140 kPa, and 100 mL/min N_2 gas feed flow rate. Weight hourly space velocity (WHSV) = 7.9 (g reactant)/(g catalyst × h)

Table 1 Products of conversion of eugenol catalyzed by HY zeolite and Pt/γ-Al_2O_3 (liquid product streams)[a]

Product	Selectivity to product in reaction catalyzed by HY zeolite[c]	Selectivity to product in reaction catalyzed by Pt/Al_2O_3 without H_2[c]	Selectivity to product in reaction catalyzed by Pt/Al_2O_3 with H_2[b]
Guaiacol	0.058	Trace	Trace
4-Methylguaiacol	0.012	Trace	Trace
4-Ethylguaiacol	0.005	Trace	Trace
4-Propylguaiacol	0.15	0.042	0.93
4-Allylphenol	–	0.072	0.013
4-Propylphenol	–	–	0.01
cis-Isoeugenol	0.16	0.21	0.010
trans-Isoeugenol	0.61	0.68	0.035

[a] Data were extrapolated to zero time on stream, and thus represent approximate initial selectivities determined at a weight hourly space velocity of 7.9 (g of reactant)/(g of catalyst × h), a pressure of 140 kPa, and a temperature of 573 K. Selectivity is defined as yield (mol product formed/mol of organic reactant fed)/conversion (mol of organic reactant consumed/mol of organic reactant fed)

[b] 100 mL/min gas feed rate, 10% H_2/90% N_2, feed molar ratio of H_2 to the organic reactant was 5

[c] 100 mL/min gas feed rate, 100% N_2

p-vinylguaiacol, 1,2-dimethoxy-4-*n*-propylbenzene (4-propylveratrole), and 4-propylcatechol. Methane, ethane, propane, and propene were identified in the gas-phase products.

Initial conversions, obtained by extrapolating the conversion data to zero time on stream, as shown in Fig. 3, were used to determine catalyst performance prior to significant deactivation. In the absence of H_2, the initial conversion of eugenol catalyzed by HY zeolite was greater ($X = 0.11$) than that catalyzed by Pt/γ-Al_2O_3 ($X = 0.04$).

The data show that the deactivation behaviors of the two catalysts were similar, characterized by approximately 50% loss in conversion in 90 min on stream. We infer that coke formed on each catalyst, because the catalysts became darker during operation. The accumulated masses of deposits (presumed to be coke) formed on the catalyst in 4 h of operation of the flow reactor in the conversions catalyzed by HY zeolite and by Pt/γ-Al_2O_3 were 0.01 and 0.006 g, respectively.

Initial selectivities to the most abundant products formed with each catalyst are summarized in Table 1. In the reactions catalyzed by Pt/γ-Al_2O_3 in the presence of H_2, the initial conversion was substantially greater ($X = 0.70$, data not shown) than in the reactions without H_2 in the feed. The conversion in the presence of H_2 was associated mainly with the hydrogenation of eugenol to form 4-propylguaiacol and the HDO of eugenol to form 4-allylphenol.

Isomerization reactions giving *cis*- and *trans*-isoeugenol were found to be important with each catalyst. Reactions catalyzed by HY zeolite gave guaiacol, likely by deallylation. Several saturated substituted guaiacols, including 4-methylguaiacol, 4-ethylguaiacol, and 4-propylguaiacol, were also formed (without H_2 formation), presumably via a combination of deallylation, dealkylation, hydrogen transfer, and alkylation reactions (as discussed below). These products were detected at only trace levels when Pt/γ-Al_2O_3 was used as the catalyst instead of the zeolite.

The data determine a reaction network for the conversion of eugenol catalyzed by HY zeolite; this is an approximation accounting only for the most abundant products. The network was determined from selectivity–conversion plots (e.g., Fig. 4) determining products as primary or not [26, 27]. The selectivity data for each product were fitted with a straight line and extrapolated to zero conversion; intercepts of regression lines significantly different from zero selectivity (analyzed with 95% confidence limits) at zero conversion indicate primary products by our criterion. These designations are empirical, falling short, for example, of providing information about intermediates that were too reactive to be detected.

