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# Highly-efficient Ru/Al-SBA-15 Catalysts with Strong Lewis Acid Sites for the Water-assisted Hydrogenation of *p*-Phthalic Acid

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The ruthenium nanoparticles supported onto the aluminum-doped mesoporous silica catalysts (Ru/Al-SBA-15) are fabricated using the hydrothermal and impregnation methods for catalysis application. Ru/Al-SBA-15-3 catalyst at a Si/Al molar ratio of 3 exhibited excellent catalytic performance for the hydrogenation of *p*-phthalic acid with high conversion efficiency (100.0%) and *cis*-isomer selectivity (84.0%) in water. Moreover, this system displays exceptional stability and recyclability through preserving the conversion efficiency as well as the *cis*-isomer selectivity of 90.2 and 83.3%, respectively, after reusing it fourteen times. Such an exceptional system can also be ideal for the hydrogenation of aromatic dicarboxylic acids and their ester derivatives in water. The strong Lewis acid sites due to doped Al species play significant roles in the hydrogenation reaction. Moreover, the isotope labeling studies indicated that the water molecules effectively participated in the hydrogenation reaction. Hydrogen and water contributed half of the hydrogen atoms for this hydrogenation reaction. In the end, a plausible mechanistic pathway of the hydrogenation of p-phthalic acid using the Ru/Al-SBA-15-3 catalyst in water is proposed.

#### 1. Introduction

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Indeed, 1,4-cyclohexanedicarboxylic acid (CHDA) is a crucial chemical intermediate and raw material for the production of drugs, polyester resin, and coating. Traditionally, CHDA can be prepared by the hydrogenation of dimethyl terephthalate, followed by hydrolysis.1 Recently, direct hydrogenation of pphthalic acid has attracted considerable attention for the synthesis of CHDA. In this context, various organic solvents, such as N-methyl-2-pyrrolidone (NMP), dimethylformamide (DMF), and isopropanol have been used, owing to the low solubility of pphthalic acid in water. Moreover, it should be noted that the processing strategies utilizing such organic solvents face limitations of environmental unfriendly and poor recyclability.<sup>2, 3</sup> These limitations could be addressed by using water as the reaction medium, which is predominantly regarded as the universal solvent for achieving green chemistry goals due to its non-toxic nature, enormous availability, and simple postprocessing, among others.<sup>4</sup> However, most of the research studies indicated that the hydrogenation of p-phthalic acid generally requires harsh conditions (high temperature and pressure) due to

the stability of the aromatic ring and its low solubility (1.5 mg/100 mL at 20 °C) in the aqueous solution.<sup>5, 6</sup> In this framework, Sumner and Gustafson<sup>7</sup> reported that the yield of CHDA was 98.4% at 195~230 °C with 0.5 wt.% Pd/C catalyst in 3 h (H2 pressure 4.5 MPa). Kayou and Nanba<sup>8</sup> performed this reaction with 5 wt.% Pd/C catalyst obtaining 99.2% conversion at 150 °C in 1 h. Yu and colleagues<sup>9</sup> reported that bimetallic catalyst Rh70Pt30/SBA-15 with 5.6 wt.% total metal loading exhibited 74.3% terephthalic acid conversion after 2 h at 80 °C (H<sub>2</sub> pressure, 5 MPa). Based on these facts of considering the high energy consumption and cost of existing catalytic systems, a highly efficient catalyst with low noble metal loading would be desirable and appropriate to execute the catalytic operations.

Ruthenium is a relatively inexpensive precious metal and exhibits high efficiency in the hydrogenation of the aromatic rings. Several efforts have been dedicated to fabricating the ruthenium nanoparticles-doped composites for catalysis applications. In a case, Wang and coworkers<sup>10</sup> demonstrated that the rutheniumbased catalyst displayed excellent catalytic performance for the hydrogenation of benzoic acid. In another instance, Zhu and Lv<sup>11</sup> used Ru/Al<sub>2</sub>O<sub>3</sub> catalyst for the hydrogenation of *p*-phthalic acid, in which the conversion efficiency reached 95.4% at 140 °C, 5.0 MPa  $H_2$  after 1.5 h. Similarly, Yen and colleagues<sup>12</sup> fabricated a highly efficient and durable nano-ruthenium catalyst Ru/MCM-41 for the hydrogenation of bisphenol A in the aqueous solution. Zahmakiran and Ozkar<sup>13</sup> reported that the ruthenium nanoclusters deposited on the zeolite frameworks displayed excellent catalytic performance for the hydrogenation of neat benzene under mild conditions. Furthermore, Liu and colleagues<sup>14</sup>

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suggested that N-doped carbon spheres impregnated with highly monodispersed ruthenium nanoparticles catalyst substantially exhibited high catalytic activity for the hydrogenation of benzoic acid. Plausibly, the predominant motive for the utilization of ruthenium-based nanoparticles in catalysis is their ability to effectively absorb and dissociate the available hydrogen in the reaction system, facilitating the hydrogenation of *p*-phthalic acid in the aqueous environment.

