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# Base promoted hydrogenolysis of lignin model compounds and organosolv lignin over metal catalysts in water

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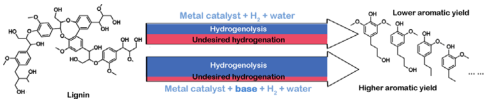
## HIGHLIGHTS

- The first systematic study of base promotional effect in lignin hydrogenolysis..
- Lignin hydrogenolysis into aromatics was carried out in pure water under mild conditions.
- The yield for monomeric aromatic compounds from lignin increased ca. 100% in the presence of base.
- Base promotional effect was observed over Ru (a typical noble metal) and Ni (a typical non-noble metal) catalysts.

## GRAPHICAL ABSTRACT



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## ABSTRACT

Herein we present a systematic investigation on the promotional effect of base in metal catalysed hydrogenolysis of lignin model compounds and organosolv lignin. The research started with the evaluation of pH effects (pH 1–14) on the hydrogenolysis of a lignin β-O-4 model compound over a Ru catalyst (a stable catalyst over a wide pH range), from which a significantly increased selectivity towards monomeric compounds was observed in the presence of base. This promotional effect was studied in detail over bimetallic $Ni_7Au_3$ nanoparticles. Addition of a strong base such as NaOH significantly enhanced the activity and selectivity for C-O bond hydrogenolysis over undesired hydrogenation reactions, not only in lignin model compounds but also in real lignin conversion. Notably, the yield for monomeric aromatic compounds from lignin over $Ni_7Au_3$ catalyst increased ca. 100% after adding NaOH as a promoter, under the same reaction conditions. Mechanistic study suggest that addition of base significantly reduced the benzene ring hydrogenation activity of the metal catalysts. The effect of adding different bases over various metal catalysts were also investigated.

## 1. Introduction

Recently, the valorisation of biomass, such as lignin,(Perlack, 2005; Huber et al., 2006; Corma et al., 2007; Stöcker, 2008; Yan et al., 2010; Long et al., 2012; Long et al., 2013; Mu et al., 2013; Sammons et al., 2013) cellulose(Ngee et al., 2014; Siankevich et al., 2014; Yabushita et al., 2014) and chitin,(Dutta et al., 2004; Chen et al., 2014; Pierson et al., 2014) as sustainable alternative for energy, fuel and chemical production becomes cumulatively interesting. Lignin is the most abundant natural aromatic polymer. New methods that can process lignin into value-added aromatic chemicals are highly desirable.(Sales et al., 2007; Marshall and Alaimo, 2010; Zakzeski et al., 2010; Murat Sen et al., 2012; Azadi

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et al., 2013; Ben et al., 2013; Gao et al., 2014) Lignin consists of interlinked arylpropane units with various functional groups like ethers, methoxy and hydroxyl groups, as well as C–C linkages. The most abundant lignin linkage is the β-O-4 linkage with 45–50% occurrence in softwood and even more than 60% in hardwood. Other important ether linkages include the α-O-4 and 4-O-5 linkages with 4–9% and 6–7% abundance in hardwood, respectively.(Chakar and Ragauskas, 2004; Zakzeski et al., 2010).

The complex structure of lignin necessitates the employment of model compounds bearing typical linkages in lignin to study the reactivity behaviour (see Fig. 1 for typical C–O linkages in lignin). Although no model compounds can precisely represent the lignin structure, this strategy facilitates the understanding of reaction pathways and mechanisms. The difficulty in breaking the ether bonds in lignin model compounds largely depend on the C–O bond energies. α-O-4 type of linkages are the weakest with a aliphatic C–O bond dissociation energy between 156 to 203 kJ/mol, followed by the β-O-4 linkage (226–303 kJ/mol) and the 4-O-5 lignin linkage (346 kJ/mol).(Dorrestijn et al., 2000; Parthasarathi et al., 2011; Younker et al., 2011) The linkages containing C–C bonds possess even higher bond dissociation energies.(Dorrestijn et al., 2000; Parthasarathi et al., 2011; Younker et al., 2011).

Hydrogenolysis of C–O linkages(Kobayashi et al., 2011; Nakagawa and Tomishige, 2012) in lignin, where $H_2$ is used to cleave the C–O bond in the presence of a metal catalyst, is regarded as an effective way to transform lignin into depolymerized aromatic platform compounds.(Ruppert et al., 2012; Li et al., 2013; Yan and Dyson, 2013) The complexity of lignin structures makes its depolymerisation a challenging issue and needs the use of appropriate catalysts.(Zakzeski et al., 2010) Early reports date back in 1938 as Harris and Adkins used copper-chromium catalyst for the hydrogenolysis of pretreated aspen hardwood.(Harris et al., 1938) Afterwards Raney Ni,(Baker and Hibbert, 1948; Brewer et al., 1948) Pd, Rh and Ru supported on carbon or $Al_2O_3$, and Cu-doped porous metal oxide(Barta et al., 2010; Matson et al., 2011; Barta et al., 2014) have been tested.(Pepper and Lee, 1969; Pepper and Fleming, 1978; Pepper and Supathna, 1978) High-temperature approaches were generally applied in these earlier reports to break down the polymer structure catalytically. A clear trend in recent study is the development of catalysts that could be operated under milder conditions in environmentally benign solvents, among which heterogeneous nickel catalysts are of particular interest.(Song et al., 2012; Song et al., 2013; Song et al., 2013) In our group a series of bimetallic NiM ($M$=Au, Ru, Rh, Pd) catalysts were developed that exhibited better performance in lignin hydrogenolysis than single component Ni catalyst, among which NiAu catalyst appears to be most effective.(Zhang et al., 2014).

