Vanadium catalyzed guaiacol deoxygenation

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Abstract

The first row transition metals (vanadium to zinc) supported on alumina were evaluated for their ability to catalyze the formation of phenol from guaiacol (2-methoxyphenol) at atmospheric pressure and 350°C. Vanadium oxide on alumina had the highest activity for phenol formation. The vanadium catalyst was studied in more detail, and the highest yields of phenol and methylated phenols, and the lowest yields of coke, were obtained when an organic reductant, such as α-terpinene, was co-fed with the guaiacol. The vanadium catalyst remained active for a significant period of time on stream (8 g of feed per g of catalyst), even with 20% coke present on the catalyst. The possible benefits of vanadium in new biomass upgrading catalysts are discussed, and a reaction mechanism is proposed. © 1999 Elsevier Science B.V. All rights reserved.

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1. Introduction

Vanadium-based catalysts are used industrially to catalyze a variety of reactions in the gas and liquid phase [1], perhaps the most dramatic of which is the air oxidation of *n*-butane to maleic anhydride [2]. Vanadium catalyzed oxidation reactions have been studied extensively, with vanadium supported on zeolites [3] and aluminophosphates [4], for the oxidations of aromatic hydrocarbons [5] and aldehydes [6], and with hydrogen peroxide as the oxidant [7]. Reductions catalyzed by vanadium, on the other hand, have been studied less, and appear to be limited to reductions of nitrogen oxides [8] and hydrazine [9].

Biomass pyrolysis produces many compounds, most of which are rich in oxygen. The high oxygen content of oils produced from biomass pyrolysis imparts undesirable properties to the oils, such as low caloric value and high reactivity. This reactivity can make the use of the oil as a fuel and its long-term storage difficult [10]. Research efforts aimed at deoxygenation of pyrolysis oils have

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focused on high pressure hydrotreating [11,12] and on the use of zeolites under low pressure conditions [13,14]. The lignin component of biomass is primarily converted by pyrolysis to aromatic monomers, many of which bear two oxygen atoms attached consecutively to the ring (guaiacyl units) or three (syringyl units) [15]. High pressure hydrodeoxygenation of lignin model compounds has been examined both with [16–18] and without [19,20] catalysts.

It would be of considerable value to those who hope to use pyrolysis products to have a way of economically removing oxygen atoms from the lignin-derived part of pyrolysis oils: first, the reactivity of the oil would be lessened, since fewer oxygen atoms on the benzene rings will make them less electron rich and less likely to undergo condensation reactions during storage; second, if the aromatic portion of the pyrolysis oil is to be used as an industrial feedstock, in most cases it will need to first be converted to a simpler benzene derivative; and third, as oxygen is removed, the caloric content of the oil, and hence its fuel value, rises.

We wish to report on our initial efforts at understanding how metals influence the activity of heterogeneous catalysts for the low pressure upgrading of pyrolysis oils. The lignin model compound guaiacol (2-methoxyphenol) was used to evaluate the first row transition metals supported on alumina for their ability to catalyze lignin deoxygenation. Vanadium oxide on alumina was found to be highly active for the selective removal of one oxygen atom from guaiacol to produce phenol and methylated phenols. Herein we give the details of the reaction, and speculate on its mechanism.

2. Experimental

Reagents were obtained from commercial suppliers. 3-Methoxyphenol and α-terpinene were distilled before use. Nitrogen gas was 99.999% pure.

The vanadium catalyst supported on γ-alumina was prepared as follows. A slurry of 4.0 g V_2O_5 in 10 ml concentrated ammonia and 50 ml water was stirred for 30 min before it was treated with 50 g γ-alumina (LaRoche V-250). More water was added until a uniform orange paste was obtained. This paste was dried overnight at 110°C, and then calcined at 538°C for 6 h. The resultant solid was ground to a fine powder, and suspended in sufficient acidic alumina hydrosol (American Cyanamid, 10% alumina) to give a final V_2O_5 content of 4.7% on a dry weight basis. The gel was made basic with concentrated ammonia and allowed to solidify. It was then dried, calcined as before, and ground to a US sieve size of $+20/-40$. A pure γ-alumina catalyst was prepared analogously to which no metal was added.

