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FURFURAL HYDROTREATMENT APPLYING ISOPROPANOL AS A SOLVENT – THE CASE OF ACETONE FORMATION

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ABSTRACT

In this study, acetone formation was investigated as a side reaction in furfural hydrotreatment applying isopropanol as a solvent. Acetone formation was observed to depend strongly on the metal and metal loading of catalysts as copper, nickel, and iron catalysts supported on activated carbon were studied. Furfural has an important role in acetone formation: the initial formation rate for acetone was high as long as furfural reacted further. After furfural was consumed the acetone formation decelerated except with the catalysts including iron. Two formation mechanisms were derived: first mechanism includes direct and transfer hydrogenation of furfural and isopropanol dehydrogenation, as mechanism two consists only of isopropanol dehydrogenation. Another novel discovery of the study was the confirmation of the formation mechanism for 2-methylfuran through transfer hydrogenation of furfuryl alcohol in the experiments. In conclusion, the acetone formation as a side product was observed significant and could not be totally prevented.

Keywords: Acetone, catalyst, furfural, hydrotreatment, isopropanol

1. Introduction

Replacing fossil based chemicals and fuels with bio-based ones is increasingly important as environmental concerns and need for energy, chemicals, and fuels are continuously increasing.¹ Platform chemicals produced from renewable feedstocks are promising chemicals for the production of desired chemicals and fuels. One excellent platform chemical produced from lignocellulosic biomass is furfural, which is produced from hemicellulosic pentose sugars with dehydration.²⁻⁴ Furfural itself is a quite unstable chemical and further refining is needed to obtain stable components. An excellent method for furfural refining is hydrotreatment. With furfural hydrotreatment many valuable chemicals such as furfuryl alcohol (FA), tetrahydrofurfuryl alcohol (THFA), 2-methylfuran (MF), and 2-methyltetrahydrofuran (MTHF) can be produced.⁵ These chemicals have many applications varying from solvents to pharmaceutical components. 2-Methylfuran with its excellent properties has recently attracted attention with potential use as a biofuel component. This chemical has a high research octane number (131), low water solubility ($7 \text{ g} \cdot \text{dm}^{-3}$), and high energy density ($31.2 \text{ MJ} \cdot \text{kg}^{-1}$) that could compete with the current octane boosting components in gasoline.⁶ The furfural hydrotreatment scheme with the most common products is presented in Figure 1.

Figure 1.

Production of MF with furfural hydrotreatment has proved to be challenging as many by-products can be produced at the same conditions. The most common product in furfural hydrotreatment is furfuryl alcohol, which is produced at mild temperatures and low hydrogen pressures.⁷ Production of MF is carried out at higher temperatures compared to furfuryl alcohol production.

Solvents used in furfural hydrotreatment studies include alcohols, alcohol-water mixtures, and water.⁸⁻¹¹ Applying pure water generates a problem as furfural has a limited water solubility. Thus, alcohols are mostly used in these studies as the solubility of furfural in alcohols is good. The most used solvent in furfural hydrotreatment studies is isopropanol.⁹ However, this solvent can be dehydrogenated in the reaction conditions to acetone and hydrogen.¹² The isopropanol dehydrogenation scheme is presented in Figure 2.

The other alcohols have a similar kind of behavior. As secondary alcohols are used as solvents they are dehydrogenated to ketones and hydrogen, whereas primary alcohols produce aldehydes and hydrogen. Thus, the use of n-propanol, ethanol, or i-butanol as a solvent will result in propanal, acetaldehyde, or butanone, respectively.⁶

In addition to dehydrogenation, the solvent can react also with furfural. The solvent can act as a hydrogen donor with furfural and produce furfuryl alcohol and acetone as products. The transfer hydrogenation reaction of furfural and isopropanol is presented in Figure 3.

Figure 2 and 3.