The analyses indicate that the following products were primary in the conversion catalyzed by HY zeolite: *cis*-isoeugenol (a), *trans*-isoeugenol (b), guaiacol (c), 4-methylguaiacol (d), 4-ethylguaiacol (e), and 4-propylguaiacol (f), each thus apparently formed directly from eugenol by

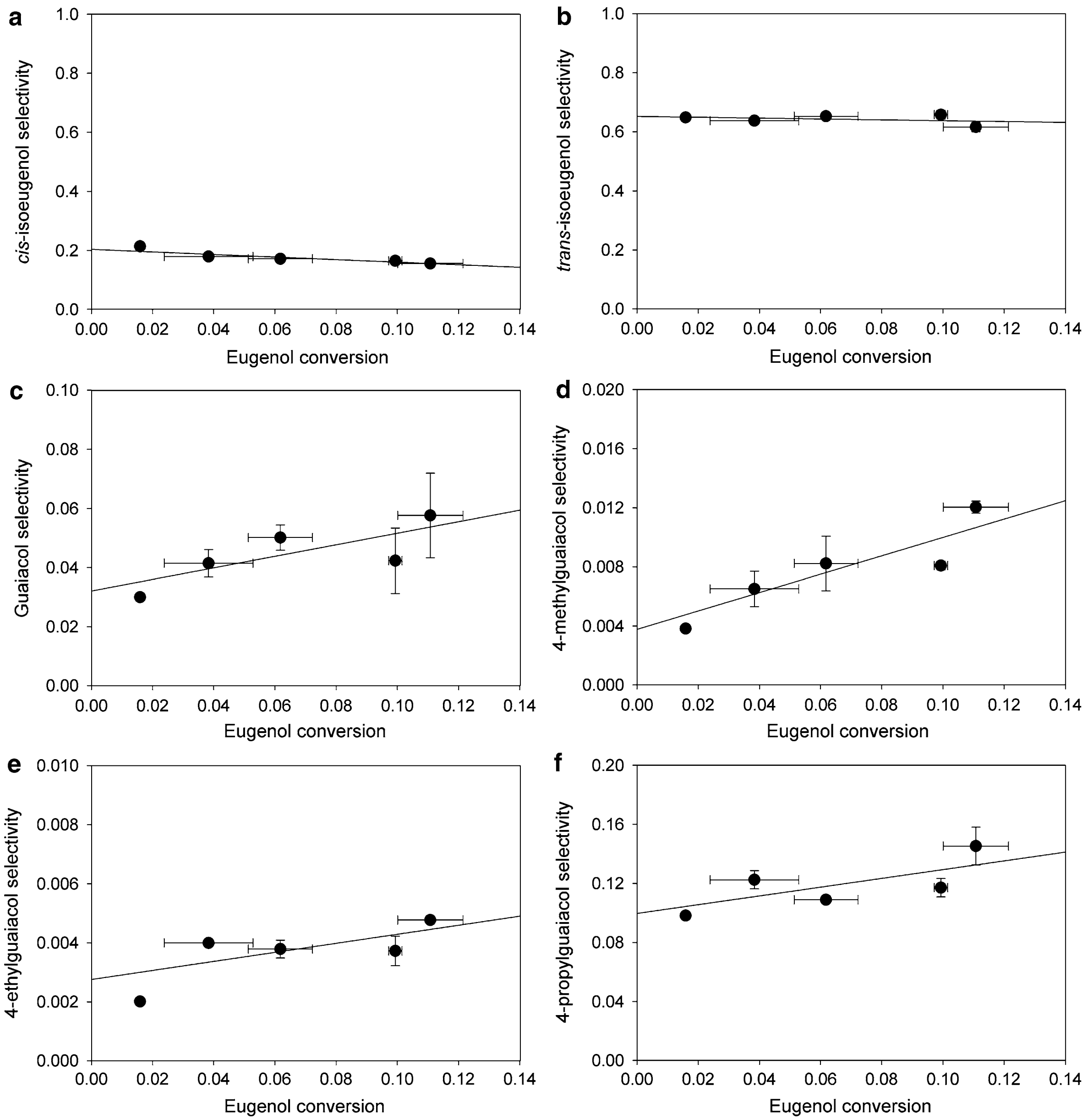


Fig. 4 Selectivity for the formation of *cis*-isoeugenol (**a**), *trans*-isoeugenol (**b**), guaiacol (**c**), 4-methylguaiacol (**d**), 4-ethylguaiacol (**e**), and 4-propylguaiacol (**f**) in the conversion of eugenol catalyzed by HY zeolite at 573 K. Data for each product were fitted with a straight line and extrapolated to zero conversion; intercepts of regression lines significantly different from zero selectivity at zero conversion (analyzed with 95% confidence limits) indicate primary products; all of these products were primary

the reactions that we infer to be those summarized in Fig. 5. We repeat that the formation of any of these products could involve multiple reactions with intermediates that were too reactive to detect.

