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## Upgrading of aromatic compounds in bio-oil over ultrathin graphene encapsulated Ru nanoparticles

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Fast pyrolysis of biomass for bio-oil production is a direct route to renewable liquid fuel, but raw bio-oil must be upgraded in order to remove those easily polymerized compounds (such as phenols and furfurals). Herein, a synthesis strategy of graphene encapsulated Ru nanoparticles (NPs) on carbon sheets (denoted as Ru@G-CS) and its excellent performance for the upgrading of raw bio-oil were reported. Ru@G-CS composites were prepared via the direct pyrolysis of mixed glucose, melamine and RuCl<sub>3</sub> at varied temperatures (500-800 °C). Characterizations indicated very fine Ru NPs (2.5 ± 1.5 nm) that encapsulated within 1-2 layered N-doped graphene were fabricated on N-doped carbon sheets (CS) in Ru@G-CS-700 (pyrolysis at 700 °C). And Ru@G-CS-700 composite was highly active and stable for hydrogenation of these unstable components in bio-oil (31 samples including phenols, furfurals and aromatics) even in aqueous media under mild conditions. This work provides a new protocol to the utilization of biomass, especially to the upgrading of bio-oil.

Bio-oil, produced by fast pyrolysis or liquefaction of biomass, is a promising renewable energy carrier.<sup>1-4</sup> However, the direct use of raw bio-oil as a liquid fuel is currently impossible because hundreds of compounds have been identified in the primary fast pyrolysis products, such as water, acids, alcohols, ethers, ketones, esters, aldehydes, phenols, saccharides, hydrocarbons, *etc.*.<sup>5-9</sup> Among these components, phenols (5–9 wt%), furfurals (18–22 wt%) and aromatics (18–24 wt%) are the dominant contents beside water (10–13 wt%) and char/ash (15–18 wt%).<sup>10–12</sup> Furthermore, phenols and furfurals are easily polymerized which always initiates the solidification of bio-oil during the storage and transportation process. Catalytic hydrogenation of phenols and furfurals to stable hydrocarbons is of great importance in the upgrading of bio-oil. At the same time, the cleavage of C<sub>aromatic</sub>–OH bond in phenols and furfurals is difficult and a challenge in academic research.  $^{\rm 13-16}$ 

In the past decades, many works have been conducted in order to find an active, stable and cheap heterogeneous catalyst for hydrogenation of phenols, furfurals and aromatics,<sup>17-30</sup> and most experiments were performed in organic solvents, such as methanol,<sup>21</sup> ethanol and 2propanol,<sup>22</sup> and dichloromethane.<sup>22,23</sup> From the viewpoint of practical application, the use of water as solvent is not only environmental friendly, but also economically viable because raw bio-oil contains a large amount of water (10-13 wt%). Savage and co-workers have made significant progresses in converting bio-oil and bio-derived molecules into liquid hydrocarbons using Pd/C under 350-500 °C and 150-305 bar in supercritical water.<sup>8,15,25</sup> Zhao and co-workers disclosed that the combined Pd/C with mineral acid  $H_3PO_4$  can catalyze the hydride oxygenation phenolic compounds to alkanes in aqueous solution at 5.0 MPa  $H_2$  and 250 °C.<sup>5</sup> Bal *et al* also found that the hydrogenation of phenol and phenolic compounds proceeded efficiently over Pt-CeO2 catalyst in aqueous medium at 100 °C.<sup>24</sup> Wang et al further reported that Pd@carbon nitride without any additives can catalyze the conversion of phenolic compounds to cyclohexanone in aqueous media under 65 °C for 2.0 h.<sup>26</sup> More recently, Huang et al developed a ruthenium-tungsten bifunctional catalyst for the selective hydrogenolysis of CAr-O bonds in phenols in aqueous media at 270 °C.<sup>27</sup> Above pioneering works have contributed a lot to the production and possible application of bio-oil and promoted the study in upgrading of bio-oil. However, metal NPs that directly deposited on supports are easily leached and/or agglomerated in aqueous media because the interaction between metal NPs and supports surface was weak.<sup>31</sup> Therefore, the development of an active, stable and cheap catalyst is of great importance for the bio-oil upgrading.

