

*Supporting information*

**Tetranuclear Ruthenium Cluster Anchored on Polyoxometalates Catalyzes  
Hydrogenation of Methyl Levulinate in Water**

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**Materials**

All solvents were dried by the standard methods and then stored in the Schlenk flask under the N<sub>2</sub> atmosphere. Ethanol (99%), methanol (99%), hydrochloric acid (35-38%), sulfuric acid (98%), n-hexane (99%), 1,4-dioxane (99%), acetonitrile (99%), tetrahydrofuran (99%) and dimethyl sulfoxide (99%) were all provided by Titan General Reagent Co., Ltd. Methyl Levulinate (99%) and deuterium oxide (99%) were provided by Shanghai Adamas Reagents Co., Ltd. Sodium tungstate dihydrate (Na<sub>2</sub>WO<sub>4</sub>·2H<sub>2</sub>O, 99%), 1,4-cyclohexadiene (98%) and Ru/C (5wt%) were bought from Aladdin Industrial Corporation. Ruthenium chloride trihydrate (RuCl<sub>3</sub>·3H<sub>2</sub>O, 99%) were purchased from Kunming Boren Metal Materials Co., Ltd. Aluminum trichloride hexahydrate (AlCl<sub>3</sub>·6H<sub>2</sub>O, 99%) were obtained from Sinopharm Chemical Reagent Co., Ltd. (Shanghai, China). High-purity H<sub>2</sub> (99.5%) and N<sub>2</sub> (99.999%) were provided by Shanghai Pujiang Specialty Gases Co., Ltd.

**Synthesis of H<sub>5</sub>AlW<sub>12</sub>O<sub>40</sub> and K<sub>5</sub>AlW<sub>12</sub>O<sub>40</sub>**

H<sub>5</sub>AlW<sub>12</sub>O<sub>40</sub> were synthesized according to the previous literature.<sup>1</sup> Na<sub>2</sub>WO<sub>4</sub>·2H<sub>2</sub>O (20.1g) and 80ml H<sub>2</sub>O were put in a 250 ml round-bottomed flask, stirred until it was

dissolved, and then hydrochloric acid (about 5-6 ml) was added dropwise into the solution until the pH was 7.7 (monitored by pH meter). The final mixture was heated and refluxed. Thereafter, aluminum chloride hexahydrate (2.66 g) was dissolved in 16ml deionized water and was added dropwise by means of the addition funnel into the reflux solution of the previous step with a drop rate of 5-6 drops/min. With the addition of aluminum chloride solution, the mixed solution will appear slightly turbidity. After all the  $\text{AlCl}_3$  has been added, the solution was kept at reflux for 1 h, cooled to room temperature, and filtered. The final pH should be approximately 7. Then 7.52 g sulfuric acid were added to the mixture, stirred constantly at the same time. The final measurement of the pH value was 0, and then additional 5 drops of concentrated sulfuric acid was added, eventually the solution was refluxed for 6 days. After the reaction, cooled it to room temperature, filtered it to get supernatant **1**. Concentrated  $\text{H}_2\text{SO}_4$  (30 mL) was added to the reaction mixture. After cooling with ice bath and transferring to a 500-mL separatory funnel, 100 mL of diethyl ether was added, and the mixture was shaken carefully. After settling until three layers separated, the bottom (heteropolyanion etherate) layer was collected. The combined etherate layers were dried through rotary evaporation to give the crude product of  $\text{H}_5\text{AlW}_{12}\text{O}_{40}$ . (Yield: 13.4 g, 92%) The crude product was then recrystallized in water. (Yield: 9.1 g, 58%) Solid-State  $^{27}\text{Al}$  NMR (130.3 MHz)  $\delta_{\text{Al}} = 71.93$  ppm (Fig. 3a).

$\text{K}_5\text{AlW}_{12}\text{O}_{40}$  was also prepared in a similar method except the supernatant **1** obtained above was rotary evaporated to remove the solvent ( $\text{H}_2\text{O}$ ), and then potassium chloride was added to extract the  $\text{K}_5\text{AlW}_{12}\text{O}_{40}$  from the solution, and then the final product was obtained by filtration, drying and recrystallization. (Yield: 9.6 g, 62%) Solid-State  $^{27}\text{Al}$  NMR (130.3 MHz)  $\delta_{\text{Al}} = 72.18$  ppm (Fig. 3b).

