ORGANIC PROCESS RESEARCH & DEVELOPMENT
OPR&D

Subscriber access provided by ST FRANCIS XAVIER UNIV

Full Paper

Mechanistic aspects of hydrodeoxygenation of para-methylguaiacol over Rh/silica and Pt/silica

Florent Bouxin, Xingguang Zhang, Iain Kings, Adam Fraser Lee,
Mark John H. Simmons, Karen Wilson, and S. David Jackson

Org. Process Res. Dev., **Just Accepted Manuscript** • DOI: 10.1021/acs.oprd.8b00211 • Publication Date (Web): 29 Aug 2018

Downloaded from http://pubs.acs.org on August 29, 2018

Just Accepted

"Just Accepted" manuscripts have been peer-reviewed and accepted for publication. They are posted online prior to technical editing, formatting for publication and author proofing. The American Chemical Society provides "Just Accepted" as a service to the research community to expedite the dissemination of scientific material as soon as possible after acceptance. "Just Accepted" manuscripts appear in full in PDF format accompanied by an HTML abstract. "Just Accepted" manuscripts have been fully peer reviewed, but should not be considered the official version of record. They are citable by the Digital Object Identifier (DOI®). "Just Accepted" is an optional service offered to authors. Therefore, the "Just Accepted" Web site may not include all articles that will be published in the journal. After a manuscript is technically edited and formatted, it will be removed from the "Just Accepted" Web site and published as an ASAP article. Note that technical editing may introduce minor changes to the manuscript text and/or graphics which could affect content, and all legal disclaimers and ethical guidelines that apply to the journal pertain. ACS cannot be held responsible for errors or consequences arising from the use of information contained in these "Just Accepted" manuscripts.

ACS Publications

is published by the American Chemical Society. 1155 Sixteenth Street N.W., Washington, DC 20036

Published by American Chemical Society. Copyright © American Chemical Society. However, no copyright claim is made to original U.S. Government works, or works produced by employees of any Commonwealth realm Crown government in the course of their duties.

Mechanistic aspects of hydrodeoxygenation of *para*-methylguaiacol over Rh/silica and Pt/silica.

Florent P. Bouxin[a], Xingguang. Zhang[b], Iain N. Kings[c], Adam F. Lee[b] , Mark J. H. Simmons[c],
Karen Wilson[b], S. David. Jackson*[a]

[a]Centre for Catalysis Research, School of Chemistry, University of Glasgow, Glasgow G12 8QQ,
Scotland

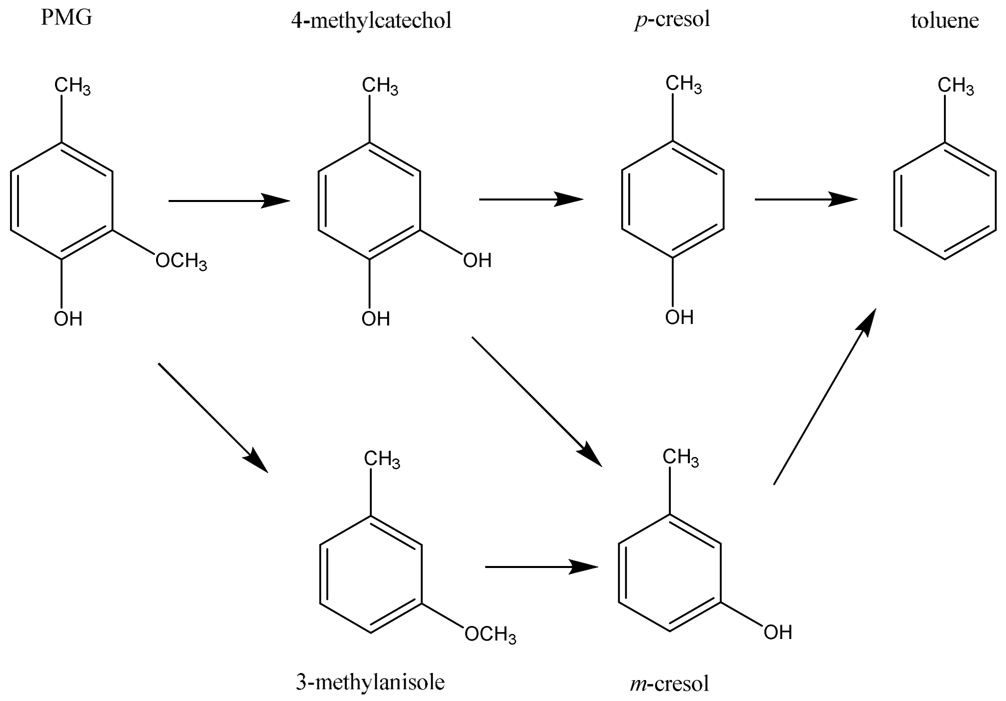
[b]School of Science, RMIT University, Melbourne VIC3001, Australia

[c]School of Chemical Engineering, University of Birmingham, Birmingham B15 2TT, UK

* Author to whom all correspondence should be addressed

david.jackson@glasgow.ac.uk

TOC Graphict



Abstract.

