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Raney® nickel-catalyzed hydrodeoxygenation and dearomatization under transfer hydrogenation conditions—Reaction pathways of non-phenolic compounds

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Graphical Abstract



Highlights

- Aromatic ketones and alcohols are reduced into cycloalkanes under TH catalyzed Raney Ni
- Reduction proceeds through pathways ketone-alcohol-alkane
- Ketones are reduced quicker than alcohols or benzaldehyde
- Decarbonylation of benzaldehyde and phenylacetaldehyde are observed
- CO demonstrates poisoning effect on Raney Ni surface

Abstract: Catalytic reduction of oxygen-containing aromatic compounds has been studied under transfer hydrogenation (TH) conditions at 150 °C in 2-PrOH as a hydrogen donor. Raney® nickel is used as a heterogeneous catalyst. The reaction of aromatic non-phenolic carbonyl compounds is most proceed likely to through the pathway "aromatic ketone (aldehyde)→aromatic alcohol→alkylaromatics→saturated alkylcyclohexane". One of the main reactions under the TH conditions is a hydrodeoxygenation (HDO) process. Unexpectedly, the hydrodeoxygenation of aromatic ketones to alkylaromatics (C=O \rightarrow CH₂) occur faster than of corresponding aromatic alcohols (HC–OH \rightarrow CH₂) that means either additional reaction pathway of its hydrodeoxygenation missing for the corresponding aromatic alcohols or specific interaction of OH functionality with Raney® nickel surface obstructing (hindering) the further reduction. Benzaldehyde is shown to be

less reactive than the aromatic ketones under the same reaction conditions. The main reason is proposed to be carbon monoxide release resulted from the decarbonylation of the aldehyde. Carbon monoxide demonstrates a poisoning effect on Raney® nickel surface that is evidenced in the catalyzed TH reaction of acetophenone. The HDO reaction of anisole under the same reaction conditions was a little slowly than of oxygen-containing non-phenolic aromatics.

Keywords: Transfer hydrogenation Raney® nickel Hydrodeoxygenation Dearomatization Oxygen-containing aromatics

1. Introduction

Lignocellulosic biomass consisting of three major components (cellulose, lignin, and hemicellulose) is the most abundant bioresource which world production is around 170 metric tons per year [1]. As a renewable chemical feedstock, lignocellulose can be converted into different valuable chemicals [2] and biofuels [3,4] along with conventional heat and electricity production. However, chemical processing of lignocellulose is complicated and difficult owing to the complex structure, chemical and biochemical stability [5], as well as an extremely high oxygen content reaching up to 40 wt% [6]. Specifically in lignin, the oxygen content can vary in a wide range of 22–45 wt% [7,8]. That is the reason why a catalytic hydrodeoxygenation process (HDO) plays an important role in lignin processing [2,9,10]. As known, HDO is a reductive transformation for removing oxygen from oxygen-containing compounds and saturating by hydrogen. The process can also proceed under transfer hydrogenation (TH) conditions [11–17] with using heterogeneous catalysts that has some clear advantages over the conventional hydrogenation or hydrogenolysis, for example, no necessity to use hazardous and flammable H₂ gas or metal hydrides, availability of various suitable *H*-donors, relative cheapness, operational simplicity of handling, and ease of removing [18,19].

Raney[®] nickel is recognized as a widely-used industrial hydrogenation catalyst for the reduction of monosaccharide sugars, nitriles, nitro- and carbonyl compounds [20,21], total hydrogenation of some aromatics and alkynes [20], as well as an alkylation of amines with alcohols, *etc.* [21,22]. Moreover, the skeletal nickel is a highly promising catalyst for the TH reaction of various substrates as demonstrated earlier [18,23–26] including the catalytic upstream biorefining of lignin [16,27]. The first stage of the last process is lignin depolymerization into a mixture of monomeric aromatic aldehydes and Hibbert's ketones which carry out the further reductive transformation (the second stage) into hydrogenated products as a key reaction. Thus, Raney[®] nickel can be very useful and effective enough to decrease oxygen content and

hydrogenate unsaturated products *via* a one-pot "disassembling hydrogenolysis" of lignin followed by the HDO process.

