Preparation of Ni-IL/SiO$_2$ and its catalytic performance for one-pot sequential synthesis of 2-propylheptanol from $n$-valeraldehyde

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A novel silica-immobilized nickel and acid ionic liquid (Ni-IL/SiO$_2$) catalyst was prepared by combining a bonding procedure with an impregnation operation and was characterized by means of X-ray diffraction (XRD). Fourier transform infrared (FT-IR) spectra, X-ray photoelectron spectroscopy (XPS) and thermogravimetric analysis (TGA) techniques. Its catalytic performance was evaluated for the one-pot synthesis of 2-propylheptanol (2-PH) via a sequential $n$-valeraldehyde self-condensation and hydrogenation reaction. As a result, Ni-IL/SiO$_2$ showed an excellent catalytic activity for the one-pot synthesis of 2-PH, affording a 2-PH selectivity of 75.4% at a $n$-valeraldehyde conversion of 100% and the sum of 2-PH and pentanol selectivity reached 98.6% under the suitable reaction conditions.

1. Introduction

2-Propylheptanol (2-PH), an important plasticizer alcohol, can be used for synthesizing a series of plasticizers by esterification with phthalic anhydride, trimellitic anhydride and adipic acid, etc. Bis(2-propylheptyl) phthalate (DPHP) is a major 2-PH-derived plasticizer. Compared with diocyl phthalate (DOP) derived from 2-ethylhexanol, DPHP has the advantages of low toxicity and less volatility and can meet the requirements for health, safety and environmental protection. In the industrial production of 2-PH mainly includes three reaction steps: hydroformylation of butene, self-condensation of $n$-valeraldehyde, and hydrogenation of 2-propyl-2-heptenal. One-pot synthesis of 2-PH by sequential aldol condensation and hydrogenation reaction from $n$-valeraldehyde can shorten the process flow, reduce energy consumption, and lower equipment and operating costs. So the one-pot synthesis of 2-PH is of academic and commercial importance.

The one-pot synthesis of 2-PH by sequential aldol condensation and hydrogenation from $n$-valeraldehyde is categorized as a type of reaction integration. At present, the research on the reaction integration of $n$-valeraldehyde self-condensation and 2-propyl-2-heptenal hydrogenation is rarely reported. Instead some researchers including our group have investigated a similar reaction integration of $n$-butyraldehyde self-condensation and successive hydrogenation. Liang et al. studied this reaction integration using a bifunctional catalyst of Ni/Al$_2$O$_3$ and realized one-step synthesis of 2-ethylhexanol from $n$-butyraldehyde, attaining a 2-ethylhexanol selectivity of 66.9% at a $n$-butyraldehyde conversion of 100%. Li et al. obtained similar 2-ethylhexanol selectivity and $n$-butyraldehyde conversion over Ni/La-Al$_2$O$_3$ catalyst for one-pot sequential synthesis of 2-ethylhexanol. Patankar et al. prepared a Cu-Mg-Al catalyst for this reaction integration and obtained a 2-ethylhexanol selectivity of 90% at a 30% of $n$-butyraldehyde conversion. Miao et al. obtained a 2-ethylhexanol selectivity of 73.5% at a complete $n$-butyraldehyde conversion using a Cu-Mg-Fe catalyst for one-step synthesis of 2-ethylhexanol from $n$-butyraldehyde. It can be inferred from the above researches that the reaction integration of $n$-butyraldehyde self-condensation and successive hydrogenation needs a multifunctional catalyst with both acid/base active site (for aldol condensation) and metal active site (for hydrogenation). So the reaction integration of $n$-valeraldehyde self-condensation and successive hydrogenation for one-pot synthesis of 2-PH form $n$-valeraldehyde requires a metal–acid/base multifunctional catalyst either.