Undesired benzene ring hydrogenation is a severe problem in lignin hydrogenolysis,(Song et al., 2013) which induces increased hydrogen consumption and decreased efficiency. Moreover, benzene ring hydrogenation leads to stable fully saturated products which do not readily undergo further hydrogenolysis.(He et al., 2012; Zhang et al., 2014) In a few literatures it appears the involvement of a base could improve the selectivity towards monomeric aromatics. For example, NaO$^t$Bu is found to be crucial for a Ni carbene complex catalyzed hydrogenolysis of lignin model compounds.(Sergeev and Hartwig, 2011; Sergeev et al., 2012) Wang and Rinaldi reported that a solvent which exhibits high Lewis basicity results in the formation of aromatics over saturated products over Raney Ni in the conversion of lignin model compounds and organosolv lignin.(Wang and Rinaldi, 2012) Other reports followed, concerning hydrogenolysis reactions over heterogeneous catalysts in the presence of base.(Ren et al., 2013; Zaheer et al., 2014) Despite these encouraging results, some questions remain: (I) what is the pH-activity correlation of the reaction, under otherwise identical conditions? (II) what is the optimized pH for the reaction? (III) what is the role of the base? Does the base enhance the rate of C–O bond hydrogenolysis, or does it inhibit benzene ring hydrogenation, or both? Therefore we carried out detailed studies on the influence of pH in lignin hydrogenolysis over Ru and NiAu catalysts. As mentioned above,

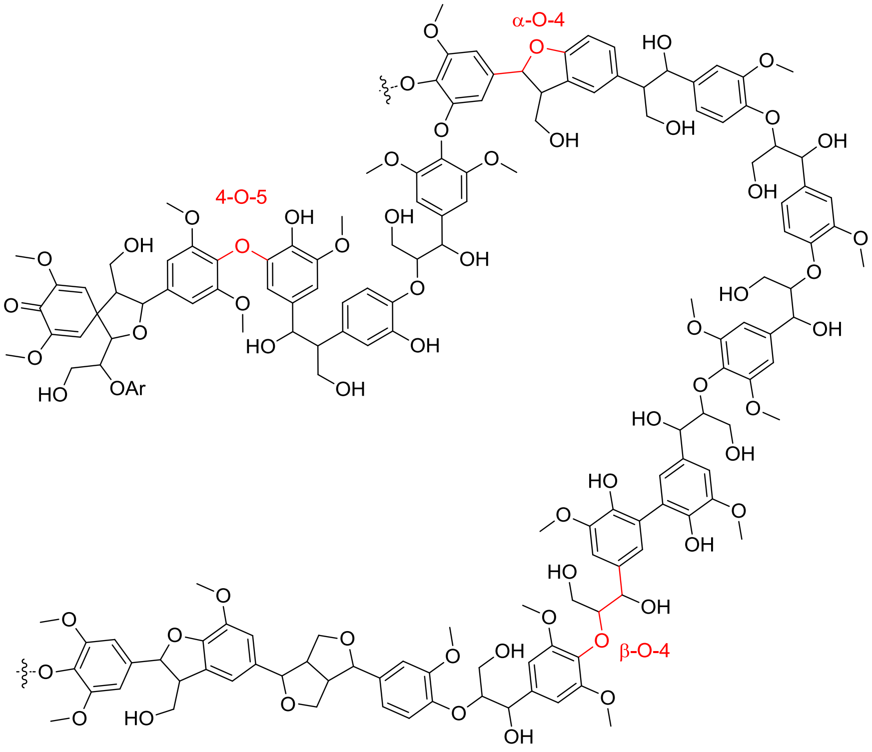


**Fig. 1.** Schematic fragment structure of hardwood lignin. (Zakzeski et al., 2010).

$Ni_7Au_3$ was recently identified as a promising catalyst for lignin hydrogenolysis,(Zhang et al., 2014) whereas Ru is stable under both acidic and basic conditions so that a wide pH range can be studied. The conversion of lignin model substrates 2-phenoxy-1-phenylethanol (β-O-4 lignin linkage), 1-(benzyloxy)-2-methoxybenzene (α-O-4 lignin linkage) and diphenyl ether (4-O-5 lignin linkage) have been systematically studied. The unique role of base in lignin hydrogenolysis was identified, which implies that adding base could be used to enhance the selectivity of certain aromatic compounds in lignin hydrogenolysis.

## 2. Experimental section

### 2.1. Solvents and reagents

Solvents and reagents were used as received without further purification if not otherwise mentioned. The chemicals 2-methoxyphenol ($\geq 98\%$), 1-hexene (98%) and polyvinylpyrrolidone (M.W.=40000) were purchased from Alfa Aesar. Sodium borohydride ($> 95\%$) was purchased from TCI, 2-bromoacetophenone (98%), phenol ($\geq 99\%$), diphenyl ether (99%), benzyl bromide (98%), 2,6-dimethoxyphenol (99%) and lithium bromide ($\geq 99\%$) were purchased from Sigma Aldrich. Chloroauric acid ($\geq 50\%$ Au) and ruthenium(III) chloride ($\geq 37\%$) were purchased from Shaanxi Kaida Chemical Engineering Co., Ltd. and nickel(II) chloride hexahydrate ($\geq 98\%$) from Sinopharm Chemical Reagent Co., Ltd.. Sodium hydroxide ($\geq 99\%$), hydrochloric acid (37%), as well as the solvent ethyl acetate (AR grade) were purchased from Merck. Potassium carbonate ($\geq 99\%$) and sodium carbonate ($\geq 99.5\%$) were purchased from Goodrich Chemical Enterprise (GCE). The solvents dichloromethane, diethyl ether, ethanol, toluene and methanol with analytical reagent grade as well as dimethylformamide (HPLC grade) were purchased from Fisher Chemical. Acetone was received from Aik Moh Paints & Chemical Pte Ltd. and tetrahydrofuran (HPLC grade) was purchased from Tedia. $H_2$ and $N_2$ (purified grade) were purchased from Singapore Oxygen Air Liquide Pte Ltd. (SOXAL).

### 2.2. General procedures

Catalyst preparations were carried out in a Vacuum Glove Box VG-800 Type Handling Manual from *Sanplatee* with nitrogen as inert gas.

### 2.3. Catalysis synthesis and hydrogenolysis of lignin model compounds

The catalyst preparation was carried out mixing 1.4 ml of 0.011 M (0.07 eq., 0.0154 mmol) $NiCl_2 \cdot 6H_2O$ stock solution with 0.6 ml of a 0.011 M (0.03 eq., 0.0066 mmol) $HAuCl_4$ (50%Au) stock solution. In this solution 48.9 mg (2 eq., 0.44 mmol) of PVP were dissolved. Then 4.2 mg (0.5 eq., 0.11 mmol) $NaBH_4$ were dissolved in 1 ml $H_2O$ and were added to the precursor solution. For the reactions without the addition of base 0.4 ml $H_2O$ were added. For the reactions with the addition of base the pH was adjusted using 10 M sodium hydroxide solution and $H_2O$ to obtain the same concentration of $c_{Cat}=6.5 \cdot 10^{-3}$ mol/L and a volume of 3.4 ml in all experiments. Then 0.22 mmol of substrate were added to the reactor with the fresh prepared catalyst solution. The reactor was sealed, charged with 10 bar $H_2$ and placed into a preheated silicon oil bath (1000 rpm) at the appropriate temperature. After the appropriate reaction time the reactor was cooled down to room temperature using water. For the reactions using base the reaction mixture was adjusted to pH 6–7 with 0.5 M hydrochloric acid. The reaction mixture was extracted with 6 ml ethyl acetate and 20 μl (0.09 mmol) *n*-dodecane as internal standard were added. The yield was determined using GC-FID.