Surface areas were measured by the BET method on a Micrometrics FlowSorb II 2300.

The other metals were supported on alumina (to obtain the same wt.% of metal for each catalyst) by slurrying 50 g γ-alumina with an aqueous solution of the metal, drying, calcination, and binding with alumina using the hydrosol process described above. The metal salts used were acetates of Cr(III), Mn(II), Co(II), Ni(II), Cu(II), and Zn(II), and $FeCl_3 \cdot 6H_2O$.

Catalytic reactions were carried out in a quartz tubular flow reactor, 1.5 cm i.d., using N_2 as the carrier gas at atmospheric pressure. Product liquids condensed on the cool walls of the reactor downstream of the furnace, and then were further cooled in a receiving flask by an ice water bath.

Liquids were introduced into the reactor with a syringe pump. Screening runs were performed by passing about 1.0 g of guaiacol over 1.0 g of catalyst at 350°C and collecting the products. In runs that included the reductant, 1.0 g of fresh catalyst (2 cm bed height) was preconditioned with 0.5 to 0.7 g of feed mixture consisting of equimolar amounts of α-terpinene and the phenol at 350°C at the

same feed rate as was used during a run. The weight hourly space velocity (WHSV) of guaiacol was $1.1 \ h^{-1}$. The carrier gas flow rate was 50 sccm.

Products were weighed, and analyzed by gas chromatography/mass spectrometry (GC/MS, HP 5890, 5970 mass selective detector, DB 1701 column). Calibrants were guaiacol, phenol, *p*-cresol (for phenolic peaks with $m/z = 108$), and 2,4-dimethyl phenol (for phenolic peaks with $m/z = 122$ or higher). Water yields were measured in a conical graduated flask. Gases were not analyzed.

Qualitative experiments with catechol, resorcinol and hydroquinone were performed by preparing aqueous solutions of the diols (0.13 g in 0.5 ml for catechol and resorcinol, 0.13 g in 2.0 ml for hydroquinone) and injecting the solutions into the reactor (diol WHSV $\approx 3 \ h^{-1}$) at the same time that α-terpinene was fed over fresh catalyst samples using a separate syringe pump. Products were taken up in methanol, and analyzed by GC/MS.

Coking was studied at lower conversions (guaiacol WHSV $= 4$–$5 \ h^{-1}$) by feeding guaiacol or equimolar guaiacol/α-terpinene over fresh catalyst samples (0.5 g) for varying periods of time on stream, collecting the liquids produced, and determining the coke on the catalyst in air to 750°C (TA Instruments, TGA 2950).

3. Results

Preliminary experiments were aimed at making qualitative assessments of the first row transition metals for their ability to deoxygenate guaiacol. Thus, the catalysts were prepared in order to rapidly screen the metals, and they were not characterized, except for the supported vanadium catalyst and the pure alumina once interesting activity was found for the vanadium. When guaiacol was passed over the catalysts at 350°C, phenol, methyl phenols, catechol, and methyl catechols were produced in each case. In order to rank the metals, the relative yields of phenol and catechol were measured. The results are shown in Fig. 1, which shows that vanadium clearly stands out for its ability to produce phenol. The amount of phenol produced over vanadium was comparable to the levels of catechol produced by the other metals, while the level of catechol for vanadium was low. Pure alumina also produced catechol from guaiacol.
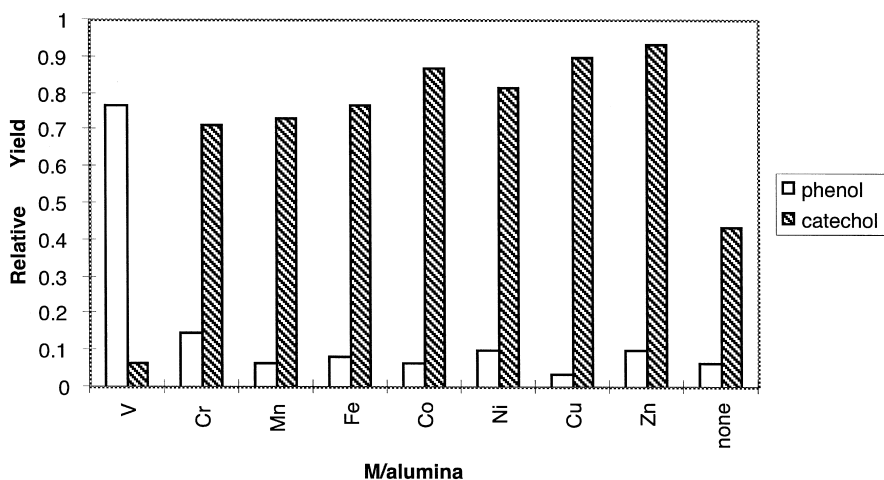

