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## Preparation of Ni-IL/SiO<sub>2</sub> 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<sub>2</sub>) 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<sub>2</sub> 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.

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### 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 dioctyl 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.<sup>1</sup> 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.<sup>2-8</sup> Liang *et al.*<sup>4</sup>

studied this reaction integration using a bifunctional catalyst of Ni/Ce-Al<sub>2</sub>O<sub>3</sub> 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.*<sup>5,6</sup> obtained similar 2-ethylhexanol selectivity and *n*-butyraldehyde conversion over Ni/La-Al<sub>2</sub>O<sub>3</sub> catalyst for one-pot sequential synthesis of 2-ethylhexanol. Patankar *et al.*<sup>7</sup> 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.*<sup>8</sup> 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 from *n*-valeraldehyde requires a metal-acid/base multifunctional catalyst either.

We once evaluated the catalytic performance of an acid ionic liquid [HSO<sub>3</sub>-*b*-N(Et)<sub>3</sub>]p-TSA in *n*-butyraldehyde self-condensation and the catalytic performance of an acid-base bifunctional ionic liquid [PEmim]Cl-0.5Zn(CH<sub>3</sub>COO)<sub>2</sub> 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<sub>3</sub>-*b*-N(Et)<sub>3</sub>]p-TSA while 2-propyl-2-heptanal selectivity of 86.6% was obtained at a *n*-valeraldehyde conversion of 94.7% over [PEmim]Cl-0.5Zn(CH<sub>3</sub>COO)<sub>2</sub>.<sup>9,10</sup> Moreover, supported Ni-based or Cu-based catalysts show excellent catalytic performance for hydrogenation of 2-propyl-2-heptenal.<sup>11-14</sup> So a combination of an acidic

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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 from *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.<sup>15,16</sup> With such ideas in mind, we prepared a silica-immobilized nickel and acid ionic liquid (Ni-IL/SiO<sub>2</sub>) catalyst and characterized its structure and property by means of FT-IR, TGA, XRD and XPS analysis. To our delight, Ni-IL/SiO<sub>2</sub> 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/SiO<sub>2</sub>

The process for preparation of Ni-IL/SiO<sub>2</sub> comprises two steps: firstly an acid ionic liquid was immobilized on silica to form silica-immobilized acid ionic liquid (IL/SiO<sub>2</sub>), and then nickel was introduced in IL/SiO<sub>2</sub> to obtain the target catalyst Ni-IL/SiO<sub>2</sub>.

(1) **Preparation of IL/SiO<sub>2</sub>.** A IL/SiO<sub>2</sub> sample was prepared by a bonding procedure.<sup>17</sup> 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, CF<sub>3</sub>SO<sub>3</sub>H 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/SiO<sub>2</sub>. The structure of IL/SiO<sub>2</sub> is presented in Scheme 1.

(2) **Preparation of Ni-IL/SiO<sub>2</sub>.** Ni-IL/SiO<sub>2</sub> catalyst was prepared by impregnating a nickel nitrate aqueous solution into

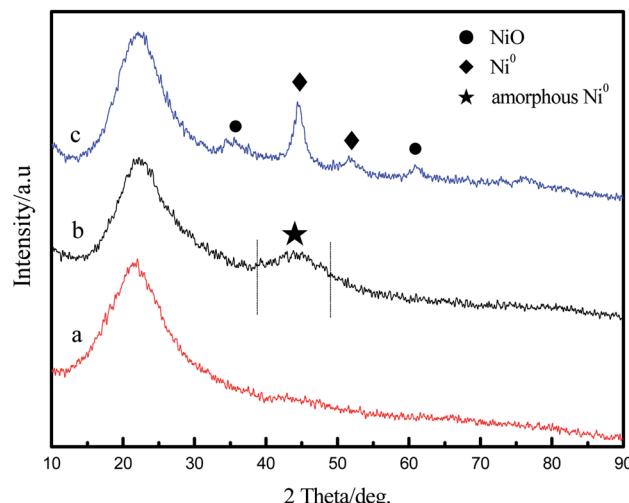


Fig. 1 XRD patterns of Ni(NO<sub>3</sub>)<sub>2</sub>-IL/SiO<sub>2</sub> and fresh and recovered Ni-IL/SiO<sub>2</sub> (a) Ni(NO<sub>3</sub>)<sub>2</sub>-IL/SiO<sub>2</sub>, (b) fresh Ni-IL/SiO<sub>2</sub>, (c) recovered Ni-IL/SiO<sub>2</sub>.