### 2.4. Hydrogenation of toluene and 1-hexene

For the hydrogenation reactions of toluene and 1-hexene the catalyst preparation and hydrogenation reaction was carried out using the representative procedure, but 2.2 mmol substrate were used. Before extraction no adjustment of the pH was carried out.

### 2.5. Depolymerisation of organosolv lignin

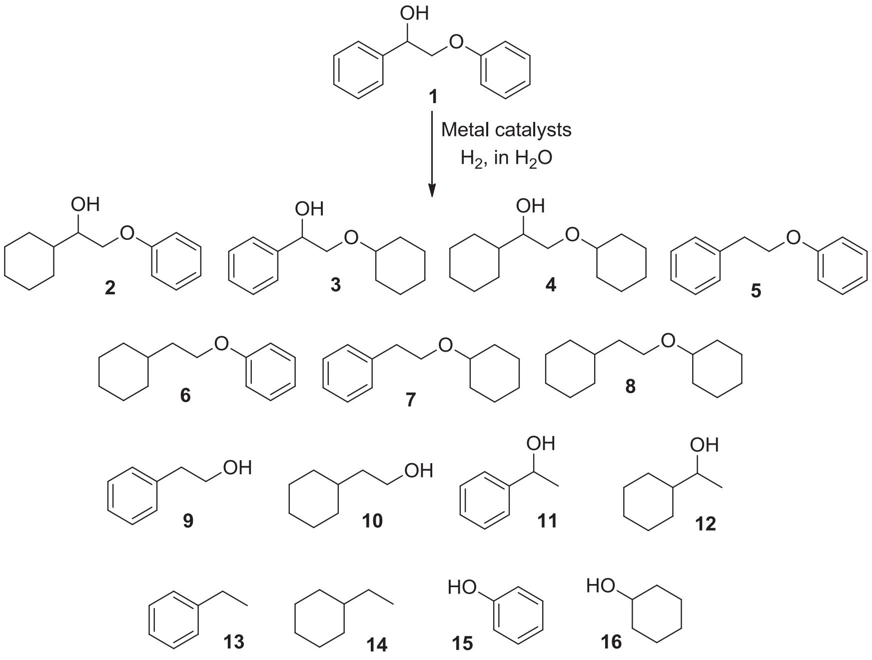
For the depolymerisation of organosolv lignin the representative procedure with 50 mg organosolv lignin were used. For determination of the monomer yield the reaction mixture was extracted three times with ethyl acetate and the solvent was evaporated under reduced pressure. To the residue 20 μl (0.09 mmol) *n*-dodecane were added as internal standard and it was dissolved in 1.5 ml dimethylformamide. The yield was determined using GC-FID. For measurement of FT-IR and GPC the reaction mixture was extracted with 25 ml dichloromethane and the solvent was evaporated under reduced pressure.

## 3. Results and discussion

### 3.1. Hydrogenolysis of lignin model compounds

2-phenoxy-1-phenylethanol (**1**) was employed as a lignin β-O-4 model compound. After reacting with $H_2$ over a metal catalysts, up to 15 products including 7 dimers (**2–8**) and 8 monomers (**9–16**), can be detected by GC-FID and GC–MS (Scheme 1). Total monomer yield can act as an indicator of hydrogenolysis activity of the catalytic system, whereas the total yield of dimers can partially represent hydrogenation activity. To investigate the pH influence on the hydrogenolysis, Ru was chosen as the catalyst.(Yan et al., 2008; Song et al., 2013) As Ru catalyst is resistant to corrosion and oxidation, it provides reliable results over the whole pH range. The catalyst was prepared by aqueous phase reduction of $RuCl_3$ by $NaBH_4$ in the presence of PVP,(Zhang et al., 2013) after which it was immediately used to catalyze the reaction between **1** and $H_2$ in water at 130 °C for 0.5 h. Experiments were carried out at an initial pH ranging from 1.1 to 13.7, adjusted with HCl to obtain an acidic and NaOH for a basic reaction medium.

Ru-catalysed reaction leads to quantitative conversion and the formation of three main products in the pH range of 3.0 to 13.0. 1-cyclohexyl-2-(cyclohexyloxy)ethan-1-ol (**4**) forms via hydrogenation of both aromatic rings. Monomers 1-cyclohexylethanol (**12**) and cyclohexanol (**16**) results from tandem hydrogenolysis/hydrogenation of the substrate. Fig. 2 shows the yield of the three main products (**4**, **12**, **16**) as well as the desired aromatic monomers 1-phenylethanol (**11**) and phenol (**15**) as a function of the pH value. Without the addition of acid or base the reaction mixture has an initial pH of 8.4. This slightly basic reaction medium is due to the decomposition byproducts of $NaBH_4$ used to reduce $RuCl_3$. A decrease of the pH to 7.1, 4.9 and 3.0 leads to a decrease of the formation of monomers and increased yield of **4**, indicating inhibition of hydrogenolysis. For instance, **4** was obtained with 93% yield at pH=3.0 whereas **12** forms in 1.4% and **16** in 2.9% yield. Thus, an increase of the acidity of the reaction medium leads to a higher selectivity for hydrogenation over hydrogenolysis. A further decrease of pH to 1.1 results in a significant decrease in activity with only 63% conversion. In addition the cleavage of the hydroxyl group moieties, probably by acid catalysed dehydration followed by C=C bond hydrogenation (the yield for each individual



**Scheme 1.** Reaction scheme of the metal catalysed hydrogenolysis/hydrogenation of β-O-4 lignin linkage 2-phenoxy-1-phenylethanol (**1**) with 15 possible selected products.