The HDO process of biomass-derived lignins is very important, but the most intensively studied only in last eight years (2011–2018). Usually "*lignin-derived phenolic compounds*" are used in the HDO study as model compounds of lignin structure, mainly anisole (methoxybenzene) and guaiacol (2-methoxyphenol). The main purpose of those studies is a C–O bond hydrogenolysis of these phenolic compounds to further convert into monocyclic hydrocarbons. However, in the alkyl side chain of phenylpropane basic units of lignin, there are some kinds of other carbon-oxygen bonds (–OH, C–O–C, C=O) different from phenolic hydroxyl groups. The relevant studies of HDO focused on the conversion of oxygen-containing phenylpropanes or, in general, phenylalkanes as another type of model compounds simulating the lignin structure are still very scant.

Herein, we report the results of the HDO reaction catalyzed by Raney® nickel under transfer hydrogenation conditions at 150 °C. Different oxygen-containing aromatic substrates have been used as non-phenolic model compounds of lignin structure: acetophenone, benzophenone, diphenylmethanol, benzaldehyde, benzyl alcohol and styrene oxide. The reference compound was anisole which catalytic HDO transformations are studied well enough excluding the process catalyzed by Raney® nickel (hydrodeoxygenation, hydrogenation, or hydrogenolysis). As a hidden hydrogen resource, 2-propanol was used which *H*-donor activity in the TH reactions is the subject of many recent studies and well-documented. The aim of this study is to investigate a comparative reactivity of abovementioned aromatics and the HDO kinetics under catalyzed TH conditions, to determine the structure of main reaction products (if not done before) as well as "substrate structure"-dependent catalytic selectivity of Raney® nickel. A plausible reaction mechanism is proposed to explain the "step-by-step" formation of the products.

2. Experimental

2.1. Chemicals and solvents

All solvents and reagents were obtained from commercial sources and used as received: 2propanol (\geq 99.5%, Sigma–Aldrich), benzophenone (99%, Sigma–Aldrich), diphenylmethanol (99%, Aldrich), acetophenone (\geq 98%, Aldrich), benzaldehyde (\geq 99%, Sigma–Aldrich), benzyl alcohol (\geq 99%, Sigma–Aldrich), styrene (\geq 99%, Aldrich), styrene oxide (\geq 97%, Aldrich), anisole (99.7%, Sigma–Aldrich), sulfolane (99%, Aldrich), aluminum-nickel alloy (Al–Ni 50:50 wt%, Sigma–Aldrich), NaOH (\geq 97%, Sigma–Aldrich).

2.2. Catalyst preparation

Raney[®] nickel was prepared according to well-known leaching method from aluminum–nickel alloy [28]. So, 0.450 g of the alloy was added portion-wise to 5.6 mL 20% aq. NaOH (a solution of 14.50 g of NaOH in 58.0 mL of distilled water) under vigorous stirring at room temperature. The temperature was kept at about 50 °C. After adding the total amount of the alloy (10–15 min), the mixture was stirred for 45–50 minutes at 50 °C until the H₂ evolution stopped. Then the skeletal nickel was washed out with distilled water (4 × 50 mL) till neutral pH and then additionally stirred with extra portion of distilled water (15 mL) for 2.5 hours. Water was decanted away and 2-PrOH was added portion-wise (4 × 50 mL) to remote residual water from prepared Raney[®] nickel. The prepared leached nickel was pyrophoric enough and usually used immediately after preparation. The catalyst was characterized by BET, X-ray powder diffraction (XRD) and X-ray fluorescence (XRF) analyses. The properties were very similar to literature data (see *Supplementary Materials*).

2.3. General experimental procedure

The batch reactor equipped with mechanical agitator MagneDrive® (Autoclave Engineers) was charged by ~3.2·mmole of ketone (or benzaldehyde, 0.39–0.60 g), 0.20–0.30 g of sulfolane (as an internal standard) and 120 mL of 2-PrOH. After adding the catalyst prepared from 0.45 g of aluminum–nickel alloy, the reactor was closed, purged with argon under stirring and heated up with the rate of ~7 °C/min to reach the reaction temperature of 150 ± 1 °C. The reaction was carried out at constant temperature of 150 °C during 5 h with permanent stirring at 800 rpm. During the reaction, probes of the reaction mixture were collected hourly to the sampler. The final reaction mixture and all other probes were analyzed by GC–MS method.