### Synthesis of $[\text{Ru}_2(\eta^6\text{-C}_6\text{H}_6)_2\text{Cl}_4]$

The hydrated ruthenium trichloride (1.0 g) and 1,4-cyclohexadiene (5 ml) were dissolved in 50 ml anhydrous ethanol in a 100 ml Schlenk bottle, heated it to reflux for 4h under nitrogen atmosphere, and then cooled it down.<sup>2</sup> Finally brown-red precipitate

was obtained at the bottom. The precipitate was filtered with suction and washed with ice anhydrous methanol for 5-6 times until the unreacted 1,4-cyclohexadiene was removed. The resulting solid was dried under vacuum. Finally the  $[\text{Ru}_2(\eta^6\text{-C}_6\text{H}_6)_2\text{Cl}_4]$  was obtained and stored it under nitrogen. (Yield: 0.865g, 90%)  $^1\text{H}$  NMR (400 MHz,  $\text{d}_6\text{-DMSO}$ )  $\delta_{\text{H}} = 4.02$  (s, 12H,  $2\text{C}_6\text{H}_6$ ).

### Synthesis of $[\text{Ru}_4(\eta^6\text{-C}_6\text{H}_6)_4\text{H}_6]\text{Cl}_2$

$[\text{Ru}_2(\eta^6\text{-C}_6\text{H}_6)_2\text{Cl}_4]$  (150 mg) and water (20 ml) were charged in a 100 ml polytetrafluoroethylene liner, placed it in an autoclave, filled with 6 MPa hydrogen, and reacted at 55 °C for 14 h. After the reaction, the autoclave was put in an ice-water bath to cool, and then hydrogen was slowly released to obtain a violet liquid with a small amount of precipitate at the bottom. After the precipitate was removed by centrifugation, then the upper layer of liquid was collected, and then the solvent was removed by rotary evaporation, and the resulting solid was finally dried it under vacuum. Since the cation  $[\text{Ru}_4(\eta^6\text{-C}_6\text{H}_6)_4\text{H}_6]^{2+}$  reacted readily with a trace of oxygen to give the tetrahydride cation  $[\text{Ru}_4(\eta^6\text{-C}_6\text{H}_6)_4\text{H}_4]^{2+}$ , the resulting dark violet powder was marked as  $[\text{Ru}_4(\eta^6\text{-C}_6\text{H}_6)_4\text{H}_4]\text{Cl}_2$ ,<sup>3</sup> which was proved by  $^1\text{H}$  NMR spectra and abbreviated as Ru<sub>4</sub>. (Yield: 82 mg, 66%).  $^1\text{H}$  NMR (600 MHz,  $\text{D}_2\text{O}$ )  $\delta_{\text{H}} = -17.4$  (s, H, Ru-H),  $\delta_{\text{H}} = -15.1$  (s, H, Ru-H, n=6), 5.96 (s, 6H,  $\text{C}_6\text{H}_6$ ) (Fig. 4a, left).

### Catalyst characterization

X-ray diffraction (XRD) recorded the diffraction patterns of catalysts, with  $2\theta$  in the range of 5-75°, on a SmartLab diffractometer (Rigaku D/MAX 2550 VB/PC) equipped with a 9 kW rotating anode Cu source at 45 kV and 100 mA (5-80°, 0.2 s<sup>-1</sup>). The Brunauer-Emmett-Teller (BET) equation and the Barrett-Joyner-Halenda (BJH) model were respectively used to calculate the BET specific surface area. A Magna 550 Fourier transform infrared spectrometer was used to obtain the Fourier transform infrared (FT-IR) spectrum of samples in the range of 4000-400 cm<sup>-1</sup>. A Netzsch STA 449C thermal analyzer was used to conduct the thermogravimetric analysis (TGA). The

FT-IR spectra of the adsorbed pyridine on various catalysts were obtained as follows: first, the samples were fully ground into uniform powder and pressed into wafers at 3.0 MPa. Then, the disc was put into a quartz IR container with calcium fluoride (CaF<sub>2</sub>) windows and placed into an IR cell connected to a sealed adsorption system. After this, the samples were heated to 400 °C under a vacuum to remove the moisture. The background spectrum of samples was gathered by a Nicolet Model 710 spectrometer after the cell cooled to 25 °C. Subsequently, pyridine was introduced in the form of steam at 25 °C, until the sample reached adsorption equilibrium. Then, the evacuation of pyridine was performed at 25 °C for 60 min. Finally, the spectrum was gathered at room temperature, and the previously recorded background was subtracted. The acid center is quantified by the following two expressions 1 and 2

$$C_B = k_B A_{1540} \frac{\pi}{IMEC_B} \left( \frac{r^2}{\omega} \right) A_{1540} \quad (1)$$

$$C_L = k_L A_{1450} \frac{\pi}{IMEC_L} \left( \frac{r^2}{\omega} \right) A_{1450} \quad (2)$$

