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Experimental study for liquid phase selective hydrogenation of furfuryl alcohol to tetrahydrofurfuryl alcohol on supported Ni catalysts

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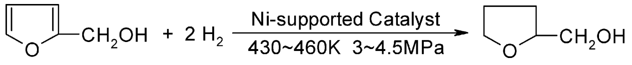
Abstract

The liquid phase hydrogenation of furfuryl alcohol (FA) to tetrahydrofurfuryl alcohol (THFA) on a series of new special supported Ni catalyst was experimentally studied while the raw material and the product were analyzed by a set of on-line GC. The reactor used in the experiment was a continuous stirred autoclave with volume of 500 mL. The operating conditions studied in the experiments were opted as the following ranges: temperature within 433–453 K, pressure within 3.0–4.0 MPa, catalyst loading 20 g/L and the stirring rate at about 1000 rpm. The experimental results show that, under the operation conditions mentioned above, the hydrogenation of FA in the presence of the catalyst QD3 can lead to a high FA conversion above 99.9% and a high selectivity of THFA higher than 98.3% within 3.5 h.

Keywords: Tetrahydrofurfuryl alcohol; Furfuryl alcohol; Supported Ni catalyst; G–L–S reaction

1. Introduction

The application of catalytic techniques for the production of downstream products of furfural is important for agricultural countries. The catalytic hydrogenation of furfural to furfuryl alcohol (FA) has been fully studied and the catalyst has been industrialized successfully. As an important downstream product of furfural, tetrahydrofurfuryl alcohol (THFA) is a preferred solvent in the pharmaceutical industry and a significant intermediate widely used in various industrial and agricultural fields [1–5]. THFA can be obtained by hydrogenation of FA in liquid phase.



Many research teams proposed a number of catalysts with high conversion and selectivity in the laboratory, but the cost of the preparation was relatively high and the catalysts were immature technically.

Aiming at reducing the preparation costs, our team has developed a new supported Ni catalyst, which is cheaper and more efficient. In this paper, we will introduce our experimental study for hydrogenation of FA to THFA on the new developed supported Ni catalyst, the catalytic behavior of the hydrogenation reaction, and the product analysis. In order to optimize the operating conditions for industrial application, the relationship between the hydrogenation results and the operating conditions is discussed (see Fig. 1).

2. Experimental

2.1. Raw material and Equipment

H_2 (industrial grade, purity above 99.5%);
FA (industrial grade, purity above 98%, produced by Heibei Baoshuo Co. Ltd. Xyful Branch);
supported Ni catalyst (QD3, must be activated strictly and protected by nitrogen in normal temperature);
Conventional WDF produced by Weihai Automatic Control Reaction Kettle Co. Ltd.

2.2. The pre-experimental procedure

FA must be distilled under vacuum conditions before each run.
The autoclave must be flushed by 100 mL clean FA twice.
Gas tightness of the entire system must be examined at 6.5 MPa weekly, and the hydrogen gas leakage should be less than 0.05 MPa per 30 min under pressure.

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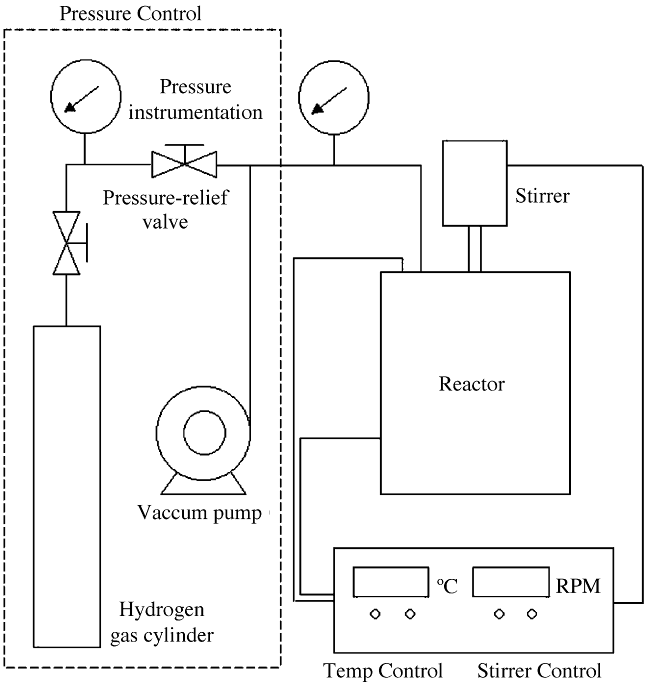