Fig. 1. Relative yields of phenol and catechol from guaiacol over metals supported on alumina.

The BET surface area of the vanadium catalyst was determined and compared to the pure alumina catalyst prepared analogously. Both catalysts had a measured surface area of 220 m^2 g^{-1}, indicating the vanadium was present as a monolayer on the support and not as crystallites [21,22].

In order to more fully characterize the reaction, and determine to what extent the vanadium catalyst can produce phenol from guaiacol, a reductant was mixed with the guaiacol in order to facilitate the removal of oxygen. When an equimolar mixture of guaiacol and α-terpinene (an inexpensive plant-derived terpene) was fed over the catalyst at 350°C, a small amount of water and a clear yellow oil were obtained in 95% yield based on the mass of the starting mixture. GC analysis of the mixture indicated that 98% of the guaiacol was converted to phenol and methyl phenols. Volumetric measurement of the aqueous phase resulted in a water yield of 83% based on the guaiacol fed. As shown in Table 1, the yield of phenol was 41%; the combined yield for phenol and methylated phenols was nearly quantitative. Also shown in Table 1 is the 'methyl balance' for the methyl group present in the guaiacol feed; the methyl group was distributed on the methylated phenols after the reaction.

The other compound present in high abundance in the mixture after the reaction was p-cymene (1-isopropyl-4-methylbenzene), which was the product expected from the oxidation of α-terpinene (vide infra). Traces of other terpene-derived products were also found by GC/MS: 4-isopropyl-1-methylcyclohexene and 4-methyl-1-isopropenylbenzene. Starting α-terpinene was converted to p-cymene nearly quantitatively.

Experiments designed to elucidate the mechanism of the reaction were performed next. When pure α-terpinene was fed over the vanadium catalyst in air (50 sccm) at 350°C, the hydrocarbon was cleanly converted to p-cymene and a lesser amount of 4-methyl-1-isopropenylbenzene.

For equimolar mixtures of 3-methoxyphenol and α-terpinene, no phenol could be found in the product liquids, which consisted of a viscous yellow oil (not analyzed) and a lighter hydrocarbon phase that was mostly unreacted α-terpinene, p-cymene and various $m/z = 136$ isomers.

Other feeds that were tested were catechol, resorcinol and hydroquinone; these solid materials were introduced into the reactor as aqueous solutions along with the reductant in short (5 min) qualitative experiments. Catechol was converted cleanly to phenol (no alkylated phenols were observed), while both resorcinol and hydroquinone yielded only traces of phenol, and emerged form the reactor largely unchanged. Significantly, the α-terpinene was converted to p-cymene to a much larger extent in the catechol reaction than in the reactions of either resorcinol or hydroquinone.

Since phenol was produced from guaiacol over the vanadium catalyst even without a reductant co-feed (Fig. 1), it was assumed that guaiacol fed alone disproportionated to produce phenol and an

Table 1

Product yield (based on guaiacol fed) and methyl balance obtained for the conversion of an equimolar guaiacol (1.1 g) and α-terpinene mixture over V_2O_5/Al_2O_3 (1.0 g)

Product	% Yield	Methyl balance (%)[a]
Phenol	41	–
Methyl phenols	38	38
Dimethyl phenols	16	32
Tri-, tetra-, pentamethyl phenols	9	28
Total	104	98

Guaiacol WHSV $= 1.1$ h^{-1}.

[a] Computed from the moles of product formed times the number of methyl groups on the product.