The mechanism of p-methylguaiacol (PMG) hydrodeoxygenation (HDO) has been examined over two Rh/silica catalysts and a Pt/silica catalyst at 300 °C and 4 barg hydrogen. Sequential conversion of PMG to 4-methyl catechol is followed by m- and p-cresol formation, and finally toluene production, although direct conversion of PMG to p-cresol is favoured over a commercial Rh/silica catalyst. Dehydroxylation and hydrogenation are shown to occur over metal functions, while demethylation and demethoxylation are favoured over the fumed silica support. A mechanistic pathway for PMG hydrodeoxygenation is proposed.

Keywords. Para-methylguaiacol; hydrodeoxygenation; rhodium; platinum; mechanism.

Introduction.

Hydrodeoxygenation (HDO) of bio-oils is an active research area in both catalysis and bioenergy,[1,2] and offers one of the methodologies capable of upgrading bio-oils into a form suitable for blending with petroleum. Previously,[3] we examined the deactivation of three catalysts for the HDO of *para*-methylguaiacol, a common component of pyrolytic bio-oils. The catalysts were 2.5 wt% Rh/silica supplied by Johnson Matthey (JM), an in-house prepared 2.5 wt% Rh/silica (A) and 1.55 wt% Pt/silica (A). All three catalysts exhibited an initial deactivation phase, although the Rh/silica (JM) achieved steady-state after ~6 h on-stream and maintained a constant activity over the subsequent test period. In contrast, the two in-house catalysts did not reach steady state within the testing timeframe, both Rh/silica (A) and Pt/silica (A) underwent continuous deactivation, albeit following different mechanisms.[3] Here we focus on the reaction mechanisms over the different catalysts, and their response to deactivation. There are no other literature studies of *p*-methylguaiacol, however guaiacol has been the subject of several investigations. Mu et al[4] studied guaiacol HDO over a Rh/C catalyst at 40 bar hydrogen and 250 °C in a batch reactor, reporting demethoxylation as the dominant process resulting in phenol as the main product (~35 % selectivity) at a modest conversion of ~13 %; other major products were cyclohexanone and cyclohexanol (~25 % selectivity). Gutierrez *et al*.[5] examined rhodium and platinum on zirconia supports for guaiacol HDO, predominantly observing hydrogenated products at 100 °C, with some deoxygenation at 300 °C, although few details were provided. Platinum catalysts have been somewhat more researched and their HDO mechanism considered. A detailed reaction network for guaiacol conversion over Pt/alumina was uncovered by Gates and co-workers,[6] wherein a wide product distribution was detected, reflecting HDO in competition with transalkylation and hydrogenolysis. In the course of our previous work it became apparent that demethylation, demethoxylation, and hydrogenation pathways were affected differently by catalyst deactivation and we were interested to put this into context mechanistically, and through the use of two metals and two silica supports, determine the active sites for each reaction.

Results and Discussion.

The three catalysts were tested for *para*-methylguaiacol HDO over an extended period of 32 h. As previously reported, the Rh/silica (JM) catalyst achieved a steady state within the timeframe of the testing, whereas Rh/silica (A) and the Pt/silica (A) both exhibited continuous deactivation resulting in significant selectivity variations between 1 h and 32 h on stream (Figures 1-3).