Herein, a novel Ru@G-CS composite, in which nano sized Ru particles were encapsulated within N-doped graphene and N-doped carbon sheets (CS) acted as a skeleton to support the Ru NPs, was synthesized and used in the upgrading of bio-oil in aqueous solution. And more interestingly, this catalyst was

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prepared via direct pyrolysis a mixture of glucose, melamine and RuCl<sub>3</sub>. It was found that Ru@G-CS-700 composite (pyrolysis at 700 °C) was highly active and stable for the hydrogenation of phenols, furfurals and aromatics in water under mild conditions.

#### **Result and discussion**

The overall synthesis strategy of hierarchical Ru@G-CS composites was illustrated in Fig. 1. Briefly, a given amount of glucose and melamine was added into an aqueous solution of RuCl<sub>3</sub> under stirring. And then, the resulting suspension was evaporated at 80 °C in air to a tawny solid powder (denoted as S80, see Fig. S1a,b, ESI<sup>†</sup>), and S80 was further calcined at 500 °C (in Ar) to a sandwich-like structure, in which Ru NPs were confined within the sandwich layers (Fig. S1c,d, ESI<sup>+</sup>). After that, the thermal pyrolysis process was performed at 500-800 °C in Ar flow. Finally, the solid mixture was washed with aqua regia solution, and the possibly exposed metal on the outside of graphene shell was removed by a strong acid leaching. The final purified composite was denoted as Ru@G-CS-x, where x means the temperature of pyrolysis. The content of Ru in prepared Ru@G-CS-x was checked via inductively coupled plasma-atomic emission spectroscopy (ICP, Plasma-Spec-II spectrometer) and summarized in Table S1 (ESI<sup>†</sup>) in electronic supplementary data.

Nitrogen adsorption-desorption isotherms of Ru@G-CS composites were shown in Fig. 2a. All of them were type IV patterns according to the International Union of Pure and Applied Chemistry (IUPAC) classification, which were reasonably associated with the presence of mesopores, possibly due to the slit-shaped pores between the parallel layers.<sup>32</sup> The surface area of Ru@G-CS-500 was 171.6 m<sup>2</sup>/g (see Table S2, ESI<sup>†</sup>), which was lower than those of composites



Fig. 2 (a)  $N_2$  sorption isotherms and (b) pores size distribution of Ru@G-CS composites prepared at varied pyrolysis temperature.





Fig. 3 SEM (a-c) and TEM (d) images of Ru@G-CS-700.

synthesized at higher temperatures, and Ru@G-CS-700 had the largest surface area (311.8 m<sup>2</sup>/g). The pore size distribution of Ru@G-CS composites was calculated and presented in Fig. 2b. Only one kind of unique pore channel (at around 2.9–4.7 nm) was detected in Ru@G-CS composites (excepted for Ru@G-CS-500), and this kind of pore channel might be attributed to the accumulation of lamellate CS. Moreover, the mesoporous volume of Ru@G-CS-700 sample (0.144 cm<sup>3</sup>/g) was higher than those of others (see Table S2, ESI<sup>†</sup>).

Scanning electron microscopy (SEM) analysis of Ru@G-CS confirmed that these samples were hierarchically lamellar structured composites like a carbon lettuce (see Fig. 3a–c and Fig. S2, ESI<sup>†</sup>), the average thickness of the solid lamellar in Ru@G-CS-700 was around 12–14 nm. Transmission electron microscopy (TEM) image of Ru@G-CS-700 found that Ru NPs dispersed highly on the surface of CS (see Fig. 3d).