Table 2

Percent weight gain due to coke and phenol yields per 15 min interval for varying times on stream for V_2O_5/Al_2O_3 catalyst with guaiacol fed alone and as an equimolar mixture with α-terpinene

Time on stream (min)	% Weight gain		Phenol yield (%)	
	Guaiacol	+ α-Terpinene	Guaiacol	+ α-Terpinene
15	19.1	16.5	3.1	34
30	19.6	18.6	3.1	13
45	23.9	18.7	2.5	10
60	24.4	20.3	2.8	16

Guaiacol WHSV = 4–5 h^{-1}.

oxidized product which was not observed, and was deposited instead as part of the coke on the catalyst. To test this, coking rates were measured with and without the reductant co-feed α-terpinene. The results are displayed in Table 2, which shows that there was significantly less coke formed and phenol yields were much higher when guaiacol was co-fed with a reductant. In addition, the catalyst retained significant activity after 1 h on stream.

4. Discussion

The results presented here show that while all of the first row transition metals supported on alumina, and even alumina alone, have some activity for guaiacol deoxygenation to form phenol, vanadium on alumina possesses an enhanced ability to catalyze the reaction. It appears that vanadium has the unique property of efficiently removing an oxygen atom from guaiacol and converting it to water. This unusual reactivity may be attributed to the oxophilic nature of the early transition metals, and to the ability of vanadium to undergo oxidation state changes easily.

Experiments with 3-methoxyphenol, catechol, resorcinol and hydroquinone over the vanadium catalyst suggest that deoxygenation occurs more readily if the oxygen atoms in the feed molecule are in the 1,2-positions, since only traces of phenol are formed from feeds with oxygen atoms in the 1,3- or the 1,4-positions. This raises the possibility that chelation of the metal during the reaction facilitates oxygen removal, and suggests that deoxygenation of 1,2-substituted substrates proceeds by a concerted pathway, and not by radical reactions [20].

The results obtained from guaiacol alone over the catalysts indicate that guaiacol disproportionates to form phenol. This implies that catechol or methyl catechols arising from demethylation–remethylation (vide infra), are oxidized to orthoquinones on the catalyst. The orthoquinones then go on to form coke. This is supported by the coking results, which show increased coking of the catalyst when the reductant co-feed is absent. With the reductant present, the catalyst maintains its activity reasonably well, even with about 20% coke present after 1 h on stream, or after about 8 g of feed has been fed over 1 g of catalyst. The reductant alone over the catalyst in the presence of oxygen cleanly oxidizes to the corresponding aromatic compound, showing that the catalyst shuttles hydrogen atoms from the reductant to oxygen. Thus, while coking and deactivation on this catalyst are problems (perhaps due to the alumina support), we suggest that vanadium might be a useful metal for incorporation in catalysts that are being developed for upgrading lignocellulosic pyrolysis oils.

These results make it possible to form a mechanistic picture of the reaction of guaiacol over the vanadium catalyst. From the results for guaiacol alone over alumina, we may conclude that the role of

the support in the vanadium catalyzed reaction is to promote the formation of catechols from guaiacol, as shown in Eq. (1). Alumina-catalyzed alkylation-dealkylation has been observed before [23].

$$\text{(1)}$$
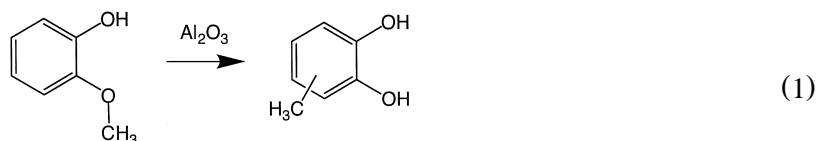
Mechanistically, the next step in the reaction involves reduction of the vanadium by α-terpinene as shown in Eq. (2). Chemical reduction of vanadium (V) oxide supported on alumina is facile [21]. The organic product is *p*-cymene, which is formed in the overall reaction with either guaiacol as the oxidant, or atmospheric oxygen.