$C_B$  and  $C_L$  denote the concentration of Brønsted and Lewis acid sites in  $\mu\text{mol} \cdot \text{g}^{-1}$ ;  $A_{1450}$  and  $A_{1540}$  are the integral areas of bands at 1450 and 1540  $\text{cm}^{-1}$  in the FT-IR spectra of pyridine adsorbed.  $K_B$  and  $K_L$  are the molar extinction constants for the Brønsted and Lewis acid sites;<sup>4</sup> 2.53 and 1.98  $\text{cm} \mu\text{mol}^{-1}$  were respectively substituted into the integrated molar extinction coefficients (IMEC) of the Brønsted and Lewis acid sites;  $r$  and  $\omega$  denote the radius (cm) and weight (g) of the wafer, respectively.

The <sup>1</sup>H NMR spectra were recorded on a Ascend 600 instrument by using D<sub>2</sub>O as solvents and TMS as reference, while the Solid-State <sup>1</sup>H NMR using adamantane as reference. The Solid-State <sup>27</sup>Al NMR spectra were recorded on 500 MHz/AVANCEIII instrument by using AlCl<sub>3</sub> as reference. Chemical shifts ( $\delta$ ) were given in parts per million and coupling constants (J) in hertz. The elemental analysis of C, H was performed on an Elementar Vario EI III elemental analyzer and ICP-AES analysis of Ru, Al and W on Agilent 725ES, respectively. Scanning Electron Microscopy was conducted on GeminiSEM 500 field emission scanning electron microscopy

(FESEM). The pH value of aqueous solution was measured by Mettler Toledo FE28 - Standard pH meter using a LE 438 pH electrode. The UV diffuse reflectance spectrum at normal temperature and pressure is determined by uv-2600 UV spectrophotometer (Shimadzu company, Japan). BaSO<sub>4</sub> was used as reference material.

### Typical reaction procedure

A typical methyl levulinate hydrogenation reaction was carried out as follows: 10 mg of catalyst, 2 mmol of substrate, and 4 ml of H<sub>2</sub>O were added to an autoclave. The assembled device was then filled with 6.0 MPa hydrogen and reacted at 25 °C for 1 h. After the reaction, the autoclave was placed under an ice-water bath. Finally, the catalyst was isolated with centrifugation and the supernatant was analyzed by gas chromatography (GC-128). Catalyst was then reused for the next run after washing three times with water and diethyl ether respectively, followed by drying under vacuum.

The products were qualitatively analyzed by an Agilent 6890/5973 GC–mass spectrometry (MS) system equipped with a HP-5MS column (30 m long, 0.25 mm i.d., and 0.25 μm film thickness) and a flame ionization detector (FID). For quantitative measurements, analysis was performed on a GC-128 gas chromatograph equipped with a free fatty acid phase capillary column (30 m long, 0.32 mm i.d., and 0.33 μm film thickness) and an FID, and 1-butanol was used as the internal standard. In the hydrogenation of ML, the conversion (Con.), selectivity (Sel.) were calculated by the following expressions 3 and 4, respectively. The GVL and 4-HPTM were detected in ML hydrogenation under the present conditions, and the content of each component can be given according to equation 5.

