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Aerobic oxidation of veratryl alcohol to veratraldehyde with heterogeneous ruthenium catalysts

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Abstract

Lignin is a complex polymeric molecule constituting various linkages between aromatic moieties. Typically, the β -O-4 linkage accounts for more than half of the linkage structures present in lignin. The present study focuses on the oxidative transformation of veratryl alcohol (VA) - a compound that can be formed by cleavage of β -O-4 linkages in lignin - to veratraldehyde (VAld) with air using ruthenium supported on γ -alumina or silica as catalyst with water or methanol as solvent in a batch reactor. Ru/Al₂O₃, prepared with ruthenium (IV) oxide hydrate showed superior catalytic activity, yielding 89 % VAld in water at 160 °C with 5 bar air pressure after 8 h of reaction. Prolonged reaction time led to significant formation of the decarbonylated product veratrol from VAld. When the reaction was completed under 20 bars of argon in methanol instead of water, the methyl ether of VA (i.e. 1,2-dimethoxy-4-(methoxymethyl)benzene) prevailed, indicating that methanol protecting the hydroxyl group in VA from being oxidized to VAld. Catalysts containing alternative transition metals (Mn, Co, Cu and Ag) supported on Al₂O₃ gave significantly lower activities compared to Ru/Al₂O₃ under identical reaction conditions. The Ru/Al₂O₃ catalyst was

reused in three consecutive reaction runs in water, but a significantly lower VAld yield was obtained after the third cycle possibly due to leaching of Ru from the support.

Keywords: Heterogeneous catalysis, Ruthenium, Oxidation, Veratryl alcohol, Veratraldehyde.

1. Introduction

Catalytic transformations of lignocellulosic biomass-derived chemicals into value-added chemicals/fuels have become increasingly important in the past decade, due to their potential application as sustainable supplement or replacement of fossil-based chemicals/fuels [1]. Most focus has been devoted to valorization of carbohydrate-based compounds originating from the cellulose and hemicellulose in biomass. Hence, numerous reports describe the conversion of glucose (model compound for cellulose) and xylose (model compound for hemicellulose) into selective products [2-5]. However, it is now recognized that suitable catalytic systems also need to be developed for conversion of the lignin fraction in order to create sustainable bio-refineries, since lignin typically constitutes 30% of the carbon content and 40% of the energy content of lignocellulosic biomass [6].

In lignocellulosic material the composition as well as the molecular weight and structure of the lignin differ from plant to plant (hard and soft wood, grass etc.), impeding the developments on lignin valorization processes [7-8]. However, three monolignol monomers p-coumaryl, coniferyl and sinapyl alcohol are common building blocks. These monomers are connected with various linkages with the most common one being the β -O-4 linkage (Fig. 1) [7]. Due to the structural complexity it is difficult to choose a unique model compound - as there is none - that can reflect/represent lignin conversion, and thus exemplify the bottleneck of the process for the

selective conversion of lignin towards targeted products. Consequently, a particular model compound is often selected to represent a specific linkage present in the lignin, and only few works have studied the reactivity of pseudo mixtures of lignin-derived model compounds [9].

One of the viable methods for the valorisation of lignin and lignin model compounds is oxidative depolymerisation with environmentally friendly oxidants such as oxygen (air) or H₂O₂. Since lignin contains many hydroxyl groups, it is susceptible to oxidation and oxidative depolymerisation. The oxidative depolymerisation/cracking cleaves aryl ether bonds, for example β -O-4 and 4-O-5, and other linkages within the lignin (Fig. 1). The major oxidation products from such cleavage would be aromatic aldehydes or carboxylic acids, depending on the severity of the reaction conditions [10]. In this connection, oxidation of methyl hydroxy (including benzylic) groups to the corresponding aldehyde or acid is of importance as such moieties are abundant in lignin [11-14].