The formation of acetone during the furfural hydrotreatment experiments can be significant. However, as the formation is not straightforward and there are two possible reaction routes for the formation, the mechanism of acetone formation during furfural hydrotreatment is still unclear. To minimize the loss of reactants in side reactions and to decrease the need of the downstream purification of the product in furfural hydrotreatment reactions it is important to know the mechanism for acetone formation.

In our study, the formation of acetone in furfural hydrotreatment reactions in the presence of isopropanol was studied. Also, the formation mechanism of acetone from isopropanol through transfer hydrogenation with furfural and dehydrogenation was studied in detail.

2. Experimental

2.1. Materials

All chemicals were purchased from Sigma-Aldrich and applied without further purification. The following chemicals were used in this study: furfural (99 %), furfuryl alcohol (98 %), tetrahydrofurfuryl alcohol (99 %), furan (≥ 99 %), 2-methylfuran (99 %), 2-methyltetrahydrofuran (anhydrous, inhibitor free, ≥ 99 %), isopropanol (ACS reagent, ≥ 99.5 %), 2-butanol (99 %), 2-pentanol (98 %), 2-pentanone (CHROMASOLV for HPLC, 99.5 %), cyclopentanol (99 %), and cyclopentanone (SAFC, ≥ 99 %).

The chemicals used for catalyst preparation were: $\text{Cu}(\text{NO}_3)_2 \cdot \text{H}_2\text{O}$ (Aldrich, trace metal basis, 99.9 %), $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (Sigma-Aldrich, puriss. p.a., ≥ 98.5 %), $\text{Fe}(\text{NO}_3)_2 \cdot 9\text{H}_2\text{O}$ (ACS reagent, ≥ 98 %). Material used as a catalyst support was steam activated carbon from Norit (Norit RB4C).

2.2. Catalyst preparation

Several catalytic materials supported on steam activated carbon (Norit RB4C) were prepared with wet incipient impregnation method. The applied metals on the catalysts were copper, nickel, and iron in mono- and bimetallic forms. The support was dried from moisture at 110 °C and the deposition of the metal precursors ($\text{Cu}(\text{NO}_3)_2 \cdot \text{H}_2\text{O}$, $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$) was performed keeping the liquid/solid ratio at $1 \text{ cm}^3 \cdot \text{g}^{-1}$. Drying of catalysts was performed at room temperature (24 h) and subsequently in a oven at 110 °C (18 h). Calcination of catalysts was done at 300 °C for 4 hours applying linear heating ramp of $5 \text{ }^\circ\text{C} \cdot \text{min}^{-1}$. The calcination was performed under air flow of $4 \text{ dm}^3 \cdot \text{h}^{-1}$. In situ reduction of catalysts was performed at 250 °C with 4 MPa pure hydrogen pressure for 90 minutes.

2.3. Furfural hydrotreatment and acetone formation studies

Experiments were performed in an Autoclave Engineers 50 cm^3 batch reactor, where the catalyst (0.2 g) was placed in a Robinson-Mahoney type of catalyst basket. 1 cm^3 of furfural or furfuryl alcohol and 15 cm^3 of solvent isopropanol with 4 MPa pure hydrogen were placed to the reactor as the reaction temperature was achieved. The same procedure was applied in isopropanol experiments except no furfural was added to the reactor. External diffusion limitations during the reaction were avoided with high stirring speed (1000 rpm), which was confirmed in pre-experiments.

During the experiments the reactions were monitored by taking liquid samples at 0, 15, 30, 60, 120, and 300 minutes. The samples were analyzed quantitatively with a GC-FID (Agilent 6890) and a Zebron ZB-wax Plus column (60 m x 0.25 mm x 0.25 μm). The temperature ramp used with GC was from 40 °C to 100 °C with heating rate of $5 \text{ }^\circ\text{C} \cdot \text{min}^{-1}$ and from 100 °C to 230 °C with heating rate of $20 \text{ }^\circ\text{C} \cdot \text{min}^{-1}$. Injection volume was 1 μl , injection temperature 230 °C and internal standard used was 2-butanol. Qualitative

analysis of unknown components was performed with a GC-MS (Agilent 7890-5975) applying similar column and method. The mass spectra was recorded in electron impact ionization at 70 eV.