In addition, the reliable support with strong acidic sites is required for the hydrogenation reaction to interacting with the aromatic ring for uneven charge distribution, leading to its activation and substantial reduction in the activation energy.<sup>15</sup> Due to their tunable morphological attributes such as even pore size distribution as well as high specific surface area, and advantageous characteristic functionalities, mesoporous silica materials, notably, the Santa Barbara Amorphous-15 (SBA-15) material shows excellent catalysis performance.<sup>16, 17</sup> Progressively, the impregnation of heteroatoms, such as Al-doped SBA-15, can provide strong surface acid sites,18-21 which are highly beneficial for the hydrogenation of *p*-phthalic acid. Furthermore, it is highly convenient to tune the acidity strength of Al-SBA-15 by adjusting the Si/Al molar ratio.<sup>22-25</sup> Motivated by these facts of relatively inexpensive and effective catalytic abilities of ruthenium metal and highly tunable Al-SBA-15 frameworks, it is expedient to fabricate a composite for the hydrogenation of p-phthalic acid under mild conditions in aqueous solution.



**Scheme 1.** Schematic illustration showing the fabrication of ordered mesoporous AI-SBA-15 and corresponding nanoparticles-supported catalyst Ru/AI-SBA-15 using subsequent hydrothermal and impregnation methods, and their high-efficient catalytic performance toward the water-assisted hydrogenation of aromatic dicarboxylic acids and their ester derivatives.

Inspired by these facts, we initially fabricated highly active composites based on ruthenium nanoparticles-supported ordered mesoporous AI-SBA-15 with highly strong acid sites using hydrothermal and impregnation methods for catalysis application. These highly efficient Ru/AI-SBA-15 catalysts could achieve hydrogenation of benzoic dicarboxylic acids and their ester derivatives in water (Scheme 1). The high total acid amount, abundant Lewis acid sites, and unique porous architectures of mesoporous silica resulted in the exceptional catalytic performance of Ru/AI-SBA-15 catalyst under mild conditions. Interestingly, hydrogen (H<sub>2</sub>) and water each contributed half of the hydrogen atoms for the hydrogenation reaction of aromatic carboxylic acids. Finally, a plausible mechanistic pathway for the hydrogenation of p-phthalic acid on the catalyst Ru/AS-3 in the

aqueous solution was proposed.

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#### 2. Experimental Section

#### 2.1. Materials

All the reagents chemicals were analytical grade without further purification. Hydrochloric acid (HCl), N,N-dimethylformamide (DMF), tetraethyl orthosilicate (TEOS), ammonia-water, and ethanol were obtained from Sinopharm Chemical Reagent Co. Ltd. (Shanghai, China). The ruthenium (III) chloride hydrate (RuCl<sub>3</sub>), aluminum isopropoxide, *o*-phthalic acid, *m*-phthalic acid, *p*-phthalic acid, dimethyl phthalate, dimethyl isophthalate, and dimethyl terephthalate were purchased from Aladdin industrial corporation (Hangzhou, China). Poly (ethylene oxide)-poly(propylene oxide)-poly(ethylene oxide) (PEO-PPO-PEO) triblock polymer (P123, Ma = 5800), *p*-phthalic acid-d<sub>4</sub>, deuterium oxide (D<sub>2</sub>O), deuterated chloroform, and dimethyl sulfoxide-d<sub>6</sub> were obtained from Sigma Co. Ltd. (St. Louis, USA).

#### 2.2. Preparation of Ru/Al-SBA-15 catalysts

Initially, Al-SBA-15 composites were prepared by a two-step hydrothermal method.<sup>26</sup> Typically, 2.0 g of P123 was completely dissolved in 70 mL of HCl (2M) solution, and 4.0 mL of TEOS and 1.22 g of aluminum isopropoxide (Si/Al ratio of 3:1) were then added to this mixture. After vigorous stirring for 24 h, the mixture was then transferred into an autoclave and kept at 100 °C for another 24 h. Then, the pH value of the cooled mixture was adjusted in the neutral range using the ammonia-water solution. Further, the mixture was subjected to hydrothermal treatment by placing it in an autoclave (100 °C) for another 24 h. The resultant product of mesoporous Al-SBA-15 supports was then collected by subsequent centrifugation and calcination at 550 °C for 6 h. These supports were denoted as AS-x, and x refers to the Si/Al molar ratio in the raw materials. Further, the Ru/AS-x catalysts were synthesized by the impregnation method. Briefly, 0.2 g of AS-x support was added to the RuCl<sub>3</sub> aqueous solution (2.0 mL, 0.02 mol/L) and stirred for 5 h. Further, the solvent was extracted by applying the rotary evaporation method. The as-synthesized catalysts were then dried and reduced under H<sub>2</sub> atmosphere at 500 °C for 2 h to obtain Ru/AS-x catalysts.

#### 2.3. Characterization

Powder X-ray diffraction (XRD) patterns at a low  $(2\theta = 0.5 \sim 5^{\circ})$  as well as wide angles  $(2\theta = 10 \sim 80^{\circ})$  with 2 $\theta$  scanning rate at 5 $^{\circ}$ /min were recorded on a Smart La X'Pert Pro powder X-ray diffractometer (Eindhoven, Netherlands). The mesostructured parameters were determined by N<sub>2</sub> adsorption-desorption isotherms based on Brunauer-Emmett-Teller (BET) analysis using a Quantachrome instruments analyzer (Florida, USA). The samples were degassed at 200 °C for 5 h before testing. The pore size distribution and the mean pore diameter of the samples were calculated using desorption isotherms by the BJH method. The specific surface area and the pore volumes of the samples were calculated from N<sub>2</sub> adsorption-desorption isotherms by the BET