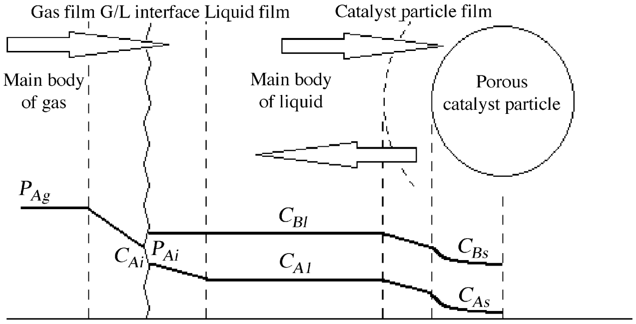
Fig. 1. Experimental flowchart.

2.3. *Liquid phase hydrogenation of FA*

Catalytic hydrogenation of FA is performed in a 500 mL stainless steel autoclave. First, the pre-activated catalyst is dispersed in 100 mL FA and sucked into the autoclave by a vacuum system in order to protect the catalyst from being oxidized by air. Then, 150 mL clean FA is fed to the reactor in the same way. Secondly, 0.5 MPa H_2 is charged to the autoclave slowly, then the vacuum pump draws the gas mixture off (manometer pressure −0.08 MPa approximately). Pressure in the autoclave is slowly increased and then rapidly decreased five times, in order to completely replace the air in the autoclave. Thirdly, the electric oven controlled by a temperature controller is used to heat the autoclave, filled with H_2 about 1.0 MPa. The temperature setting must be lower than the final desired reaction temperature about 30 °C because the hydrogenation reaction is exothermic. The stirrer is started simultaneously. After the autoclave temperature is stabilized at the setting value, other operating conditions (H_2 pressure and stirring rate) are adjusted to their desired values, and the temperature controller is slowly reset to increase the reaction temperature to the final desired value step by step. Fourthly, when all the operating conditions reach their settings, pressure drop is recorded every 5 min and the product (usually changing according to the reaction rate) is sampled every 30 min, until there is no obvious H_2 pressure drop in a 10 min period. The H_2 pressure is released and the cooling water is turned on. When the autoclave temperature falls below 40 °C, the final product is discharged.

2.4. *Product analysis*

The samples are centrifuged to separate the liquid products from the catalyst particle first. Then, the samples are analyzed by means of a gas chromatograph with TCD. The FULI GC-9790 is operated at the following conditions: COL of 413 K, TCD of 413 K, DET of 473 K and INJ of 493 K. The carrier H_2 flow rate is set at 35 mL/min in a 5 m column (3 mm × 0.5 mm) packed with 101 white support treated with poly-glycol-20000 as immobile liquid.



Sketch showing the resistances involved in the G/L reaction on a catalyst

Fig. 2. Reaction model.