2.4. Catalyzed TH reaction of acetophenone in the presence of CO at 150 °C

The batch reactor was charged by ~3.2·mmole of acetophenone (0.39 g), 0.20 g of sulfolane (as an internal standard) and 120 mL of 2-PrOH. After adding the catalyst freshly prepared from 0.45 g of aluminum–nickel alloy, the reactor was closed, purged with argon under stirring and then 80 ml of CO (at 1 atm and room temperature, ~3.2 mmol) were pumped into the reactor by using a high pressure syringe pump (Teledyne ISCO, USA). After that, the reactor was heated up with the rate of ~7 °C/min to reach the reaction temperature of 150 ± 1 °C. The reaction pressure was raised up to 9 atm. The reaction was carried out at constant temperature of 150 °C during 5 h with permanent stirring at 800 rpm. During the reaction, probes of the reaction mixture were collected hourly to the sampler and analyzed by GC–MS method.

2.5. GC–MS analysis

The identification of the products was performed by GC–MS method on a gas chromatograph Shimadzu GCMS-QP2010-SE (Japan) equipped with autosampler. A 30 m-long quartz capillary column VF-5ms with 0.25 mm i.d. was used for the analysis; the film thickness of the stationary phase (5% diphenylsiloxane – 95% dimethylsiloxane copolymer) was 0.25 μ m; helium was as the carrier gas with a constant flow rate of 1.8 mL min⁻¹; a split ratio was 1:25; the injector temperature was 270 °C; the temperature program was 1 minutes at 50 °C, 50–270 °C (12 °C min⁻¹), and 270 °C (20 min).

The qualitative analysis was carried out by comparing the retention time of the components and their experimental mass spectra with the corresponding data for the pure compounds or with the data from the NIST11 and Wiley9 mass spectral libraries. Sulfolane was used as an internal standard for the quantitative assessment of the products.

3. Results and discussion

The chemical behavior of six non-phenolic oxygen-containing aromatics together with non-oxygen styrene (which could be an intermediate in some of the reactions) were studied at 150 °C using Raney® nickel as a catalyst of transfer hydrogenation by 2-PrOH. The molar catalyst-to-substrate ratio was always 1.2/1 in the reaction mixtures and the amount of the catalyst was not optimized. At the same time, according to approximate evaluation based on specific surface area of the catalyst (see *Supplementary Materials*), less than 5% of all nickel atoms are on the working catalyst surface. Thus, it is highly possible to decrease the amount of the catalyst used.

All reactions were carried out in the same manner to each other under oxygen-free conditions to avoid the oxidation (deactivation) of the pyrophoric catalyst and repeated twice. The conversion time was 5 h, but, for kinetic information, probes of the each reaction mixture were collected hourly starting from zero reaction time at which the reaction mixture reaches the reaction temperature (150 °C) after heating. These results were compared with the TH reduction of anisole as a phenolic model compound (**Table 1**).

The early study on the TH mechanism by ATR–IR spectroscopy reveals that 2-PrOH is chemically adsorbed on the metal catalyst surface with further O–H bond dissociation. The elimination of hydrogen atom from α -*C* position of 2-PrOH (*surface*–O–C(CH₃)₂–<u>H</u>) leads to acetone formation (O=C(CH₃)₂) and hydrogen stays bonded on the metal surface (see, for example, Refs. [16,18]). This is a necessary condition for initiation of the TH reaction. Oxygen-containing aromatic substrates can also be adsorbed on the Raney® nickel surface [16]. Both functional groups participate in interaction with the metal surface that makes possible the total hydrogenation.

At the first stage, all oxygen-containing substrates underwent the reductive deoxygenation to form the non-oxygen aromatics (**Table 1**). The conversion in the total deoxygenation achieved 100% after 5 h excluding anisole (90%). Also in the anisole HDO reaction, oxygen-containing product (methoxycyclohexane, 22%) was found in the final reaction mixture. As expected, monoaromatic rings are not chemically stable under the TH reaction conditions and react further to form substituted cyclohexanes. But for 5 h of the reaction, none of deoxygenated intermediates achieved the exhaustive hydrogenation to give fully saturated products.

Table 1.

Both acetophenone and styrene have the same HDO products in the final reaction mixture – ethylbenzene and ethylcyclohexane in a similar content. More than 80% of the all products are the same in the reaction of styrene oxide too. It could mean that styrene is the common intermediate in the reaction of acetophenone and styrene oxide. For a deeper insight into the reaction mechanisms, kinetics (the dependence of all products yield *vs*. reaction time) was studied for the all reactions that helped to detect some obvious difference in the TH reaction of the chosen substrates.