Raman spectra of Ru@G-CS composites were shown in Fig. 4a. D-band (~1350 cm<sup>-1</sup>, evidence of defects such as disorders, edges and boundaries of carbon), G-band (~1580 cm<sup>-1</sup>, the vibration of  $E_{2g}$  phonons of sp<sup>2</sup> C atoms), 2D-band (~2700 cm<sup>-1</sup>, information on the number of layers of the carbon material) and G'-band (~2950 cm<sup>-1</sup>, the cooperation between D- and G-band) were detected in all samples.<sup>33–35</sup> The relative intensities of the D-band ( $I_D$ ), G-band ( $I_G$ ) and 2D-band ( $I_{2D}$ ) provide the evidence for studying the characteristic of the carbon materials. Carbon materials with high quality have a low  $I_D/I_G$  ratio and a high  $I_{2D}/I_G$  ratio, which means low defects and highly dispersed carbon layers.<sup>35</sup> It was found that Ru@G-CS-700 had the lowest of  $I_D/I_G$  (1.03) and the highest  $I_{2D}/I_G$  (0.38) (see Table S1, ESI†), which means that the carbon sheets in Ru@G-CS-700 was the best.

X-ray diffraction (XRD) pattern of Ru@G-CS composites that prepared at various pyrolysis temperatures were shown in Fig. 4b. The significant and sharp peaks at 38.3, 42.2, 44.0, 58.3, 69.4 and 78.4° were assigned to the typical diffractions of the (100), (002), (101), (102), (110) and (103) crystalline planes of the hexagonal close-packed (hcp) Ru (JCPDS 06-0663), respectively.<sup>36,37</sup> The mean crystalline particle size of Ru was calculated from the broadening of the Ru (101) plane using Scherrer's equation and summarized in Table S1 (ESI<sup>†</sup>). It was

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**Fig. 4** (a) Raman spectra, (b) XRD patterns, XPS spectra of (c) N1s and (d) Ru 3p of Ru@G-CS composites prepared at varied pyrolysis temperature.

found that the mean crystalline size of Ru decreased continuously with the increasing pyrolysis temperature from 500 °C (18.5 nm in Ru@G-CS-500) to 700 °C (2.5 nm in Ru@G-CS-700). But further increase the pyrolysis temperature to 800 °C would bring the sintering of Ru (8.4 nm in Ru@G-CS-800). Other peaks at 17–30° in all samples were assigned to the diffraction of (002) plane of graphite, and these diffraction peaks were broad, indicating that the little dense and well-exfoliated state of the CS. These results indicated that pyrolysis temperature played a crucial role in the dispersion of Ru NPs and in the graphitization (composition) of the carbon sheets.

X-ray photoelectron spectroscopy (XPS) analysis revealed the presence of C, N, O and Ru in all Ru@G-CS composites (see Fig. S3, ESI<sup>†</sup>), and the surface composition and Ru content were summarized in Table S3 (ESI<sup>†</sup>). C1s spectra can be deconvoluted into several peaks, and the peaks at 285.8 and 287.5 eV were attributed to the  $sp^2$  and  $sp^3$  C-N, respectively, indicating that the carbon framework of prepared CS was successfully doped by N (see Fig. S4, ESI<sup>†</sup>).<sup>38,39</sup> Deconvolution of N1s spectra (see Fig. 4c) further disclosed the formation of pyridinic N (398.6 eV), pyrrolic N (399.8 eV) and graphitic N (401.2 eV) in Ru@G-CS-700.<sup>40-44</sup> As it was reported, pyridinic N atoms at the edge of graphitic layers are generally believed to be connected with catalytic activity because pyridinic N can reduce the energy barrier for reactants adsorption on adjacent carbon atoms, and accelerate the rate-limiting first-electron transfer, which led to a significant enhancement of catalytic activity of carbon surface.<sup>45,46</sup> At the same time, recent reported results also indicated that doping graphitic N into graphene structure can lead to a non-uniformed electron distribution, especially when two graphitic N atoms are doped into the same hexagon, leading to a significant enhancement of catalytic activity of carbon surface.<sup>42</sup> That is, N atoms in graphene shell not only brought imperfect and porous graphene encapsulation around metal cores, but also enhanced catalytic activity of carbon surface around Ru core. XPS spectra of the Ru 3p peaks (see Fig. 4d) also confirmed the