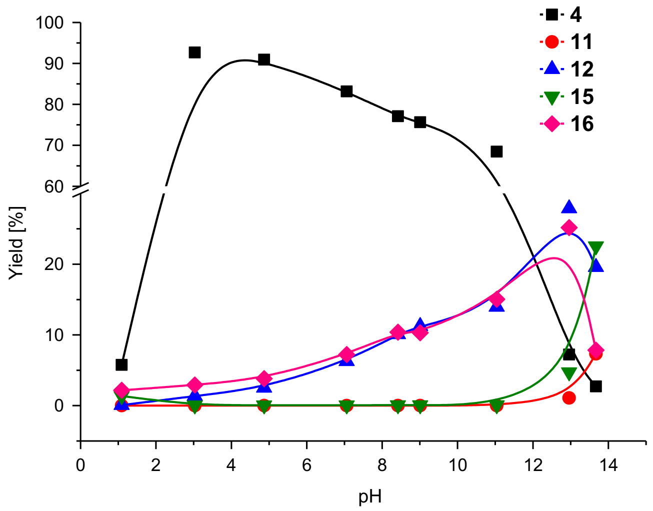


**Fig. 2.** Yields of main products after hydrogenolysis of 2-phenoxy-1-phenylethanol (**1**) over Ru as a function of pH. Reaction conditions: 10 mol% Ru, 10 bar $H_2$, $H_2O$, 130 °C, 0.5 h.

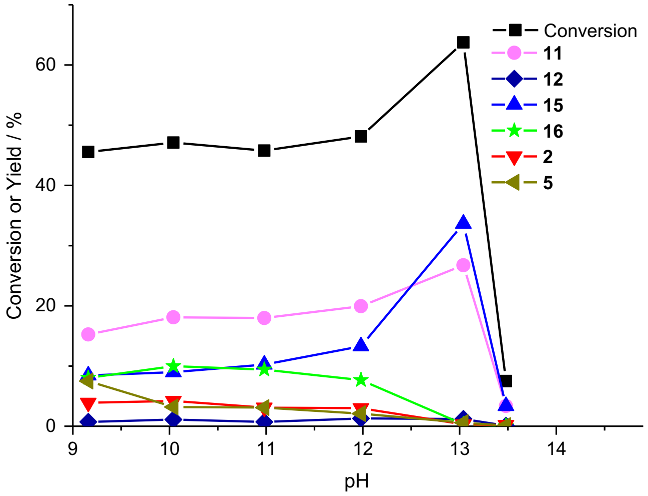


**Fig. 3.** Yields of main products after hydrogenolysis of 2-phenoxy-1-phenylethanol (**1**) over $Ni_7Au_3$ as a function of pH. Other products < 1% yield. Reaction conditions: 10 mol% $Ni_7Au_3$, NaOH, 10 bar $H_2$, $H_2O$, 130 °C, 0.5 h.

product is provided in Table S1). By a sharp contrast, change the pH to higher values of 9.0, 11.0 and 13.0 induced a decrease in the formation of **4** and accordingly, enhanced yield of the monomers **12** and **16**. In addition, at pH 13.0 slightly increased yields of the aromatic monomers **15** and **11** were also observed. An even higher pH of 13.7 led to a reduced conversion and higher product diversity. Nevertheless, the highest yields of the aromatic monomers was obtained under this condition, that is, 7.3% of **11** and 22.6% of **15**, respectively.

These results indicate low pH is detrimental to the hydrogenolysis of **1** resulting in saturated dimers as the main product. Adding base can increase the selectivity towards hydrogenolysis, especially at a pH range of 10–14. We next switch the focus to $Ni_7Au_3$ catalyst, which is much more effective in lignin hydrogenolysis than Ru under the same reaction conditions. $Ni_7Au_3$ catalyst decomposes under acidic conditions but is stable in the presence of a base.

$Ni_7Au_3$ catalyst is prepared in a similar way as the Ru catalyst, except that $HAuCl_4$ and $NiCl_2{\bullet}6H_2O$ were applied as the catalyst precursor. This catalyst exhibits a Au@Ni core-shell structure with electron enriched surface Ni.(Zhang et al., 2014) The entire synthetic procedure was conducted in a glovebox to prevent initial oxidation of the catalyst. Hydrogenolysis of **1** over $Ni_7Au_3$ catalyst was evaluated at pH 9.2, 10.0, 11.0, 12.0, 13.0 and 13.5, respectively at 130 °C (see Fig. 3 and detailed results in Table S2).

Again, the reaction turned out to be more effective at basic conditions. The conversion increased from 45.6% at pH 9.2 to 63.7% at pH 13, corresponding to ca. 40% increase in activity. Further increasing the pH to 13.5, however, dramatically decreased the conversion to 7.5%. Aggregation of $Ni_7Au_3$ nanoparticles was observed under this extreme basic condition, which is responsible for the low activity. Increase the pH from 9.2 to 13.0 also affected the product selectivity. At pH 9.2 a variety of products, including fully and half saturated dimers, aromatic dimers as well as aromatic and saturated monomers, are all present with appreciable yields.

On the contrary, aromatic monomers become the dominant products as pH increases. **11** and **15** which are formed by hydrogenolysis of the C-O bond, reach their maximum at pH 13.0 with yields of 26.7% and 33.6%, respectively. At the same time the products whose formation involves the aromatic ring hydrogenation, such as like 1-cyclohexylethanol (**12**) and cyclohexanol (**16**) are significantly reduced.

Next, the pH range between 12 and 13 was investigated in more detail (Table 1 and detailed results in Table S3). As the catalyst is freshly prepared for every reaction and the reducing agent $NaBH_4$ influences the pH, this value can differ slightly for every single experiment. For the following experiments, the NaOH amount is given in equivalents with regard to the substrate **1** which covers the pH range between 12.0 and 13.0. Moreover, in these optimisation studies the temperature was reduced to 100 °C to prevent any catalyst deactivation. From pH 12 to 13 a slightly increase in the conversion of the β-O-4 lignin linkage is observable, reaching its maximum at 1.8 and 2.7 eq. of NaOH. Between the two, 2.7 eq. of NaOH seems to be more effective in inhibiting the formation of saturated products (as indicated by a larger **15**:**16** ratio) and therefore was chosen for further investigations.