The semi-logarithmic plot of the fraction of eugenol unconverted in the presence of the acidic zeolite catalyst as a function of inverse space velocity (Fig. 6a) is nearly linear, indicating that the overall conversion of eugenol is well-represented by first-order kinetics over the observed conversion range. The pseudo-first-order rate constant for the disappearance of eugenol was found to be 12.4 L (g of catalyst)/h. Because the conversion range was small ($X = 0.02–0.11$), we emphasize that the data do not provide a good determination of the reaction order, and we have chosen first-order kinetics because it is a convenient and simple representation that matches the data well.

By using a similar approach (Fig. 6b, c), we determined the pseudo-first-order rate constants for HY zeolite-catalyzed formation of each of the relatively abundant products, as summarized in Table 2.

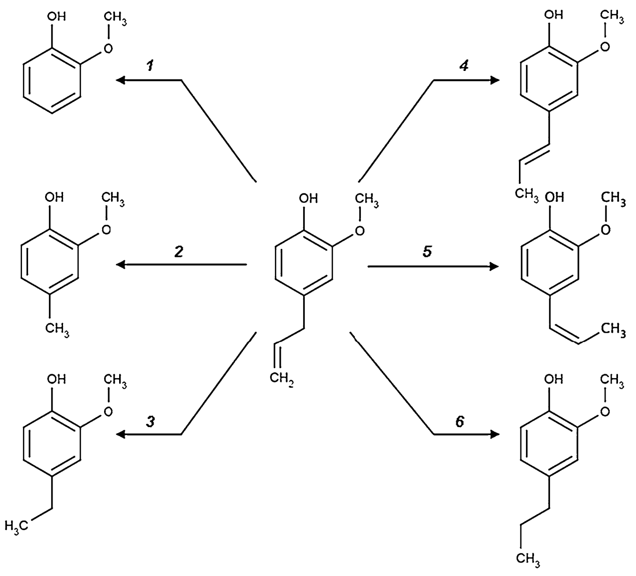


Fig. 5 Approximate reaction network accounting for the formation of abundant products determined from analysis of selectivity–conversion plots for the conversion of eugenol catalyzed by HY zeolite at 573 K. The co-products are omitted for simplicity (see the “Discussion” section)