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Fig. 5 HRTEM images (a-e), schematic illustration structure (c), the number of graphene layer over Ru NPs (f), HAADF-STEM image and EDX mapping (g), and line scanning EDS elemental analysis (h) of Ru@G-CS-700.

relative proportion of Ru(0) in Ru@G-CS-700 was higher than those of other composites ( see Table S3, ESI†). Above results indicated that 700 °C is more favorable for the growth of CS from glucose and melamine and the formation of metallic Ru in this study.

High-resolution TEM (HRTEM) analysis of Ru@G-CS-700 disclosed that all detected Ru particles distributed homogenously in the range of  $2.5 \pm 1.0$  nm in diameter, and the average particle size of counted 500 Ru particles was 2.6 nm (see Fig. 5a). At the same time, it is quite interesting to find that most Ru particles were encapsulated within 1 or 2 layered graphene (see Fig. 5b-e), and schematic illustration of the Ru@G-CS-700 structure was shown in Fig. 5c. Fig. 5d,e also displayed the well-defined lattice fringes of Ru, and the insertion was the corresponding Fast Fourier Transform (FFT) of a single Ru crystal which showed sharp spots due to wellcrystallized Ru. Moreover, the detected lattice spacing values, 0.231 and 0.214 nm, were corresponding to the 101 and 002 planes of a single-crystal Ru, respectively. The spacing of the adjacent lattice planes in graphene layer was 0.342 nm, corresponding to the (002) plane of graphite.<sup>47,48</sup> Fig. 5f presented the distribution proportion of the number of graphene layers that encapsulated around Ru particles. Highangle annular dark-field scanning transmission electron microscopy (HAADF-STEM) also confirmed that formation of N-doped CS, N-doped graphene shell and Ru deposited mainly on the surface of N-doped CS, as C (red) and N (orange) distributed homogenously on the whole surface of CS and Ru (green) also homogenously distributed on the whole CS surface (Fig. 5g). Line scanning energy dispersive spectrometer (EDS) elemental analysis (Fig. 5h) also confirmed that the resulting N-doped CS served as a support uniformly decorated with N-doped graphene encapsulated Ru NPs.

SEM and TEM images of Ru@G-CS composites prepared at

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Table 1. Hydrogenation of phenol over different catalysts. <sup>a</sup>

	OH	Catalyst	<b></b> ►	$\sim^{c}$	Н		
$20 {}^{\circ}\text{C}, 1.0 \overline{\text{MPa H}_2}$							
Entry	Sample	Conv. (%)	Selectivity (%)				
			C-OH	C=0	Others <sup>b</sup>		
1	None	0	-	-	-		
2	CS	0	-	-	-		
3	Ru NPs	38.5	72.6	27.4	0		
4	Ru@G-CS-500	41.6	88.5	11.5	0		
5	Ru@G-CS-600	75.7	85.6	14.4	0		
6	Ru@G-CS-700	100	100	0	0		
7	Ru@G-CS-800	88.5	93.3	6.7	0		
8	Ru/AC	71.6	83.5	16.5	0		
9	Ru/SiO₂	58.3	87.3	10.6	2.1		
10	$Ru/Al_2O_3$	51.4	78.2	18.6	3.2		
11	$Ru/Fe_3O_4$	42.7	61.4	27.5	11.1		
12	Ru/MgO	34.9	68.1	21.3	10.6		

 $^{o}$  Reaction condition: Phenol, 0.2 mmol; Ru, 5.0 mol% ( relative to phenol); H\_2O, 5.0 mL; H\_2, 1.0 MPa; 20  $^{\circ}$ C; 1.0 h.