Kinetic experiments over a period of 2 h, both in the presence and absence of 2.7 eq. of NaOH, were carried out to understand the reaction as a function of time (Fig. 4). The $Ni_7Au_3$ catalyst is stable under the condition, irrespective of base addition, as suggested by continuously increased substrate conversion over a period of 2 h at 100 °C. Almost quantitative yield was achieved when base was added, in comparison with 61.1% conversion without NaOH, further testifying that $Ni_7Au_3$ catalyst is intrinsically more active and selective when NaOH is added. Furthermore, using base significantly improves the selectivity. The total monomer yield after 2 h is about 90.3% whereas the total monomer yield without the addition of base is just 37.1%. A closer inspection on the yield of aromatic (**9**, **11**, **13**, **15**) and saturated (**10**, **12**, **14**, **16**) monomers (Table S4 and S5) reveals that using base as additive hinders the formation of saturated monomers. The experiment with base results in the formation of 90.3% total monomers yield with 76.9% aromatic units and only 13.4% hydrogenated monomers after 2 h. Without base, the total monomer yield (37.1%) consists of 17.9% aromatic and 19.1% saturated monomers. The kinetic experiments also suggest that the rate of cleavage of fully saturated dimers is low due to the absence of an observable decrease of these compounds as the reaction progresses (Table S4 and S5).

**Table 1**
Conversion of the hydrogenolysis of 2-phenoxy-1-phenylethanol (1) over $Ni_7Au_3$ with different NaOH amounts (pH 9.2, 12.0-13.0). Ratio of aromatic monomers 15 to corresponding hydrogenated monomer 16 as a function of the NaOH amount.

| Entry | NaOH [eq.] | Conversion [%] | Phenol **15** [%] | Cyclohexanol **16** [%] | Ratio **15**/**16** |
|---|---|---|---|---|---|
| 1 | 0 | 21.9 | 2.5 | 3.8 | 0.7 |
| 2 | 0.5 | 23.2 | 8.0 | 1.9 | 4.3 |
| 3 | 1 | 26.9 | 9.7 | 0.7 | 14.1 |
| 4 | 1.8 | 33.9 | 15.9 | 0.7 | 24.5 |
| 5 | 2.7 | 33.6 | 15.0 | 0.4 | 34.1 |
| 6 | 4.6 | 17.1 | 8.2 | $< 0.1$ | 104.8 |

Reaction conditions: 10 mol% $Ni_7Au_3$, 10 bar $H_2$, $H_2O$, 100 °C, 0.5 h.

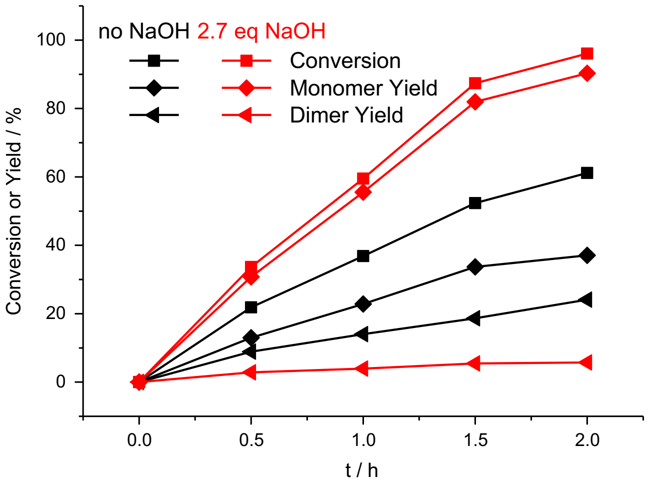


**Fig. 4.** Kinetic studies of the hydrogenolysis of 2-phenoxy-1-phenylethanol (**1**) over $Ni_7Au_3$ without base and the addition of 2.7 eq. NaOH. Reaction conditions: 10 mol% $Ni_7Au_3$, 10 bar $H_2$, $H_2O$, 100 °C. Conversion, yield of monomers (**9–16**) and dimers (**2–8**).

Lignin contains a plenty of methoxy and hydroxyl groups. Thus, model compounds containing a $C_\gamma$-OH or hydroxyl and methoxy groups at the aryl moiety, are very convenient to mimic its reactivity.(Zakzeski et al., 2010) As such, the influence of NaOH on the hydrogenolysis of methoxy-substituted β-O-4 lignin linkage model compounds, 2-(2-methoxyphenoxy)-1-phenylethanol (**1a**) and 2-(2,6-dimethoxyphenoxy)-1-phenylethanol (**1b**), were tested (Scheme S1). To our delight, the addition of base also results in a higher rate of the hydrogenolysis reaction and enhanced selectivity for these two substrates (Table S8 and S9).

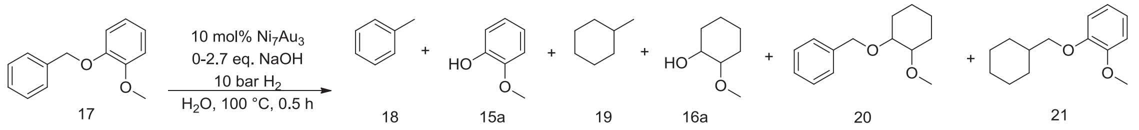
The reactivity behaviour of other typical lignin linkages was also investigated. In lignin, the α-O-4 linkage represents the weakest ether bonds to cleave due to the lower bond dissociation energy compared to the β-O-4 linkage.[7, 11] In Table 2, the addition of 0 to 2.7 eq. NaOH (pH 9.2–12.8) did not change the activity significantly, and base addition exhibited negelible influence on the selectivity of aromatic monomers (**18** and **15a**). Nonetheless, the partical hydrogenated product yield (**16a**, and **21**) decreased with increasing base addition, indicating hindrence effect of base to hydrogenation of benzene ring. This suggest the base promotional effect in lignin hydrogenolysis to be an indirect effect, i.e., through the inhibition of benzene ring hydrogenation instead of directly activiting the C-O bond. As such, for the α-O-4 linkage which is intrincically weak, no base promotional effect in C-O bond hydrogenolysis could be observed.

The third most abundant ether bond in lignin is the 4-O-5 linkage, featured by the direct connection of one aromatic ring on each side of oxygen (see Table 3 for the structure). Compared to the ether bonds in β-O-4 and α-O-4 linkages, this is the most challenging bond to cleave, because of a higher bond dissociation energy.(Zakzeski et al., 2010; Parthasarathi et al., 2011) At 100 °C after 5 h reaction time the conversion of **22** decreased from 33.7% to 22.8% by adding 2.7 eq. NaOH (Table 3, entries 1 and 2). Nevertheless, the selectivity improved dramatically. In the reaction without base only trace amount of phenol was detected (Table 3, entry 1), but becomes one of the major products when 2.7 eq. NaOH was added.