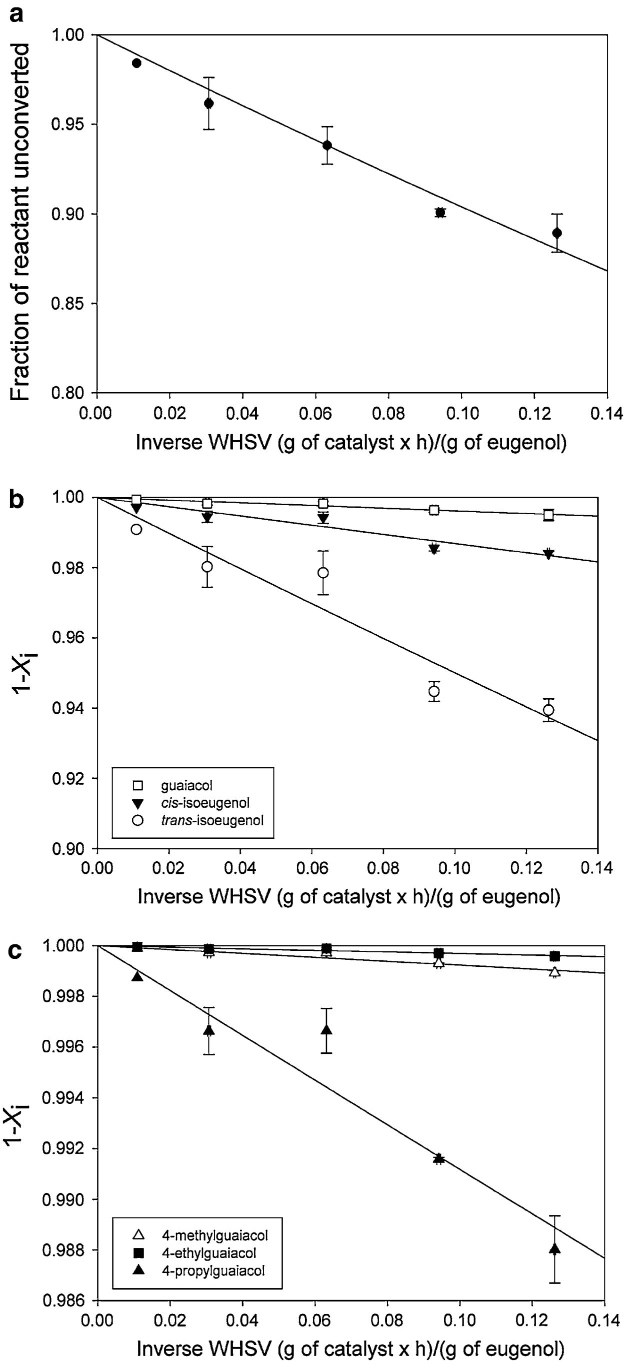


Fig. 6 Demonstration of first-order kinetics of the overall conversion of eugenol (**a**) and (**b** and **c**) the conversion of eugenol to each of the primary products shown; the catalyst was HY zeolite, and the reaction conditions are stated in Table 1. The term X_i represents the conversion of eugenol to product i. This value was calculated by dividing the number of moles of product i produced by the number of moles of eugenol fed. The inverse space velocity was varied by changing the catalyst mass in the packed-bed reactor

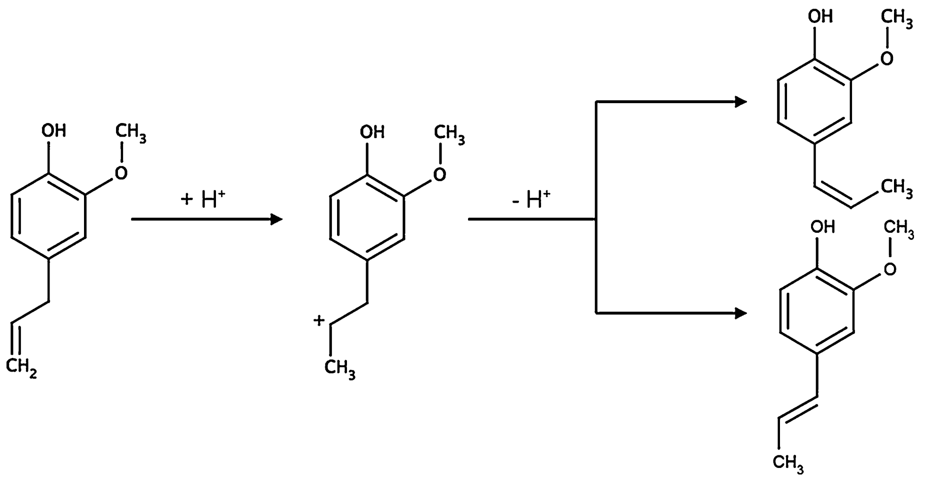
In contrast to the experiments done with the HY zeolite catalyst, those carried out with the Pt/γ-Al_2O_3 catalyst operating in the presence of H_2 gave substantially higher eugenol conversions at the same space velocity ($X = 0.11$ in the reaction with HY zeolite vs $X = 0.70$ in the reaction with Pt/γ-Al_2O_3 in the presence of H_2). The selectivity data show that relatively fast hydrogenation of the alkenyl group in eugenol led to the relatively high eugenol conversions with the supported metal catalyst. The higher conversions observed with this catalyst limited our ability to determine which reactions were primary and to elucidate a reaction network.