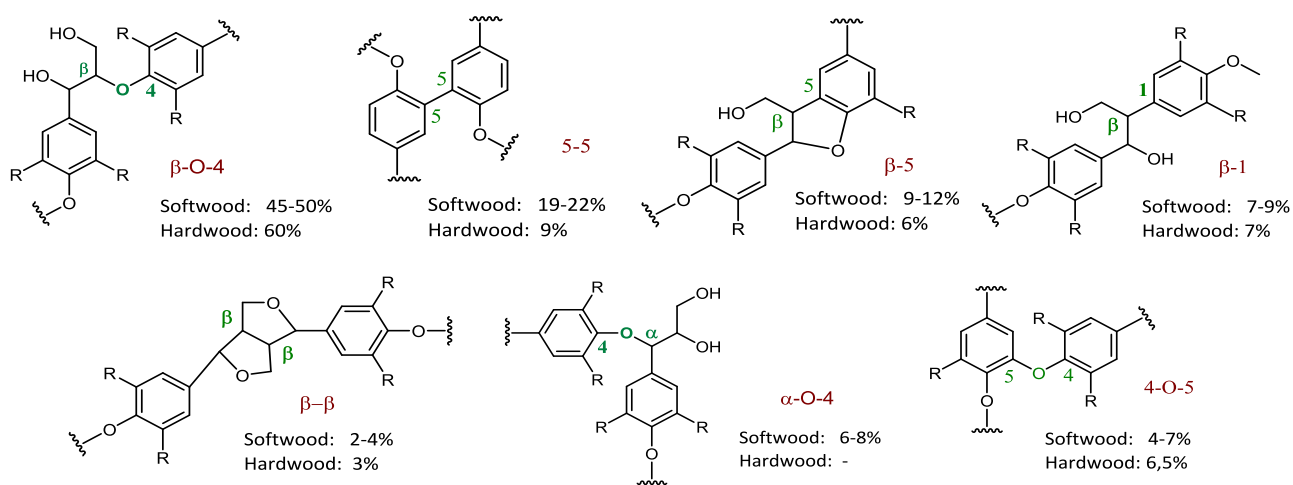


Fig. 1 Representative linkages and abundance of lignin present in soft and hardwood [7].

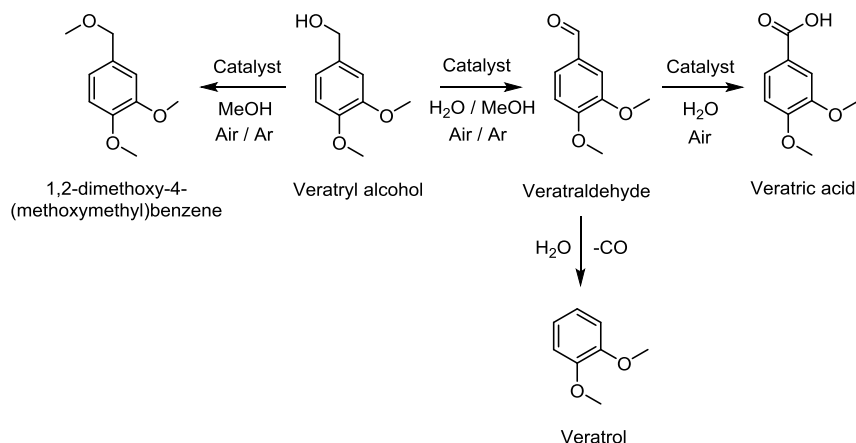
A reaction system representing the oxidative cleavage of β -O-4 linkages in lignin is the oxidation of veratryl alcohol (3,4-dimethoxybenzyl alcohol, VA) to the corresponding veratraldehyde (3,4-dimethoxybenzaldehyde, VALd) (Scheme 1). VALd is a useful flavorant and odorant and its formation has been comprehensively studied by both enzymatic and homogeneous catalyst systems.

Kirk and Farrell have reviewed early work up to 1987 on enzymatic degradation of lignin and lignin model compounds, including the catalytic oxidation of VA to VAld by ligninase [16]. Díaz-González et al. have later extensively studied the enzymatic oxidation of VA with laccase in the presence of several phenolic compounds as mediator/enhancer, but in all cases the yields to VAld remained low ($\leq 20\%$) [11]. Larson et al. have recently improved the laccase mediated oxidation and reported 94% of isolated VAld yield under optimized reaction condition [17]. Despite the advanced made on establishing enzymatic transformations of lignin and lignin model compounds these reaction systems suffer from well-known drawbacks such as, e.g. poor thermal stability, narrow pH operating range and enzyme deactivation over time making periodic replacement of enzyme necessary to maintain a good activity, which limit their general use.