Gas phase in the reactor was analyzed as the reactor had cooled down to the room temperature. The gas samples were collected to a container under vacuum and analyzed with GC-FID/TCD containing gas pneumatics (Agilent 6890). CO, CO₂, H₂, and N₂ were analyzed quantitatively with TCD applying HP-PLOT/Q (30 m x 0.53 mm x 40 µm) and HP Molesieve (30 m x 0.53 mm x 25 µm) columns. Hydrocarbons were analyzed with FID applying HP-AL/KCL column (50 m x 0.32 mm x 8 µm).

3. Results and discussion

3.1. Furfural hydrotreatment studies

Furfural hydrotreatment studies were performed with a variety of monometallic and bimetallic catalysts, testing also the effect of reaction temperature and metal loading of the catalyst. The acetone formation was monitored closely during reactions and differences between catalysts and operating conditions were observed, as there are two possible reaction routes for acetone formation.

3.1.1. Effect of metal on acetone formation

Monometallic 5 wt-% Cu/C and Ni/C, and bimetallic 2/2 wt-% CuNi/C, CuFe/C, and NiFe/C were tested in furfural hydrotreatment experiments. Figure 4 presents the acetone formation as a function of contact time in each of these experiments. The acetone concentration was monitored as a function of contact time to avoid differences caused by different metal loading between the catalysts. Contact time indicates the reaction time multiplied with the metal loading of the catalyst. The highest concentration of acetone was observed with bimetallic CuFe/C catalyst. With this catalyst the acetone concentration after 300 minutes was as high as initial furfural concentration in the beginning of the experiment. In each experiment the acetone formation in the beginning had a very high reaction rate and it was noticed to cease after conversion of furfural had achieved over 90 % (typically in 60-120 minutes). This indicates that either equilibrium state is achieved or the reactants for the reaction are running out or that the formed acetone is reacting

further. However, the iron containing catalysts had a constantly increasing trend in acetone formation throughout the whole experiment (300 min), whereas the formation of acetone was observed to stabilize with the catalysts without iron. This indicates that formation of acetone has at least two mechanisms.

With nickel catalyst even a decreasing trend of acetone formation can be observed after 60 minutes of experiment clearly indicating further reactions of acetone. Known reactions of acetone include for example condensation reaction of acetone with furfural or furfuryl alcohol to furanmethanol acetate (FMA) and aldol condensation of acetone to methyl isobutyl ketone (MIBK). MIBK formation was observed in quantitative GC-FID analysis and the results indicated that with the iron containing catalysts MIBK was formed. With the 5 wt-% Ni/C the further reaction of acetone was mainly caused by FMA formation.

Figure 4.

3.1.2. Effect of metal loading on acetone formation

Effect of metal loading on acetone formation was studied with all the catalyst options and it was observed that each catalyst had a characteristic trend in acetone formation as a function of metal loading. The highest amount of acetone formed during the experiments with each catalyst is presented in Figure 5.

With monometallic nickel catalyst metal loadings of 2, 5, and 10 wt-% were tested. The difference in acetone formation between 2 and 5 wt-% catalysts was low but with higher metal loading (10 wt-%) remarkably more acetone was formed. With all the tested nickel catalysts acetone concentration started to stabilize after 60 minutes of reaction time, when most of the furfural was consumed as described above.

With monometallic copper increasing the metal loading from 2 wt-% to 5 wt-% decreased the amount of formed acetone. Furthermore, due to the low overall activity of copper catalysts neither the stabilization of acetone concentration nor the complete conversion of furfural were reached during the experiments, which supports that furfural is involved in the acetone formation mechanism. The lower activity of copper in the acetone formation and furfural hydrotreatment reactions can be explained with a weaker adsorption of furfural on copper as well as with poor dissociation of hydrogen on copper surface compared to nickel and

iron.^{13,14} E.g. Pozzo and Alfe¹⁴ studied H₂ dissociation and calculated that the activation energies for H₂ dissociation on copper, nickel, and iron were 0.56, 0.06, and 0.03 eV, respectively.