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method. Transmission electron microscope (TEM) images, as well as its high-resolution prototype (HR-TEM) images, were captured on a JEM 2100F instrument (Tokyo, Japan). The amounts of ruthenium, silicon, and aluminum in the catalysts were measured using inductively coupled plasma optical emission spectroscopy (ICP-OES, PerkinElmer 8300, Waltham, USA). NH<sub>3</sub>-TPD experiments were measured on a Micromeritics AutoChem 2920II instrument (Norcross, USA). Typically, the sample (120 mg) was placed into a U-shaped quartz tube. Then, it was heated from ambient temperature to 300 °C at 10 °C/min for drying pretreatment. Before cooling to 50 °C, the He gas was introduced (30 mL/min) for 2 h. Then, NH<sub>3</sub> (10%) and He were introduced to attain saturation. Subsequently, the He gas (30 mL/min) was switched and purged further for 1 h to remove  $NH_3$  from the sample completely. Finally, the temperature was increased to 700 °C at a rate of 10 °C/min under Helium (He) gas atmosphere to desorb NH<sub>3</sub>. <sup>27</sup>Al magic angle spinning (MAS) Nuclear Magnetic Resonance (NMR) spectra were recorded on an Agilent 600 DD2 spectrometer (Broadway Lubbock, Germany) operating at a Larmor frequency of 600 MHz for  ${\rm ^1H.\ ^{27}Al}$  experiments were carried out at a Larmor frequency of 156.25 MHz. Pyridine-FTIR spectral measurements were recorded using a Thermo Nicolet 380. The samples were dried at 400 °C for 2 h under 0.001 Pa, and pure pyridine vapor was instilled at 50 °C for 20 min. Finally, the FTIR spectra were recorded after evacuating the system at 150 and 400 °C.

#### 2.4. Catalytic performance

Typically, 0.03 g of catalyst, 0.3 g of p-phthalic acid and 25 mL of water were added to an autoclave (100 mL) equipped with a magnetic stirrer. It should be noted that strict anaerobic atmospheric conditions were maintained by hydrogen purging for 6 times with an initial hydrogen pressure adjusted to 5 MPa. Further, the reaction was conducted at a constant temperature (80 °C) for 2 h at the stirring speed of 1000 rpm. After the completion of the reaction, water in the mixture was removed by rotary evaporation, and then the product was dissolved using DMF. Further, the catalyst was centrifuged and washed before the next run. The product was analyzed by GC-FID (Echrom A90, Shanghai, China) equipped with a capillary column (HP-5, 30m×0.32mm×0.25µm, Agilent Technologies, Palo Alto, USA) to understand the product yield and the conversion efficiency. In addition to the catalytic performance efficiency, the cis-isomer selectivity of the resultant products was determined by <sup>1</sup>H NMR (Methyl sulfoxide-d<sub>6</sub>, 500 MHz).

#### 3. Results and discussion

#### 3.1. Characterization of supports and catalysts

The  $N_2$  adsorption-desorption isotherms of supports and catalysts were recorded to analyze their porosity and specific surface area (Fig. 1). All the samples have exhibited type-IV adsorption isotherms with an H1 hysteresis loop, indicating that these supports and catalysts possessed a mesoporous structure with narrow pore size distribution. With the incorporation of a small

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amount of aluminum into SBA-15, the final specific surface area of the catalyst was increased from 578 to 728 9hi 2/g1(Table 1) Enthies 1 and 2), due to which incorporated AI might introduce additional mesoporous and micropores in the support.<sup>27</sup> However, the specific surface area, pore volume, and area of the hysteresis loop of supports and catalysts decreased noticeably after further doping with aluminum in the mesoporous siliceous frameworks (Table 1 and Table S1), indicating that the excessive Al cluster was distorted in the pore channels.<sup>22</sup> To this end, the pore diameter distribution curves (Fig. 1B and 1D) have depicted that the pore diameters of AS-x (x = 50, 10, 5, 3, 1 and 0.5) and Ru/AS-x (x = 50, 10, 5 and 3) were at around 6.5 nm (Table 1 and Table S1), suggesting that ruthenium nanoparticles have not blocked the channels in Ru/AS-x (x = 50, 10, 5 and 3). Moreover, the pore diameter of Ru/AS-1 and Ru/AS-0.5 was smaller compared to that of the AS-1 and AS-0.5 and was centered at around 5.6 nm (Table 1 and Table S1). These consequences happened plausibly due to the partial aggregation of ruthenium nanoparticles inside the pore channels of AS-1 and AS-0.5. However, the large pore size of the solid supports favors the ease of mass transfer during the catalysis.



Fig. 1 Graphical representation showing the  $N_2$  adsorptiondesorption isotherms (A and C) and pore diameter distribution curves (B and D) of various designed supports and Ru-based catalysts, respectively.

Furthermore, the Si/Al ratio and ruthenium content in these catalysts were determined by ICP-OES analysis (Table 1). It was evident from the experimental results that the tendency of the Si/Al ratio of the catalysts was consistent with the theoretical amounts of the raw material composition. This indicated that most of the added aluminum was incorporated in the composites. On the other hand, the ruthenium content was nearly identical with the theoretical value (2.0 wt.%), signifying no loss of ruthenium during the preparation process.