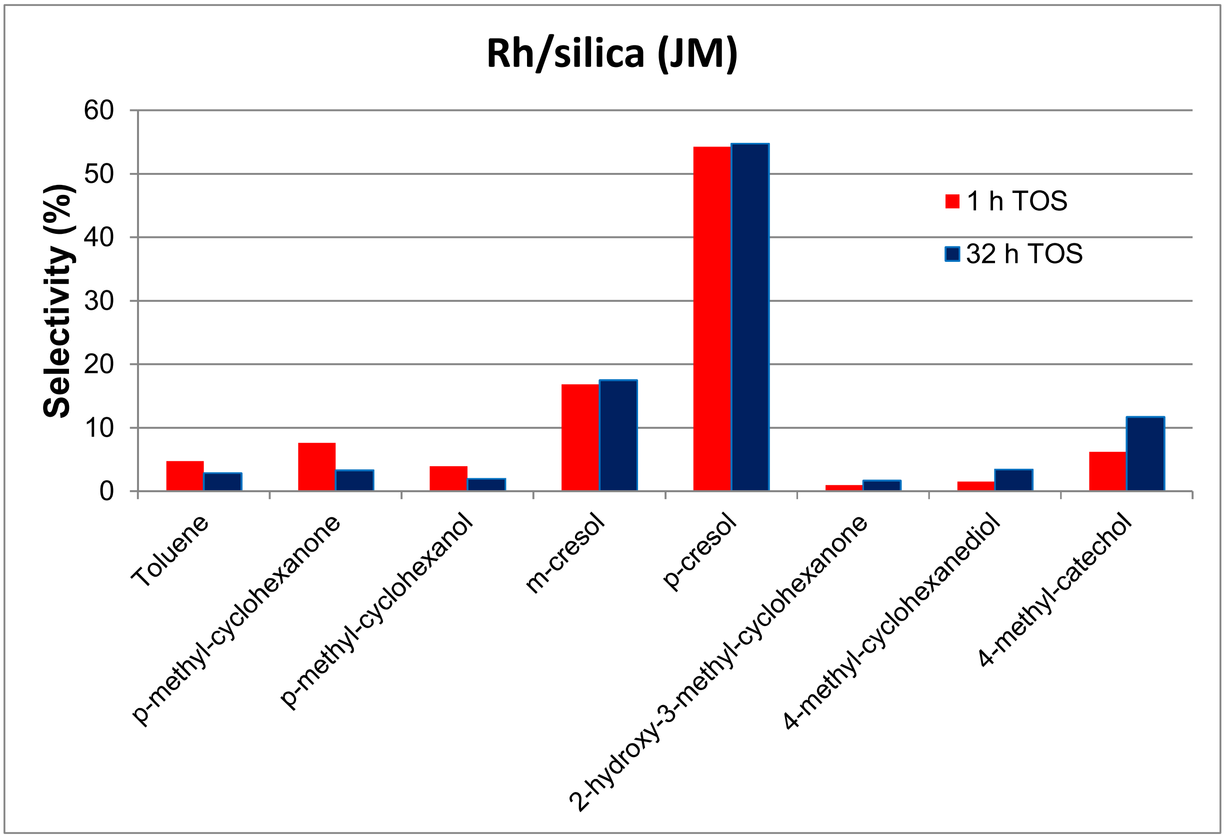


Figure 1. Product distribution for *p*-Methylguaiacol HDO over Rh/silica (JM); 47 % and 34 % conversion after 1 h and 32 h time on stream respectively.

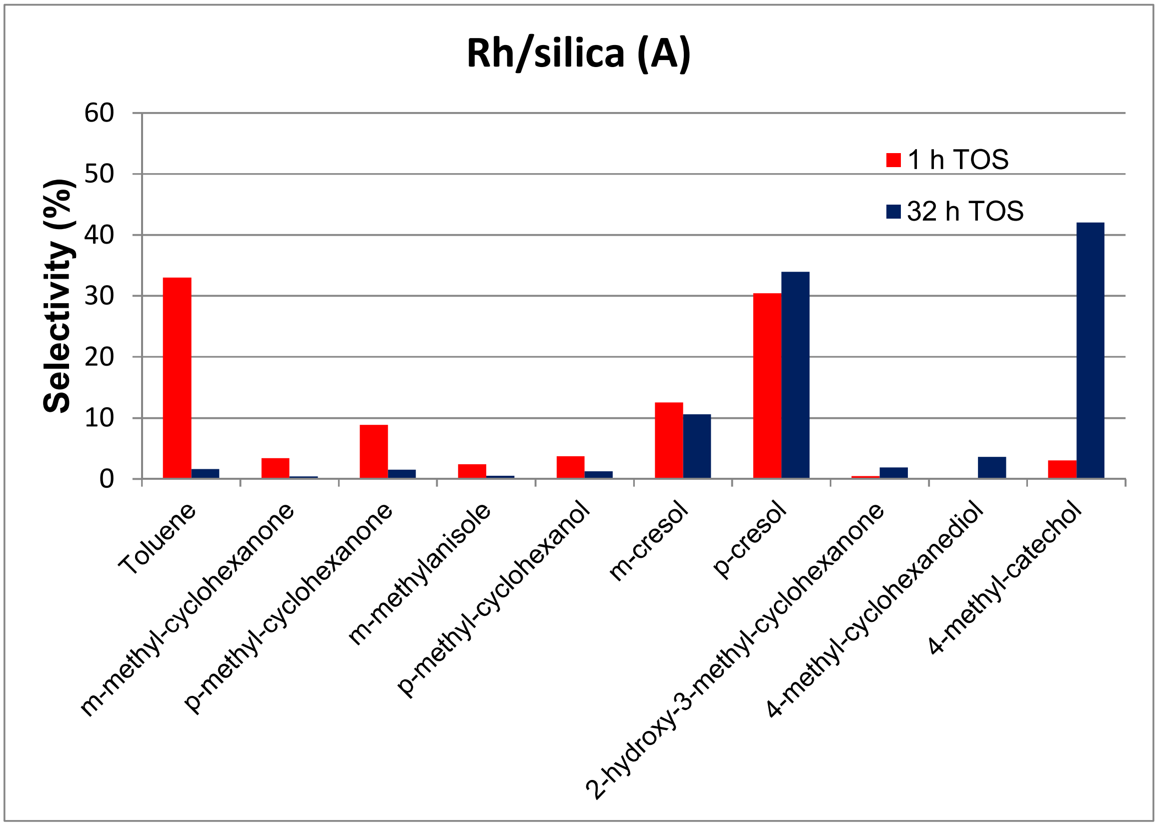


Figure 2. Product distribution for *p*-Methylguaiacol HDO over Rh/silica (A); 50 % and 26 % conversion after 1 h and 32 h time on stream respectively.