With bimetallic catalysts significant differences in acetone formation were detected as the metal loading was altered (Figure 5). From these results it can be concluded, that with bimetallic catalysts containing copper (CuNi/C and CuFe/C) the increase of copper loading actually decreased the amount of acetone formed. This trend is in line with the monometallic copper catalyst. With bimetallic nickel catalysts (CuNi/C and NiFe/C) the acetone formation was similar as with monometallic nickel catalyst, the increase of nickel loading increased also the amount of acetone formed. The highest amount of acetone formed during the experiment was observed with the 5/5 wt-% NiFe/C catalyst. As iron was observed to increase acetone formation, acetone concentration can be assumed to increase also in case of CuFe/C with increasing iron loading.

Figure 5.

3.1.3. Effect of reaction temperature on acetone formation

To observe how acetone formation is affected as a function of temperature the reaction was studied at reaction temperatures of 200 and 230 °C. With most of the catalysts an increasing temperature led to an increased amount and rate of acetone formation, as can be assumed with the law of Arrhenius (Figure 6). The only exception was CuNi/C, as with this catalyst a decrease in acetone concentration as a function of reaction temperature was observed. This is mostly due to the above mentioned further reactions of acetone. In this case no MIBK formation was observed in either reaction temperature but the FMA formation was significant. In conclusion, higher temperatures promoted the furfural hydrotreatment reactions to furfuryl alcohol (and other products) as well as acetone formation. Thus, higher temperatures are needed to achieve the best result for the furfural hydrotreatment although the side reaction to acetone intensifies as well.

Figure 6.

3.2. Isopropanol dehydrogenation

Acetone formation can also be a result from the solvent dehydrogenation to acetone and hydrogen. All the chosen metals in this study have also been studied earlier in isopropanol dehydrogenation with good results.^{12,15-18} Most of the reported catalysts for dehydrogenation have had oxide supports or they have been in oxide form themselves. This has been reported to be beneficial for isopropanol dehydrogenation. Especially iron has been reported as a good dehydrogenation catalyst, which would support our results of the massive acetone production with our iron catalyst.^{12,16-20} To study the acetone formation mechanism more deeply, the formation of acetone from isopropanol was studied with experiments applying only the solvent isopropanol and with experiments applying an intermediate product of furfural hydrogenation (furfuryl alcohol) as a reactant to disregard the furfural transfer hydrogenation and furfural hydrogenation routes.

An experiment with pure isopropanol was performed with 10 wt-% Ni/C catalyst at 230 °C and 4 MPa hydrogen pressure, i.e. in the same reaction conditions as the furfural hydrogenation experiments. In this dehydrogenation experiment the acetone concentration was observed to increase constantly as a function of reaction time. However, signs of acetone concentration stabilization were seen as the experiment proceeded further (Figure 7). As the experiment was compared to the furfural hydrogenation experiments performed with the same catalyst at the same reaction conditions it was discovered, that in the presence of furfural the initial acetone formation reaction rate was higher and the acetone concentration stabilized much earlier than with pure isopropanol as a feed. In addition, the amount of acetone remains lower as furfural is present in the experiment. It is assumed that in the case of pure isopropanol the amount of catalytically active sites for dehydrogenation is higher than in the case of furfural/isopropanol mixture experiments as furfural is not competing on the available sites on the catalyst and dehydrogenation can occur more efficiently until the equilibrium state is reached.

Figure 7.