3. Reaction model

The hydrogenation of furfuryl alcohol to tetrahydrofurfuryl alcohol on Supported Ni catalysts can be abstracted to the following simple expression:

$$\mathrm{A(g} \xrightarrow{\text{dissolve}} \mathrm{l)} + \mathrm{B(l)} \xrightarrow{\text{catalyst}} \text{products}$$

As the mass transfer of three-phase is very complicated, the following basic assumptions were used in the modeling of the reactor (see Figs. 2) to simplify analysis:

- Thermodynamic equilibrium is assumed to dominate at the gas–liquid interface.
- The mass transfer resistance in liquid is neglected.
- The mass and heat transfer at the gas–liquid interface is described by the two-film theory and Fick’s Law.
- The catalyst particle is assumed to be completely wetted; thus the contribution of gas phase hydrogenation is ignored.
- With 473 K, 4.5 MPa, catalyst load 35 g cat/L, and finally the reaction time 4 h.
- The liquid and gas phases in the reactor are completely back-mixed due to vigorous agitation. The concentration and temperature gradients appear inside the catalyst particle only.

4. Results and discussion

4.1. *Typical reaction on catalyst QD3*

The graphs shown in Figs. 3 and 4 are different hydrogenation results obtained in different operating conditions on the same catalyst QD3. In Fig. 3, FA conversion was less than 96%, the selectivity of THFA about 78%. The result shown in the Fig. 4 was performed at the optimum operating conditions. FA conversion was above 99.5%, and selectivity of THFA 98.2% and the reaction time about 3 h. The average reaction time and

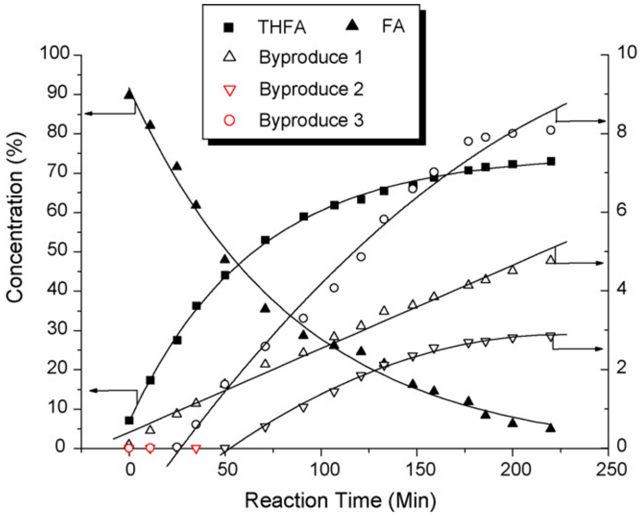


Fig. 3. Before finding optimum condition.

the selectivity of THFA are more important than the conversion for the industrial application. Fig. 5 shows the selectivity drop of THFA as a function of time in a typical reaction under the optimum operating condition.

4.2. Measures to minimize the effect of mass transfer

The FA hydrogenation to THFA falls into the category of gas–liquid–solid three-phase reaction. Hydrogen is in the gas phase; reactant FA and product THFA are in the liquid phase; and Supported Ni catalyst is in solid phase (as shown in Eq. (1)).

$$H_2(\text{gas} \rightarrow \text{liquid}) + \text{FA} \xrightarrow{\text{catalyst}} \text{THFA} \tag{1}$$

4.2.1. Theoretical criteria

In order to estimate the mass transfer iMPact in different phases, we adopt the criteria proposed by Ramachandran and Chaudhari [6]:

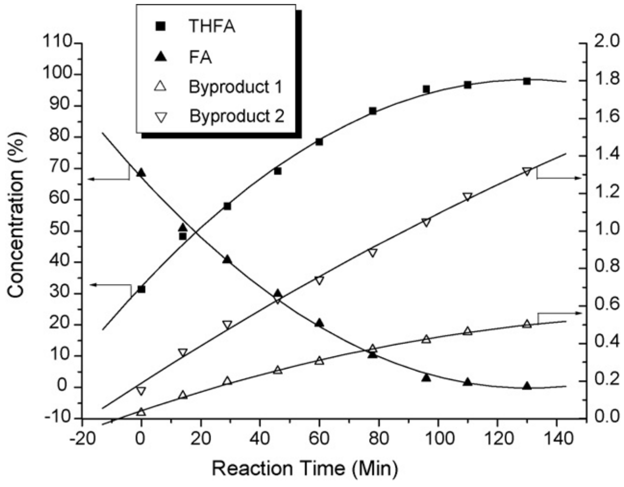


Fig. 4. After finding optimum condition (with 443 K, 4.0 MPa, catalyst load 25 g cat/L, and finally the reaction time 3.5 h).