Various types of homogeneous catalyst systems comprising porphyrins, Schiff-bases, polyoxometalates and other metal salts have been applied as alternatives to enzymes for the transformation of VA to VAld in the presence of stoichiometric oxidants (H_2O_2 , t-BuOOH, NaClO, PhIO, KHSO_5 , etc.) [18-23]. Thus, M-porphyrin based catalysts with $M = \text{Mn}$, Fe or Co all gave good yields (up to 90%) of VAld in the presence of H_2O_2 at room temperature [23]. In contrast, comparative lower yields of ≤ 7 and 43% were obtained with Co-sulphosalen [24-25] and Co-salen complexes [26], respectively. Quantitative conversion was, however, obtained with Cu-9,10-diamine-phenanthrene [27] as well as when using hexacyanoruthenate(II) in combination with either laccase or an electrolysis cell [28]. Several other catalyst systems based on Co, Cu or Ru salts have also been reported to provide VAld yields in the range 73-84% [29-30]. Despite excellent catalytic performance of many of the reported homogeneous catalyst systems they are inherently difficult to recover and recycle, which limit their general usability.

In contrast to homogeneous catalysts, solid catalysts with supported metals/metal oxides can easily be recovered from liquid reaction mixtures. Moreover, such catalysts can often be recycled provided that the metal leaching is negligible and applied at elevated reaction temperatures. For the aerobic oxidation of VA a combined Ru-imidazolite/CuO ionic liquid catalyst system has been reported to yield up to 95% of VAld at 130 °C [31]. However, the recyclability of the catalyst system was not documented. Recently, Yamaguchi and Mizuno have reported RuO_x supported on γ -alumina to be an effective and reusable heterogeneous catalyst for aerobic oxidation of both activated and non-activated alcohols in presence of sulfur, nitrogen and carbon-carbon double bonds [32]. Moreover, Ru-based catalysts have been demonstrated to play an important role in hydrogenation and hydrogenolysis reactions [31-36]. Combined, this makes Ru-based catalysts interesting to examine in the context of lignin valorization.

In the present work we have prepared, characterized and examined the performance of RuO_x supported on silica (Ru/SiO₂) and alumina (Ru/Al₂O₃) as catalysts for the oxidation of VA to VAld with air in both water and methanol. Analogous M/Al₂O₃ catalysts (M = MnO_x, CoO_x, CuO_x and AgO_x) were also prepared and applied in the oxidation reaction for comparison. Important reaction parameters such as temperature, time and solvent effect were optimized with the Ru/Al₂O₃ catalyst in order to limit the formation of by-products such as veratrol (Scheme 1). The recyclability of the catalyst was further examined by performing consecutive reaction runs in order to demonstrate the viability of the system.



Scheme 1 Catalytic oxidation of veratryl alcohol (VA) to veratraldehyde (VAld) and other products.

2. Experimental

2.1 Materials

Veratryl alcohol (> 96%, VA), veratraldehyde (99%, VAld), veratrol (99%) manganese(II)acetate tetrahydrate (> 99%), cobalt(II)nitrate hexahydrate (p.a.), copper(II)acetate monohydrate (p.a.), silver(I)nitrate (p.a.), ruthenium(IV)oxide hydrate (> 99.9%), ruthenium(III)acetylacetonate (> 97%) and silica gel 60 were purchased from Sigma Aldrich. γ -Aluminium oxide (> 99%) was provided by Saint Gobain as a generous gift. Compressed air (~21% oxygen) and argon (> 99.99%) was purchased from Air Liquide, Denmark. All chemicals and gasses were used as received.

2.2 Catalyst preparation

The supported catalysts were prepared by wet impregnation. Appropriate amounts of ruthenium or other metal (manganese, cobalt, copper and silver) precursors were dissolved in water and either alumina or silica was slowly added to the aqueous solution of metal precursor and stirred for 3 h. The slurry was then dried at 80 °C overnight in order to remove the water. Finally, the dried catalysts were calcined at 450 °C for 6 h in static air to get metal oxide (5 wt.% with respect to

metal) supported catalysts. The catalysts were stored in a desiccator and not pre-activated before use.

2.3 Catalyst characterization

TEM images of the Ru supported catalysts were recorded on a FEI Tecnai Transmission Electron Microscope at 200 kV with samples deposited on a carbon support. EDS analysis was performed with an Oxford INCA system. Surface areas of the supported catalysts were determined by nitrogen sorption measurements at liquid nitrogen temperature on a Micromeritics ASAP 2020. The samples were outgassed in vacuum at 150 °C for 4 h prior to the measurements. The total surface areas were calculated according to the BET method.