### 3.2. Depolymerisation of organosolv lignin

The valorisation of lignin into smaller molecular weight compounds is often more challenging and requires harsh reaction conditions.(Zakzeski et al., 2010) We next evaluated the combination of NaOH and $Ni_7Au_3$ catalyst for real lignin hydrogenolysis into aromatic compounds. The organosolv lignin from birch sawdust was used. At 100 °C no monomers could be detected, thus higher temperatures from 120–160 °C were tested (Table S10). By GC–MS analysis products **25–28** were identified as the major monomeric products (Table 4, Fig. S1–S4). The total monomer yield results from the sum of the identified monomers **25–28** (the actual total monomer yield should be higher as there are unidentified monomers, despite in small amount).

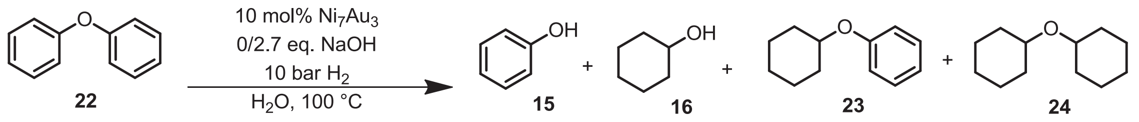
**Table 2**
Conversion and main product yields of the hydrogenolysis of 1-(benzyloxy)-2-methoxybenzene (**17**) over $Ni_7Au_3$ as a function of the NaOH amount.



| Entry | NaOH [eq.] | Conversion [%] | **18** [%] | **15a** [%] | **19** [%] | **16a** [%] | **20/21** [%] |
|---|---|---|---|---|---|---|---|
| 1 | 0 | 51.2 | 10.8 | 17.5 | 0.5 | 0.4 | 0.1 |
| 2 | 0.4 | 48.9 | 8.0 | 13.8 | 0.4 | 0.2 | 0.1 |
| 3 | 1.0 | 53.4 | 10.1 | 17.7 | 0.5 | 0.1 | 0.1 |
| 4 | 1.8 | 54.0 | 11.5 | 19.5 | 0.2 | 0.0 | 0.0 |
| 5 | 2.7 | 46.8 | 7.0 | 13.0 | 0.3 | 0.0 | 0.0 |

Reaction conditions: 10 mol% $Ni_7Au_3$, 0–2.7 eq. NaOH, 10 bar $H_2$, $H_2O$, 100 °C, 0.5 h.

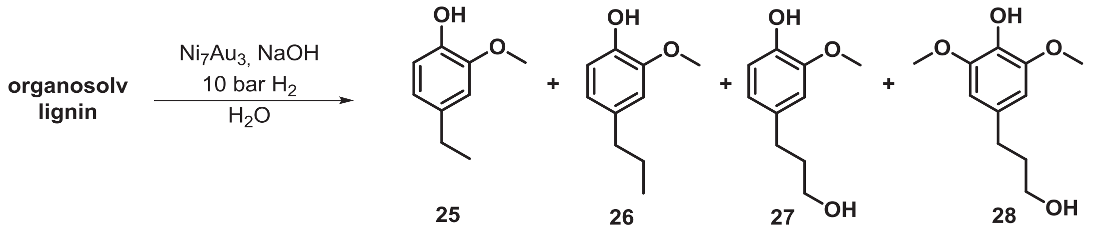
**Table 3**
Conversion and main products yield of the hydrogenolysis of diphenyl ether (**23**) over $Ni_7Au_3$ as a function of the pH amount.



| Entry | NaOH [eq.] | t [h] | Conversion [%] | **15** [%] | **16** [%] | **23** [%] | **24** [%] |
|---|---|---|---|---|---|---|---|
| 1 | 0 | 5 | 33.7 | 0.2 | 17.3 | 2.2 | 0.5 |
| 2 | 2.7 | 5 | 22.8 | 4.1 | 5.4 | 0.8 | 0.1 |
| 3 | 2.7 | 15 | 37.2 | 6.5 | 12.3 | 1.4 | 0.2 |

Reaction conditions: 10 mol% $Ni_7Au_3$, NaOH, 10 bar $H_2$, $H_2O$, 100 °C.

**Table 4**
Conversion and main products yield of the hydrogenolysis of organosolv lignin over $Ni_7Au_3$.



| Entry | NaOH [eq.] | t [h] | **25** [%] | **26** [%] | **27** [%] | **28** [%] | total [%] |
|---|---|---|---|---|---|---|---|
| 1a | 0 | 2 | 0.02 | 0.01 | 0.26 | 1.02 | 1.5 |
| 2a | 2.7 | 2 | 0.03 | 0.03 | 0.76 | 1.85 | 3.0 |
| 3b | 0 | 4 | 0.07 | 0.13 | 1.64 | 5.08 | 7.6 |
| 4b | 2.7 | 4 | 0.48 | 0.44 | 1.95 | 6.05 | 10.9 |

Reaction conditions: 0.022 mmol $Ni_7Au_3$, 50 mg organosolv lignin, 10 bar $H_2$, $H_2O$, $^a$130 °C and $^b$160 °C.

Table 4 shows the total monomer yield as a function of the NaOH amount at 130 °C and 160 °C. Encouragingly, the base additive promotes the total monomer yield at both temperatures after adding NaOH, which is in perfect agreement with the experiments with lignin model substrates. As the promotional effect does not change significantly with temperatures, 130 °C was chosen for further investigations as the catalyst is more stable under this condition. Table S11 shows the time dependent total monomer yield of the depolymerisation reaction of organosolv lignin using the selected reaction conditions of 0.6 mmol NaOH at 130 °C. The kinetic studies show after 14.5 h a total monomer yield of 5.4 wt%. Without base 3.3 wt% monomers were obtained under the same condition (Table S11).