As shown in Fig. 2A and 2B, the XRD patterns of supports (SBA-15, and AS-x) and catalysts (Ru/SBA-15 and Ru/AS-x) at a low angle exhibited three distinct planes (100), (110), and (200), corresponding to p6mm hexagonal symmetry of mesoporous

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materials, indicating that the supports and catalysts possessed highly ordered mesoporous structures.<sup>24</sup> It was also observed from the XRD diffraction patterns that the peak intensities were decreased with the increase of aluminum content in the mesoporous materials (Fig. 2A and 2B). At the reduced Si/Al ratio to 0.5, the mesoporous supports were completely disordered, which exhibited excessive aluminum damage to the mesoporous architectures, as shown in Fig. 1 and 3F.

As depicted in Fig. 2C, the XRD patterns in the wide-angle of supports resulted in the broad peak at a  $2\theta$  of around  $22.5^{\circ}$ , indicating the characteristic patterns of the amorphous silica.<sup>28</sup> Moreover, no prominent characteristic peaks of alumina in the

wide-angle XRD patterns illustrated that the aluminar thad in the aluminar thad in the second second

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Entry	Catalyst	Si/Al ratio <sup>a</sup>	S <sub>BET</sub> (m²/g)	D <sub>p</sub> (nm)	V (cm³/g)	Ru (wt.%)ª	Mean D <sub>Ru</sub> b (nm)
1	Ru/SBA-15	-	578	6.6	1.2	2.0	4.3
2	Ru/AS-50	90	728	6.5	1.0	2.0	5.8
3	Ru/AS-10	7.8	611	6.6	0.9	1.9	6.0
4	Ru/AS-3	1.9	558	6.5	0.9	2.0	5.9
5	Ru/AS-1	0.8	368	5.6	0.6	1.9	7.7
6	Ru/AS-0.5	0.5	252	5.6	0.4	1.9	14.5

<sup>a</sup> Si/Al molar ratio and ruthenium content in catalysts were determined by ICP-OES; <sup>b</sup> The mean diameters of ruthenium nanoparticles were estimated by TEM; D<sub>p</sub> and V represent pore diameter and pore volume, respectively.



**Fig. 2** Graphical representation showing the low angle XRD patterns of supports (A) and catalysts (B), and the wide-angle XRD patterns of the supports (C) (SBA-15 and AS-x) and catalysts (D) (Ru/SBA-15 and Ru/AS-x).

Moreover, Fig. 3 displays TEM images of various designed Ru/AS-x catalysts and AS-3, as well as the HR-TEM image and the particle size distribution of ruthenium nanoparticles of Ru/AS-3. It was observed from the TEM observations that all the catalysts whose Si/Al ratio higher than 1 retained their original ordered mesoporous structure (Fig. 3A-E). And the mean size of ruthenium nanoparticles (Ru/AS-x; x = 50, 10, and 3) was around 6.0 nm (Table 1). With the decrease of the Si/Al ratio, the well-ordered structure of the catalysts and the uniform distribution of the Ru metal were reduced. The ruthenium nanoparticles tended to be



**Fig. 3** TEM images of (A) Ru/SBA-15, (B) Ru/AS-50, (C) Ru/AS-10, (D) Ru/AS-3, (E) Ru/AS-1, (F) Ru/AS-0.5 and (G) AS-3; (H) HR-TEM image of Ru/AS-3; (I) Graphical representation showing the particle size distribution of ruthenium nanoparticles in the sample Ru/AS-3.

aggregated (Fig. 3F). Moreover, the mean size of ruthenium nanoparticles in Ru/AS-0.5 reached 14.5 nm, in which their dispersion was related to the low pore volume and specific surface area of the AS-0.5 (Table 1 and Table S1, Entry 6). Typically, the relatively large pore diameter and high dispersion of the ruthenium nanoparticles in the solid supports are highly beneficial for the hydrogenation reaction. In addition, the crystal

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plane spacing, *i.e.*, 0.21 nm of nanoparticles, could correspond to the characteristic plane (101) of ruthenium (JCPDS 06-0663, Fig. 3H). These results were in the explicit agreement with the wide-angle XRD data (Fig. 2D).

<sup>27</sup>AI MAS NMR spectroscopy was used to further explore the aluminum chemical environment in the bulk phase of Ru/AS-x (Fig. 4A). The broad and strong peaks at 53, 28, and 0 ppm could correspond to the tetrahedral coordinated Al (Al<sub>tetra</sub>), pentahedral coordinated AI (AIpenta), and octahedral coordinated Al (Al $_{\text{octa}}$ ), respectively.<sup>26, 32</sup> Al $_{\text{tetra}}$  originated from the Al metals in SBA-15 framework.<sup>26, 32</sup> Al<sub>penta</sub> is regarded to be distorted from the framework and exists as the amorphous silica-alumina phase.<sup>33, 34</sup> Al<sub>octa</sub> is attributed to extra-framework amorphous alumina phase.<sup>26, 32</sup> With the decrease in the Si/Al ratio below 3, the Alpenta content of the catalysts increased gradually (Fig. 4A), indicating to the enhancement of disordered arrangement (Fig. 2B and 3B-F). However, combined with the low angle XRD (Fig. 2B) and TEM (Fig. 3B-E), Ru/AS-x (x refers to 50, 10, 3, and 1) still held well-ordered SBA-15 architecture. Besides SBA-15 phase, amorphous alumina phase and amorphous silica-alumina phase also existed, but were homogeneously distributed (Fig. 2B, 3B-E, and 4A). But, for Ru/AS-0.5, the ordered SBA-15 structure ultimately disappeared (Fig. 2B and 3F), implying that the amorphous silica-alumina phase composed of Alpenta and Alocta became the main phases in Ru/AS-0.5, while Al<sub>tetra</sub> species might exist as fragment or pre-phase of SBA-15. These consequences eventually resulted in the low specific surface area and pore volume of AS-0.5 and Ru/AS-0.5 (Table 1 and Table S1). In general, the  $AI_{tetra}$  and  $AI_{octa}$  tend to form strong Brønsted and Lewis acid sites, respectively.<sup>35</sup> In addition, the Al<sub>penta</sub> mainly contributes to the weak Lewis acid sites.34