2.4 Catalytic oxidation reactions

Catalytic experiments were performed in an autoclave (Microclave 50 ml reactor, Autoclave Engineers) charged with an appropriate amount of VA, catalyst (100 mg) and water or methanol (10 ml) as solvent. The reactor was pressurized with air (5 bars) or argon (20 bars) and heated to the desired reaction temperature. Mechanical stirring of the reactor (300 rpm) was started when a temperature 20 °C below the set-point was reached. After the reaction, the autoclave was quenched in cold water where after filtered aliquots of the reaction mixture was subjected to GC-FID analysis (Agilent 6890N instrument, HP-5 capillary column 30.0 m × 320 μm × 0.25 μm) to quantify the conversion and product yield. The conversions of VA and yields of VAld were calculated based on series of individual standard solutions. The products were identified by GC-MS.

3. Results and Discussion

Initially, blank experiments without catalyst and with silica and alumina supports alone were carried out for the oxidation of VA to VAld in water. As expected, very poor yields of VAld (< 3%) were

obtained confirming that the oxidation reaction did practically not occur in absence of a catalytically active metal (Table 1).

Table 1 Oxidation of VA to VAld over various supported catalysts in water^a

Catalyst	BET surface area (m ² /g)	Conversion of VA (%)	Product yield (%)		TON
			VAld	Veratrol	
Ru/Al ₂ O ₃ (1) ^b	166	93	67	3	8
Ru/Al ₂ O ₃ (2) ^c	152	77	37	<1	4
Ru/SiO ₂ ^b	422	96	46	<1	6
Mn/Al ₂ O ₃	152	69	17	<1	1
Al ₂ O ₃	204	46	3	0	-
SiO ₂	472	59	3	0	-
-	-	34	2	0	-

^a Reaction conditions: 100 mg VA, 100 mg catalyst (5 wt.% metal), 10 ml water, 160 °C, 5 h, 5 bar air. ^b Catalyst prepared using ruthenium(IV) oxide hydrate precursor. ^c Catalyst prepared using ruthenium(III) acetylacetonate precursor. TON = mmol formed VAld/mmol metal in catalyst.

The yield of VAld increased significantly from 3 to 37% when the Ru/Al₂O₃ (2) catalyst made with ruthenium(III) acetylacetonate was applied in the reaction. Encouragingly, the VAld yield was improved even further to 67% (62% selectivity) for the Ru/Al₂O₃ (1) catalyst made with ruthenium(IV) oxide hydrate. In comparison, the activity as well as the selectivity (25%) of the Mn/Al₂O₃ catalyst was much lower than Ru/Al₂O₃ (1) and a corresponding yield of 17% VAld was only observed. TONs were calculated for the reactions based on the formation of VAld with respect to the total amount of metal present in the catalyst and are also given in Table 1. The TON for

Ru/Al₂O₃ (1) was found to be 8, which was much higher than Ru/Al₂O₃ (2) (TON = 4) as well as Mn/Al₂O₃ for the formation of VAld.

In order to understand the discrepancy in activity of the Ru/Al₂O₃ catalysts synthesised with the two different precursors, the catalysts were subjected to surface area measurement and microscopic studies. As shown in Table 1, no significant difference in the surface area of Ru/Al₂O₃ (1) and Ru/Al₂O₃ (2) was found. However, a considerable change in particle sizes on the Ru/Al₂O₃ catalysts was observed from TEM images (Fig. 2). Here, it can be inferred that Ru/Al₂O₃ (1) contained RuO_x particles with a size range between 20-30 nm, whereas Ru/Al₂O₃ (2) had particles with 5-10 fold larger size ranging from 100-200 nm. This suggests that RuO_x particle sizes played a significant role on the conversion of VA to VAld, thus signifying the importance of choosing the suitable metal precursor when making active Ru/Al₂O₃ catalysts. When changing the support from Al₂O₃ to SiO₂ the comparable VAld yield (46%) of catalysts made with the ruthenium(IV) oxide hydrate precursor decreased by 20% after 5 h of reaction, thus revealing a possible support role. However, the Ru/SiO₂ catalyst had a much higher surface area than Ru/Al₂O₃ (1) making a direct comparison difficult.