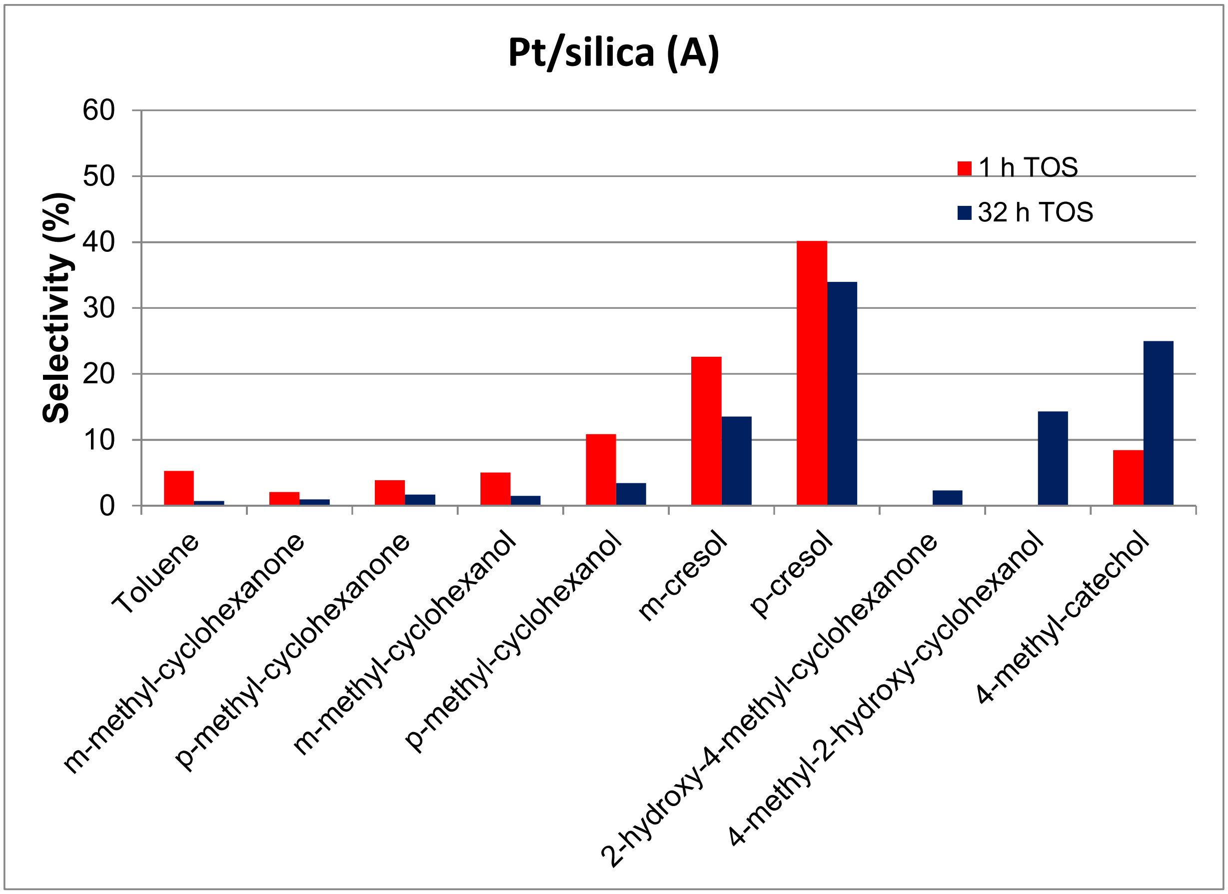
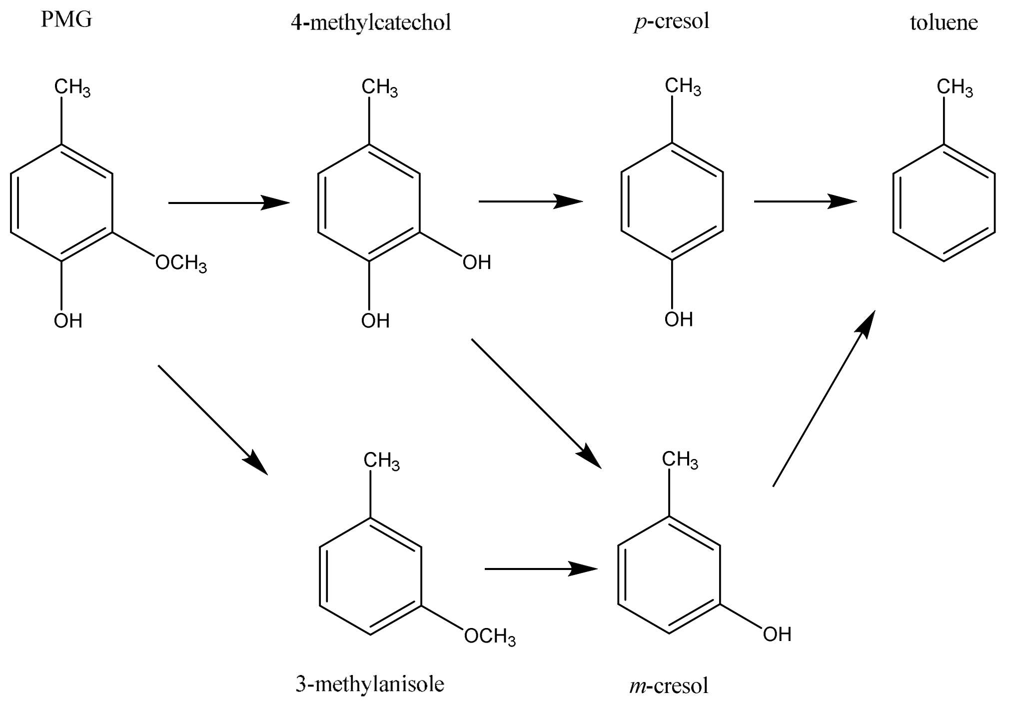