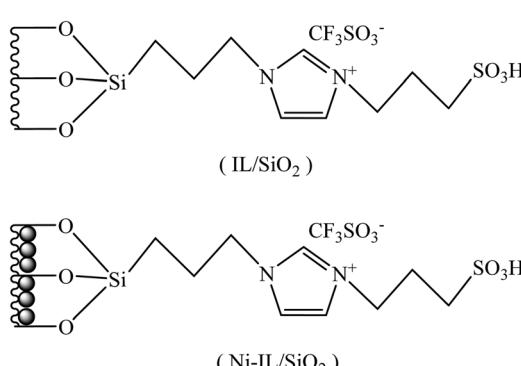
the IL/SiO<sub>2</sub> sample and then reduction by NaBH<sub>4</sub> under 40 °C for 4 h. The structure of Ni-IL/SiO<sub>2</sub> is shown in Scheme 1 either.

### 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<sup>-1</sup> at a resolution of 4 cm<sup>-1</sup>. The thermal stability of samples was determined using a SDT Q600 simultaneous thermal analyzer (TA Instruments Corp., USA). The test was carried out under a flowing air atmosphere (40 mL min<sup>-1</sup>) with a heating rate of 10 °C min<sup>-1</sup> 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 K $\alpha$  radiation at 100 mA and 40 kV. The scan range covered from 5° to 90° at a rate of 6° min<sup>-1</sup>.

### 2.3. Catalytic performance evaluation

The catalytic performance of Ni-IL/SiO<sub>2</sub> 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/SiO<sub>2</sub> 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 H<sub>2</sub> 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 H<sub>2</sub> pressure. After the completion of reaction, the mixture solution was filtered to remove the catalyst and the filtrate was analyzed on a gas chromatograph



Scheme 1 Structure diagrams of IL/SiO<sub>2</sub> and Ni-IL/SiO<sub>2</sub>.



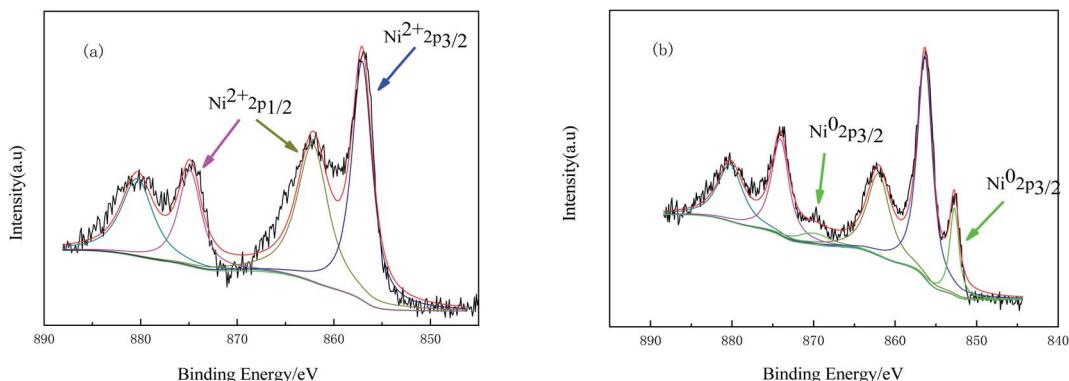


Fig. 2 XPS Ni 2p spectra of (a)  $\text{Ni}(\text{NO}_3)_2$ -IL/SiO<sub>2</sub> and (b) Ni-IL/SiO<sub>2</sub>.