We once evaluated the catalytic performance of an acid ionic liquid [HSO$_3$-b-N(Et)$_2$]$_p$-TSA in $n$-butyraldehyde self-condensation and the catalytic performance of an acid–base bifunctional ionic liquid [PEmim]Cl-0.5Zn(CH$_3$COO)$_2$ in $n$-valeraldehyde self-condensation. Pretty good results were attained: 2-ethyl-2-hexenal selectivity of 87.8% was achieved at a $n$-butyraldehyde conversion of 89.7% over [HSO$_3$-b-N(Et)$_2$]$_p$-TSA while 2-propyl-2-heptenal selectivity of 86.6% was obtained at a $n$-valeraldehyde conversion of 94.7% over [PEmim]Cl-0.5Zn(CH$_3$COO)$_2$. Moreover, supported Ni-based or Cu-based catalysts show excellent catalytic performance for hydrogenation of 2-propyl-2-heptenal. So a combination of an acidic
ionic liquid or an acid–base bifunctional ionic liquid with supported Ni or Cu catalyst will be expected to show a good catalytic performance for the one-pot synthesis of 2-PH form n-valeraldehyde. Besides, the immobilization of ionic liquid can reduce the usage of ionic liquid, simplify separation and purification operation, and impose a specially designed environment around the catalytic site, being beneficial to inhibit the side reactions and enhance the product selectivity.15,16 With such ideas in mind, we prepared a silica-immobilized nickel and acid ionic liquid (Ni-IL/SiO2) catalyst and characterized its structure and property by means of FT-IR, TGA, XRD and XPS analysis. To our delight, Ni-IL/SiO2 showed an excellent catalytic performance for the one-pot synthesis of 2-PH from n-valeraldehyde, laying a foundation for establishing a new green technology for 2-PH synthesis.

2. Experimental

2.1. Preparation of Ni-IL/SiO2

The process for preparation of Ni-IL/SiO2 comprises two steps: firstly an acid ionic liquid was immobilized on silica to form silica-immobilized acid ionic liquid (IL/SiO2), and then nickel was introduced in IL/SiO2 to obtain the target catalyst Ni-IL/SiO2.

(1) Preparation of IL/SiO2. A IL/SiO2 sample was prepared by a bonding procedure.17 The mixture of silica, toluene and 3-chloropropyl triethoxysilane was stirred for 6 h under reflux of toluene to obtain a chloropropyl functionalized silica (Intermediate Product-1, IP-1). Then IP-1, potassium iodide and excess imidazole were dispersed in anhydrous toluene and the mixture was refluxed at 110 °C for 16 h to give a 3-(1-imidazole) propyl functionalized silica (IP-2). Next, IP-2 was mixed with a solution of 1,3-propane sultone and toluene and then the mixture was stirred at 100 °C for 6 h to attain a silica-immobilized amphoteric salt (IP-3). After that, CF3SO3H was added dropwise into a mixture of IP-3 and toluene. The resulting mixture was heated to 80 °C and kept for 5 h to afford an immobilized sulfonic acid functional ionic liquid, IL/SiO2. The structure of IL/SiO2 is presented in Scheme 1.

(2) Preparation of Ni-IL/SiO2. Ni-IL/SiO2 catalyst was prepared by impregnating a nickel nitrate aqueous solution into the IL/SiO2 sample and then reduction by NaBH4 under 40 °C for 4 h. The structure of Ni-IL/SiO2 is shown in Scheme 1 either.

2.2. Catalyst characterization

A NICOLET NEXUS 470 infrared spectroscopy (Thermo Electron Corp., USA) was used for the FTIR measurement of samples. The spectra were recorded between 400 and 4000 cm⁻¹ at a resolution of 4 cm⁻¹. The thermal stability of samples was determined using a SDT Q600 simultaneous thermal analyzer (TA Instruments Corp., USA). The test was carried out under flowing air atmosphere (40 mL min⁻¹) with a heating rate of 10 °C min⁻¹ in the range from room temperature to 700 °C. The binding energy of Ni on the catalyst surface was measured using a Kratos Axis Ultra DLD photoelectron spectrometer (Kratos Analytical, Manchester, England). All the binding energy data were calibrated with C 1s = 284.6 eV as an internal standard. X-ray diffraction (XRD) patterns were recorded with a Rigaku D/ max-2550 diffractometer (Rigaku International Corp., Japan) using Cu Kz radiation at 100 mA and 40 kV. The scan range covered from 5° to 90° at a rate of 6° min⁻¹.