In all the reactions with the VA and the Ru catalysts the by-product veratrol (see Scheme 1) was only found in low yields < 3% (also at ≤ 140 °C, results not shown), even though previous reports have shown that Ru-based catalysts are efficient for decarbonylation of aromatic and aliphatic aldehydes as applied here [37-38]. The pH of the reaction mixture was measured before and after the reaction. Here a change from pH of 7-8 before reaction to 5-6 after reaction was found, suggesting us to speculate that veratric acid (not detectable by our GC, GC-MS and HPLC equipment) was formed by over oxidation, as also observed in previous studies [12]. Veratric acid thus also accounts for some of the missing material in the carbon balance.

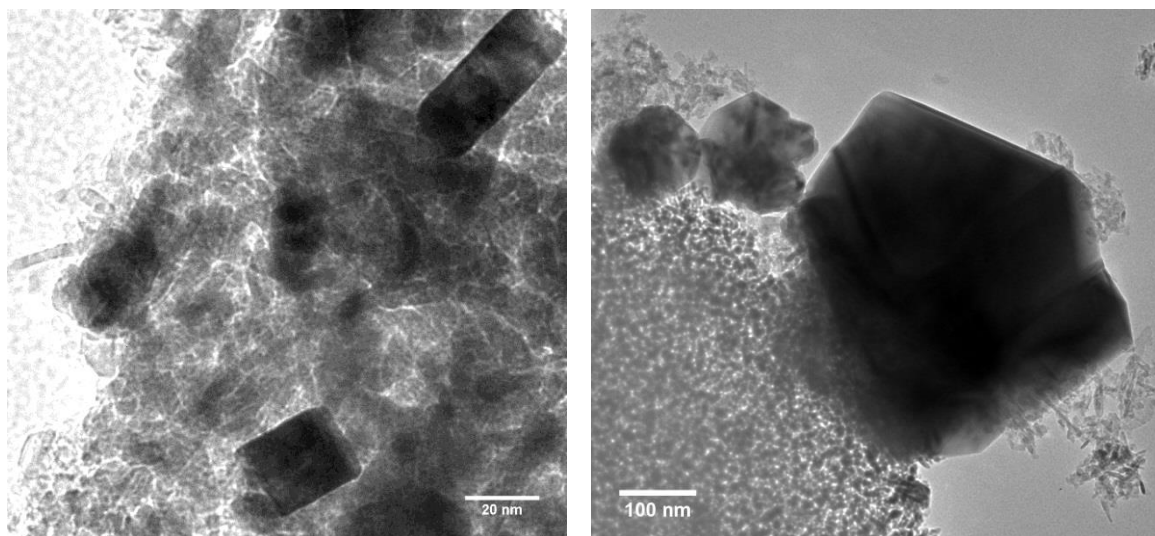


Fig. 2 High-resolution TEM images of (left) 5 wt.% Ru/Al₂O₃ (1) and (right) 5 wt.% Ru/Al₂O₃ (2).

In order to examine in more detail how VALd and veratrol formation developed during the reaction in water the reaction time was prolonged to 20 h in Ar, and the results are summarised in Table 2 and in the accompanying time-course study on Fig. 3. The results showed that Ru/Al₂O₃ (1) yielded 69% of VALd along with 27% of veratrol and full conversion after 20 h of reaction, with the former being essentially the same as the yield obtained after 5 h of reaction. Likewise, Ru/SiO₂ yielded 69% of VALd and less than 1% of veratrol along with quantitative VA conversion. Catalysts with alternative metals (Co, Cu, Ag and Mn) supported on Al₂O₃ gave VALd yields between 5 and 26% and low amounts of veratrol ($\leq 6\%$). TONs for all the metal supported catalysts were calculated and are also reported in Table 2. Apparently, it can here be seen that the TONs for Ru/Al₂O₃ (1) and Ru/SiO₂ were similar and significantly higher than the TONs for the catalysts based on the alternative metals. Notably, the time-course study further revealed that an excellent VALd yield of 89% could be reached after about 8 h of reaction, where the veratrol yield was less than 2%. When the reaction time exceeded 8 h, the veratrol yield increased at the expense of the VALd yield corroborating that decarbonylation of VALd to veratrol occurred. In a separate experiment using

VAlD as substrate, a very low yield of veratrol (< 2%) was obtained after 5 h in line with the results from the time course-study.