4 Discussion

There are several reports of the isomerization of eugenol catalyzed by alkalis in alcoholic solutions [28], by solid bases [29–31], and by metal complexes [32]. Catalysis by bases is used industrially to catalyze the conversion of eugenol to isoeugenol [29].

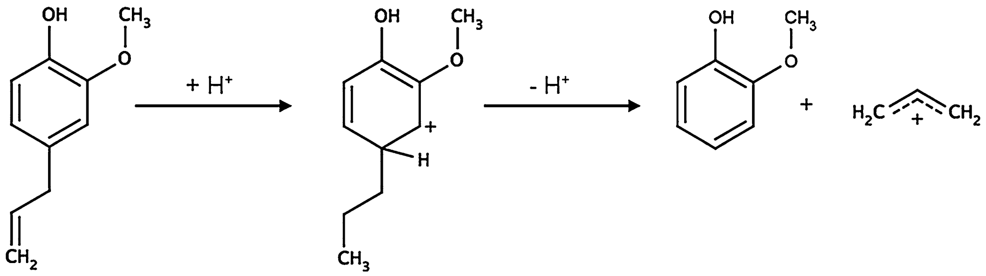
In our work, the acidic HY zeolite was found to catalyze the isomerization of eugenol, consistent with the recent report by Binder et al. [7]. These authors reported that the reactions of eugenol (including isomerization) are catalyzed by acids including HY zeolite in ionic liquids under high H_2 partial pressures. Our results are broadly consistent with the report in terms of the observed reaction classes, but the reported conversions and selectivities are different from ours. We suggest that the differences are associated with the lower reaction temperature (473 K), the higher pressure (6.9 MPa), and the presence of ionic liquids and H_2 in the reported work.

We infer that the acid-catalyzed isomerization of eugenol involves carbenium ion chemistry, as illustrated below (this is a conventional alkene isomerization):



Under our operating conditions, isomerization was the most significant reaction class in the conversion catalyzed by HY zeolite, as the selectivities for the formation of *cis*- and *trans*-isoeugenol were the highest of any (Table 1). The molar ratio of *cis*- to *trans*- isoeugenol produced was approximately 1:4, consistent with typical observations that the more thermodynamically *trans*-isomer predominates.

Consistent with the proposal of Binder et al. [7], we also suggest that the formation of guaiacol takes place by deallylation of eugenol, as illustrated below:



As a result, the allyl cation is formed along with guaiacol. The data are not sufficient to determine the fate of the allyl cation; it might have contributed to coke formation.

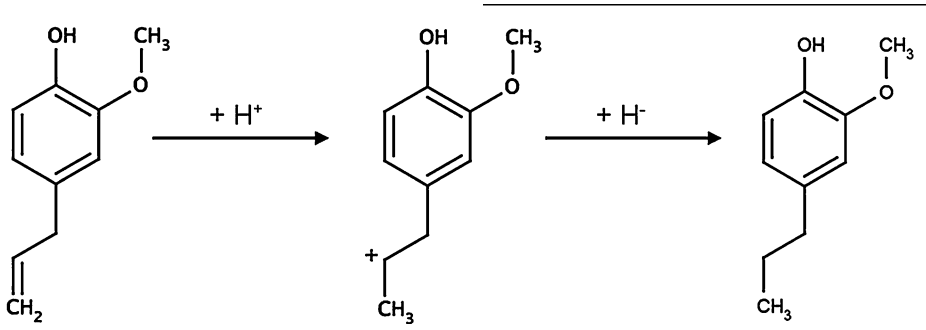
Notwithstanding the absence of H_2 in the feed, the selectivity for formation of 4-propylphenol was high relative to that of other products, excluding isoeugenol. These results indicate a hydrogen transfer reaction, as typically occurs in zeolite-catalyzed cracking of alkanes, for example [33–35]. Carbenium ions formed from alkenes (products of alkane cracking) abstract hydrogen (hydride) from alkanes and from species such as coke precursors in cracking reactions [36]; thus, we suggest that carbenium ion formation from eugenol is following by hydride abstraction from such hydrogen sources as the coke or coke precursors on the catalyst surface.