Figure 3. Product distribution for *p*-Methylguaiacol HDO over Pt/silica (A): 70 % and 47 % conversion after 1 h and 32 h time on stream respectively.

In the early stages of the test Rh/silica (A) is selective to toluene (33 %) and *para*-cresol (30 %) but after 32 h time on stream the major products are 4-methylcatechol (41 %) and *para*-cresol (34 %). This is in marked contrast to Rh/silica (JM), where toluene selectivity (< 5 %) and 4-methylcatechol selectivity (< 10 %) are both low throughout the test. Pt/silica (A) displays a less pronounced switchover from *meta*- and *para*-cresol to 4-methylcatechol production.

Mechanistically, the results for both Rh catalysts reflect sequential hydrogenolysis reactions as shown in Scheme 1. As Rh/silica (A) deactivates, it loses hydrogenolysis/HDO activity, such that the demethylation product 4-methycatechol is increasingly favoured. This selectivity switching mirrors the relative ArO-CH_3 versus Ar-OCH_3 bond strengths of ~381 kJ.mol^{-1} versus 419 kJ.mol^{-1} respectively. None of the catalysts promoted C-C bond scission and concomitant benzene generation, and only products of cresol hydrogenation (*p*- and *m*-methylcyclohexanone) were observed, but not methylcyclohexane. 3-Methylanisole was only formed as a minor product over Rh/silica (A), suggesting that dehydroxylation of PMG to 3-methylanisole (and subsequent demethylation to m-cresol) is generally an unfavourable pathway consistent with its high energy barrier of ~431 kJ.mol^{-1}. Demethylation of PMG to 4-methylcatechol was unaffected by deactivation, presumably reflecting the weaker bonds to be cleaved. *p*-Cresol may form by either direct demethoxylation of PMG, or (very energetically unfavourable) dehydroxylation of 4-methylcatechol. Since *p*-cresol production was largely unaffected by deactivation, we conclude it forms through the former (less energy intensive) direct demethoxylation. Rh/silica (JM) is never effective for complete PMG dehydroxylation (toluene selectivity <5 %), indicating a lack of the



Scheme 1. Mechanism of hydrogenolysis/HDO of PMG.

highly active sites requisite for such a challenging bond cleavage, which may in part underlie its superior stability. To test the proposed mechanism the catalyst was operated under a range of space velocities. As the space velocity was increased conversion and selectivity to secondary products decreased, however selectivity to 4-methylcatechol increased (yield also increased except for the highest space velocity) as shown in Figure 4, confirming 4-methylcatechol as a primary product.