In addition to the experiment with pure isopropanol, experiments with the furfural hydrotreatment intermediate furfuryl alcohol were performed. These experiments were performed to avoid reactions of furfural, but to offer more comparable reaction conditions for isopropanol dehydrogenation that are present in furfural hydrotreatment experiments. The acetone formation experiments with furfuryl alcohol were performed at two different temperatures (210 and 230 °C) and from these experiments it was discovered that the acetone concentration increased with the increasing temperature (Figure 8). At the higher temperature (230 °C) some sign of stabilization for the acetone concentration was noticed. However, the amounts of formed acetone are much lower than in the furfural/isopropanol or isopropanol experiments. This indicates that in the furfuryl alcohol experiments a similar situation occurs as in furfural experiments, the catalytically active sites of catalysts are more actively occupied by FA than isopropanol, and less acetone is formed by isopropanol dehydrogenation. The low amount of acetone in the FA experiment compared to the furfural experiment can be explained with higher affinity of FA on the catalyst compared to furfural and isopropanol, as reported in previous studies.^{13,21,22} The decrease in acetone concentration at 230 °C can be explained with further reactions of acetone, as MIBK formation was observed to increase as a function of temperature in the FA experiments.

Figure 8.

3.3. Comparison of acetone formation routes

3.3.1. Thermodynamic calculations

With three main reaction routes present in the reaction media during the experiments and two of them producing acetone as a product, it is important to know the thermodynamic limitations of the reactions. For comparison of the routes thermodynamic calculations were performed with HSC Chemistry 6 simulation software.²³ The equilibrium constants were calculated with the software at reaction temperature (230 °C) in the gas phase and the results are presented in Table 1. In our system the reaction takes place in liquid phase, but thermodynamic calculations in gas phase give a good indication of the equilibrium although the

values are not directly applicable for the liquid phase. From the results it can be concluded that the only reaction that was limited by equilibrium at 230 °C was isopropanol dehydrogenation.

Table 1.

3.3.2. Experimental results

As the thermodynamics of all three known reactions were calculated the results were compared to the experiments performed. Also, more comparisons were made to discover which of the reaction routes prevail in the experiments. In furfural transfer hydrogenation, one mole of furfuryl alcohol is formed as one mole of acetone is formed according to the stoichiometry. Thus, the maximum of formed furfuryl alcohol and acetone moles during the catalyst experiments were compared (Figure 9). The maximum of FA and acetone were not usually achieved at the same reaction time, the maximum of FA formation was usually reached in 15 to 60 minutes as the maximum of acetone appeared somewhat later between 30 and 300 minutes. Furthermore, the experiments indicated that with most of the catalysts a lower amount of acetone was formed compared to the furfuryl alcohol amount, although one exception of this were the iron containing catalysts discussed earlier. For more thorough investigation, the acetone concentration with all the metal catalysts was compared as a function of FA concentration and as a function of furfural conversion. Both these comparisons confirmed the same information, with Cu/C, Ni/C, and CuNi/C catalysts the acetone formation ceased as the formation of furfuryl alcohol achieved its maximum and most of the furfural was consumed. However, as iron was included in the catalyst acetone formation was observed to increase significantly after the raw material furfural and most of the intermediate product FA had reacted further. This implies that isopropanol dehydrogenation occurs significantly at least in the presence of iron.

In conclusion, furfural hydrogenation reaction with hydrogen is present during the experiments and produces at least part of the furfuryl alcohol along this route. As acetone is nevertheless produced in large quantities, also transfer hydrogenation of furfural or/and isopropanol dehydrogenation reactions occur during experiments. All these observations indicate of two mechanisms. The first mechanism takes place in the beginning of the experiments with high reaction rate and it includes all three reactions presented

above. After total furfural conversion mechanism two with slower reaction rate takes place. This mechanism is confirmed to consist only of isopropanol dehydrogenation and it occurs only with the iron containing catalysts. As the results were compared to the thermodynamic calculations, the amounts of acetone and FA were observed to be in the same order of magnitude as expected.

Figure 9.