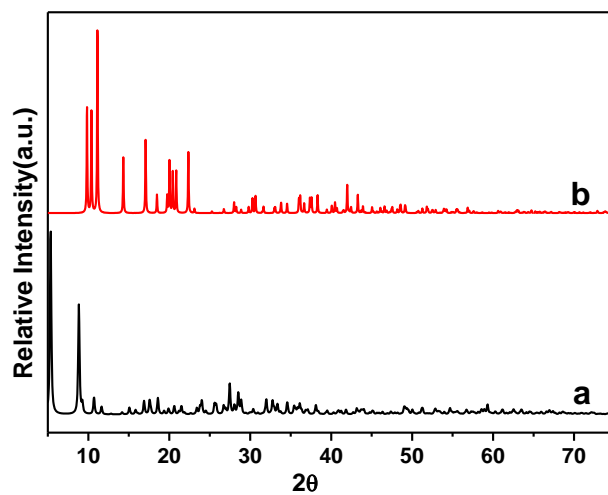
$$Con. (\%) = \frac{\text{Amount of Methyl levulinate converted (mole)}}{\text{Initial amount of Methyl levulinate (mole)}} \times 100\% \quad (3)$$

$$Sel. (\%) = \frac{\text{Amount of product (mole)}}{\text{Amount of Methyl levulinate converted (mole)}} \times 100\% \quad (4)$$

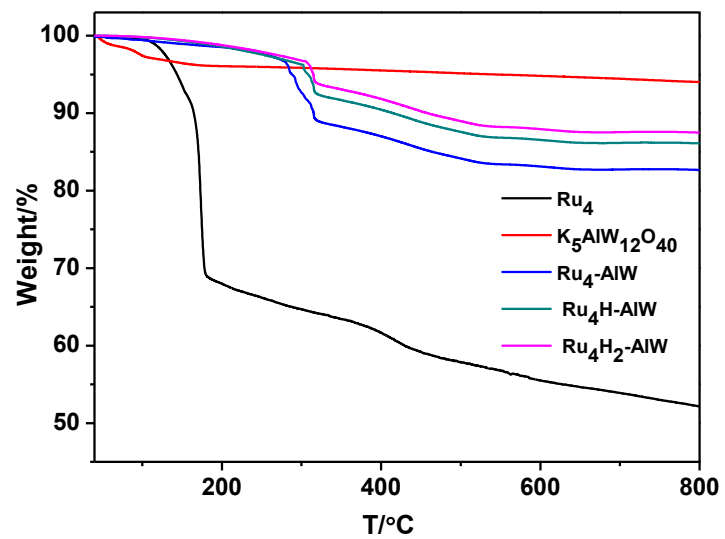
$$Content (\%) = \frac{\text{Amount of component (mole)}}{\text{Total amount of components (mole)}} \times 100\% \quad (5)$$

**Table S1.** Elemental analysis of the catalysts.

Catalysts		C	H	Al	W	Ru	Molecular formulas
Ru <sub>4</sub> -AlW	Cal. (%)	15.41	1.51	0.57	47.19	21.62	[Ru <sub>4</sub> (η <sup>6</sup> -C <sub>6</sub> H <sub>6</sub> ) <sub>4</sub> H <sub>4</sub> ] <sub>2.5</sub>
	Found (%)	15.32	1.56	0.52	46.6	20.71	[AlW <sub>12</sub> O <sub>40</sub> ]
Ru <sub>4</sub> H-AlW	Cal. (%)	13.36	1.33	0.62	51.11	18.73	[Ru <sub>4</sub> (η <sup>6</sup> -C <sub>6</sub> H <sub>6</sub> ) <sub>4</sub> H <sub>4</sub> ] <sub>2</sub>
	Found (%)	13.98	1.42	0.60	50.77	17.84	H[AlW <sub>12</sub> O <sub>40</sub> ]
Ru <sub>4</sub> H <sub>2</sub> -AlW	Cal. (%)	10.93	1.12	0.68	55.76	15.33	[Ru <sub>4</sub> (η <sup>6</sup> -C <sub>6</sub> H <sub>6</sub> ) <sub>4</sub> H <sub>4</sub> ] <sub>2.5</sub>
	Found (%)	11.27	1.25	0.65	52.37	16.21	H <sub>2</sub> [AlW <sub>12</sub> O <sub>40</sub> ]