Table 2 Oxidation of VA in water and methanol over various metal supported catalysts^a

Catalyst	VA Conversion (%)	Product Yield (%) ^b			TON
		VAlD	Veratrol	VA-Ether ^d	
Ru/Al ₂ O ₃ (1) ^c	>99 (90)	69 (22)	27 (17)	(36)	9 (3)
Ru/SiO ₂ ^c	99 (96)	69 (10)	<1 (<1)	(67)	8 (1)
Co/Al ₂ O ₃	61 (56)	13 (7)	4 (6)	(16)	2 (1)
Cu/Al ₂ O ₃	>99 (56)	5 (13)	1 (8)	(37)	<1 (2)
Ag/Al ₂ O ₃	34 (89)	26 (2)	<1 (22)	(34)	3 (<1)
Mn/Al ₂ O ₃	81 (47)	23 (24)	6 (<1)	(22)	3 (3)

^a Reaction conditions: 170 mg VA, 170 mg catalyst (5 wt.% metal), 10 ml water, 160 °C, 20 bar argon, 20 h. ^b Numbers in parenthesis are results from experiments performed in methanol (10 ml). ^c Catalyst prepared using ruthenium(IV) oxide hydrate precursor. ^dVA-ether refers to 1,2-dimethoxy-4-(methoxymethyl)benzene. TON = mmol of VAlD formed/mmol of metal in catalyst.

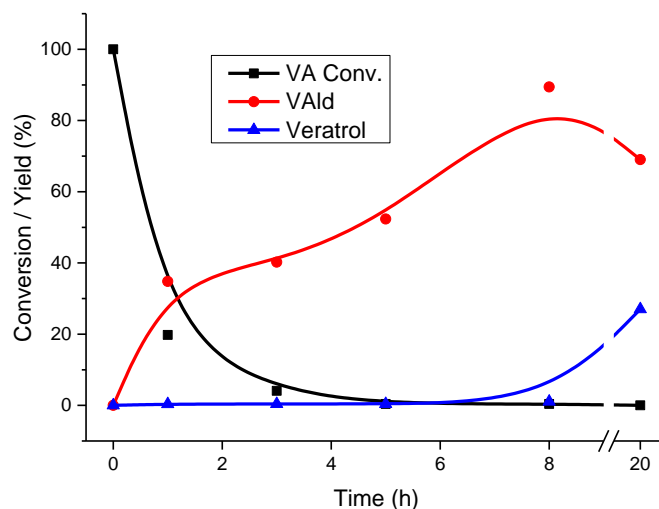


Fig. 3 Time-course study for VA conversion into VAld with Ru/Al₂O₃ (1) in water. Reaction conditions: 100 mg VA, 100 mg catalyst (5 wt.% metal), 10 ml water, 160 °C, 5 bar air. Each set of data on the time axis is from individual experiments.

When the solvent was changed from water to methanol, the yield of VAld obtained with Ru/Al₂O₃ (1) (at 160 °C and 20 bar Ar) drastically reduced from 69 to 22%. Instead the formation of the methyl ether by-product of VA, 1,2-dimethoxy-4-(methoxymethyl)benzene (VA-ether) prevailed (see Scheme 1). The highest yield of VA-ether (67%) was obtained over Ru/SiO₂. Concomitantly, the yield of VAld was reduced to 10% with the latter catalyst, which was about five times lower than the corresponding yield attained in water with 5 bar of air after 20 h reaction (Table 2). This substantiate that the presence of oxygen favoured the conversion of VA to VAld by oxidation rather than dehydrogenation which, on the other hand, prevailed under argon atmosphere. Moreover, when the experiment was carried out in methanol at 5 bar air pressure, no improvement in VAld yield (15%) was observed (results not shown), inferring that water was the preferred solvent for the oxidation of VA to VAld in the presence of air.

Catalyst recyclability is important for the viability of a catalyst system. Accordingly, the Ru/Al₂O₃ (1) catalyst was subjected to reuse studies in the VA oxidation reaction. After each reaction run the catalyst was recovered by filtration, thoroughly washed with water, dried overnight at 80 °C and finally calcined at 450 °C for 6 h before being used in the next reaction. As depicted in Fig. 4, the conversion of VA and the yield to VAld decreased noticeably after three reaction cycles from 93 to 65% and 67 to 34%, respectively, while the VAld selectivity remained above 50%. Part of the loss of catalytic activity could be due to loss of catalyst during the separation or due to increase in particles size of ruthenium during the additional calcinations, as previously observed in supported Ru catalysts [39]. The used Ru/Al₂O₃ (1) catalyst was after the consecutive reactions subjected to

surface area measurement. Here the BET surface area was found to be increased almost 20% from the original 166 to 201 m²/g, which resembled the alumina support alone (204 m²/g). Combined, the activity drop as well as the increased surface area could indicate possible Ru leaching from the support to the reaction solutions. However, leaching of Ru from this type of catalyst materials under similar conditions has previously shown to be a minor issue [39-40].