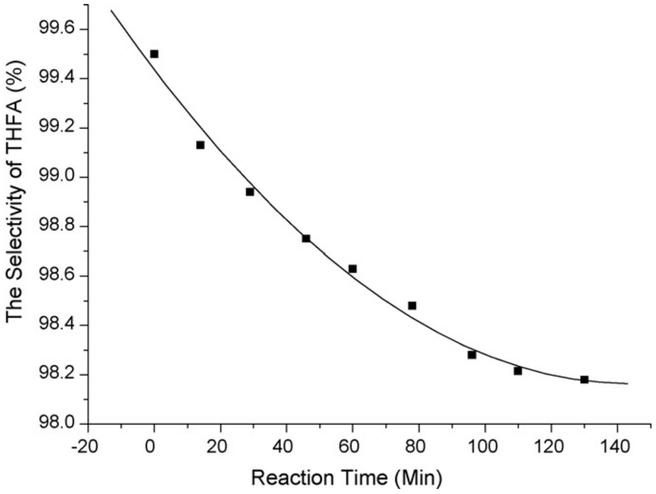


Fig. 5. Selectivity at optimal condition (with 443 K, 4.0 MPa, catalyst load 25 g cat/L, and finally the reaction time 3.5 h).

(1) The mass transfer between gas and liquid phases can be negligible, if

$$\alpha_1 = \frac{R_{H_2}}{k_L a_b C^*_{H_2}} < 0.1 \tag{2}$$

where R_{H_2} is hydrogen consumption rate, k_L is mass transfer coefficient between gas and liquid phases, a_b is activity of FA,$C^*_{H_2}$ is hydrogen concentration in liquid phase.

(2) The mass transfer between liquid and solid phases can be neglected, if

$$\alpha_2 = \frac{R_{H_2}}{k_s a_p C^*_{H_2}} < 0.1 \quad \text{and} \quad a_p = \frac{6w}{\rho_p d_p} \tag{3}$$

where R_{H_2} is hydrogen consumption rate, k_s is mass transfer coefficient between liquid and solid phases, w is catalyst loading, ρ_p is catalyst particle size, d_p is nominal diameter of catalyst.

(3) The mass transfer within the solid phase can be neglected, if

$$\phi_{\exp} = \frac{d_p}{6}\left[\frac{(m+1)}{2D_e}\frac{\rho_p R_{H_2}}{wC^*_{H_2}}\right]^{1/2} < 0.2 \tag{4}$$

where D_e is diffusion coefficient, $D_e = D_M\varepsilon/\tau$, and D_M can be determined by the correlation proposed by Wilke and Chang [7].

(4) Resulting from the mass transfer between gas and liquid phases, $k_L a_b$ is determined by the correlation of stirring tank reactor proposed by Bern [8]

$$k_L a_b = 1.099 \times 10^{-2} N^{1.16} d_I^{1.797} u_g^{0.32} V_L^{-0.52} \tag{5}$$

where N is stirring rate of tank reactor; d_I is the diameter of turbine blade; u_g is gas velocity; V_L is volume of liquid phase in reactor.