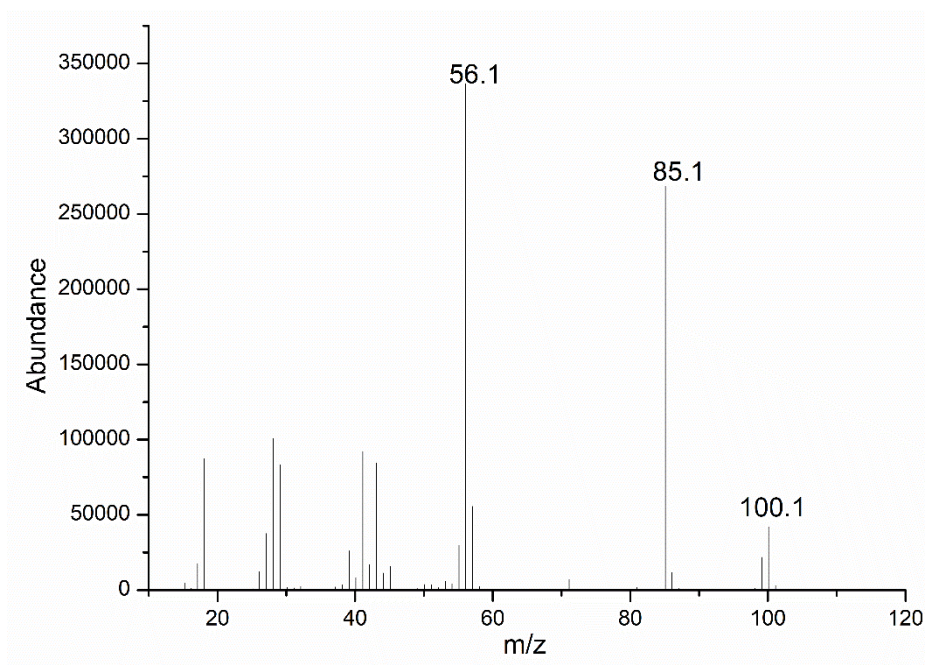


**Fig. S1.** The simulated X-ray diffraction patterns of the a)  $K_5AlW_{12}O_{40}$ ,<sup>1</sup> b)  $Ru_{4.3}$ .<sup>3</sup>

