

## Supporting Information

### **Aqueous phase hydrogenation of levulinic acid to 1,4-pentanediol**

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## 1. Preparation of catalysts

M/SiO<sub>2</sub> (M = Rh, Ir, Pt, Pd, Ru) catalysts were prepared according to Tomishige *et al.*<sup>1</sup> by the incipient wetness impregnation of SiO<sub>2</sub> (Qingdao Ocean Chemical Ltd., BET surface area 509 m<sup>2</sup> g<sup>-1</sup>) with the aqueous solution of RhCl<sub>3</sub> • 3H<sub>2</sub>O, H<sub>2</sub>IrCl<sub>6</sub> • 6H<sub>2</sub>O, H<sub>2</sub>PtCl<sub>6</sub> • 6H<sub>2</sub>O, PdCl<sub>2</sub> and RuCl<sub>3</sub> • 3H<sub>2</sub>O respectively then dried at 393 K for 12 h. Mo modified M/SiO<sub>2</sub> catalysts were prepared by incipient wetness impregnation after the drying procedure with aqueous solution of (NH<sub>4</sub>)<sub>6</sub>Mo<sub>7</sub>O<sub>24</sub> • 4H<sub>2</sub>O. For comparison, MoO<sub>x</sub>/SiO<sub>2</sub> was also prepared by impregnation SiO<sub>2</sub> with aqueous solution of (NH<sub>4</sub>)<sub>6</sub>Mo<sub>7</sub>O<sub>24</sub> • 4H<sub>2</sub>O. The content of Mo in MoO<sub>x</sub>/SiO<sub>2</sub> was controlled as 0.485% which is same as that in the 4%Rh-MoO<sub>x</sub>/SiO<sub>2</sub> (Mo/Rh = 0.13). All catalysts were dried at 393 K overnight then calcined in air at 773 K for 3 h. To facilitate the comprehension, the noble metal contents in the catalysts are denoted by their weight percentage. For example, 4% Rh-MoO<sub>x</sub>/SiO<sub>2</sub> accounts for the Rh-MoO<sub>x</sub>/SiO<sub>2</sub> catalyst with Rh content of 4% by weight.

## 2. Activity test

The reaction was carried out in a 316L stainless steel tubular flow reactor described in literature<sup>2, 3</sup>. Before the reaction, the catalysts were reduced *in-situ* in the reactor by flowing hydrogen from the bottom at 160 mL min<sup>-1</sup> at 573 K and 6 MPa for 2 h. After cooling down to reaction temperature (353 K), the aqueous solution of biomass derived carboxylic acid or  $\gamma$ -valerolactone (GVL) was feed into the reactor from the bottom by a HPLC pump along with hydrogen at a flow rate of 60 mL min<sup>-1</sup>. The

products from the reactor tube passed through a gas-liquid separator, and became two phases. The gaseous products flowed through a back pressure regulator to maintain the pressure in reaction system and were analyzed on-line by an Agilent 6890N GC. CO<sub>2</sub> in the gaseous products was analyzed by a Thermal Conductivity Detector (TCD) equipped with an Alltech HAYESEP DB 100/120 packed column (30 feet, 1/8 inch O.D., 2.0 mm I.D.). Alkanes in the gaseous products were analyzed with a flame ionized detector (FID) equipped with an Rt<sup>®</sup>-Q-BOND capillary column (30 m, 0.32 mm I.D., 10µm film). Liquid products were drained from the gas-liquid separator after reaction for 6 h and analyzed by another Agilent 6890N GC equipped with a HP-INNOWAX capillary column (30 m, 0.25 mm I.D., 0.5 µm film) and FID detector.

### 3. Characterization

#### 3.1 XRD

XRD patterns of different catalysts were obtained by a PW3040/60X' Pert PRO (PANalytical) diffractometer equipped with a Cu K<sub>α</sub> radiation source ( $\lambda=0.15432$  nm) at 40 kV and 40 mA. Figure S2 shows the XRD patterns of 4% Rh/SiO<sub>2</sub> and 4% Rh-MoO<sub>x</sub>/SiO<sub>2</sub> catalysts after reduction in hydrogen flow at at 573 K for 2 h. From them, we can only see the peaks of SiO<sub>2</sub> support and metallic Rh. According to this result, 473 K is enough for the reduction the Rh species to metallic state. From the XRD patterns of different 4% Rh-MoO<sub>x</sub>/SiO<sub>2</sub> catalysts, no peak of Mo or its oxides was observed, indicating that the Mo species is well dispersed on the catalysts. By Scherrer's equation, the average Rh particle sizes on 4% Rh-MoO<sub>x</sub>/SiO<sub>2</sub> catalysts

were estimated. From the results illustrated in Table S4, the modification of 4% Rh/SiO<sub>2</sub> with Mo increases the size of Rh particles at low Mo/Rh atomic ratio (< 0.25). With the further increase of Mo/Rh atomic ratio, such a effect becomes less evident. After being used for the aqueous phase hydrogenation of acetic acid for 30 h (the reaction conditions were shown in Figure S1), there is no evident change for the average size of Rh particles on 4% Rh-MoO<sub>x</sub>/SiO<sub>2</sub> (Mo/Rh = 0.13) catalyst.