2.3. Catalytic performance evaluation

The catalytic performance of Ni-IL/SiO2 for one-pot synthesis of 2-PH by sequential n-valeraldehyde self-condensation and hydrogenation was evaluated in a 100 mL stainless steel autoclave. In a typical procedure, 30 mL (about 24 g) of n-valeraldehyde and 4.5 g of Ni-IL/SiO2 catalyst were added into the autoclave, and the air inside was replaced by nitrogen. The mixture was heated to 200 °C and held for 1.5 h with stirring. Then H2 was introduced into the reaction system without cooling and separation. The hydrogenation reaction was carried out for 8.0 h under 3.0 MPa of H2 pressure. After the completion of reaction, the mixture solution was filtered to remove the catalyst and the filtrate was analyzed on a gas chromatograph.
equipped with a FID and a KB-1 capillary column and quantified by the internal standard analysis method.

3. Results and discussion

3.1. Characterization of Ni-IL/SiO₂ catalyst

The XRD patterns of Ni(NO₃)₂-IL/SiO₂ and Ni-IL/SiO₂ are shown in Fig. 1. No characteristic peaks of Ni(NO₃)₂ are observed in Ni(NO₃)₂-IL/SiO₂, indicating that the supported Ni(NO₃)₂ has small particle sizes and is homogeneously dispersed on the surface of IL/SiO₂. For Ni-IL/SiO₂ catalyst, a very weak and broad characteristic peak centered at 2 theta of 44.5°C corresponds to amorphous Ni⁰, indicating that Ni²⁺ has been reduced to Ni⁰ successfully in Ni-IL/SiO₂. After the reaction, some diffraction peaks are observed at around 2 theta of 44.5°C and 52.0°C (Fig. 1(c)), which attribute to the Ni⁰(100) and Ni⁰(220) planes.

There are two possible explanations for the change in characteristic peak of Ni⁰: further reduction under H₂ atmosphere, or aggregation and growth of Ni grains.

To further analyze the chemical states of nickel, the samples were characterized by XPS analysis. Fig. 2 displays Ni 2p spectra of the catalyst before and after reduction. It can be seen from Fig. 2(a) that the binding energies of Ni 2p₃/₂ and Ni 2p₁/₂ in Ni(NO₃)₂-IL/SiO₂ are respectively 857.2 eV and 874.8 eV, which are ascribed to Ni²⁺ of Ni(NO₃)₂. There are two valence states of nickel in Ni-IL/SiO₂ (Fig. 2(b)). The binding energies at around 852.7 eV and 870.0 eV for the Ni 2p₁/₂ are attributed to Ni⁰ (metallic Ni) whereas the Ni 2p₃/₂ and Ni 2p₁/₂ peaks at 856.2 eV and 873.9 eV are attributed to Ni²⁺ of NiO. An absence of Ni²⁺ of Ni(NO₃)₂ in Ni-IL/SiO₂ indicates Ni(NO₃)₂ has been completely reduced by NaBH₄. It also demonstrates that the enhancement of XRD diffraction peaks of Ni⁰ in the recovered catalyst is caused by the aggregation and growth of Ni grains. The presence of NiO in Ni-IL/SiO₂ may be due to the reoxidation of metallic nickel by contacting air in the analysis process.