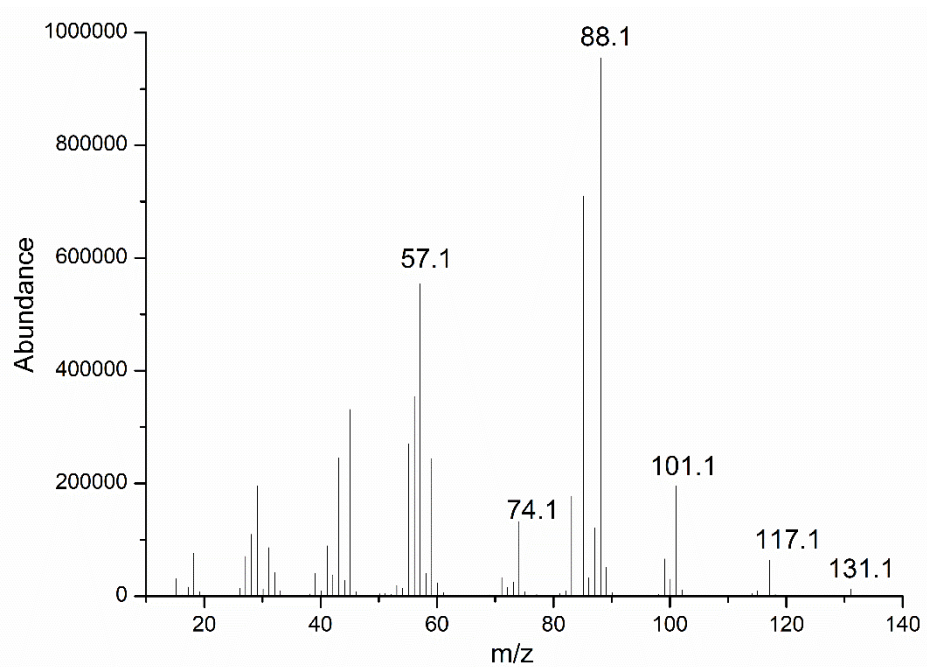


**Fig. S2.** The TG curves of the catalysts.

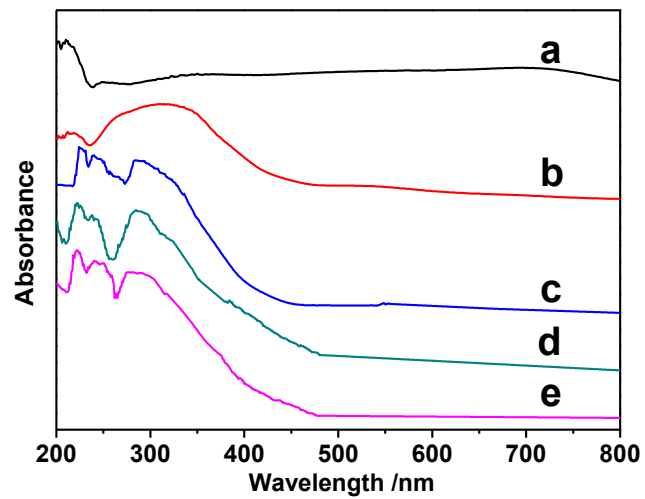




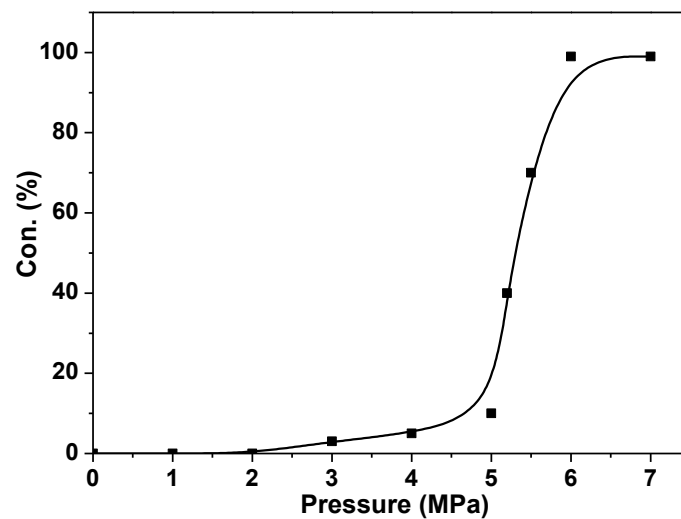
**Fig. S3.** MS spectra of GVL ( $m/z = 100.1$ ).



**Fig. S4.** MS spectra of 4-HPTM ( $[M-H]^+$ ,  $m/z = 131.1$ ).



**Fig. S5.** DR UV-vis spectra of the a) Ru<sub>4</sub>, b) K<sub>5</sub>AlW<sub>12</sub>O<sub>40</sub>, c) Ru<sub>4</sub>H<sub>2</sub>-AlW, d) Ru<sub>4</sub>H-AlW, e) Ru<sub>4</sub>-AlW.



**Fig. S6.** Effect of H<sub>2</sub> pressure on hydrogenation of ML. Reaction conditions: ML 2.0 mmol, catalyst Ru<sub>4</sub>-AIW 10.0 mg, water 4.0 ml, 25°C, 1h.

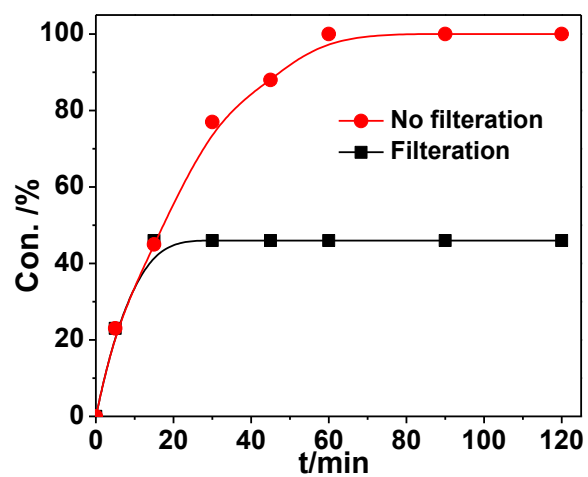
**Table S2.** Performance of various solvents on the ML hydrogenation over Ru<sub>4</sub>-AIW catalyst.

Entries	Solvent	Con.(%)	Sel.(%)	
			4-HPTM	GVL
1	CH <sub>3</sub> OH	100	-	100
2	CH <sub>3</sub> CH <sub>2</sub> OH	100	-	100
3	H <sub>2</sub> O	100	-	100
4	CH <sub>3</sub> CN	0	-	-
6	n-hexane	23	-	99
7	1,4-dioxane	76	-	99
8	DMSO	54	-	99