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/SiO<sub>2</sub> catalyst

The XRD patterns of  $\text{Ni}(\text{NO}_3)_2$ -IL/SiO<sub>2</sub> and Ni-IL/SiO<sub>2</sub> are shown in Fig. 1. No characteristic peaks of  $\text{Ni}(\text{NO}_3)_2$  are observed in  $\text{Ni}(\text{NO}_3)_2$ -IL/SiO<sub>2</sub>, indicating that the supported  $\text{Ni}(\text{NO}_3)_2$  has small particle sizes and is homogeneously dispersed on the surface of IL/SiO<sub>2</sub>. For Ni-IL/SiO<sub>2</sub> catalyst, a very weak and broad characteristic peak centered at 2 theta of 44.5° corresponds to amorphous Ni<sup>0</sup>, indicating that Ni<sup>2+</sup> has been reduced to Ni<sup>0</sup> successfully in Ni-IL/SiO<sub>2</sub>. After the reaction, some diffraction peaks are observed at around 2 theta of 44.5° and 52.0° (Fig. 1(c)), which attribute to the Ni<sup>0</sup>(100) and Ni<sup>0</sup>(220) planes.<sup>18</sup> There are two possible explanations for the change in characteristic peak of Ni<sup>0</sup>: further reduction under H<sub>2</sub> 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 2p<sub>3/2</sub> and Ni 2p<sub>1/2</sub> in  $\text{Ni}(\text{NO}_3)_2$ -IL/SiO<sub>2</sub> are respectively 857.2 eV and 874.8 eV, which are ascribed to Ni<sup>2+</sup> of  $\text{Ni}(\text{NO}_3)_2$ . There are two valence states of nickel in Ni-IL/SiO<sub>2</sub> (Fig. 2(b)). The binding energies at around 852.7 eV and 870.0 eV for the Ni 2p<sub>3/2</sub> are attributed to Ni<sup>0</sup> (metallic Ni) whereas the Ni 2p<sub>3/2</sub> and Ni 2p<sub>1/2</sub> peaks at 856.2 eV and 873.9 eV are attributed to Ni<sup>2+</sup> of NiO.<sup>19</sup> An absence of Ni<sup>2+</sup> of  $\text{Ni}(\text{NO}_3)_2$  in Ni-IL/SiO<sub>2</sub> indicates  $\text{Ni}(\text{NO}_3)_2$  has been completely reduced by NaBH<sub>4</sub>. It also demonstrates that the enhancement of XRD diffraction peaks of Ni<sup>0</sup> in the recovered catalyst is caused by the aggregation and growth of Ni grains. The presence of NiO in Ni-IL/SiO<sub>2</sub> may be due to the reoxidation of metallic nickel by contacting air in the analysis process.<sup>14</sup>

The FT-IR spectra of silica and the prepared IL/SiO<sub>2</sub> and Ni-IL/SiO<sub>2</sub> are shown in Fig. 3. The broad band around 3445 cm<sup>-1</sup> belongs to asymmetric stretching vibration of -OH on the support surface. The band at 1625 cm<sup>-1</sup> is associated with the bending vibration of H-O-H. The bands at 809 cm<sup>-1</sup> and 1099 cm<sup>-1</sup> are assigned to symmetrical and asymmetric stretching vibration of Si-O-Si while the bending vibration of

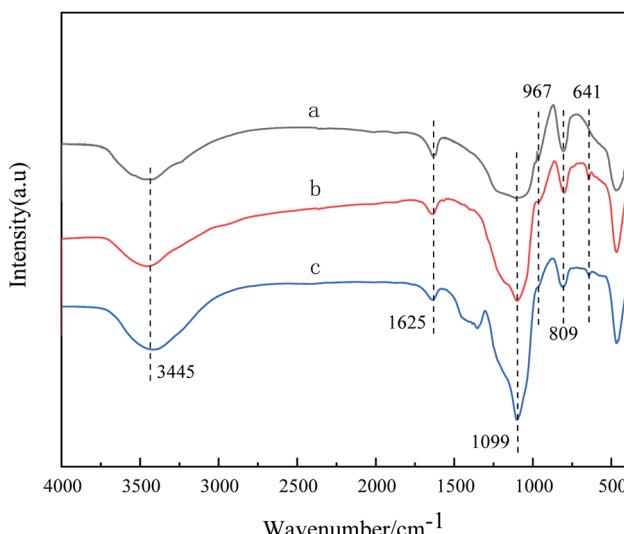


Fig. 3 FT-IR spectra of silica, IL/SiO<sub>2</sub> and Ni-IL/SiO<sub>2</sub> (a) silica, (b) IL/SiO<sub>2</sub>, (c) Ni-IL/SiO<sub>2</sub>.