The FT-IR spectra(Suni et al., 2010; Azadi et al., 2012; Mao et al., 2012; Sammons et al., 2013) of organosolv lignin, and the recovered residues after the reaction are compiled in Fig. 5. In organosolv lignin the band at 2939 $cm^{-1}$ and 2843 $cm^{-1}$ can be assigned to the C-H stretching vibrations in methyl and methylen groups. The reaction with the addition of NaOH shows nearly the same bands, except a slight shift from 2939 $cm^{-1}$ to 2933 $cm^{-1}$. In the case of the reaction without base one additional vibration at 2961 $cm^{-1}$ appears. Moreover, the bands at 2939 $cm^{-1}$ and 2843 $cm^{-1}$ are shifted to 2924 $cm^{-1}$ and 2853 $cm^{-1}$, respectively. The fact that the stretching vibration bands for $CH_3$ and $CH_2$ are shifted and increase in intensities supports the assumption of a higher hydrogenation activity resulting in saturated rings preventing the depolymerisation in the absence of NaOH. In addition, the stretching vibration of C-O bond in guaiacyl units shifted from 1271 $cm^{-1}$ to 1260 $cm^{-1}$ and the in plane deformation vibrations

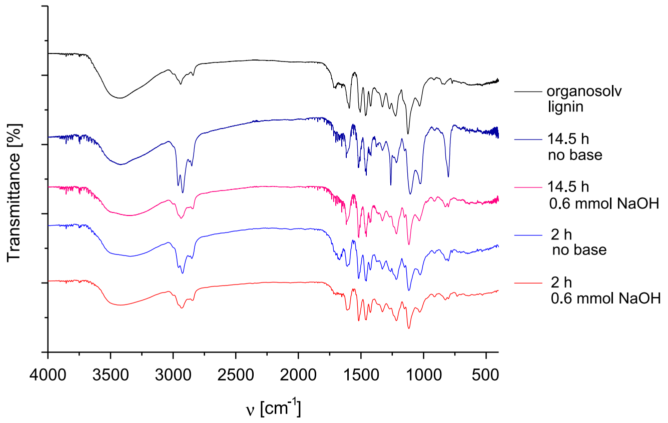


**Fig. 5.** FT-IR spectra of organosolv lignin and depolymerisation reactions of lignin catalysed by $Ni_7Au_3$. Reaction conditions: 50 mg organosolv lignin, 0.022 mmol $Ni_7Au_3$, 10 bar $H_2$, $H_2O$, 130 °C.

of C-H bonds in guaiacyl units and stretching vibration of C-O bonds in primary alcohols shifted from 1029 $cm^{-1}$ to 1022 $cm^{-1}$, respectively, in the absence of base. All those results indicate that adding NaOH better preserve the lignin structure, enabling a more selective depolymerisation.

### 3.3. *Mechanistic studies*

Reaction in the absence of $Ni_7Au_3$, but with identical amount of PVP, $NaBH_4$ and 2.7 eq. NaOH, at 130 °C showed only 0.1% conversion of the **1** after 0.5 h. Under the same condition, organosolv lignin provided merely 0.1 wt% of 4-(3-hydroxypropyl)-2-methoxyphenol (**27**) after 4 h reaction (see SI for detailed control experiments procedure). These results suggest the reaction follows a metal-catalysed reaction pathway, instead of a base-catalysed hydrolysis. $Ni_7Au_3$ catalyst was characterised using TEM, UV–vis and XPS measurements (Fig. S7-11), revealing there is no appreciable differences in these spectra at pH 9 and 13. Thus, the catalyst itself does not experience structural or chemical changes after the addition of NaOH.

At higher pHs, phenols are existing as phenolates in water solution, which has a much higher solubility. The calculated energy gap of the hydration energy for phenol and phenolate is 6.38 eV,(Ghosh et al., 2012) indicating that phenolate is much better solvated than phenol in water. Consequently, the reaction barrier for phenolate to be absorbed and hydrogenated over the catalyst surface would be higher. This is likely to be part of the reason that the selectivity towards aromatic compounds is higher under basic conditions. Nevertheless, we observed that the hydrogenation of all aromatic compounds were inhibited at higher pHs, indicating solvation is not the only reason for the inhibition effect. Thus, hydrogenation reactions of toluene and 1-hexene over $Ni_7Au_3$ were carried out to obtain insight into the hydrogenation behaviour of C=C bonds with base additive (Fig. 6). Toluene was used as simple aromatic substrate whereas 1-hexene has a non-hindered terminal C=C bond.

For the hydrogenation of toluene to methylcyclohexane, the reaction rate was significantly reduced in the presence of base. In addition, the apparent activation energy was calculated using the Arrhenius plot which showed no significant change as in both cases the value for the apparent activation energy results in about $E_A = 46.1–47.9$ kJ/mol (Fig. S12). These values correlate with literature data for hydrogenations of toluene over heterogeneous catalysts. (Keane and Patterson, 1996; Prechtl et al., 2008) On the other hand, the pre-exponential factor A, which provides information on the collision rate of the molecules and particles, changed considerably. (Atkins and de Paula, 2006) For the reaction without base, the value of A is 812, which is ca. five times higher than that in the presence of base ($A = 151$). In view of the reaction mechanism this indicates a hindered coordination of the aromatic ring on the catalyst surface.