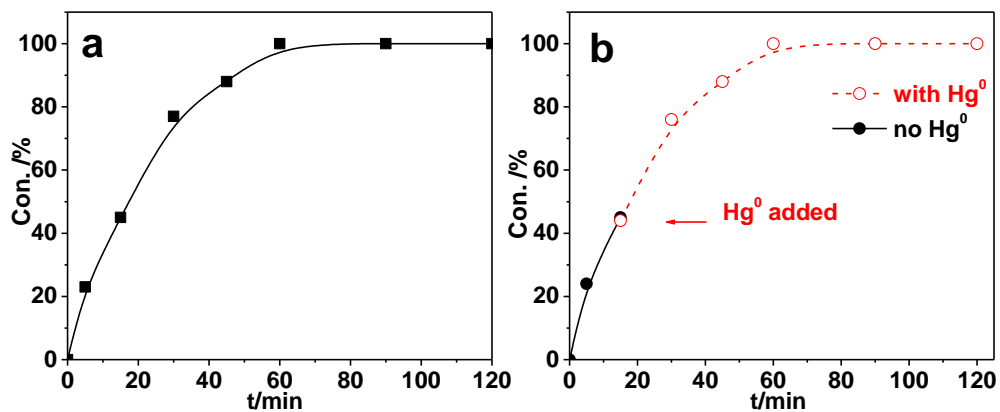
Reaction conditions: ML 2.0 mmol, Ru<sub>4</sub>-AIW 10.0 mg, solvent 4.0 ml, 25°C, H<sub>2</sub>(6.0 MPa), 1h.

**Table S3.** Acidic properties of different catalysts

Entries	Catalyst	$C_B$ ( $\mu\text{mol} \cdot \text{g}^{-1}$ )		$C_L$ ( $\mu\text{mol} \cdot \text{g}^{-1}$ )
		Calculated	Found	
1	$\text{H}_5\text{AlW}_{12}\text{O}_{40} \cdot 15\text{H}_2\text{O}$	Calculated	1588	-
		Found	1618	28
2	$\text{Ru}_4\text{H}_2\text{-AlW}$	Calculated	505	-
		Found	488	106
3	$\text{Ru}_4\text{H-AlW}$	Calculated	253	-
		Found	228	153
4	$\text{Ru}_4\text{-AlW}$	Calculated	-	-
		Found	-	206

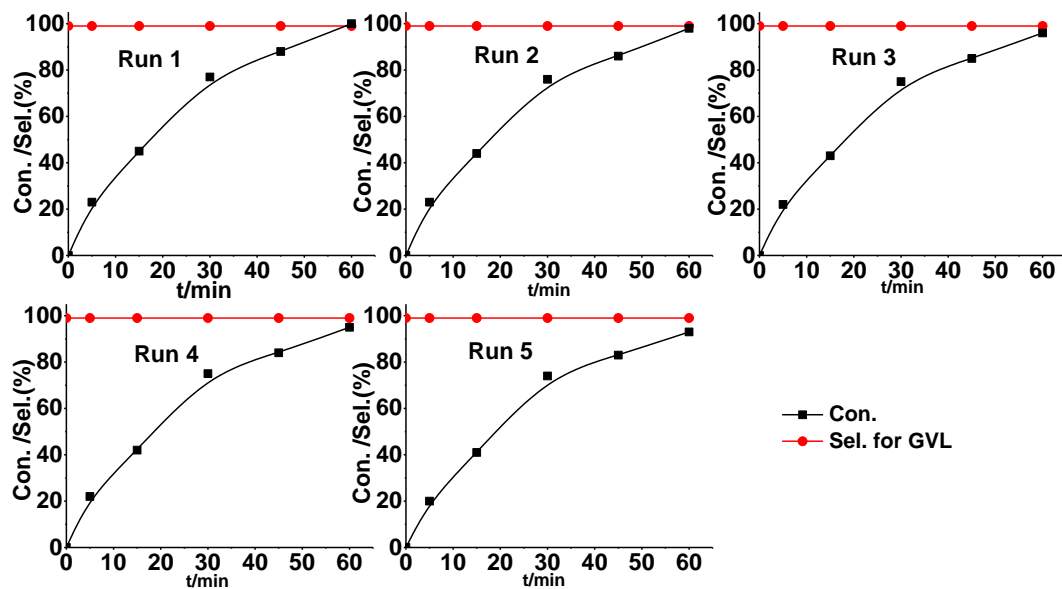


**Fig. S7.** Hot filtration curve. Reaction conditions: ML (2.0 mmol), Ru<sub>4</sub>-AIW (10mg), H<sub>2</sub>O (4.0 ml), 25°C, 6.0 MPa H<sub>2</sub> pressure.