Additional experiments were performed to get more information about the reactions. Furfural experiments without any additional hydrogen and without any catalyst were performed at 230 °C and compared to the experiment with 10 wt-% Ni/C catalyst. Based on the results from the experiment without any catalyst it can be concluded that thermal reactions are not significant in these conditions and a catalyst is needed for the reactions to proceed. In the experiment without any additional hydrogen, the reactor was pressurized with 4 MPa of nitrogen. The amount of acetone formed remained lower and stabilized later than in the experiment with H₂ (Figure 10). Furfuryl alcohol was produced as efficiently in both experiments, but the formation of further hydrogenation products was decelerated and obviously needs additional hydrogen to occur efficiently. Thus it can be concluded, that furfuryl alcohol can be produced efficiently without any additional hydrogen, which would make this process safer. In these Ni/C experiments with and without any added hydrogen, only the first mechanism proposed above was visible. In the case of iron containing catalysts the mechanism two with isopropanol dehydrogenation would be significant and acetone concentration would increase also after total conversion of furfural.

Figure 10.

As transfer hydrogenation is also possible with the intermediate products of furfural hydrogenation, experiments with furfuryl alcohol were performed. The catalyst used in the experiments was 10 wt-% Ni/C and the reactor was pressurized either with 4 MPa of H₂ or N₂. Interesting results were obtained, as without any additional hydrogen the main product was MF, and only traces of THFA and other hydrotreatment products of MF were detected. As these results were compared to the FA experiments with additional hydrogen, the difference was significant as much THFA and MTHF were formed. The results indicate that

MF is actually formed from FA through transfer hydrogenation, but for the other products direct hydrogenation route is dominant. The amount of acetone was observed significantly lower in the FA experiments with additional H₂ compared to the FA experiments without H₂. The reason for this may be that the additional hydrogen occupies the active sites and suppresses the isopropanol dehydrogenation reaction or the equilibrium limited isopropanol dehydrogenation reaches the equilibrium state due to excess amount of hydrogen. The acetone formation in the furfural and furfuryl alcohol experiments with and without additional hydrogen is presented in Figure 11. It was observed that the amount of acetone produced in the furfural experiments was higher than in the FA experiments. This can be explained as in the case of furfural there are two transfer hydrogenation reactions from the reactant to MF, whereas with FA as a reactant there is only one transfer hydrogenation step present.

Figure 11.

4. Conclusions

Furfural hydrotreatment to many valuable products is an important reaction route to replace many fossil based chemicals and fuels with renewable options. Acetone formation was observed to be prominent during the liquid phase furfural hydrotreatment experiments. The acetone formation in furfural hydrotreatment has not been studied deeply and is the purpose of this study.

Acetone formation was observed to occur in furfural hydrotreatment reactions as long as a metal catalyst was applied in the experiments. Differences in acetone formation were noticed between metals as copper, nickel, and iron in mono- or bimetallic combinations were tested. The lowest activity was observed with nickel, copper was slightly more active, and iron was observed to be significantly more active. Metal loading of these tested catalysts was also observed to have a significant effect on the acetone formation. With nickel and iron the increase of metal loading increased the amount of acetone, but with copper the amount of acetone decreased with the increasing metal loading. This can be explained with poor dissociation of hydrogen on copper surface as well as with weaker adsorption of furfural on copper.

Acetone formation can occur through two reaction routes and discovering the actual reaction route for the formation has appeared very challenging. From the performed experiments the first conclusion is that acetone formation appears to apply two mechanisms, and furfural has an important role in the acetone formation. With all the catalysts the reaction rate for acetone formation is very high in the beginning of the experiment as furfural hydrogenates further. After furfural is almost completely consumed the reaction rate for acetone formation decelerates or even ceases with copper and nickel catalysts. With catalysts including iron the acetone formation was noticed to continue and even intensify after all furfural had reacted. Thus, in the case of iron, isopropanol dehydrogenation is apparent. This has been found to be in line with literature, as iron oxides are presented as good dehydrogenation catalysts. From experiments performed with furfuryl alcohol it was discovered that the MF production from FA occurs through transfer hydrogenation as the other reactions (to THFA or MTHF) need additional hydrogen for hydrogenation. This has not been earlier tested or discovered.