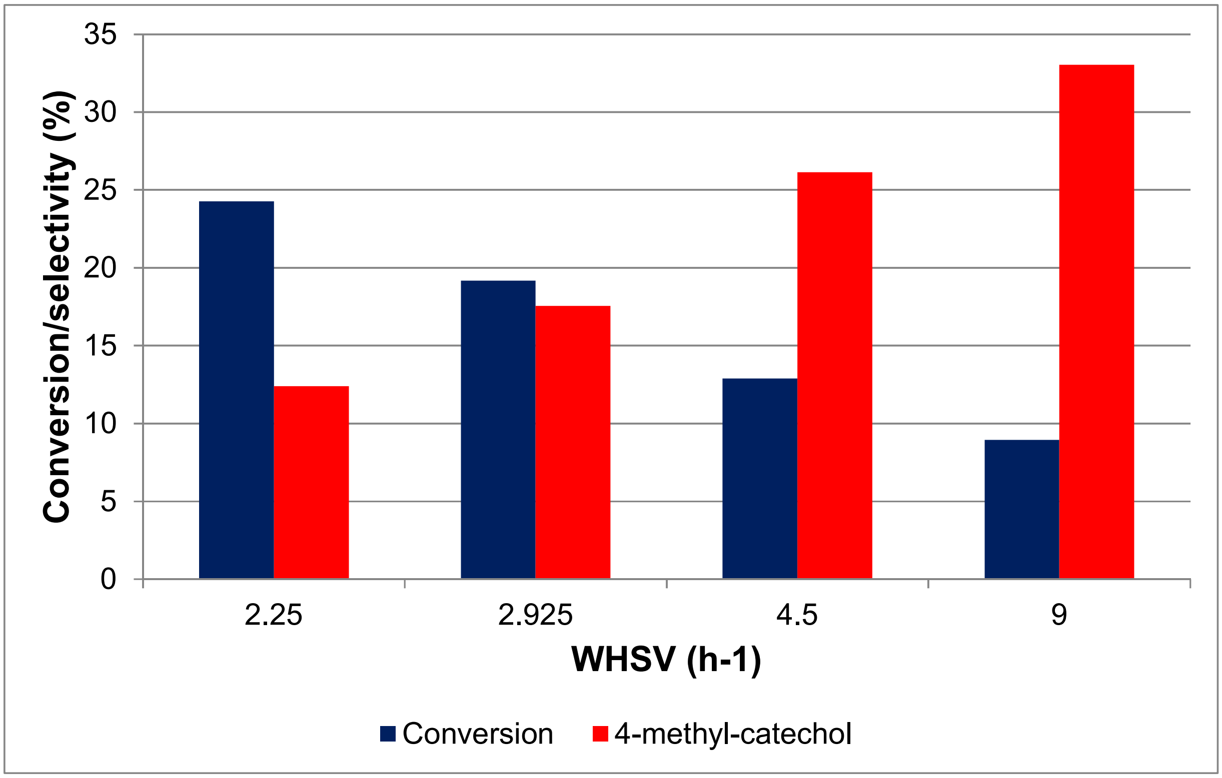
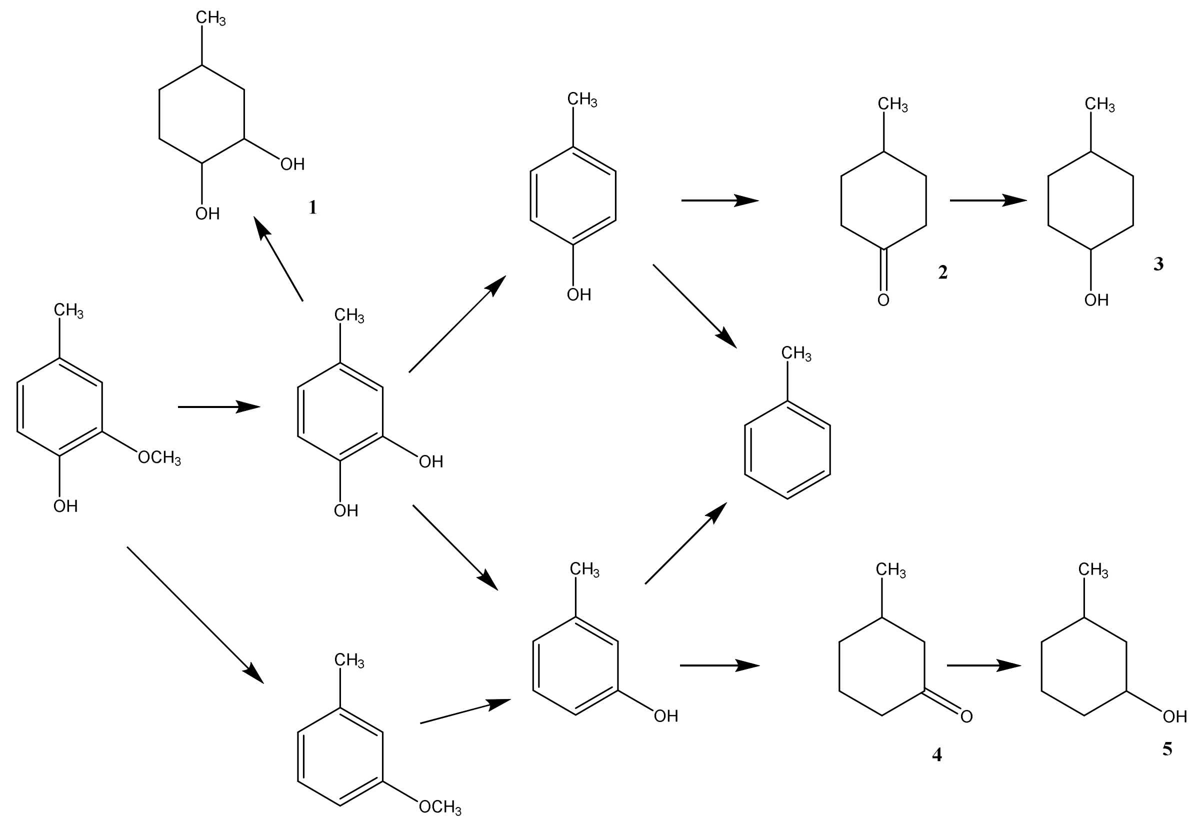


Figure 4. Conversion of PMG and selectivity to 4-methylcatechol. Conditions: 280 °C, 4 barg H_2.