<sup>b</sup> Mainly intermediates.

500, 600 and 800 °C were presented in Fig. S2 and S5 (ESI<sup>+</sup>), respectively. Ru@G-CS-500 was a wrinkled multi-carbon sheets-like structure with significant agglomeration (see Fig. S2a, ESI † ), and uneven dispersed Ru particles were encapsulated with incomplete graphene layers (shown in Fig. S5a,b). Raising the pyrolysis temperature to 600 °C, the CS became thinner and Ru particles were smaller than those of Ru@G-CS-500 (see Fig. S2b and Fig. S5c,d, ESI<sup>†</sup>). However, further increase the pyrolysis temperature to 800 °C may damage the graphene layers that formed on the outer surface of Ru particles, and result in the formation of big Ru particles in Ru@G-CS-800 (Fig. S5e,f, ESI †). These results further indicated that the pyrolysis temperature played a critical role in the structure of Ru@G-CS composites, and it is reasonable to speculate that 700 °C is more favourable for the formation of highly dispersed, ultrathin graphene encapsulated Ru NPs on CS support.

The performance of Ru@G-CS composites for the upgrading of bio-oil was first tested using phenol as a model compound at 20 °C, 1.0 MPa H<sub>2</sub> and 1.0 h. Table 1 summarized the activity of phenol hydrogenation over Ru@G-CS composites and compared with those Ru catalysts on traditional supports. Under mild reaction conditions, the main product was cyclohexanol (C-OH), and the byproducts were were cyclohexanone (C=O) and other mainly intermediates. As it can be seen from Table 1, no reaction happened without catalyst (Entry 1) and Ru (Entry 2), and the activity of supportfree Ru colloidal NPs (Entry 3) was quite low. It is quite interesting to note that the selectivity of cyclohexanol reached 100% with a complete conversion of phenol over Ru@G-CS-700 (Entry 6). These results indicated that CS support played an important role in enhancing the activity of Ru and increasing the selectivity of desired product. Other Ru@G-CS catalysts (Entries 4 to 7) also exhibited good activity for the selective hydrogenation of phenol to cyclohexanol. When

700. <sup>a</sup>						
Entry	Substrate	<i>Т</i> (°С)	Time (h)	Conv. (%)	Product	Yield (%)
1	OH	20	6	100	OH	99.1
2	OH	20	6	100	OH	99.7
3	$\square$	20	6	100	$\langle $	100
4	ОНОН	30	7	100	OH	97.4
5	OH OH	30	5	100	ОН	95.6
6	OH	30	7	100	ОН	99.1
7	OH OH	20	8	99.7	OH OH	90.3
8		20	8	100		93.5
9		20	8	99.2		94.8
10	OH	40	6	100	OH	99.2
11	OH	60	7	100		96.7
12		60	12	100		98.1
13	OH OH	60	10	99.6	ОН	91.4
14	Ç	70	8	100	$\widehat{\mathbb{Q}}$	99.2
15	OH C	120	10	98.7	OH	98.1
16	OH ON	120	12	95.4	- Vn	94.8
17 <sup>b</sup>		180	2	100		89.5
18 <sup>b</sup>	но	200	3	100	$\checkmark$	82.6

Table 2. Hydrogenation of phenols and furfurals in bio-oil over Ru@G-CS-

 $^{\it a}$  Reaction condition: Substrate, 0.2 mmol; Ru (5.0 mol% relative to substrate); H2O, 5.0 mL; H2, 1.0 MPa.