In conclusion, the acetone formation as a side product when applying isopropanol as a solvent in furfural hydrotreatment experiments is significant and cannot be prevented as copper, nickel, and iron catalysts are applied. The furfuryl alcohol production can be performed efficiently without any additional hydrogen utilizing the solvent as hydrogen donor. This would make the process safer and simultaneously the amount of acetone could be slightly decreased. Same applies also for the direct MF production from furfuryl alcohol. However, for the production of other hydrogenation products like THFA or MTHF, applying additional hydrogen is necessary for efficient production.

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Figure titles:

Figure 1. Furfural hydrotreatment.

Figure 2. Isopropanol dehydrogenation to acetone and hydrogen.

Figure 3. Transfer hydrogenation of furfural to furfuryl alcohol with isopropanol as hydrogen donor.

Figure 4. Acetone concentration as a function of contact time in furfural hydrotreatment experiments with varying catalysts. $T = 230\text{ }^{\circ}\text{C}$, $p = 4\text{ MPa H}_2$, $t = 300\text{ min}$, $m(\text{cat}) = 0.2\text{ g}$.

Figure 5. Maximum acetone concentration in furfural hydrotreatment experiments with varying metal loadings. $T = 230\text{ }^{\circ}\text{C}$, $p = 4\text{ MPa H}_2$, $t = 300\text{ min}$, $m(\text{cat}) = 0.2\text{ g}$.

Figure 6. Maximum acetone concentration in furfural hydrotreatment experiments at temperatures of 200 and 230 $^{\circ}\text{C}$. $P = 4\text{ MPa H}_2$, $t = 300\text{ min}$, $m(\text{cat}) = 0.2\text{ g}$.

Figure 7. Acetone concentration as a function of reaction time in furfural and isopropanol experiments with 10 wt-% Ni/C. $T = 230\text{ }^{\circ}\text{C}$, $p = 4\text{ MPa H}_2$, $t = 300\text{ min}$, $m(\text{cat}) = 0.2\text{ g}$.

Figure 8. Acetone concentration as a function of reaction time in furfuryl alcohol experiments with 10 wt-% Ni/C at 200 and 230 $^{\circ}\text{C}$. $P = 4\text{ MPa H}_2$, $t = 300\text{ min}$, $m(\text{cat}) = 0.2\text{ g}$.

Figure 9. A ratio of maximum acetone concentration and maximum furfuryl alcohol concentration with various metal catalysts. $T = 230\text{ }^{\circ}\text{C}$, $p = 4\text{ MPa H}_2$, $t = 300\text{ min}$, $m(\text{cat}) = 0.2\text{ g}$.

Figure 10. Acetone and furfuryl alcohol (FA) concentrations as a function of reaction time in furfural hydrogenation experiments with 10 wt-% Ni/C, with and without additional hydrogen. $T = 230\text{ }^{\circ}\text{C}$, $t = 300\text{ min}$, $m(\text{cat}) = 0.2\text{ g}$.

Figure 11. Acetone concentration as a function of reaction time in furfural and furfuryl alcohol (FA) experiments, with and without additional hydrogen. $T = 230\text{ }^{\circ}\text{C}$, $t = 300\text{ min}$, $m(\text{cat}) = 0.2\text{ g}$.

370 **Table titles:**

371 Table 1. Reaction enthalpies and equilibrium constants of reaction routes at reaction temperature of 230 °C.

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Reaction	Reaction enthalpy ΔH / $\text{kJ}\cdot\text{mol}^{-1}$	Equilibrium constant
Isopropanol dehydrogenation	-0.406	$1.36\cdot 10^{-1}$
Transfer hydrogenation of furfural	-68.919	$1.66\cdot 10^3$
Furfural hydrogenation to furfuryl alcohol	-68.513	$1.22\cdot 10^4$

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