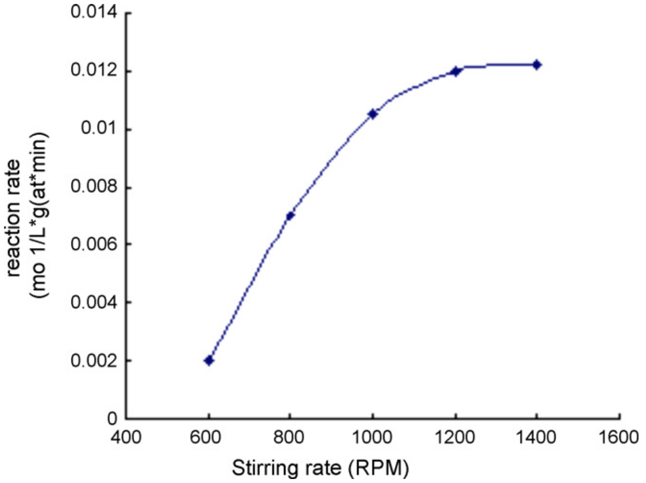


Fig. 6. Reaction rate via stirring rate (with 448 K, 4.0 MPa, catalyst loading, 20 g/L, and stirring rate 1200 rpm).

(5) To determine k_s in the Eq. (3) α_2, Sano's correlation [9] is used:

$$\frac{k_s d_p}{D F_c} = 2 + 0.4\left[\frac{e d_p^4 \rho_L^3}{\mu_L^3}\right]^{0.25}\left[\frac{\mu_L}{\rho_L D_M}\right]^{0.333} \qquad (6)$$

where F_c is factor of particle shape; e is affinity between liquid and solid phase, which can be calculated by Calderbank's correlation [10].

Given the data from publications and the experimental conditions chosen in this paper, which include reaction temperature (433–453 K), hydrogen pressure (3.0–4.0 MPa), catalyst loading (20 g/L), stirring rate (1200 rpm), and reactor dimension, α_1, α_2 and ϕ_{exp} are estimated about 0.08, 0.001 and 0.16, respectively, all less than each limit value in Eqs. (2)–(4). Therefore, the iMPact of mass transfer across phases can be considered negligible.

4.2.2. *Experimental support*

4.2.2.1. Stirring rate. To eliminate the impact of external diffusion, several stirring rates were tested in experiments, though it also can affect the mass transfer in other phases. Other factors were pre-defined as temperature 448 K, hydrogen pressure 4.0 MPa, catalyst loading 20 g/L. Test result is shown in Fig. 6. Reaction rate increases as stirring rate revs up. After stirring rate reaches 1100 rpm, reaction rate has no significant increase. So the impact of external diffusion is considered not dominant any more.

但随着搅拌转速的增大，
反应釜内液滴飞溅现象逐渐增大。因此，
为了保证研究结果的可靠性，搅拌转速通常采用
1000-1100RPM.

With the stirrer revved up, the gas–liquid interfacial area is increased and the gas film and the liquid film beside the interface become thinner, which intensifies the dissolution of H_2. At the same time, the suspending solid catalyst particle moves more quickly in liquid and so the liquid film on the active sites of catalyst refresh more frequently and the mass transfer through the film was intensified. In other words, at high stirring rate, the mass transfer was intensified and the reaction was accelerated. At low stirring rate, not only the reaction time increased, but also the selectivity of THFA dropped in the final stage of the reaction. This drop may be explained that the insufficient adsorption rate cause excessive residence time of THFA on active sites and then create undesirable byproducts. So increasing stirring rate not only increases the reaction rate, but also improves the FA conversion and the selectivity of THFA.

Table 1
Diameters of each particle size

Particle size number	Diameter (mm)
1	<0.15
2	0.15–0.2
3	0.2–0.3
4	0.3–0.5

4.2.2.2. Catalyst particle size. Several catalyst particle sizes were used to test the internal diffusion impact, as showed in Table 1, though changing catalyst particle size can also affect external diffusion. Result is shown in Fig. 7, where the diameter of each particle size is listed in Table 6. It can be observed that internal diffusion is no longer dominated when particle size is chosen and no significant improvement when particle 1 is used. The catalyst used in this paper is easy to reach the size range and able to neglect the iMPact of internal mass transfer.