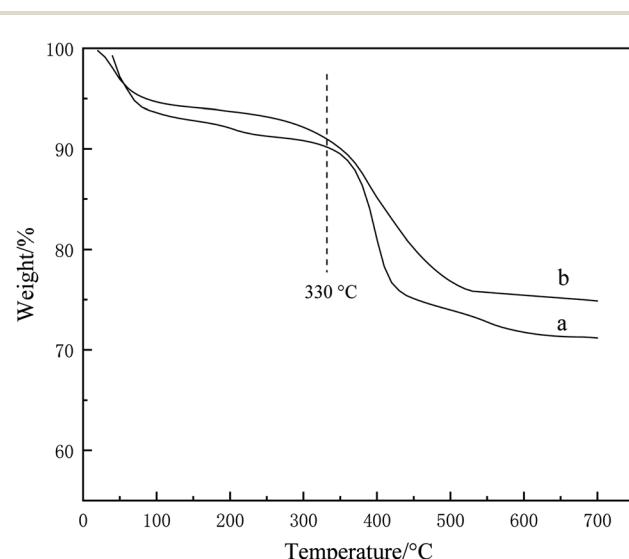


Fig. 4 TGA curves of IL/SiO<sub>2</sub> and Ni-IL/SiO<sub>2</sub> (a) IL/SiO<sub>2</sub>, (b) Ni-IL/SiO<sub>2</sub>.



**Table 1** Effect of catalyst amount on the catalytic performance of Ni-IL/SiO<sub>2</sub><sup>a</sup>

Catalyst amount/%	X <sub>V</sub> /%	S <sub>PO</sub> /%	S <sub>2-PHEA</sub> /%	S <sub>2-PHA</sub> /%	S <sub>2-PH</sub> /%
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

<sup>a</sup> Reaction conditions:  $T = 200\text{ }^{\circ}\text{C}$ ; *n*-valeraldehyde self-condensation:  $t = 1.5\text{ h}$ ; hydrogenation:  $P_{\text{H}_2} = 3\text{ MPa}$ ,  $t = 8\text{ h}$ . V: *n*-valeraldehyde; PO: pentanol; 2-PHEA: 2-propyl-2-heptenal; 2-PHA: 2-propylheptanal; 2-PH: 2-propylheptanol. X: conversion; S: selectivity.

**Table 2** Effect of hydrogen pressure on the catalytic performance of Ni-IL/SiO<sub>2</sub><sup>a</sup>

Reaction pressure/MPa	X <sub>V</sub> /%	S <sub>PO</sub> /%	S <sub>2-PHEA</sub> /%	S <sub>2-PHA</sub> /%	S <sub>2-PH</sub> /%
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

<sup>a</sup> Reaction conditions:  $T = 200\text{ }^{\circ}\text{C}$ , a weight percentage of catalyst = 15%; *n*-valeraldehyde self-condensation:  $t = 1.5\text{ h}$ ; hydrogenation:  $t = 8\text{ h}$ . V: *n*-valeraldehyde; PO: pentanol; 2-PHEA: 2-propyl-2-heptenal; 2-PHA: 2-propylheptanal; 2-PH: 2-propylheptanol. X: conversion; S: selectivity.

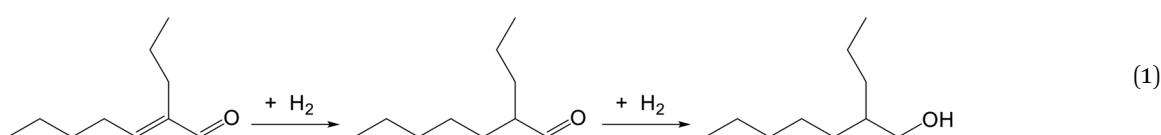
Si-OH is observed at  $967\text{ cm}^{-1}$ .<sup>20</sup> Compared with silica support, a new band at  $641\text{ cm}^{-1}$  attributed to the bending vibration of C-F appears in IL/SiO<sub>2</sub> while the bending vibration of Si-OH

amount per unit mass of sample because of the introduction of nickel for Ni-IL/SiO<sub>2</sub>.