3.1. Reaction of ketones and benzaldehyde

The first stage of acetophenone transformation is the transfer hydrogenation of C=O group, which leads to 1-phenylethanol. So, at zero reaction time, the acetophenone conversion achieves 94% (**Fig. 1**). But the amount of firstly formed 1-phenylethanol is already decreased to 16% due to its further hydrogenolysis and hydrogenation into a mixture of ethylbenzene and ethylcyclohexane those amounts are highly anti-correlated with each other. Selectivity on ethylbenzene is reached maximum of 88–89% for 0.5 h of the reaction at 100% conversion of acetophenone and then gradually decreased to 50% at the end of the reaction. A trace amount of 1-cyclohexylethanol is also detected in the reaction mixture, which concentration is changed very little during the reaction (< 1%).

Fig. 1.

To compare the reaction under milder conditions, the catalyzed transfer hydrogenation of acetophenone was studied at 50°C: no conversion was observed for 5 h of the reaction. At the same time, in the non-catalytic reaction at 150°C, less than 1% of initial acetophenone was converted into

any hydrogenation products for 5 h. Thus, Raney® nickel catalyst and reaction temperature are crucial conditions for successful TH reaction of acetophenone.

The transfer hydrogenation of C=O group in benzophenone molecule leads to diphenylmethanol which content at zero reaction time is already decreased to 20% at 98% conversion of benzophenone (**Fig. 2**). After 1 h of the reaction, no diphenylmethanol detects in the reaction mixture. But at the same reaction time, the amount of diphenylmethane formed directly from diphenylmethanol *via* hydrogenolysis is also about zero being totally converted into other products. For example, selectivity on cyclohexylphenylmethane is reached maximum of 89% for 1 h of the reaction and then gradually decreased to 65% at the end of the reaction. The amount of fully saturated dicyclohexylmethane is gradually increased and reached 34% at the end of the reaction. Trace amounts of cyclohexylphenylketone and cyclohexylphenylmethanol are also detected in the reaction mixture.

Fig. 2.

Compared with ethylbenzene, diphenylmethane is shown to have higher reactivity in the hydrogenation of benzene ring. But the total hydrogenation of cyclohexylphenylmethane derived directly from diphenylmethane after one ring reduction undergoes slow enough. Although the two aromatic rings in diphenylmethane molecule are isolated (non-conjugated aromatics) and react independently, first among them is hydrogenated much faster than the second one. This result is in good agreement with reported elsewhere [6] and more research is clearly needed to be explained.

The conversion of benzaldehyde achieves only 44% at zero reaction time. The maximum content of benzyl alcohol (50%) is reached after 30 min and then decreased to zero for 2.5 hours of the reaction (**Fig. 3**). The amount of cyclohexylmethanol formed directly from benzyl alcohol *via* the total hydrogenation of benzene ring (dearomatization) is changed very little during the reaction (< 1%).

Interestingly, the reductive conversion of benzaldehyde passes through two independent pathways (parallel ones): 1) without changing the carbon skeleton; 2) with shortening the carbon chain of the products. According to the first pathway, the TH reaction of benzaldehyde proceeds as follows: "benzaldehyde \rightarrow benzyl alcohol \rightarrow toluene \rightarrow methylcyclohexane". The second pathway includes, at the first stage, the well-known decarbonylation of benzaldehyde to benzene (for example, during a catalytic reaction at 150 °C [29]) which is further hydrogenated to cyclohexane. Unexpectedly, both toluene and benzene are low-reactive enough under the TH

reaction conditions: their further hydrogenation to methylcyclohexane and cyclohexane, respectively, occurs very slowly after reaching the maximum content for 1-2 h of the reaction.

Fig. 3.

Surprisingly, the hydrodeoxygenation of benzaldehyde as a first stage occurs slower than of acetophenone and benzophenone: this result differs from general conception of the TH reaction, in which aldehydes are much more reactive than ketones. Moreover, the total hydrogenation of aromatic rings of intermediates (toluene and benzene) also slows down in the reaction. In our opinion, the decarbonylation can cause the low rate of further hydrogenation due to partial deactivation of Raney® Ni. As known [16], CO is adsorbed on metal nickel surface and, perhaps, stays bonded similar to Fischer–Tropsch species [30]. These species block centers of 2-PrOH adsorption and hinder the process.