4.2.2.3. Catalyst loading. By changing catalyst loading under the condition in Sections 4.2.2.1 and 4.2.2.2, it is found that reaction rate is proportional to catalyst loading with a correlation coefficient of 0.992, as shown in Fig. 8, which supports the fact that either external diffusion or internal diffusion is not the dominant step in this reaction by choosing proper operating conditions.

4.3. *Influence of temperature*

In our experiment, when the reactor temperature rose up to 398 K, an obvious H_2 pressure drop appeared. The product was

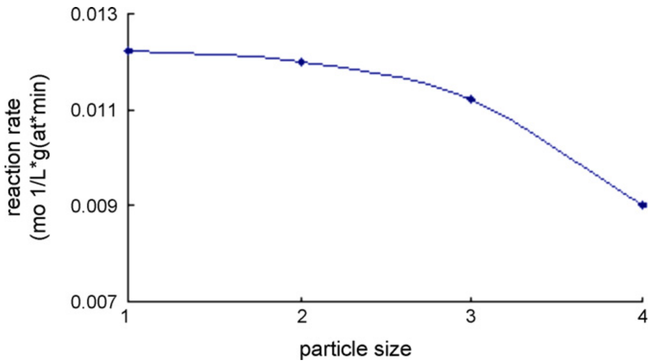


Fig. 7. Reaction rate via particle size (with 448 K, 4.0 MPa, catalyst loading, 20 g/L, and stirring rate 1200 rpm).

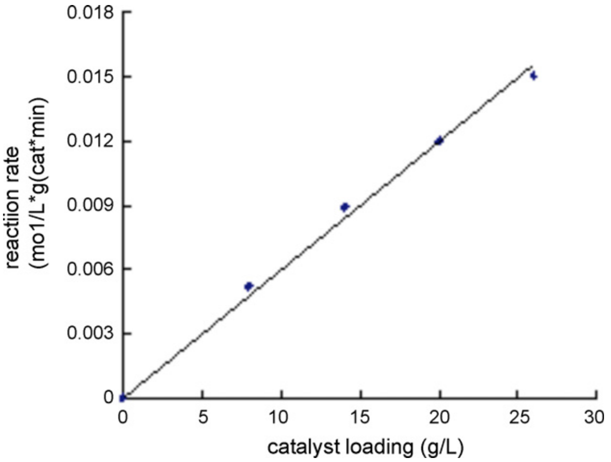


Fig. 8. Reaction rate via catalyst loading. (with 448 K, 4.0 MPa, catalyst loading, 20 g/L, and stirring rate 1200 rpm).

nearly all THFA, even though the reaction rate is very low. But the reaction activity continuously declined to zero before the FA conversion reached 60–70% at this low reaction temperature, and the selectivity of THFA was above 98.5%. When the reaction temperature rose up to 458 K, the hydrogenation performed almost completely, but the following gas chromatographic analysis showed that the selectivity of THFA was below 83% and the byproducts increased to 17%.

At the proper temperature range (423–453 K), the catalysts can perform desirable hydrogenation. The FA conversion is above 98%, and the selectivity of THFA is more than 97%, and reaction terminates within 2–6 h. Within this range, as temperature increases, the reaction continuously accelerates, while the selectivity of THFA declines slowly. The amount of byproducts slightly increased. In order to obtain the optimum operating temperature with respect to the industrial application, more attention should be paid to the reaction rate, since higher temperatures can result in lower selectivity and conversion.

The experiments show that the reaction temperature affects the reaction more than other factors. It is directly related to the FA conversion, THFA selectivity and reaction rate. It is very important to optimize the temperature. It can be seen in Table 2 that the best overall performance is achieved at 443 K.

The data in Table 2 also shows that the reaction rate increases 30–50%, as temperature rises every 10 K. According to the Arrhenius' Law, apparent activation energy in this catalytic hydrogenation is about 40–60 KJ/mol.