<sup>b</sup> Substrate 0.2 mmol, Ru 5.0 mol %; 1-butanol, 20.0 mL; H<sub>2</sub>, 3.0 MPa.

activated carbon (AC) was used as the support, the conversion of phenol was 71.6% (Entry 8). On the surface of other

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commonly used supports, such as SiO<sub>2</sub> (Entry 9), Al<sub>2</sub>O<sub>3</sub> (Entry 10),  $Fe_3O_4$  (Entry 11) and MgO (Entry 12), the conversion of phenol decreased to 58.3%, 51.4%, 42.7% and 34.9%, respectively, and selectivity towards cyclohexanol was low. These results indicated that the nature of support played an important role in the activity and selectivity of phenol hydrogenation. The predominant performance of Ru@G-CS-700 might be attributed to the synergetic interaction between Ru NPs and protective ultrathin graphene layers. In other words, both Ru NPs and the surrounding graphene shell would be active towards the catalytic reaction; moreover, the doping N into the carbon lattice further increased the projected density of states near Fermi level and reduced the local work function theory.<sup>38,49–51</sup> At the same time, the micropore-free structure, higher surface area of Ru@G-CS-700 and the well dispersion of Ru NPs can also promote the hydrogenation reaction.

Table 2 summarized the performance of Ru@G-CS-700 for the hydrogenation of those phenols and furfurals in bio-oil. It was found that Ru@G-CS-700 exhibited excellent performance for the hydrogenation of all tested phenols to corresponding cyclohexanols with higher yield (> 90.3%) under mild condition ( $\leq$  100 °C) in aqueous solution. In detail, methylsubstituted phenols were hydrogenated smoothly to the corresponding cyclohexanol derivatives with up to 99% yields (Entries 1-3). Hydrogenation of pyrocatechol (Entry 4), resorcinol (Entry 5) and hydroquinone (Entry 6) yielded the synthetically very valuable hydroxylcyclohexanols, again with high conversion and yield. The presence of functional groups such as methoxyl (Entries 7,8), ethyoxyl (Entry 9) and tert-butyl (Entry 10) did not influence the hydrogenation reactions, which also obtained good yields of products. The disubstituted and tri-substituted phenols were also investigated, and they were hydrogenated to the corresponding substituted cyclohexanols with excellent yields (Entries 11,12). However, relatively higher temperature and longer reaction time were needed in order to gain good yields due to the steric hindrance (Entrv 12). for example. 2.6-di-tert-butyl-4-methylcyclohexanol obtained from 2,6-di-tert-butyl-4was methylphenol within 12 h. Additionally, 2-naphthol, a polycyclic arene, was also reduced to the corresponding polyalicyclic product with 91.4% yield (Entry 13). Finally, three represents phenols with unsaturated band (C=C bond) were also investigated. For 4-vinyl phenol (Entry 14), the hydrogenation reaction was performed at 70 °C for 8 h, and the detected conversion was 100% with a 99.2% product yield. However, for 2-methoxy-4-vinyl phenol (Entry 15) and 2methoxy-4-propenyl phenol (Entry 16) with both -hydroxyl and -methoxy, the higher temperature and longer time were required to achieve the maximum conversion of the phenols, and the cleavage of C-OMe occurred during the reactions (120 °C, ≥10 h).

On the other hand, the hydrogenation of furfural (Entry 17) and 5-hydroxymethylfurfural (Entry 18) over Ru@G-CS-700 was difficult. These experiments were carried in organic solvents at high temperature, it was found that furfural and 5-

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$R \xrightarrow{\Pi} \frac{Ru@G-CS-700}{H_2, H_2O} R $							
Entry	Substrate	<i>Т</i> (°С)	Time (h)	Conv. (%)	Product	Yield (%)	
<b>1</b> <sup>b</sup>	C ( ,	80	3.5	100	$\bigcirc$	96.2	
2 <sup><i>b</i></sup>	<i>t</i> Bu	80	3.5	100	tBu	98.7	
3		60	6.0	98.4	$\bigcirc$	89.4	
4	$\tilde{\mathbf{A}}$	80	5.0	99.4	$\tilde{\bigcirc}$	95.1	
5		80	4.0	98.6	$\bigcirc \bigcirc \bigcirc$	93.4	
6		60	5.5	100	$\mathbf{X}$	93.7	
7		60	5.0	99.1	$\left( \right)$	95.8	
8	$\bigcirc$	60	5.0	97.8	$\Diamond$	96.9	
9 <sup>c</sup>	CO <sub>2</sub> H	80	4.0	98.5	CO <sub>2</sub> H	94.3	
10 <sup>c</sup>	H <sub>2</sub> N CO <sub>2</sub> H	80	4.0	100	H <sub>2</sub> N CO <sub>2</sub> H	95.7	
11 <sup>c</sup>		100	7.0	93.6		91.5	
12 <sup>c</sup>		100	7.0	95.7		94.1	