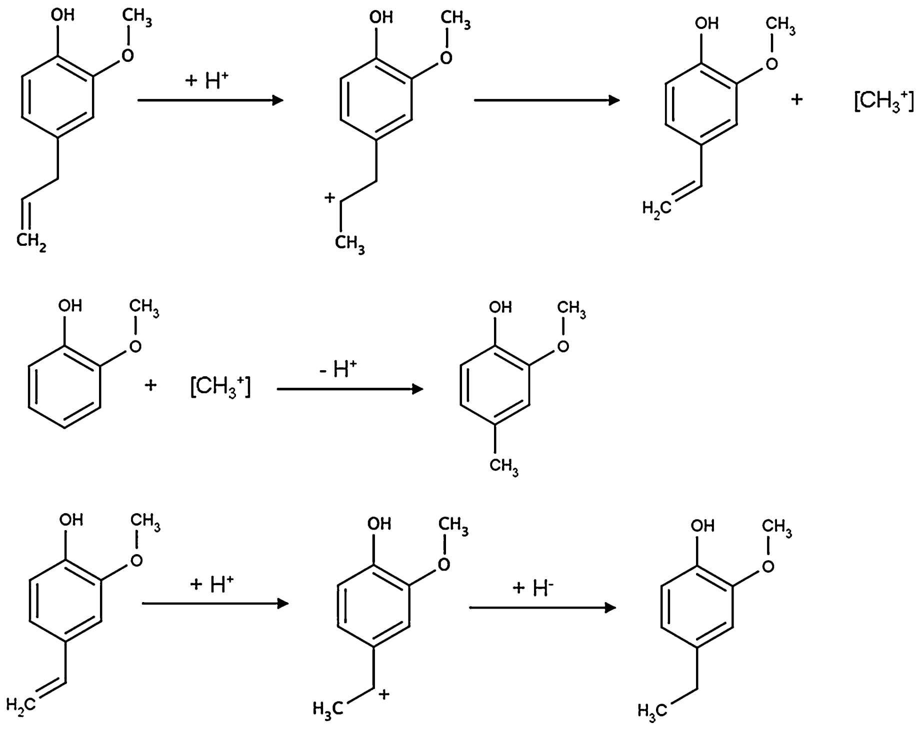
Table 2 Pseudo-first-order rate constants for the formation of abundant products produced in the reactions of eugenol catalyzed by HY zeolite

Reaction number (keyed to Fig. 5)	Product	Rate constant[a]
1	Guaiacol	0.47
2	4-Methylguaiacol	0.095
3	4-Ethylguaiacol	0.038
4	*trans*-Isoeugenol	6.3
5	*cis*-Isoeugenol	1.6
6	4-Propylguaiacol	1.1

[a] Rate constants in L (g catalyst)$^{-1}$ h^{-1}

Alkenes are an important source of coke in isomerization and cracking reactions [37–39]. Owing to its alkenyl side chain, eugenol molecules can potentially form coke on the zeolite surface beginning with the dimerization of eugenol. As this polymerization continues in parallel with reforming reactions, species including cycloalkenes, dienes, trienes, and aromatics could be formed [40, 41]. These hydrogen-deficient species are usually formed in association with the formation of saturated compounds, inferred in our case to include 4-propylguaiacol.





According to the selectivity–conversion plots shown in Fig. 4, 4-methylguaiacol and 4-ethylguaiacol are primary products. However, there is no plausible favorable single reaction for the formation of these two products. As illustrated schematically above we suggest that 4-vinylguaiacol is formed first. The guaiacol could be alkylated in a concerted reaction giving predominantly 4-methylguaiacol because the electrophilic aromatic substitution occurs preferentially at the 4-position [42, 43]. (Formation of the primary cation is meant only schematically; it would be avoided in the concerted reaction.) 4-Ethylguaiacol can be formed subsequently via hydrogen transfer involving hydrogen sources, such as those mentioned above. The selectivity–conversion analysis might imply that the rates of formation of 4-methylguaiacol and of 4-ethylguaiacol are relatively high in comparison with the rate of 4-vinylguaiacol formation. These hypotheses account for the appearance of these two products as apparently primary products.