Although the major products over Pt/silica (A) after 1 h time on stream were *m*-cresol and *p*-cresol, there is also marked hydrogenation activity, evidenced by significant selectivity to hydrogenated cresols. The initial total selectivity to *p*-methylcyclohexanone and *p*-methylcyclohexanol is ~11 % (with proportionally lower values for the *meta*-isomers). After 32 h, when the catalyst has deactivated, the selectivity changes to favour 4-methylcatechol and the hydrogenated form 4-methyl-2-hydroxy-cyclohexanol. Overall Pt/silica (A) is the most active hydrogenation catalyst, which is maintained even during deactivation.[3] The mechanism outlined in Scheme 1 can be extended to give Scheme 2 taking into account the platinum hydrogenation activity.



Scheme 2. Extended mechanism of hydrogenolysis/HDO/hydrogenation of PMG. The aromatic species are as in Scheme 1; compound 1, 1,2-dihydroxy-4-methyl-cyclohexanol; compound 2, 4-methyl-cyclohexanone; compound 3, 4-methyl-cyclohexanol; compound 4, 3-methyl-cyclohexanone; compound 5, 3-methyl-cyclohexanol.

The above discussion considers the behaviour of the catalysts with time and changes in their selectivity; however it is also worthwhile to compare the selectivity at equivalent conversion. The results are shown in Figure 5. What is immediately noticeable is that the yield/selectivity of 4-methycatechol is the same for both Rh/silica (A) and Pt/silica, the catalysts with the same support. This suggests that the demethylation reaction (the breaking of the ArO-CH_3 bond) is favoured over

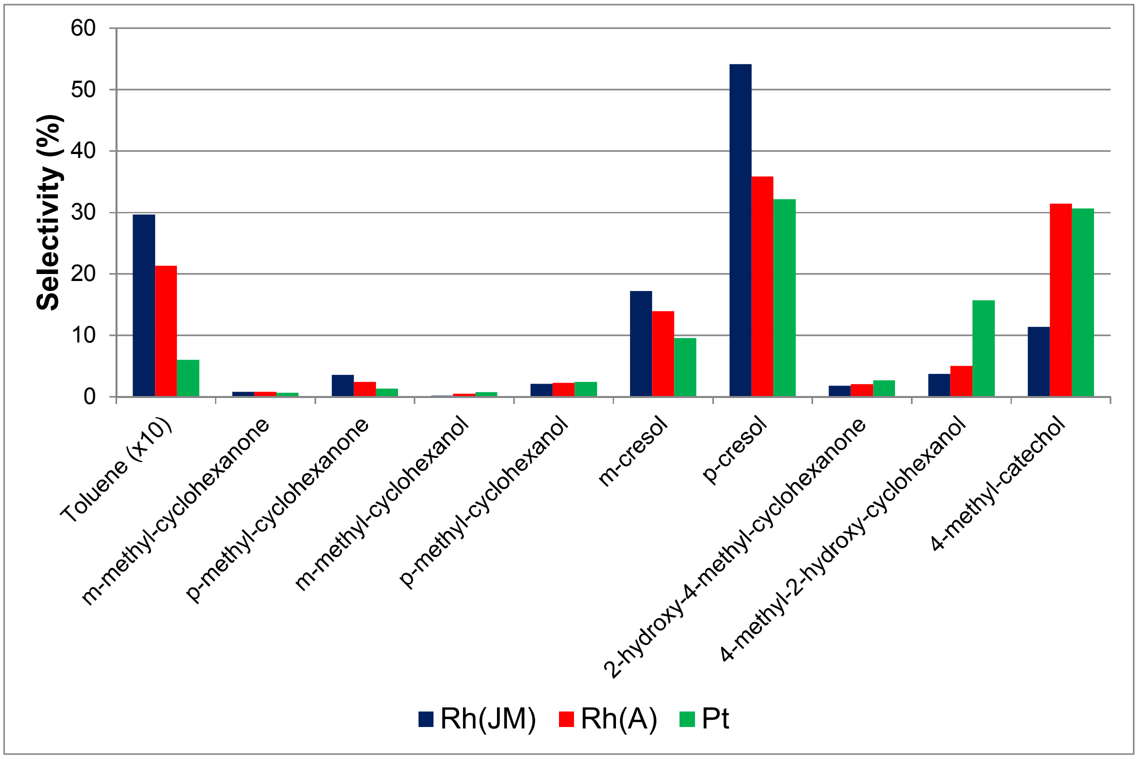


Figure 5. Selectivity to products at ~32 % conversion.

the fumed silica support rather than the metal function. In contrast dehydroxylation (breaking Ar-OH bonds) appears to take place over the metal function. This is suggested at by the selectivity of toluene, where the Rh catalysts give a similar figure but is confirmed by the selectivity to *m*-cresol and *m*-anisole (Rh/silica (JM) and Rh/silica (A) selectivity 0.6 %, Pt/silica selectivity 0.4 %). This in agreement with Nimmanwudipong *et al*. who suggested dehydroxylation was performed over the metal function.[6] It is also consistent with the deactivation study, where demethylation activity was the least affected by carbon deposition.[3] There are two routes to the formation of *p*-cresol, through 4-methylcatechol by dehydroxylation and by demethoxylation direct from PMG. Given that dehydroxylation is a difficult process, the high selectivity to *p*-cresol over the Rh/silica (JM) suggests that demethoxylation of PMG to give *p*-cresol takes place over the support.