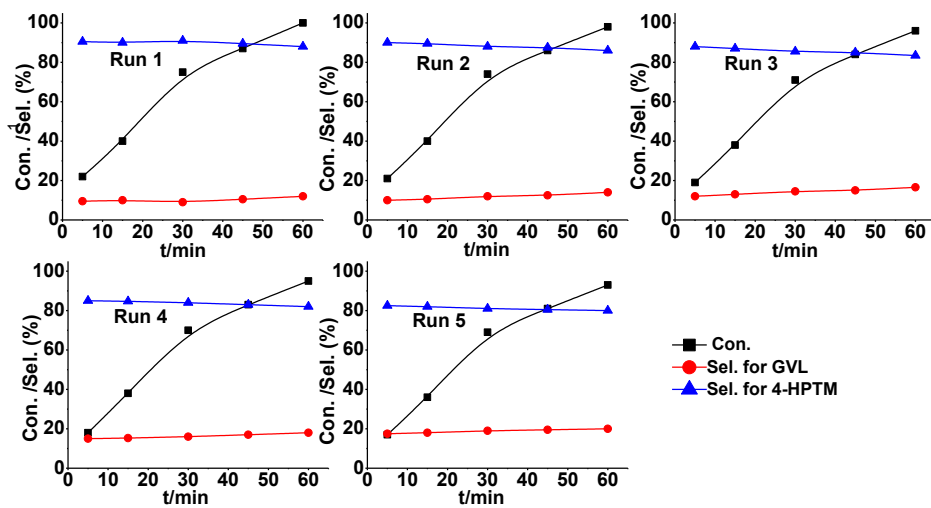


**Fig. S8.** (a) ML conversion/time profiles. Reaction conditions: ML (2.0 mmol), Ru<sub>4</sub>-AlW (10mg), H<sub>2</sub>O (4.0 ml), 25°C, 6.0 MPa H<sub>2</sub> pressure. (b) Hg<sup>0</sup> poisoning test. Reaction was carried out under the identical conditions but Hg<sup>0</sup> (0.2 g) was added after the reaction started for 20 min.

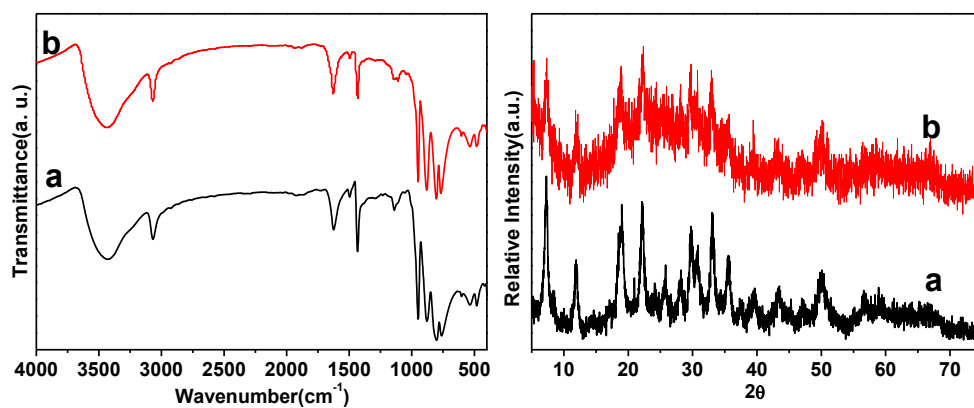




**Fig. S9.** Time profiles of ML hydrogenation over Ru<sub>4</sub>-AIW catalyst in each run. Reaction conditions: ML (2.0 mmol), catalyst(10mg), H<sub>2</sub>O (4.0 ml), 25°C, 6.0 MPa H<sub>2</sub> pressure.



**Fig. S10.** Time profiles of ML hydrogenation over Ru<sub>4</sub>H<sub>2</sub>-AIW catalyst in each run. Reaction conditions: ML (2.0 mmol), catalyst(10mg), H<sub>2</sub>O (4.0 ml), 25°C, 6.0 MPa H<sub>2</sub> pressure.



**Fig. S11.** FT-IR Spectra and X-ray diffraction patterns of the used catalysts a) Ru<sub>4</sub>-AIW  
b) Ru<sub>4</sub>H<sub>2</sub>-AIW

### References

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