**Fig. 4** Analysis of bulk phase and surface acidity properties of Ru/SBA-15 and Ru/AS-x through <sup>27</sup>AI MAS NMR, NH<sub>3</sub>-TPD, and Pyridine-FTIR measurements. (A) <sup>27</sup>AI MAS NMR spectra were obtained for analyzing the chemical environment of aluminum in Ru/AS-x bulk phase; (B) NH<sub>3</sub>-TPD profiles showing the strength distribution of weak, medium and strong solid acid sites on catalyst surface; Pyridine-FTIR spectra of various designed catalysts at (C) 150 °C and (D) 400 °C. B, Bronsted-bound pyridine; L, Lewis-bound pyridine.

Indeed, the desorption temperature of  $NH_3$  represents the strength of solid acid sites. From the NH<sub>3</sub>-TPD profiles of the catalysts in Fig. 4B, the peak below 200 °C, could correspond to the NH<sub>3</sub> physical absorption and weak acid sites. The peak at the desorption temperature range from 200 °C to 400 °C could be ascribed to the medium acid sites stemming from Al<sub>tetra</sub>.<sup>35</sup> The peak ranging from 400 °C to 600 °C could be contributed by the strong acid sites originating from the Al<sub>octa</sub>.<sup>35</sup> As shown in Fig. 4B, all catalysts exhibited weak acid sites. Both Ru/SBA-15 and Ru/AS-50 catalysts have also shown no significant desorption peak at around 270 °C, implying that the number of medium acidic sites was relatively lesser. It should be noted that with the increase of Al content, Ru/AS-10, Ru/AS-3, Ru/AS-1, Ru/AS-0.5 catalysts showed distinct peaks at about 270 °C and 450 °C, indicating that these catalysts possessed medium and strong acid sites. In addition, the desorption temperature of Ru/AS-3 shifted to slightly higher than other catalysts, implying that it could exhibit relatively strong medium and strong acid sites. Moreover, as shown in Table 2, Ru/AS-3 possessed the most substantial amount of total acid sites and strong acid sites among these samples. These acid sites help to create more transition metal activity sites.<sup>36, 37</sup> Meanwhile, the strong acidic catalyst could enhance the interaction with the aromatic ring and promote the uneven distribution of electrons to activate the aromatic ring. Furthermore, the strong acid sites are also beneficial to improve the ability of the catalyst toward the hydrogenolysis/isomerization and hydrogenation.

**Table 2.** Determination of acidity sites of the catalyst using the  $NH_3$ -TPD approach.

	Catalust		Acid sites (mmol/g)						
Entr	y Calaly	/SL	Weak	Med	Medium		g Total		
1	Ru/SBA	-15	0.38	0.1	.4	-	0.52		
2	Ru/AS-50		0.86	0.51		-	1.37		
3	Ru/AS-	Ru/AS-10		0.56		0.21	1.60		
4	Ru/AS	Ru/AS-3		0.6	50	0.32	1.92		
5	Ru/AS-1		0.47	0.8	33	0.13	1.43		
6	Ru/AS-	0.5	0.25	0.3	37	0.18	0.80		
"_"	represents	no	distinct	acid	site	was	detected.		

Pyridine-FTIR spectra of catalysts were recorded in the wavenumber range 1700-1300 cm<sup>-1</sup> at 150 °C and 400 °C to investigate the effect of doped aluminum on surface acid type of catalyst (Fig. 4C and 4D, respectively). The peaks at 1443 cm<sup>-1</sup> and 1575 cm<sup>-1</sup> could be ascribed to Lewis acid sites, and the peak at 1542 cm<sup>-1</sup> could be attributed to pyridine adsorbed onto the Brønsted acid sites. Moreover, the peak at 1488 cm<sup>-1</sup> could be attributed to adsorbed pyridine onto both Brønsted and Lewis acid sites, and the vibrations of hydrogen-bonded pyridine were in the

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wavenumber range of 1590-1600 cm<sup>-1</sup>. <sup>38</sup> As shown in Fig. 4C and 4D, no significant peak at 1542 cm<sup>-1</sup> and a small peak at 1488 cm<sup>-1</sup> indicate that there existed only a slight amount of Brønsted acid sites on the surface of the catalyst. Furthermore, distinct peaks at 1443 cm<sup>-1</sup> and 1575 cm<sup>-1</sup> implied that the surface of these catalysts mainly had shown Lewis acid properties. Under the same catalyst composition and test conditions, the peak strength after degassing at 150 and 400 °C could represent the relative amount of total and strong acid, respectively. Moreover, as shown in Fig. 4C, the catalyst Ru/AS-3 exhibited the highest peak intensity, attributing to higher total acidity amounts than other catalysts. After degassing at 400 °C, the peaks of Ru/SBA-15 were nearly disappeared (Fig. 4D), representing that this catalyst has no strong Lewis acid sites. In addition, all the peaks were retained in Ru/AS-x samples, indicating the presence of strong L acid sites compared to Ru/SBA-15. In particular, Ru/AS-3 still maintained the highest relative peak intensity, which could probably possess excellent catalytic performance.