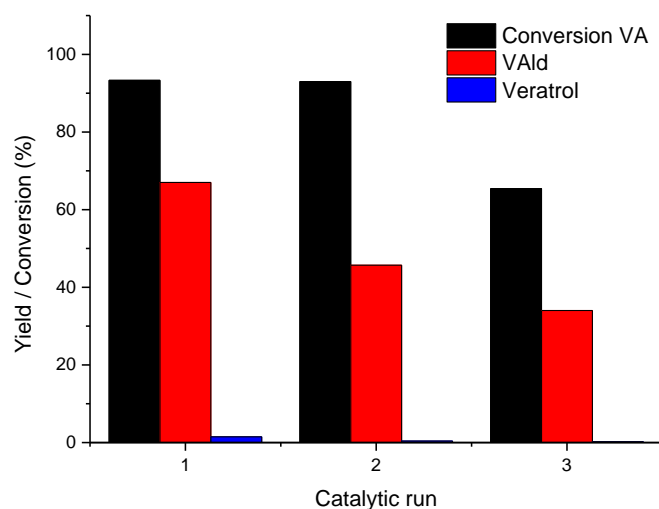


Fig. 4 Reuse of Ru/Al₂O₃ (1) catalyst for three consecutive VA oxidation reactions in water. Reaction conditions: VA to catalyst mass ratio = 1.04, 10 ml water, 160 °C, 5 h, 5 bar air.

4. Conclusions

Ru/Al₂O₃ (1) (prepared with ruthenium(IV)oxide hydrate precursor) demonstrated to give the highest yield to VAld (89 %) at full conversion of VA in water at 160 °C and 5 bar air after 8 h of reaction. An analogous catalyst prepared with ruthenium(III) acetylacetonate precursor gave a 30% lower VAld yield, which by TEM analysis was correlated with the presence of larger RuO_x particles in the latter catalyst. A significant amount of veratrol by-product was formed by decarbonylation of VA with Ru/Al₂O₃ after prolonged reaction time, suggesting that control of the

reaction time was necessary to obtain VAld in high yield. Moreover, by conducting the reaction in methanol instead of water with 20 bars of Ar resulted in a lower yield of VAld (by dehydrogenation), while VA-ether formation was facilitated (36% yield). TONs for the conversion of VA to VAld was found to be 8 with Ru/Al₂O₃ (1) in air, which was about 50% higher than the TONs obtained with Ru/Al₂O₃ (2) and Ru/SiO₂. The TON increased slightly with Ru/Al₂O₃ (1) at longer reaction time when the reaction was carried out under Ar due to dehydrogenation of VA to VAld. It was possible to recycle the Ru/Al₂O₃ (1) catalyst and apply it in three consecutive reaction runs. However, the VA yield decreased significantly between each run, probably due to insufficient catalyst stability under the reaction conditions. The unsatisfying recyclability is a major drawback, which obviously hamper implementation of the Ru/Al₂O₃ catalyst for lignin valorisation. Continuation of the work is currently in progress in search for a suitable water-tolerant and stable supported catalyst.

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References

- [1] The oil drum, discuss about energy and our future (2013) Luis de Soussa, Luxemburg. <http://www.theoil drum.com/node/10009>.
- [2] Corma A, Iborra S, Velty A (2007) Chem. Rev. 107: 2411-2502.
- [3] Saravanamurugan S, Holm MS, Taarning E (2010) Science 328: 602-605.