Because first-order kinetics satisfactorily represents the data characterizing the reactions leading to the formation of guaiacol, isoeugenol, 4-methylguaiacol, 4-ethylguaiacol, and 4-propylguaiacol under our operating conditions (Fig. 6), we can use the pseudo-first-order rate constants as a basis for analyzing the selectivity data. These rate constants show that the isomerization reaction to give *trans*-isoeugenol formation is kinetically the most significant, followed by *cis*-isoeugenol formation. The rate constant characterizing 4-propylguaiacol formation is comparable to that characterizing *cis*-isoeugenol formation, possibly implying that the rate of coke formation on the surface could be substantial as coke or coke precursors are inferred to be potential hydrogen sources for hydrogen transfer reactions. Deallylation of eugenol is relatively slow in comparison with isomerization and hydrogen transfer, as the rate constant for guaiacol formation is approximately 17 times less than that for isoeugenol formation (the enantiomers combined) and two times lower than that of 4-propylguaiacol formation. The rate constants for 4-methylguaiacol and 4-ethylguaiacol formation are relatively small in comparison with those characterizing the other abundant products.

The results suggest that the acidic γ-Al_2O_3 support catalyzes reactions giving products matching those formed in the reactions catalyzed by the acidic zeolite (i.e., guaiacol, 4-methylguaiacol, 4-ethylguaiacol, 4-propylguaiacol, and isoeugenol). In the absence of H_2, the weaker acidic sites of γ-Al_2O_3 led to lower rates of formation of these products than were observed with the zeolite and to a lower eugenol conversion ($X = 0.04$ vs. 0.11).

When the Pt/γ-Al_2O_3 catalyst was used with H_2 added to the feed with eugenol, the selectivity for 4-propylguaiacol formation increased, indicating that hydrogenation of eugenol occurred readily with H_2 as the hydrogen source. We infer that the reactions to form 4-propylguaiacol (mostly hydrogenation) account for most of the eugenol conversion (selectivity = 0.93 at $X = 0.70$).

Hydrodeoxygenation of eugenol takes place as 4-allylphenol is produced, regardless of whether H_2 is present in the feed (Table 1). As H_2 is necessary for HDO of aromatic oxygenates [16, 17], the data might be suggested to imply that H_2 was produced in situ on the metal surface and consumed in the reactions (as we did not observe H_2 in the gas product stream).

Because it was observed only when H_2 was co-fed, we infer that 4-propylphenol was produced via hydrogenation of 4-allylphenol. However, we do not disregard the possibility that 4-propylphenol could also be formed by a hydrogen transfer reaction of 4-allylphenol, comparable to the formation of 4-propylguaiacol from eugenol in reactions catalyzed by HY zeolite, mentioned above.

We infer that understanding of the catalytic reactions of prototypical compounds that represent those derived from lignin may facilitate the development of better catalysts and processes for lignin conversion. In contrast to more widely investigate lignin-derived prototypes, such as guaiacol [15–18], anisole [12–15], and phenol [9, 10], eugenol contains an alkenyl group. Our data show that several useful products can be produced from eugenol, including guaiacol (an important intermediate for alkylaromatics production [16, 17]) and isoeugenol (used as an additive in pharmaceuticals and fragrances [30]). The data show that the alkenyl group is highly reactive with H_2 and important in determining the H_2 consumption—it would be expected to be responsible for high H_2 consumptions in processes in which HDO is a desired goal, as is typical in bio-oils upgrading.

Thus, we suggest that to optimize overall H_2 consumption, one might first use a solid acid catalyst to eliminate unsaturated side chains, followed by removal of oxygen via HDO in the presence of a supported metal catalyst used with H_2 as a co-reactant.

5 Conclusions

The catalytic conversion of eugenol catalyzed by HY zeolite involves two major reaction classes: isomerization and deallylation, resulting in three main products, *cis*- and *trans*-isoeugenol and guaiacol. Saturation of the propenyl side-chain of eugenol occurs even in the absence of H_2 in the feed and a metal catalyst function, possibly via acid-catalyzed hydrogen transfer reactions. Under our operating conditions, Pt/γ-Al_2O_3 is highly active for hydrogenation reactions, leading to substantial formation of 4-propylguaiacol. Isomerization and minimal HDO were also observed, regardless of whether H_2 was present in the feed.

The results highlight the effect of an alkenyl substituent on the catalytic conversion of lignin-derived compounds. The data complement those reported for other compounds representative of lignin-derived products.

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