<sup>*a*</sup> Reaction condition: Substrate, 0.2 mmol; Ru (10.0 mol% relative to substrate); H<sub>2</sub>O, 5.0 mL; H<sub>2</sub>, 5.0 MPa.

<sup>b</sup> H<sub>2</sub>, 1.0 MPa.

<sup>c</sup> Substrate, 0.1 mmol.

hydroxymethylfurfural could convert completely to methylfuran (89.5%) and 2,5-dimethylfuran(82.6%) at 180 and 200 °C (Entries 17 and 18, see Table 2), respectively.

Table 3 summarized the performance of Ru@G-CS-700 for the hydrogenation of aromatics in bio-oil. Once again, Ru@G-CS-700 showed high activity for the hydrogenation of alkyl benzenes and the yield of cyclo-paraffin reached 96–99% (Entries 1 and 2). Cumene (Entry 3) and biphenyl (Entries 4 and 5) were successfully converted into the corresponding cyclohexane derivatives with good yields. It is noteworthy that the hydrogenation of di-substituted aromatic (Entries 6–8) also occurred with excellent yields under lower temperature compared with mono-substituted aromatics. Ru@G-CS-700 catalyst also showed high activity for the hydrogenation of benzoic acids (Entries 9 and 10), ethyl benzoate (Entry 11) and cyclohexyl propyl formate (Entry 12). In brief, the hydrogenation of alkylbenzene and biphenyl, as well as benzoic acids can be realized over Ru@G-CS-700 catalyst.

Fig. S6 (ESI<sup> $\dagger$ </sup>) presented the performance of recycled Ru@G-CS-700 for the hydrogenation of phenol in water. As it can be separated easily from the reaction solution by simple centrifugation, the result of recycling tests demonstrated that

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there was no obvious decrease in the conversion of phenol during the ten runs. The prolonged stability of the catalyst can be ascribed to the fact that the Ru NPs were well encapsulated with the N-doped graphene layers.

#### Conclusions

In summary, a novel one-step strategy for the synthesis of Ru@G-CS composites by controlled pyrolysizing a mixture of RuCl<sub>3</sub>, glucose and melamine was developed. It was confirmed that well dispersed, ultrathin graphene layers (only 1–2 layers) encapsulated Ru NPs that anchored on the surface of carbon sheets could be synthesized at 700 °C, and Ru@G-CS-700 catalyst exhibited predominant performance for the hydrogenation of those phenols, furfurals and aromatics in bio-oil under mild conditions. These findings paved a way for the concise preparation of stable nano-hybrid catalysts and also for the feasible upgrading of bio-oil over one versatile catalyst.

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### **Graphical abstract**

Upgrading of aromatic compounds in bio-oil over ultrathin graphene encapsulated Ru nanoparticles

A novel Ru@G-CS composite, in which 1-2 layered N-doped graphene encapsulated nano sized Ru ( $2.5 \pm 1.5 \text{ nm}$ ) particles, was fabricated on carbon sheets (CS), *via* the direct pyrolysis of mixed glucose, melamine and RuCl<sub>3</sub>. And Ru@G-CS-700 (pyrolysis at 700 °C ) is highly active, selective and stable for the hydrogenation of those model compounds (such as phenols, furfurals and aromatics) in bio-oil in water under mild conditions.