Thus, the reduction of C=O groups in acetophenone, benzophenone and benzaldehyde molecules seems to proceed mainly *via* the pathway: "*aromatic ketone (aldehyde)→aromatic alcohol→alkylaromatics→saturated alkylcyclohexane*" (structures **1**, **2**, **3**, and **4**, **Scheme 1**). This "mainstream" is accompanied with minor reduction of aromatic rings giving the trace amount of non-aromatic both ketone and alcohol like structures **5** and **6**, correspondingly (**Scheme 1**). We believe that both aliphatic ketone and alcohol **5** and **6** are not main precursors of final alkylcyclohexanes. Unlike aromatic 1-phenylethanol and diphenylmethanol (**2**, R = CH₃ or Ph), HDO of low-reactive aliphatic alcohols like **6** (R = CH₃ or Ph) catalyzed by Raney® nickel at 150 °C is much more difficult to undergo [31].

Scheme 1.

3.2. Reaction of aromatic alcohols

As diphenylmethanol and benzyl alcohol are the primary product of the HDO derived from the corresponding carbonyl compound, it was important to study their kinetics (conversion dynamics) under the same reaction conditions.

Both diphenylmethanol and benzyl alcohol demonstrate lower reactivity than corresponding carbonyl compounds: only 44% and 27% of the conversion, respectively, at zero reaction time (**Fig. 4** and **Figure 5**). The TH reaction of diphenylmethanol proceeds through the same pathway as diphenylketone (**Fig. 4**). Selectivity on cyclohexylphenylmethane reaches its maximum of 93% for 2 h of the reaction. Diphenylmethane content achieves maximum of 42% for 30 min and then is decreased being

converted into cyclohexylphenylmethane. Cyclohexylphenylmethane and dicyclohexylmethane are found in the final reaction mixture in ratio 87:13. The trace amount of cyclohexylphenylmethanol is also detected.

Fig. 4.

Selectivity on toluene reaches up to 96% for 1 h of the TH reaction of benzyl alcohol (**Figure 5**). The amount of methycyclohexane is gradually increased during the reaction achieved 25% in the final reaction mixture. Only a trace amount of cyclohexylmethanol is detected. In contrast to the reaction of benzaldehyde, the decarbonylation products are not found in the reaction mixture. It means that solely benzaldehyde underdoes the decarbonylation process, not benzyl alcohol. Additionally, this confirms a weak *H*-donor ability of primary aliphatic alcohols including benzyl alcohol (as compared with secondary 2-PrOH) in the presence of Raney® nickel [6,31]. A much faster toluene reduction in the reaction of benzyl alcohol as compared with the TH of benzaldehyde is an argument demonstrating CO poison effect on Raney® nickel surface when the decarbonylation process of aldehyde occurs.

Figure 5.

3.3. Reaction of styrene and styrene oxide

The epoxide functionality is not "native" for lignin structure, but may be formed after some thermal and/or chemical exposures on lignin molecules, for example as a result of the dehydration of vicinal diol moiety to epoxy group [32] or of some other chemical pretreatment [33]. On the other hand, behavior of epoxides under TH conditions could be interesting from a synthetic viewpoint [34–36].

Earlier styrene oxide was studied under TH reaction conditions [37,38], but those reactions have differed from present one: other catalysts and reductants were used. Now styrene oxide is reduced with using 2-PrOH as a hydrogen donor and Raney® nickel as a heterogeneous catalyst. Styrene oxide is active enough under the reaction conditions to be successful converted into the products. The conversion achieves 78% already at zero reaction time (**Fig. 6**). Among the products, aromatic ethylbenzene and toluene, as well as fully saturated ethylcyclohexane and methylcyclohexane are the main ones. The minor products are styrene and 2-phenylethanol (β -phenethyl alcohol). The content of ethylbenzene and ethylcyclohexane are highly anti-correlated with each other after 1 h of the reaction.

Fig. 6.

The chemical composition of the products is rather different from that obtained in the conventional hydrogenation of styrene oxide catalyzed by Raney® nickel [39]. For example, under our reaction conditions, selectivity on ethylbenzene reaches up to 78% for 1 h, while selectivity on 2-phenylethanol is only 3% for the same reaction time. Liquid-phase hydrogenation of styrene oxide at 50 °C catalyzed by Raney® nickel gives quite opposite result: selectivity on ethylbenzene was only 10% for 1 h of the reaction, while selectivity on 2-phenylethanol reached up 90% for the same reaction time [39]. Additionally, our reaction mixture contains no 1-phenylethanol (α -phenethyl alcohol) which is common enough for the conventional hydrogenation of styrene oxide [40].