Table 2
Influence of temperature (with 4.0 MPa, Catalyst load 40 g/L and stirring rate 1000 rpm)

Temperature (K)	FA conversion (%)	THFA selectivity (%)	Reaction time (h)
398	67.4	98.9	Approx. 8.5
423	98.2	98.7	Approx. 5.5
433	99.4	98.4	Approx. 3.7
443	99.6	98.4	Approx. 2.5
453	99.8	98.0	Approx. 1.7

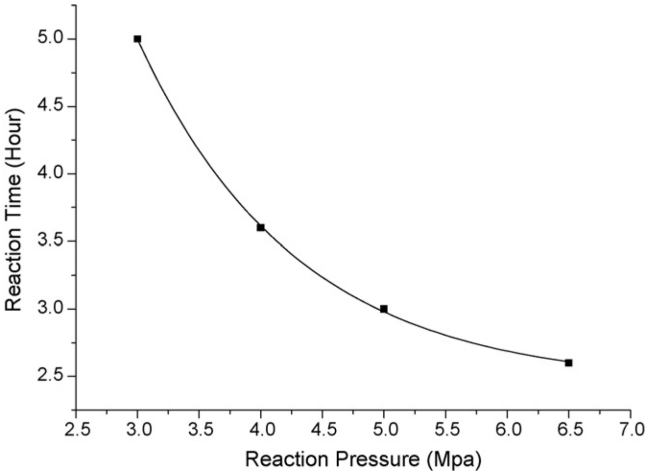


Fig. 9. Influence of pressure (with 448 K, catalyst loading 40 g/L and stirring rate 1000 rpm).

In order to maximize the throughput of a production facility without compromising product quality, the reaction temperature could be set higher in the beginning, e.g. 453 K, to accelerate the reaction; and lower at the end, e.g. 433 K, to minimize the amount of byproduct. Lower temperature for reactor will favor the catalytic hydrogenation when the reaction approaches the end, since hydrogenation is exothermic and the rate of heat release is higher in the beginning than at the end.

4.4. *Influence of pressure*

Experiments show that reaction rate increases as H_2 pressure becomes higher, when H_2 pressure is within the range of 2.0–4.0 MPa, FA conversion rate and THFA selectivity show no relation to H_2 pressure, meanwhile catalyst performs at high efficiency.

As pressure increases, more hydrogen is dissolved in FA, which results in higher hydrogen concentration in the liquid phase and interface between liquid phase and catalyst, therefore, intensifies the reaction (as shown in Fig. 9). It is also noted that the increase in the reaction rate slows down after the pressure reaches a certain value, and has no significant change when pressure is above 5.0 MPa.

It can be included that increasing hydrogen pressure favors hydrogenation. This also agrees with experiments done by others that reaction rate was not as much as expectation when H_2 continuously increases, because the controlling step is switching from G/L mass transfer to other kind of mass transfers. Pressure around 4.0 MPa can be chosen in order to accelerate the reaction; and that between 2.5 and 3.7 MPa can result in a moderate reaction process.

Hydrogen pressure is directly related to the reaction rate, and has no significant effect on product quality. In industrial production, hydrogen pressure can be kept lower when production load is moderate, so as to save operation cost; accordingly, higher pressure can be chosen to increase facility throughput when production load increases.

Table 3
Overall influences of reaction temperature, hydrogen pressure and catalyst loading

Number	Reaction temperature (K)	Hydrogen pressure (MPa)	Catalyst loading (g/L)	FA conversion (%)	THFA selectivity (%)
1	433	2.6	16	45.67	98.67
2	433	3.3	24	51.03	97.94
3	433	4.0	32	62.30	98.88
4	443	2.6	24	68.00	99.08
5	443	3.3	32	76.49	99.09
6	443	4.0	16	68.58	98.67
7	453	2.6	32	91.07	98.98
8	453	3.3	16	71.13	99.09
9	453	4.0	24	98.76	96.37

Table 4
Average relative iMPact of reaction temperature

Reaction temperature (K)	FA conversion (%)	THFA selectivity (%)
433	53.01	98.49
443	72.02	98.95
453	86.99	98.15

Maximum difference of FA conversion $R = 33.98\%$, maximum difference of THFA selectivity $R' = 0.8\%$.