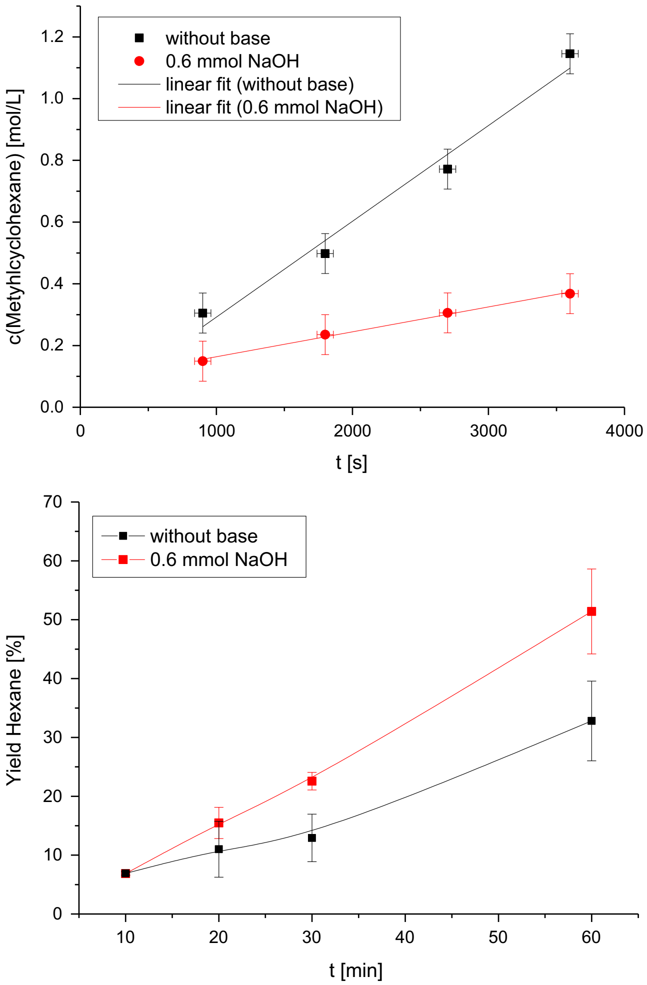


**Fig. 6.** (a) Hydrogenation of toluene over $Ni_7Au_3$ without base and the addition of 0.6 mmol NaOH. Linear fit with margin of error: $\Delta t = \pm 60$ s, $\Delta c = \pm 0.06$ mol/L. Reaction conditions: 2.2 mmol toluene, 0.022 mmol $Ni_7Au_3$, 10 bar $H_2$, $H_2O$, 130 °C. (b) Hydrogenation of 1-hexene over $Ni_7Au_3$ without base and the addition of 0.6 mmol NaOH. Reaction conditions: 2.2 mmol 1-hexene, 0.022 mmol $Ni_7Au_3$, $H_2O$, 30 °C. Lines are just shown for visualisation.

In agreement with this, no hindered hydrogenation of 1-hexene was observed in the presence of base. In fact, the addition of base seems to accelerate the hydrogenation reaction of the terminal alkene. Combining these two studies, the inhibiting effect of the base on the aromatic ring hydrogenation is due the increased hindrance caused by competitive adsorption of base on catalyst surface.

The promotional effect in hydrogenolysis of **1** were tested over various bases (Table 5 and detailed results in Table S6). KOH and LiOH exhibited similar results of the enhancement in activity and selectivity. These strong bases resulted in a high pH value of 12.3–12.9 and similar concentration of hydroxyl ions in the reaction media. The addition of the much weaker bases such as $K_2CO_3$ or $Na_2CO_3$ resulted in a decrease of activity. The organic base $Et_3N$ exhibited negligible effect in activity, but the selectivity for the formation of aromatics such as phenol increased. Overall it appears that $OH^-$ is crucial for the enhanced activity and selectivity, further suggesting the proposed competitive absorption between aromatic rings and hydroxyl ions.

Investigations on different metal catalysts revealed that the base promotional effect in lignin hydrogenolysis appears to be

**Table 5**
Hydrogenolysis of of 2-phenoxy-1-phenylethanol (**1**) over $Ni_7Au_3$ with different bases.

| Entry | Base | pH | Conversion [%] | Yield [%] | |
|---|---|---|---|---|---|
| | | | | **11** | **15** |
| 1 | – | 9.2 | 36.9 | 9.9 | 3.1 |
| 2 | NaOH | 12.8 | 59.5 | 24.4 | 26.6 |
| 3 | KOH | 12.9 | 56.1 | 20.9 | 30.0 |
| 4 | LiOH | 12.3 | 68.5 | 25.6 | 33.6 |
| 5 | $K_2CO_3$ | 11.0 | 28.3 | 10.9 | 12.2 |
| 6 | $Na_2CO_3$ | 10.9 | 27.4 | 10.3 | 10.7 |
| 7 | $Et_3N$ | 11.0 | 34.5 | 12.7 | 8.0 |

Reaction conditions: 10 mol% $Ni_7Au_3$, 2.7 eq. base, 10 bar $H_2$, $H_2O$, 100 °C, 1 h.

**Table 6**
Hydrogenolysis of 2-phenoxy-1-phenylethanol (**1**) over various metal catalysts.

| Entry | [M] | NaOH [eq.] | Conversion [%] | Yield [%] | |
|---|---|---|---|---|---|
| | | | | **11** | **15** |
| 1 | $Ni_7Au_3$ | – | 61.1 | 14.0 | 2.5 |
| 2 | | 2.7 | 96.0 | 35.5 | 40.9 |
| 3 | Ni | – | 36.5 | 6.1 | 4.0 |
| 4 | | 2.7 | 59.1 | 21.3 | 30.4 |
| 5 | $Ni_{85}Ru_{15}$ | – | 96.3 | 10.9 | 0.5 |
| 6 | | 2.7 | 99.9 | 17.0 | 31.7 |

Reaction conditions: 10 mol% [M], NaOH, 10 bar $H_2$, $H_2O$, 100 °C, 2 h.

applicable to a few other metals (Table 6 and detailed results in Table S7). Over pure Ni catalyst, the addition of 2.7 eq. NaOH increased the conversion from 36.5% to 59.1%, and the yield of the two aim products, **11** and **15**, were significantly increased from 10.1% to 51.7% (entry 3-4). Another bimetallic catalyst, $Ni_{85}Ru_{15}$, (Zhang et al., 2014) was also evaluated. Despite a high conversion (96.3%), the yield towards aim products was very low (11.4%) in the absence of a base. After the addition of 2.7 eq. NaOH, full conversion was achieved, and the yields of **11** and **15** reached 17.0% and 31.7%, respectively.

## 4. Conclusions

We presented a systematic investigation on the influence of pH in the hydrogenolysis of lignin. Low pH is detrimental to both activity and aromatic product selectivity, whereas high pH, in particular in the range of pH 12-13, exhibits significant promotional effect. For all tested model substrates a basic reaction medium leads to an increase in selectivity towards aromatic compounds and inhibition for arene hydrogenation. For the β-O-4 linkage model compounds, additionally a promoting effect for $C_{Alkyl}$-O bond hydrogenolysis was observed, resulting in a higher activity. More importantly the depolymerisation of organosolv lignin into aromatic monomers is also enhanced considerably using NaOH as an additive.

The catalyst characterisation using TEM, UV–vis and XPS, as well as the apparent $E_A$ of the hydrogenation of toluene suggest that there is no change in the nature of the catalyst after adding base. On the other hand, the hydrogenation behaviour towards toluene and 1-hexene indicates that a high amount of the hydroxyl groups in the reactions mixture could adsorb weakly on the catalyst surface and thus hinder the coordination of the bulky aromatic ring. This results in a decreased hydrogenation of arenes and a higher selectivity towards aromatic compounds in the hydrogenolysis of the lignin model compounds and lignin. The synergistic effect of metal catalyst and a base is at least applicable to Ru (a typical noble metal) and Ni (a typical non-noble metal) catalysts, thus providing a potential strategy to enhance aromatic product yield in lignin hydrogenolysis.

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## Appendix A. Supporting information

Supplementary data associated with this article can be found in the online version at http://dx.doi.org/10.1016/j.ces.2014.10.045.

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