Toluene (methylbenzene) and methylcyclohexane formation evidences in the decarbonylation reaction of 2-phenylacetaldehyde. Thus, the first stage of the reaction is a well-known Meinwald rearrangement of oxirane to aldehyde [29,41] resulted in the formation of phenylacetaldehyde **8** from styrene oxide (**Scheme 2**). The further reaction of phenylacetaldehyde gives either 2-phenylethanol **9** *via* the TH reduction or toluene **13** due to the decarbonylation. 2-Phenylethanol can be dehydrated into styrene **10** or converted into ethylbenzene **11** due to the HDO reaction catalyzed by Raney® nickel [42]. Another possible precursor of styrene **10** is styrene oxide which may be directly deoxygenated on Raney® nickel surface (*cf.* [42]). The total hydrogenation of toluene and ethylbenzene occurs slowly enough under these reaction conditions. Our reason is the same one: CO poisoning effect on Raney® nickel surface when the decarbonylation process of aldehyde occurs.

Scheme 2.

The TH reaction of styrene is carried out to prove the reaction pathways of styrene oxide conversion. Expectedly, non-aromatic conjugated C=C double bond of styrene is reduced quickly under the TH conditions and the total conversion achieves at zero reaction time (**Fig. 7**). The reaction mixture contains only two products – ethylbenzene and ethylcyclohexane which contents are fully anti-correlated with each other and gradually changed during the reaction reaching the final ratio equal to 2/3. As there are no toluene and methylcyclohexane in the reaction mixture, therefore, these products resulted from some rearrangement (carbon-chain shortening) of oxygen-containing derivatives of ethylbenzene those one could observed in the reaction of styrene oxide.

Fig. 7.

To test the reaction under milder conditions, the catalyzed transfer hydrogenation of styrene was studied at 50°C. Similar to acetophenone reaction, there was no conversion for 5 h under the reaction conditions. But in the non-catalytic reaction at 150°C, less than 10% of styrene was converted into hydrogenation products. Thus, the reactivity of styrene under the same non-catalytic conditions is slightly more than that of acetophenone.

3.4. Influence of CO on the TH reaction of acetophenone

To prove the inhibiting effect of CO on the catalytic properties of Raney® nickel in the reaction, the catalyzed transfer hydrogenation of acetophenone was studied in the presence of equimolar amount of CO at 150 °C.

The difference between the reactions in the presence of CO and without it is shown in **Figs. 1** and **8**. The most pronounced effects are demonstrated for acetophenone conversion, partial reduction of acetophenone into ethylbenzene and its total hydrogenation into ethylcyclohexane. So, at zero reaction time the acetophenone conversion reduced from 94% in the catalyzed reaction without CO (**Fig. 1**) down to 21% in the presence of CO (**Fig. 8**), *i.e.* CO inhibited the hydrogenation of C=O group that may be due to competitive adsorption of CO and C=O group of acetophenone molecule on the catalyst surface. The similar competition of CO with benzene ring (π -conjugated aromatic system) for active metal centers of the catalyst (*cf.* [16]) caused the decrease of reactivity of intermediate ethylbenzene, which content in the reaction mixture reached maximum of 92% after 1 h of the reaction and remained almost unchanged until the end of the reaction. That is why intermediate ethylbenzene doesn't further reduce into fully hydrogenated ethylcyclohexane. Thus, the inhibition effect of CO is quite pronounced.

Fig. 8

3.5. Reaction of anisole

Anisole is well-known and widely used model compound to study the catalytic HDO reaction of lignins. Surprisingly, there are very poor experimental data on the hydrodeoxygenation, hydrogenation, and hydrogenolysis of anisole catalyzed by Raney® nickel. To compare the HDO efficiency of Raney® nickel towards both non-phenolic and phenolic model compounds of lignin structure, the TH reaction of anisole was carried out at the same reaction conditions.

Unlike other oxygen-containing compounds, the anisole conversion is only 90% reached for 5 h of the reaction (**Fig. 9**). Two parallel reaction routes are realized under the conditions – HDO and dearomatization. The main product of direct HDO process is benzene (22% after 0.5 h of the reaction) which is further dearomatizated to cyclohexane: the cyclohexane and benzene contents in the final reaction mixture are 63% and 7%, respectively. Evidently, the fully both conversion of anisole and benzene dearomatization can be achieved under the reaction conditions with increased reaction duration (see trend of kinetic curves, **Fig. 9**). Direct dearomatization of anisole results in 1-methoxycyclohexene (up to 1%) and methoxycyclohexane (19% after 5 h) formation, but this process catalyzed by Raney® nickel is minor. The same is true for cyclohexanol ($\leq 1\%$), which formation results from the combination of demethylation and dearomatization of anisole. Methoxycyclohexane, which content is correlated with cyclohexane may undergo the same demethylation reaction to convert into cyclohexanol.