Table 6
Average relative impact of hydrogen pressure

Hydrogen pressure (MPa)	FA conversion (%)	THFA selectivity (%)
2.6	68.25	98.91
3.3	71.22	98.70
4.0	76.55	97.97

Maximum difference of FA conversion $R = 10.33\%$, maximum difference of THFA selectivity $R' = 0.94\%$.

4.5. Overall influence of catalyst loading, reaction temperature and hydrogen pressure

It is easy to test the effect of reaction temperature and hydrogen pressure individually, but it is hard to optimize the catalyst loading, since it is highly related to specific reaction temperature and hydrogen pressure. In order to find the optimal catalyst loading, we design a set of experiments as following (Table).

There are several factors highly related to FA conversion rate and THFA selectivity. They include reaction temperature, hydrogen pressure, reaction time, catalyst loading, stirring rate, and catalyst particle size.

In order to minimize the number of experiments, we set same stirring rate, reaction time and catalyst particle size, and consider the impact of reaction temperature, hydrogen pressure and catalyst loading.

Based on the experiments done before, stirring rate of 1200 rpm and reaction time of 1.5 h are preset. Result is shown in Table 3.

The average relative impacts of reaction temperature, hydrogen pressure and catalyst loading are shown in Tables 3–5 separately.

Among three factors, reaction temperature is most closely related to FA conversion. As shown in Table 4, its maximum difference of FA conversion is 33.98%. THFA selectivity would slightly diminish as the reaction temperature becomes too high.

Table 5
Average relative iMPact of catalyst loading

Catalyst loading (g)	FA conversion (%)	THFA selectivity (%)
16	61.79	98.81
24	72.59	97.80
32	76.63	98.98

Maximum difference of FA conversion $R = 14.87\%$, maximum difference of THFA selectivity $R' = 1.18\%$.

Catalyst loading is most closely related to THFA selectivity. As shown in Table 5, the maximum difference of THFA selectivity reaches 1.18%. The number of active centers increases due to higher catalyst loading, which accelerates hydrogenation, and prevents the generation of the byproduct. In other words, larger catalyst loading favors hydrogenation, not the byproduct reactions.

Compared to reaction temperature and catalyst loading, hydrogen pressure has a more significant contribution to the optimization of the reaction condition once the previous condition is defined; nevertheless, higher hydrogen pressure can be used to adjust the reaction rate, which is shown in Table 6.

In an industrial process, more catalyst loading would result in higher production cost; similarly, higher hydrogen pressure could mean larger capital investment, even though, it can be used to control reaction rate; but the temperature manipulation can be accomplished quite economically and efficiently.

5. Conclusions

In this paper, Supported Ni catalyst QD3 for FA hydrogenation to THFA is studied; impacts of different factors on the FA hydrogenation are considered. It is found that temperature is the most important factor to FA conversion, catalyst loading directly affects THFA selectivity, and hydrogen pressure has a relatively weak impact on FA conversion and THFA selectivity.

Different stirring rates and catalyst particle sizes are also considered. Under the operating conditions proposed in this paper, high linear correlation between reaction rate and catalyst loading also shows that the impact of external and internal diffusion can be neglected by choosing proper stirring rate and catalyst particle size.

Higher temperature proved to increase the reaction rate at the cost of the low selectivity of THFA. Increasing catalyst loading and stirring rate were effective to intensify the reaction rate without reducing the conversion and selectivity, but the increment caused proportionally higher production costs. Proper pressure is integrant condition to hydrogenation reaction.

The optimum operating condition for catalyst QD3 is obtained as follows, temperature of 433–453 K, pressure of 3.0–4.0 MPa, stirring rate of 1000–1200 rpm and catalyst loading of 20 g/L.

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