- [4] Holm MS, Pagan-Torres, YJ, Saravanamurugan S, Riisager A, Dumesic JA, Taarning E (2012) *Green Chem.* 14: 702-706.
- [5] Saravanamurugan S, Riisager A (2013) *ChemCatChem* 5: 1754-1757.
- [6] Patil PT, Armbruster U, Richter M, Martin A (2006) *Energy & Fuels* 311: 4713-4722.
- [7] Zakzeski J, Bruijninx PCA, Jongerius AL, Weckhuysen BM (2010) *Chem. Rev.* 110: 3552-3599.
- [8] Amen-Chen C, Pakdel H, Roy C (2001) *Bioresour. Technol.* 79: 277-299.
- [9] Zhao C, Lercher JA (2012) *ChemCatChem* 4: 64-68.
- [10] Q. Xiang, Y. Y. Lee, *Appl. Biotechnol.* 2000 153: 84-86
- [11] Díaz-González M, Vidal T, Tzanov T (2011) *Appl. Microbiol. Biotechnol.* 89: 1693-1700
- [12] Crestini C, Crucianelli M, Orlandi M, Saladino R (2010) *Catal. Today* 156: 8-22.
- [13] Jha A, Chandole T, Pandya R, Roh HS, Rode CV (2014) *RSC Adv.* 4: 19450-19455.
- [14] Lange H, Decina S, Crestini C (2013) *Eur. Polymer. J.* 49: 1151-1173.
- [15] Shannon S. Stahl, Alireza Rahimi (2014) US Patent 2014/0235838
- [16] Kirk TK, Farrell RL (1987) *Ann. Rev. Microbiol* 41: 465-505.
- [17] Larson TM, Anderson M, Rich JO (2013) *Biotechnol. Lett.* 35: 225-231.
- [18] Cui F, Dolphin D (1995) *Biorg. Med. Chem.* 3: 471-477.
- [19] Labat G, Meunier B (1989) *J. Org. Chem.* 54: 5008-5011.
- [20] Zhu W, Ford WT (1993) *J. Mol. Catal.* 78: 367-378.

- [21] Zucca P, Sollai F, Garau A, Rescigno A, Sanjust E (2009) *J. Mol. Catal. A: Chem.* 306: 89-96.
- [22] Kumar A, Jain N, Chauhan SMS (2007) *Synlett* 34: 411-414.
- [23] Zucca P, Mocci G, Rescigno A, Sanjust E (2007) *J. Mol. Catal. A: Chem.* 278: 220-227.
- [24] Sena-Martins G, Almeida-Vara E, Duarte JC (2008) *Ind. Crops Prod.* 27: 189-195.
- [25] Sippola V, Krause O, Vuorinen T (2004) *J. Wood Chem. Technol.* 24: 323-340.
- [26] Kervinen K, Korpi H, Mesu JG, Soulimani F, Repo T, Rieger B, Leskelä M (2005) *Eur. J. Inorg. Chem.* 13: 2591-2599.
- [27] Lahtinen P, Korpi H, Haavisto E, Leskelä M, Repo T (2004) *J. Comb. Chem.* 6: 967-973.
- [28] Rochefort D, Boubonnais R, Leech D, Paice MG (2002) *Chem. Commun.* 1182-1183.
- [29] Kervinen K, Korpi H, Leskelä M, Repo T (2003) *J. Mol. Catal. A: Chem.* 203: 9-19.
- [30] Ambrose K, Bitu BB, Singer RD (2013) *Can. J. Chem.* 91: 1258-1261.
- [31] Fan H, Yang Y, Song J, Ding G, Wu C, Yang G, Han B (2014) *Green Chem.* 16: 600-604.
- [32] Yamaguchi K, Mizuno N (2002) *Angew. Chem. Int. Ed.* 41: 4538-4542.
- [33] Zhan BZ, White MA (2003) *J. Am. Chem. Soc.* 125: 2195-2199.
- [34] Gorbanev YY, Kegnæs S, Riisager A (2011) *Top. Catal.* 54: 1318-1324.
- [35] Nie J, Xie J, Liu H (2013) *J. Catal.* 301: 83-91.
- [36] Ruppert A, Weinberg K, Palkovits R (2012) *Angew. Chem. Int. Ed.* 51: 2564-2601.
- [37] Domazetis G, Tarpey B, Dolphin D, James BR (1980) *J. Chem. Soc., Chem. Commun.* 20: 939-940.

[38] Allen CL, Willams MJJ (2010) *Angew. Chem. Int. Ed.* 49: 1724-1725.

[39] Gorbanev YY, Kegnæs S, Hanning CW, Hansen TW, Riisager A (2012) *ACS Catal.* 2: 604-612.

[40] Gorbanev YY, Kegnæs S, Riisager A (2011) *Catal. Lett.* 141: 1752-1760.