#### 3.2. Catalytic performance of Ru/AS-x for the hydrogenation of pphthalic acid and other substrates

The hydrogenation results of p-phthalic acid using Ru/AS-x

catalysts are listed in Table 3. With the decrease of the Si/Al ratio, the conversion rate was increased initially and then are duced while the selectivity was slightly changed. Moreover, the Ru/AS-3 catalyst achieved the best catalytic performance with 84.0% CHDA selectivity and complete conversion of p-phthalic acid in the aqueous solution (80 °C, 2h). The extraordinary catalytic performance could be ascribed to the excellent structure characteristics, well-dispersed ruthenium nanoparticles, and strong Lewis acid sites. Initially, the appropriate textural properties, including size as well as the volume of pores, and final BET specific surface area (Table 1) could favor the mass transfer process during the catalysis. Moreover, under optimal Si/Al ratio condition, Ru/AS-3 exhibited the strong Lewis acid sites (Fig. 4B-D) (mainly originating from support), which could improve the ruthenium nanoparticles activity through influencing the ruthenium electronic structure.<sup>34, 37</sup> On the other hand, Lewis acid sites could interact with -COOH functional group to adsorb and carbon atoms of the aromatic ring of the substrate molecules to make it highly electron-deficient and thus activated.<sup>15</sup> Finally, ruthenium nanoclusters activated by Lewis acid sites could effectively adsorb and dissociate hydrogen to form ruthenium hydride active species, which inserted into the carbon-carbon double bonds in the benzene ring to generate cyclohexane.<sup>39</sup>

	<b>Table 3.</b> Reaction results of hydrogenation of <i>p</i> -phthalic acid with catalysts.								
Entry	Catalyst	Temperature (°C)	Time (h)	Metal Loading (wt.%)	Conv. (%) <sup>a</sup>	<i>Cis</i> -isomer Selectivity (%) <sup>b</sup>			
1	Ru/SBA-15	80	2.0	2.0	32.1	78.0			
2	Ru/AS-50	80	2.0	2.0	50.5	80.3			
3	Ru/AS-10	80	2.0	1.9	71.4	83.3			
4	Ru/AS-3	80	2.0	2.0	100.0	84.0			
5	Ru/AS-1	80	2.0	1.9	81.3	81.5			
6	Ru/AS-0.5	80	2.0	1.9	26.7	80.0			
7	Rh <sub>70</sub> Pt <sub>30</sub> /SBA-15 <sup>9</sup>	80	2.0	5.6	74.3	40.0			
8	Ru/Al <sub>2</sub> O <sub>3</sub> <sup>11</sup>	140	1.5	5.0	95.4	-			
9	Rh <sub>0.5</sub> Ni <sub>1.5</sub> /Al <sub>5</sub> -SBA-15 40	140	6.0	2.0	69.8	-			
<sup>a</sup> Conver	sions were calculated by GC. <sup>t</sup>	<sup>o</sup> Selectivity was calculat	ed by NMR.						

Compared with the reported Rh<sub>70</sub>Pt<sub>30</sub>/SBA-15,<sup>9</sup> Ru/Al<sub>2</sub>O<sub>3</sub>,<sup>11</sup> and Rh<sub>0.5</sub>Ni<sub>1.5</sub>/Al<sub>5</sub>-SBA-15 <sup>40</sup> catalysts the Ru/AS-3 used in the present study exhibited excellent catalytic performance under mild reaction conditions (80 °C) with a lower noble metal loading of 2.0 wt.%. The supports such as SBA-15 and Al<sub>2</sub>O<sub>3</sub> in the Rh<sub>70</sub>Pt<sub>30</sub>/SBA-15  $^{\rm 9}$  and Ru/Al\_2O\_3  $^{\rm 11}$  catalyst showed none and weak Lewis acid sites, respectively, resulting in their relatively weak catalytic activity. It should be noted that the Ru/AS-x sample is different from  $Rh_{0.5}Ni_{1.5}/Al_5$ -SBA-15  $^{40}$  in terms of the synthesis and performance of the catalyst. The aluminum-doped silica support (Al<sub>5</sub>-SBA-15),<sup>40</sup> was synthesized by using the impregnation method with aluminum solution, which resulted in the incorporation of only a few aluminum species in the composite. Owing to the facts of the low amount of aluminum atoms and weak interactions between aluminum species and SBA-15 framework, both Al<sub>5</sub>-SBA-15 and  $Rh_{0.5}Ni_{1.5}/Al_5$ -SBA-15 exhibited little and weak acid sites as evident from their Pyridine-FTIR spectra.40 Nevertheless, in this work, we anticipated that various characteristic attributes,

including the amount of aluminum, catalytic stability, and acidity property, were noticeably different owing to the hydrothermalassisted synthesis. Abundant aluminum species were introduced into the composites Ru/AS-x through strong interaction, and offered the increased number of total and strong Lewis acid sites (Fig. 4C and 4D). In addition, the Ru/AS-3 catalyst system possessed excellent pore structure, evenly dispersed ruthenium nanoparticles, high total acidity amounts, (Table 2, entry 4) and strong Lewis acid sites (Fig. 4D), which significantly improved its hydrogenation performance of p-phthalic acid in water. Notably, the ruthenium is more beneficial in terms of cost than rhodium and platinum, and could potentially be well-suited to explore them for industrial applicability.