In conclusion, we have clarified and simplified the mechanism for PMG hydrodeoxygenation and hydrogenation. Dehydroxylation and hydrogenation are shown to occur over metal functions, while demethylation and demethoxylation are favoured over the fumed silica support. Only one catalyst (Rh/silica (A)) gave significant yields of toluene, the full HDO product but the sites responsible were rapidly deactivated. Overall rhodium was a more effective HDO metal than platinum.

Experimental

Three catalysts were used in this study 2.5 % Rh/SiO_2 (JM), 2.5 % Rh/SiO_2 (A) and 1.55 % Pt/SiO_2. All catalysts were prepared by impregnation and details of their preparation is reported elsewhere [3]. The catalysts were ground and sieved to between 350 and 850 μm before use and all reagents and solvents were purchased from Sigma-Aldrich and used without further purification.

Conversion and yield are defined in equations 1, 2 and 3

Conversion = ((Σ moles products + moles PMG out)-(moles PMG out))/(Σ moles products + moles PMG out) (Equation 1)

Selectivity = moles product/Σ moles products (Equation 2)

Yield = moles product/(Σ moles products + moles PMG out) (Equation 3)

The catalytic testing and analysis methodology has been reported elsewhere [3] but briefly the tests were performed in a continuous-flow, fixed-bed reactor. The catalysts (~0.5 g) were pre-reduced *in-situ* before reaction at 300 °C for 2 h under 100 mL min^{-1} of 40 % H_2/Ar. After the catalysts were reduced, *p*-methylguaiacol (PMG) was pumped into the gas flow and vaporised at 200 °C. The reaction temperature was 300 °C with a hydrogen partial pressure of 4 barg giving a H_2:PMG ratio of 15. The total pressure was made up to 10 barg using argon. Typical weight hourly space velocity (WHSV) of PMG was 2.5 h^{-1}, while the gas hourly space velocity (GHSV) was 7200 h^{-1}. The products were trapped in a condenser at 5 °C before sampling.

A full description of the analysis methodology is reported elsewhere [3]. In brief to fully quantify the products three distinct solutions were prepared from the same mixture of products. Firstly two internal standards were added, (decane at 0.86 and heptadecane at 10.2 g L^{-1}) before two aliquots were silylated. Analysis of the three solutions using this technique permitted a full quantification of minor and major products. The quantitative analyses were performed on an HP 5890 gas chromatograph fitted with a Supelco DB-5 capillary column (30m × 0.32 mm, 1 mm thickness).

Acknowledgments

UK Catalysis Hub is kindly thanked for resources and support provided via our membership of the UK Catalysis Hub Consortium and funded by EPSRC (grants EP/K014706/1, EP/K014668/1, EP/K014854/1, EP/K014714/1 and EP/M013219/1).

References

(1) Lup, A. N. K.; Abnisa, F.; Daud, W. M. A. W.; Aroua, M. K. A review on reaction mechanisms of metal-catalyzed deoxygenation process in bio-oil model compounds, *Appl. Catal. A*, **2017**, *541*, 87–106

(2) Lup, A. N. K.; Abnisa, F.; Daud, W. M. A. W.; Aroua, M. K. A review on reactivity and stability ofheterogeneous metal catalysts for deoxygenation of bio-oil model compounds, *J. Ind. Eng. Chem*. **2017**, *56*, 1–34

(3) Bouxin, F. P.; Zhang, X.; Kings, I. N.; Lee, A. F.; Simmons, M. J. H.; Wilson, K.; Jackson, S. D. Deactivation study of the hydrodeoxygenation of p-methylguaiacol over silica supported rhodium and platinum catalysts, Appl. Catal. A: **2017**, *539*, 29–37

(4) Mu, W.; Ben, H.; Du, X.; Zhang, X.; Hu, F.; Liu, W.; Ragauskas, A. J.; Deng, Y. Noble metal catalyzed aqueous phase hydrogenation and hydrodeoxygenation of lignin-derived pyrolysis oil and related model compounds, *Bioresource Tech*. **2014**, *173*, 6–10

(5) Gutierrez, A.; Kaila, R. K.; Honkela, M. L.; Slioor, R.; Krause, A. O. I. Hydrodeoxygenation of guaiacol on noble metal catalysts*, Catal. Today*, **2009**, *147*, 239–246

(6) Nimmanwudipong, T.; Runnebaum, R. C.; Block, D. E.; Gates, B. C. Catalytic Conversion of Guaiacol Catalyzed by Platinum Supported on Alumina: Reaction Network Including Hydrodeoxygenation Reactions**,** *Energy Fuels,* **2011**, *25*, 3417–3427