The FT-IR spectra of silica and the prepared IL/SiO₂ and Ni-IL/SiO₂ are shown in Fig. 3. The broad band around 3445 cm⁻¹ belongs to asymmetric stretching vibration of –OH on the support surface. The band at 1625 cm⁻¹ is associated with the bending vibration of H–O–H. The bands at 809 cm⁻¹ and 1099 cm⁻¹ are assigned to symmetrical and asymmetric stretching vibration of Si–O–Si while the bending vibration of...
Si–OH is observed at 967 cm\(^{-1}\).\(^{20}\) Compared with silica support, a new band at 641 cm\(^{-1}\) attributed to the bending vibration of C–F appears in IL/SiO\(_2\) while the bending vibration of Si–OH weakens obviously, indicating the reaction of Si–OH with the coupling agent and the immobilization of ionic liquids on the support. Fortunately, the FT-IR spectrum changes little for the supported nickel catalyst Ni-IL/SiO\(_2\). Combined with the results of XRD and XPS, it is confirmed that the ionic liquid and nickel has been successfully grafted onto the surface of silica.

Fig. 4 presents the TGA curves of IL/SiO\(_2\) and Ni-IL/SiO\(_2\). There are two steps of weight loss for the two samples. The first weight loss occurs at about 70 \(^\circ\)C, which is attributed to the physically adsorbed water and residual organic solvents during the process for preparation of catalysts. The second weight loss at higher than 330 \(^\circ\)C is related to the decomposition of the ionic liquids on the surface of supports.\(^{21}\) The analysis results demonstrate that Ni-IL/SiO\(_2\) shows the same thermal stability as IL/SiO\(_2\) and its weight loss rate is slightly lower than that for IL/SiO\(_2\). This could be attributed to the decline in ionic liquid amount per unit mass of sample because of the introduction of nickel for Ni-IL/SiO\(_2\).

### 3.2. Catalyst performance of Ni-IL/SiO\(_2\) for one-pot synthesis of 2-PH

The catalytic performance of Ni-IL/SiO\(_2\) for one-pot synthesis of 2-PH was evaluated at 200 \(^\circ\)C for 1.5 h first and then H\(_2\) was introduced for hydrogenation under 3.0 MPa of H\(_2\) pressure for 8.0 h. As a result, the selectivity of 2-PH and pentanol was respectively 58.7% and 25.6% at a \(n\)-valeraldehyde conversion of 100%. The catalytic performance of Ni-IL/SiO\(_2\) is affected greatly by the reaction conditions. To improve the catalytic performance of Ni-IL/SiO\(_2\), the effects of reaction conditions such as Ni-IL/SiO\(_2\) dosage, hydrogen pressure, reaction temperature and reaction time were investigated.

#### 3.2.1 Effect of catalyst dosage

The results of effect of Ni-IL/SiO\(_2\) dosage are listed in Table 1. With an increase of weight percentage of Ni-IL/SiO\(_2\), \(n\)-valeraldehyde conversion increased from 95.3% to 100% while the selectivity of 2-PH increased first, reached its highest point at a weight percentage of Ni-IL/SiO\(_2\) of 15%, and then decreased. The selectivity of 2-propylheptanal changed adversely with 2-PH. The results suggest that the hydrogenation of 2-propyl-2-heptenal to 2-PH proceeds in two steps: C\(=\)C bond of 2-propyl-2-heptenal is hydrogenated to 2-propylheptanal first and then C\(=\)O bond of 2-propylheptanal is hydrogenated to 2-PH, as shown in eqn (1). The selectivity of 2-propyl-2-heptenal was quite low and changed little, indicating that the hydrogenation of C\(=\)C bond is easier than that of C\(=\)O bond and thus the hydrogenation of C\(=\)O bond is the controlling step.

#### 3.2.2 Effect of hydrogen pressure

The effect of hydrogen pressure was investigated and the results are listed in Table 2. When the hydrogen pressure was 2.0 MPa, there was a certain amount of 2-propylheptanal left after the reaction, which demonstrates once again the hydrogenation of C\(=\)C bond is easier than that of C\(=\)O bond. With increasing hydrogen pressure, the catalytic activity for the hydrogenation of C\(=\)O bond was improved: the selectivity of both 2-propyl-2-heptenal and 2-propylheptanal decreased and 2-PH selectivity increased obviously. When the hydrogen pressure was 4.0 MPa, the highest 2-PH selectivity of 75.4% was reached and the sum of the selectivity of 2-PH and pentanol was 98.6%.