$$\text{(2)}$$
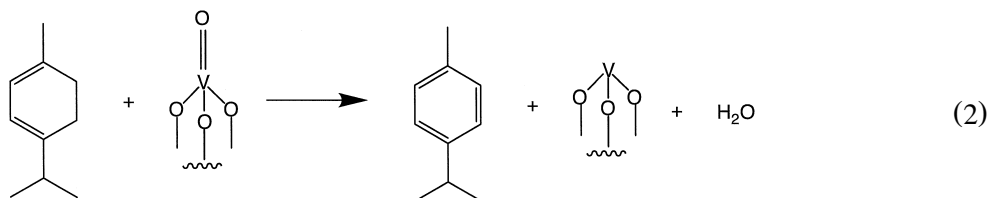
The V(III) is now in a position to complex with a molecule of catechol, and formally at least, accept an oxygen atom from the catechol and be reoxidized to V(V) (Eq. (3)).

$$\text{(3)}$$
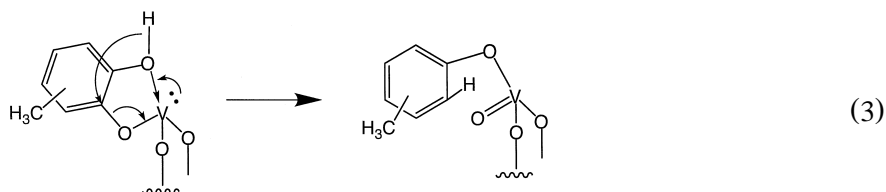
The reaction is drawn as a concerted hydride transfer to an aryl carbon, in recognition of the fact that the external reductant, when it is present, could donate hydride directly to the vanadium chelate. The participation of the second oxygen atom on catechol in a vanadium chelate is of course speculative, but is supported by the fact that substrates possessing oxygen atoms in the 1,3- or 1,4-positions, which cannot form an analogous chelate, are not reduced to phenol efficiently. This chelation also helps to explain the selectivity of the reaction to mono-oxygenated products, since non-specific electron transfer to oxygenates would be expected to produce at least some benzene and methyl benzenes, as has been observed in the catalytic hydrodeoxygenation of anisole [18].

The overall reaction, which is the combination of Eqs. (2) and (3) if the organovanadium compounds are hydrolyzed and the catalyst is omitted, is shown in Eq. (4).

$$ \text{(4)} $$
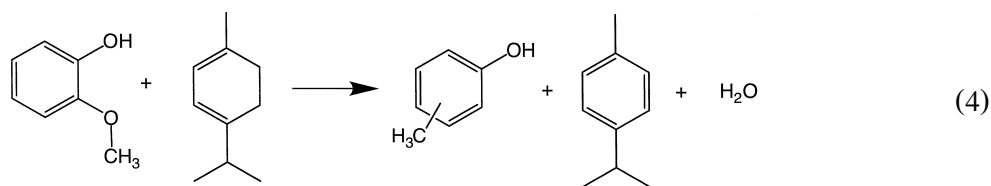
The high yield of phenol suggests that the methyl groups are distributed among the products independently of the deoxygenation step (probably on the alumina) since reaction at a single site would favor the formation of mono-methylphenols. Note that methanol formed in the above reaction would rapidly alkylate phenols present in the reaction mixture over the alumina [23], which accounts for the methyl balance in Table 1 near 100%.

5. Conclusion

We have discovered that vanadium oxide supported on alumina is effective for the atmospheric pressure deoxygenation of the simple lignin derivative, guaiacol, as long as there are reducing equivalents in the form of hydrogen atoms in the feed to combine with the liberated oxygen atom. We have chosen the inexpensive plant-derived hydrocarbon α-terpinene as the reductant, but other reductants, such as tetralin or hydrogen gas, could possibly be used instead. Even in the absence of a reductant co-feed, the reaction is successful, but in this case, the yield of deoxygenated products is less, and a greater amount of coke forms on the catalyst. The formation of phenol and methyl phenols from guaiacol occurs to some extent with all the first row transition metals (vanadium to zinc) supported on alumina (and even over plain alumina), but deoxygenation is much more facile for vanadium on alumina. Vanadium thus should be considered for its ability to catalyze reductions, and specifically for its ability to deoxygenate aromatic substrates with oxygen atoms in the 1,2-positions, when catalysts for the upgrading of biomass pyrolysis oils are being designed.

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