In addition, it should be noted that Ru/AS-3 catalyst could be reused at least eleven times with complete p-phthalic acid conversion and no significant loss of CHDA selectivity (Fig. 5). Moreover, after fourteen times of its utilization, it could still be able to maintain a high p-phthalic acid conversion (90.2%) and cisPublished on 18 March 2020. Downloaded by University of Reading on 4/8/2020 10:05:59 AM

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isomer selectivity (83.3%). As depicted in Fig. S1, it was evident that the fabricated Ru nanoparticles were not aggregated in the Ru/AS-3-U catalyst, after reusing for fourteen times. Moreover, the mean size of Ru nanoparticles decreased to 2.8 nm, might be due to leaching of Ru during the high speed agitation, which could also be a reason for the reduction of catalytic performance. Besides, the content of Ru in the Ru/AS-3 catalyst declined from 2.0 to 1.64 wt.% during the above reusing process, confirmed through the ICP analysis. Together, these experimental results indicated that the excellent reusability is due to its exceptional stability of the catalyst in water. Moreover, the exceptional stability in water is advantageous as the provided reaction conditions in terms of temperature and type of solvent are similar to the hydrothermalassisted synthetic conditions.

Ru/AS-3 catalyst was also applied in the hydrogenation of benzoicdicarboxylic acids and their ester derivatives in the aqueous solution. As shown in Table 4, all the substrates could be completely hydrogenated under mild conditions. Indeed, the *o*-phthalic acid was relatively easy to undergo hydrogenation and obtain higher selectivity in comparison to the *m*-phthalic acid and *p*-phthalic acid. However, the compound, *m*-phthalic acid, could

be completely hydrogenated within 4 h at 80 °C or 2h at 100 °C of 2h at 100 °C of 2h solubility of these benzoic dicarboxylic acids in water. The solubility parameters of *o*-phthalic acid, *p*-phthalic acid, and *m*-phthalic acid included 0.6 g, 1.5 mg, and nearly insoluble per 100 mL at 20 °C in water, respectively.<sup>40</sup> In addition, the Ru/AS-3 catalyst has exhibited the highest catalytic activity toward the hydrogenation of dimethyl phthalate, dimethyl isophthalate, and dimethyl terephthalate under further mild conditions. It is worth mentioning that the dimethyl phthalate is completely hydrogenated with the *cis*-isomer selectivity up to 100%.



**Fig. 5** The catalytic recyclability of Ru/AS-3 for the hydrogenation of *p*-phthalic acid in water (conversion (A) and cis-isomer selectivity (B)).

Table 4. Catalytic performance of Ru/AS-3 for the hydrogenation of other substrates in aqueous solution.

Entry	Substrate	Temperature (°C)	Time (h)	Conversion (%)	Cis-isomer Selectivity (%)
1	o-phthalic acid	60	1	100.0	92.6
2	<i>m</i> -phthalic acid	80	2	64.5	80.2
3	<i>m</i> -phthalic acid	80	4	100.0	76.6
4	<i>m</i> -phthalic acid	100	2	100.0	80.0
5	<i>p</i> -phthalic acid	80	2	100.0	84.0
6	Dimethyl phthalate	50	1	100.0	100.0
7	Dimethyl isophthalate	60	1	100.0	75.0
8	Dimethyl terephthalate	60	1	100.0	83.3

#### 3.3. Reaction mechanism

To explore the mechanism of *p*-phthalic acid hydrogenation in aqueous solution, we monitored the reaction process by <sup>1</sup>H NMR spectra. In addition, the isotope labeling experiments were also carried out to reveal the source of hydrogen in the product. In comparison, <sup>1</sup>H NMR spectra (Fig. S2) of standard substances trans-CHDA ( $\delta$  = 12.08 (s, 2H), 2.13~2.17 (m, 2H), 1.87~1.93 (m, 4H) and 1.27~1.36 ppm (m, 4H)) and *cis*-CHDA ( $\delta$  = 12.08 (s, 2H), 2.35~2.40 (m, 4H), 1.66~1.74 (m, 4H) and 1.54~1.61 ppm (m, 4H)) were tested. As anticipated, hydrogenation of *p*-phthalic acid in H<sub>2</sub>O with catalyst Ru/AS-3 yielded the product with peak area ratio 2:2:4:4 at the above four chemical shifts (Fig. S3). As shown in Fig. S4 and S5, after processing for 10 or 30 min, the hydrogenation was not completed, and no organic intermediate could be detected while only the end product CHDA was formed, indicating that the whole aromatic ring endured instantaneous hydrogenation, with first double bond hydrogenation as the control step in this reaction. Meanwhile, as shown in Fig. S6, the reaction of *p*-phthalic acid in D<sub>2</sub>O obtained CHDA with partial deuteration, indicating that solvent H<sub>2</sub>O high effectively participates in this hydrogenation system.