#### 3.2.3 Effect of reaction time

The effect of reaction time listed in Table 3 shows that reaction time has a significant influence on the catalytic performance. A low 2-PH selectivity of 47.1% at a reaction time of 6 h was obtained because 2-

| Reaction pressure/MPa | \(X_v/%\) | \(S_{PO}/%\) | \(S_{2-PHEA}/%\) | \(S_{2-PHA}/%\) | \(S_{2-PH}/%\) |
|-----------------------|----------|---------------|-----------------|----------------|----------------|
| 2                     | 100      | 28.2          | 2.3             | 36.8           | 28.3           |
| 3                     | 100      | 27.4          | 0.9             | 2.3            | 69.0           |
| 4                     | 100      | 23.2          | 0.4             | 0.5            | 75.4           |
| 5                     | 100      | 24.9          | 0.2             | 0.1            | 70.5           |

\(^{20}\) Reaction conditions: \(T = 200^\circ\)C; \(n\)-valeraldehyde self-condensation: \(t = 1.5\) h; hydrogenation: \(P_H_2 = 3\) MPa, \(t = 8\) h. V: \(n\)-valeraldehyde; PO: pentanol; 2-PHEA: 2-propyl-2-heptenal; 2-PHA: 2-propylheptanal; 2-PH: 2-propylheptanal. X: conversion; S: selectivity.

| Catalyst amount/% | \(X_v/%\) | \(S_{PO}/%\) | \(S_{2-PHEA}/%\) | \(S_{2-PHA}/%\) | \(S_{2-PH}/%\) |
|-------------------|----------|---------------|-----------------|----------------|----------------|
| 5                 | 95.3     | 20.4          | 0.7             | 70.6           | 3.4            |
| 10                | 100      | 25.6          | 0.8             | 12.8           | 58.7           |
| 15                | 100      | 27.4          | 0.9             | 2.30           | 69.0           |
| 20                | 100      | 24.7          | 0.9             | 10.4           | 63.0           |

\(^{21}\) Reaction conditions: \(T = 200^\circ\)C; \(n\)-valeraldehyde self-condensation: \(t = 1.5\) h; hydrogenation: \(t = 8\) h. V: \(n\)-valeraldehyde; PO: pentanol; 2-PHEA: 2-propyl-2-heptenal; 2-PHA: 2-propylheptanal; 2-PH: 2-propylheptanol. X: conversion; S: selectivity.
propylheptanal was not fully hydrogenated. With the prolonging of reaction time, 2-PH selectivity increased while 2-propylheptanal selectivity decreased. When the reaction proceeded for 8 h, 2-propylheptanal was almost completely hydrogenated to 2-PH. With further prolonging reaction time, some side-reactions of 2-PH and n-valeraldehyde could be promoted, resulting in the decrease of 2-PH selectivity.⁵

### 3.2.4 Effect of reaction temperature.⁶ Table 4 shows the effect of reaction temperature. The highest 2-PH selectivity of 75.4% was obtained with a n-valeraldehyde conversion of 100% at 200 °C. A decrease of reaction temperature mainly reduced the hydrogenation rate of C=O bond, resulting in an increase of 2-propylheptanal selectivity. However, deep self-condensation of n-valeraldehyde could be accelerated at a reaction temperature above 200 °C, affecting the generation of pentanol and 2-PH. Thus an improved catalytic performance of Ni-IL/SiO₂ was attained by investigating the effect of reaction conditions: a 2-PH selectivity of 75.4% was obtained with a n-valeraldehyde conversion of 100% and the sum of 2-PH and pentanol selectivity reached 98.6% under the suitable reaction conditions. The hydrogenation of C=O bond of 2-propyl-2-heptenal is more difficult than that of C=C bond, and is the controlling step.