### 3.2. Catalytic performance of Ni-IL/SiO<sub>2</sub> for one-pot synthesis of 2-PH

The catalytic performance of Ni-IL/SiO<sub>2</sub> for one-pot synthesis of 2-PH was evaluated at  $200\text{ }^{\circ}\text{C}$  for  $1.5\text{ h}$  first and then  $\text{H}_2$  was introduced for hydrogenation under  $3.0\text{ MPa}$  of  $\text{H}_2$  pressure for  $8.0\text{ h}$ . 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<sub>2</sub> is affected greatly by the reaction conditions. To improve the catalytic performance of Ni-IL/SiO<sub>2</sub>, the effects of reaction conditions such as Ni-IL/SiO<sub>2</sub> 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<sub>2</sub> dosage are listed in Table 1. With an increase of weight percentage of Ni-IL/SiO<sub>2</sub>, *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<sub>2</sub> 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.



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<sub>2</sub>. 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<sub>2</sub> and Ni-IL/SiO<sub>2</sub>. There are two steps of weight loss for the two samples. The first weight loss occurs at about  $70\text{ }^{\circ}\text{C}$ , 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  $330\text{ }^{\circ}\text{C}$  is related to the decomposition of the ionic liquids on the surface of supports.<sup>21</sup> The analysis results demonstrate that Ni-IL/SiO<sub>2</sub> shows the same thermal stability as IL/SiO<sub>2</sub> and its weight loss rate is slightly lower than that for IL/SiO<sub>2</sub>. This could be attributed to the decline in ionic liquid

**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  $2.0\text{ MPa}$ , 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  $4.0\text{ MPa}$ , 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  $6\text{ h}$  was obtained because 2-



**Table 3** Effect of reaction time on the catalytic performance of Ni-IL/SiO<sub>2</sub><sup>a</sup>

Reaction time/h	X <sub>V</sub> /%	S <sub>PO</sub> /%	S <sub>2-PHEA</sub> /%	S <sub>2-PHA</sub> /%	S <sub>2-PH</sub> /%
6	100	25.7	3.1	23.8	47.1
8	100	23.2	0.4	0.5	75.4
10	100	22.4	0.1	0	72.9

<sup>a</sup> Reaction conditions: a weight percentage of catalyst = 15%, *T* = 200 °C; *n*-valeraldehyde self-condensation: *t* = 1.5 h; hydrogenation: *P*<sub>H<sub>2</sub></sub> = 4 MPa. V: *n*-valeraldehyde; PO: pentanol; 2-PHEA: 2-propyl-2-heptenal; 2-PHA: 2-propylheptanal; 2-PH: 2-propylheptanol. X: conversion; S: selectivity.

**Table 4** Effect of reaction temperature on the catalytic performance of Ni-IL/SiO<sub>2</sub><sup>a</sup>

Reaction temperature/°C	X <sub>V</sub> /%	S <sub>PO</sub> /%	S <sub>2-PHEA</sub> /%	S <sub>2-PHA</sub> /%	S <sub>2-PH</sub> /%
190	99.8	27.1	3.6	24.6	43.8
200	100	23.2	0.4	0.5	75.4
210	100	22.1	0	0.2	65.8

<sup>a</sup> Reaction conditions: a weight percentage of catalyst = 15%; *n*-valeraldehyde self-condensation: *t* = 1.5 h; hydrogenation: *P*<sub>H<sub>2</sub></sub> = 4 MPa, *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.<sup>5</sup>

**3.2.4 Effect of reaction temperature.** 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 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/SiO<sub>2</sub> was attained by investigating the effect of reaction conditions: a 2-PH selectivity of 75.4% with a *n*-valeraldehyde conversion of 100% under the conditions of 15 wt% of Ni-IL/SiO<sub>2</sub>, a hydrogen pressure of 4 MPa, 200 °C, and 8 h. The Ni/Ce-Al<sub>2</sub>O<sub>3</sub> catalyst reported in our previous work of one-pot synthesis of 2-ethylhexanol<sup>4</sup> was applied in the one-pot synthesis of 2-PH via sequential self-condensation and hydrogenation from *n*-valeraldehyde under the above suitable reaction conditions. A 2-PH selectivity of 69.3% with a complete *n*-valeraldehyde conversion was obtained, indicating that the catalytic performance of Ni-IL/SiO<sub>2</sub> is better than that of Ni/Ce-Al<sub>2</sub>O<sub>3</sub> for one-pot synthesis of 2-PH.

## 4. Conclusions

A novel Ni-IL/SiO<sub>2</sub> 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(NO<sub>3</sub>)<sub>2</sub> was reduced to Ni completely by NaBH<sub>4</sub>, and Ni-IL/SiO<sub>2</sub> 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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