To further investigate the specific source of hydrogen atoms in the CHDA, the hydrogenation of p-phthalic acid- $d_4$  was performed using H<sub>2</sub>O and D<sub>2</sub>O as the solvents, respectively, and the products were esterified to dimethyl 1,4-cyclohexanedicarboxylate.<sup>41</sup> Fig. S7 shows <sup>1</sup>H NMR spectra of standard substances trans-dimethyl 1,4cyclohexanedicarboxylate ( $\delta$  = 3.60 (s, 6H), 2.22~2.24 (m, 2H), 1.97~1.99 (m, 4H) and 1.33~1.40 ppm (m, 4H)) and cis-dimethyl 1,4cyclohexanedicarboxylate ( $\delta$  = 3.61 (s, 6H), 2.38~2.42 (m, 2H), 1.79~1.86 (m, 4H) and 1.57~1.63 ppm (m, 4H)). As shown in Fig. S8 and S9, the hydrogenation of p-phthalic acid- $d_4$  in H<sub>2</sub>O and D<sub>2</sub>O yielded the products with peak area ratio approximately 6:2:0:4 and 6:1:0:2 at the above four chemical shifts, respectively. The disappeared peaks at 1.79~1.86 ppm could be attributed to the four D atoms originating from deuterated *p*-phthalic acid, indicating that they were chemical equivalent in the product, CHDA. From the results of Fig. S8 and S9, it was evident that three H atoms from H<sub>2</sub> and other three from  $H_2O$  were derived for the hydrogenation of pphthalic acid. The H atoms from both H<sub>2</sub> and H<sub>2</sub>O were furnished at  $\alpha$  and  $\beta$  positions of -COOH equally for the hydrogenation reaction.

Based on the above isotope labeling studies and the catalyst characterization results, one probable mechanistic pathway for

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hydrogenation of *p*-phthalic acid on catalyst Ru/AS-3 in aqueous solution is proposed in Scheme 2. Initially, the interactions of Lewis acid sites with the carboxyl groups of substrates and aromatic ring result in the attraction of substrates (*p*-phthalic acid) onto Ru/AS-3 surface. Upon addition of H<sub>2</sub>, the heterolytically dissociated hydrogen molecule could generate Ru-H and proton with the cooperation of Ru and *p*-phthalic acid. Moreover, the proton generated from H<sub>2</sub> might be associated initially with the carboxylic acid group, and then form H<sub>3</sub>O<sup>+</sup> with water. The hydrogenation reaction might take place *via* insertion of ruthenium hydride on carbon-carbon double bond of the aromatic ring followed by protonation to generate cyclohexa-1,3-diene-1,4-

dicarboxylic acid intermediate. Following that, the introduction of hydride at one of the  $\alpha$  positions of -COOH and protonation of another double bond lead to the 1,4-addition intermediate cyclohex-2-ene-1,4-dicarboxylic acid, which could be further hydrogenated quickly to the final products. Notably, *cis* 1,4addition resulted in the *cis* diastereomer of the final product, while the *trans*-1,4-addition generated *trans* diastereomer. In addition, the peak integral resulted in *trans*-dimethyl 1,4cyclohexanedicarboxylate (Fig. S8 and S9), which was not following the above rule for *cis*-isomer, indicating that the *p*-phthalic acid underwent another reaction pathway to form *trans*-CHDA.



**Scheme 2.** The plausible mechanism of hydrogenation of *p*-phthalic acid in the aqueous solution. The bottom planes stand for the catalyst surfaces, while the purple multisphere with Ru indicates ruthenium nanoparticle and yellow hemisphere with the letter L refers to Lewis acid site. Green arrows indicate the directions of electron transfer. Combined with the proton (red) from  $H_3O^+$ , Ru-H (green), which originated from heterolytic dissociation of  $H_2$  on ruthenium nanoparticles conducts the hydrogenation. That is the reason for the equal contribution of Ru-H and proton derived from  $H_2$  and  $H_2O$ , respectively.

#### 4. Conclusions

In summary, a series of Ru/AS-x catalysts were synthesized by hydrothermal and impregnation methods. Among them, the Ru/AS-3 catalyst showed excellent catalytic performance for the hydrogenation of *p*-phthalic acid in aqueous solution under mild conditions. The conversion efficiency and cis-isomer selectivity were up to 100.0 and 84.0%, respectively. Furthermore, this catalyst exhibited extraordinary stability, which could be reused at least fourteen times with a slight loss of the conversion and constant selectivity. In particular, the catalytic efficiencies of these composites happened to be favorable at a lower metal loading amount in this catalyst and with milder reaction conditions compared to current reported studies. Moreover, this catalyst also exhibited excellent catalytic performance in the hydrogenation of benzoic dicarboxylic acids and their ester derivatives in water. Unique structural properties, textural attributes and highly dispersed ruthenium nanoparticles significantly enabled excellent catalytic performance of the composites. The tunable acidity of the catalyst and the strong Lewis acid sites by altering the doping aluminum played critical roles in the catalytic process. In addition, hydrogen and water each contributed half of the hydrogen atoms for this hydrogenation reaction. Finally, a plausible mechanistic pathway for hydrogenation of p-phthalic acid on the catalyst Ru/AS-3 in aqueous solution was proposed. Together, this study offers a new perspective for an eco-friendly fabrication of catalyst as well as

its utilization for the hydrogenation of the aromatic ring in the aqueous solution.

#### **Conflicts of interest**

There are no conflicts to declare.

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Ru/Al-SBA-15 catalyst with excess Lewis acid sites displayed excellent efficiency (100%), high *cis*-isomer selectivity (84%), and exceptional stability towards hydrogenation of p-phthalic acid in water.