Fig. 9.

3.6. Reusability of Raney ® nickel catalyst

It has been shown that the Raney® nickel catalyst can be reused at least during three consecutive runs (5 h reaction time each) in the transfer hydrogenation of acetophenone to any hydrogenated products at 150 °C. For each cycle, the catalyst was recovered by decantation of the reaction mixture (the procedure is described in *Supplementary Materials*).

The recovered catalyst exhibited no significant loss of catalytic activity after three runs. So, after 3^{rd} cycle, the acetophenone conversion for 5 h of the reaction remains 100% similar to freshly prepared Raney® nickel. Minor difference was only observed in products selectivity: the ethylcyclohexane-to-ethylbenzene ratio (*i.e.* a ratio of fully hydrogenated product to partially hydrogenated one) was 50:50 after 1^{st} cycle, 48:52 after 2^{nd} cycle and 44:56 after 3^{rd} cycle, respectively. (*It is worthy to note that, in our case, decreasing the catalyst amount because of the separation procedure was ca. 15 wt% after third cycle.*) Therefore, the Raney® nickel catalyst can be successfully reused, but limited numbers of runs. The decrease in chemoselectivity may be ascribed to partial oxidation of the catalyst surface during the separation procedure. Recovering the Raney® nickel catalyst is well-known procedure that was studied many times including for some hydrogen transfer processes – hydrogenation, hydrogenolysis and hydrogen-borrowing reactions [22,23,43].

4. Conclusions

The seven non-phenolic aromatic substrates and one phenolic compound (anisole) have been studied as model compounds of lignin structure at 150 °C under transfer hydrogenation conditions. It has been shown that the combination of Raney® nickel as a catalyst and 2-PrOH as an H-donor can be effective for both HDO process and dearomatization reaction of different oxygen-containing aromatics. The chemical processes observed under the reaction conditions have significant difference with those in the conventional hydrogenation catalyzed by the same catalyst. If the oxygen functionality is in a side alkyl chain, the HDO process is recognized as a primary reaction, while the dearomatization reaction is a secondary one. The structure of all products was determined and plausible reaction pathways were proposed. It was shown that aldehydes undergo the decarbonylation reaction as an alternative process and carbon monoxide released is able to act as a poison of the Raney® nickel surface decreasing the conversion. The inhibiting effect of CO on the transfer hydrogenation of both C=O group and benzene ring was demonstrated in the TH reaction of acetophenone catalysed by Raney® nickel at 150 °C.

Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.XXX.2018.XX.XXX.

Notes

The authors declare no competing financial interest.

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Table Caption

Table 1

The main reaction products.^a





^a Reaction conditions: 3 mmol of substrate, Raney® Ni prepared from 450 mg of Al-Ni alloy, 120 mL of 2-PrOH, 5 h, 150 °C, 11 atm.

^b Conversion is 100% in all reactions excepting anisole conversion (90%).

^c Cyclohexylmethanol is formed only in a trace amount ($\leq 1\%$).

Figure and Scheme Captions

Figure 1. Acetophenone conversion and products content.

Figure 2. Benzophenone conversion and products content.

Figure 3. Benzaldehyde conversion and products content.

Figure 4. Diphenylmethanol conversion and products content.

Figure 5. Benzyl alcohol conversion and products content.

Figure 6. Styrene oxide conversion and products content.

Figure 7. Styrene conversion and products content.

Figure 8. Acetophenone conversion in the presence of CO.

Figure 9. Anisole conversion and products content.

Scheme 1. Plausible mechanism of TH reaction of aromatic carbonyl compounds.

Scheme 2. Plausible mechanism of TH reaction of styrene oxide.



Figure 1.









Figure 3.





Figure 4.



Figure 5.



Figure 6.



Figure 7.



→ 1-cyclohexylethanol; -★- acetylcyclohexane;
 → 1-phenylethanol; -▶ 1-ethylcyclohexene;

Figure 8.





Figure 9.