### 4. Conclusions

A novel Ni-IL/SiO₂ catalyst was prepared for one-pot synthesis of 2-PH via sequential self-condensation and hydrogenation from n-valeraldehyde. The characterization results demonstrate that Ni(NO₃)₂ was reduced to Ni completely by NaBH₄, and Ni-IL/SiO₂ has a good thermal stability below 330 °C. The prepared catalyst shows an excellent catalytic performance in one-pot synthesis of 2-PH: the selectivity of 2-PH attained 75.4% at a n-valeraldehyde conversion of 100% and the sum of 2-PH and pentanol selectivity reached 98.6% under the suitable reaction conditions. The hydrogenation of C=O bond of 2-propyl-2-heptenal is more difficult than that of C=C bond, and is the controlling step.

### Conflicts of interest

There are no conflicts to declare.

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### References

1. L. Zhao, H. An, X. Zhao and Y. Wang, *Ind. Eng. Chem. Res.*, 2016, 55, 12326.
2. T. Seki, J.-D. Grunwaldt and A. Baiker, *Chem. Commun.*, 2007, 34, 3562.
3. C. A. Hamilton, S. D. Jackson and G. J. Kelly, *Appl. Catal., A*, 2004, 263, 63.
4. N. Liang, X. Zhang, H. An, X. Zhao and Y. Wang, *Green Chem.*, 2015, 17, 2939.
5. Y. Li, X. Liu, H. An, X. Zhao and Y. Wang, *Ind. Eng. Chem. Res.*, 2016, 55, 6293.
6. Y. Li, X. Liu, H. An, X. Zhao and Y. Wang, *J. Chem. Ind. Eng.*, 2017, 68, 1381.
7. S. C. Patankar and G. D. Yavad, *Catal. Today*, 2017, 291, 223.
8. S. Miao, H. An, X. Zhao and Y. Wang, *React. Kinet., Mech. Catal.*, 2019, 128, 395.
9. X. Zhang, H. An, H. Zhang, X. Zhao and Y. Wang, *Ind. Eng. Chem. Res.*, 2014, 53, 16707.
10. H. An, Y. Kong, Q. Yang, X. Zhao and Y. Wang, *J. Chem. Technol. Biotechnol.*, 2020, 95, 710.
11. Z. Sun, *J. Chem. Ind. Eng.*, 2007, 28, 8.
12. Z. Tang, Y. Zhou and Y. Feng, *Appl. Catal., A*, 2004, 273, 171.
13. T. Zhang, J. Shi and S. Zhang, *Petroleum Technol.*, 2012, 41, 653.
14. L. Zhao, PhD thesis, Hebei University of Technology, 2018.
15. A. Dhar, N. S. Kumar, M. Khimani, A. S. Al-Fatesh, A. A. Ibrahim, A. H. Fakeeha, H. Patelc and R. L. Vekariya, *RSC Adv.*, 2020, 10, 15282.
16. A. S. Amarasekara, *Chem. Rev.*, 2016, 116, 6133.
17 H. An, J. Tian, X. Zhao and Y. Wang, *J. Chem. Ind. Eng.*, 2015, **66**, 171.
18 S. K. Sharma and R. V. Jasra, *Indian J. Chem.*, 2015, **54**, 451.
19 C. C. Torres, J. B. Alderete, C. Mella and B. Pawelec, *J. Mol. Catal. A: Chem.*, 2016, **423**, 441.
20 P. Han, H. Zhang, X. Qiu, X. Ji and L. Gao, *J. Mol. Catal. A: Chem.*, 2008, **295**, 57.
21 M. Vafaezadeh, Z. B. Dizicheh and M. M. Hashemi, *Catal. Commun.*, 2013, **41**, 96.