### 3.2 CO chemisorption

The metal dispersions of Rh on different catalysts were measured with a Micromeritics AutoChem II 2920 Automated Catalyst Characterization System by the molar ratios of the amounts of CO chemisorption to Rh in the catalysts. These values correspond to the ratios of surface Rh atoms to total Rh atoms assuming that the stoichiometry of adsorbed CO to surface metal atom is one. Before each test, the sample was heated in He flow at 423 K for 1 h to remove the physically adsorbed water. Then, the sample was reduced in H<sub>2</sub> flow at 573 K for 1 h, purged in He flow at 583 K for 1 h and cooled down in He flow to 313 K. After the stabilization of baseline, the CO adsorption was carried out by the pulse adsorption of 5% CO in He. From the data listed in Table S4, we can see that the modification of 4% Rh/SiO<sub>2</sub> with small amount of Mo decreases the available Rh sites on the catalyst, which can be explained by the increasing of Rh particle size and/or the coverage of Rh particles by MoO<sub>x</sub> species. At higher Mo content (Mo/Rh = 0.5), such effect becomes inconspicuous. This result can be rationalized by the weaker interaction between Rh and Mo species at high Mo/Rh atomic ratio. No significant difference were observed for the

accessible Rh sites on the fresh and used 4% Rh-MoO<sub>x</sub>/SiO<sub>2</sub> (Mo/Rh = 0.13) catalyst, which can be one reason for its stable performance for the hydrogenation of acetic acid.

### 3.3 TEM

The TEM images of the catalysts were obtained with a TECNAI G<sup>2</sup> Spirit FEI Transmission Electron Microscopy operated at 120 kV. Figure S4 shows the TEM images of 4% Rh/SiO<sub>2</sub>, fresh and used 4% Rh-MoO<sub>x</sub>/SiO<sub>2</sub> (Mo/Rh = 0.13) catalysts. From the statistic result shown in Table S4, the modification of 4% Rh/SiO<sub>2</sub> with small amount of Mo increases the average size of Rh particles. There is no evident variation on the Rh particles size on 4% Rh-MoO<sub>x</sub>/SiO<sub>2</sub> (Mo/Rh = 0.13) catalyst after being used for the aqueous phase hydrogenation of acetic acid for 30 h. These results are consistent with what we observed from the XRD and CO chemisorption experiments.

### 3.4 NH<sub>3</sub>-TPD

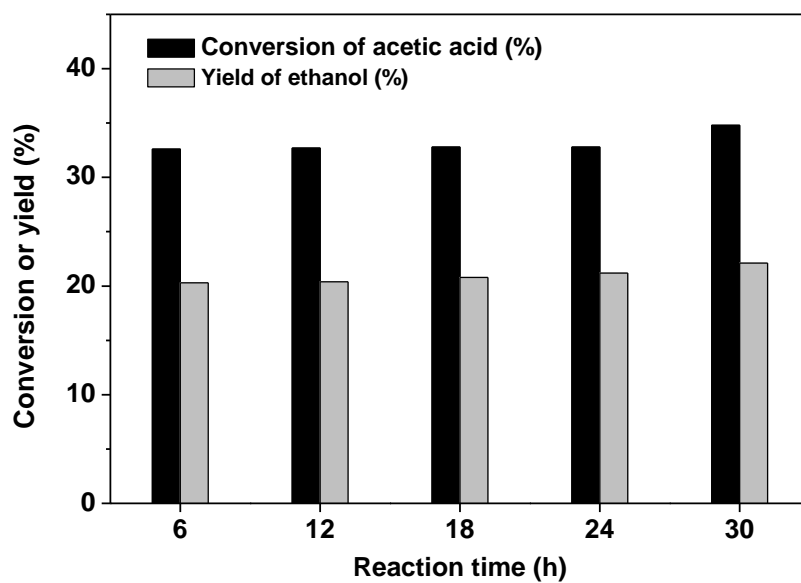
NH<sub>3</sub>-TPD tests of the fresh and used 4% Rh-MoO<sub>x</sub>/SiO<sub>2</sub> (Mo/Rh = 0.13) catalyst were carried out with a Micromeritics AutoChem II 2920 Automated Catalyst Characterization System. Before the test, the sample was reduced in H<sub>2</sub> flow at 573 K for 1 h, purged in He flow at 583 K for 30 min and cooled down in He flow to 373 K. After the saturated adsorption of NH<sub>3</sub>, the sample was heated at 373 K in He for 45 min to remove the physically adsorbed NH<sub>3</sub>. Desorption of NH<sub>3</sub> was conducted in He flow from 373 K to 973 K at a heating rate of 10 K min<sup>-1</sup>. The desorbed NH<sub>3</sub> molecules were detected by a mass spectrometry (MS) OminiStar equipped with the

software quadstar 32-bit. From the results listed in Table S5, the amount of acid sites over the 4% Rh-MoO<sub>x</sub>/SiO<sub>2</sub> (Mo/Rh = 0.13) catalyst decreased from 0.31 mmol g<sup>-1</sup> to 0.11 mmol g<sup>-1</sup> after being used in the hydrogenation of acetic acid for 30 h. However, no evident change was observed for the acetic acid conversion and ethanol yield over the 4% Rh-MoO<sub>x</sub>/SiO<sub>2</sub> (Mo/Rh = 0.13) catalyst (see Figure S1). According to these results, we believe that such a decrease in acidity has no evident effect on the performance of Rh-MoO<sub>x</sub>/SiO<sub>2</sub> catalyst for the hydrogenation of acetic acid. The decrease of NH<sub>3</sub> desorption over the used Rh-MoO<sub>x</sub>/SiO<sub>2</sub> catalyst can be attributed to the competitive adsorption of water and alcohol (or polyol) which were strongly adsorbed on the Rh-MoO<sub>x</sub>/SiO<sub>2</sub> catalyst during the reaction. As we know, water and alcohol (or polyol) have lone pair electron and can be consider as Lewis bases. Therefore, they can compete with NH<sub>3</sub> for acid sites.

### 3.5 ICP analysis

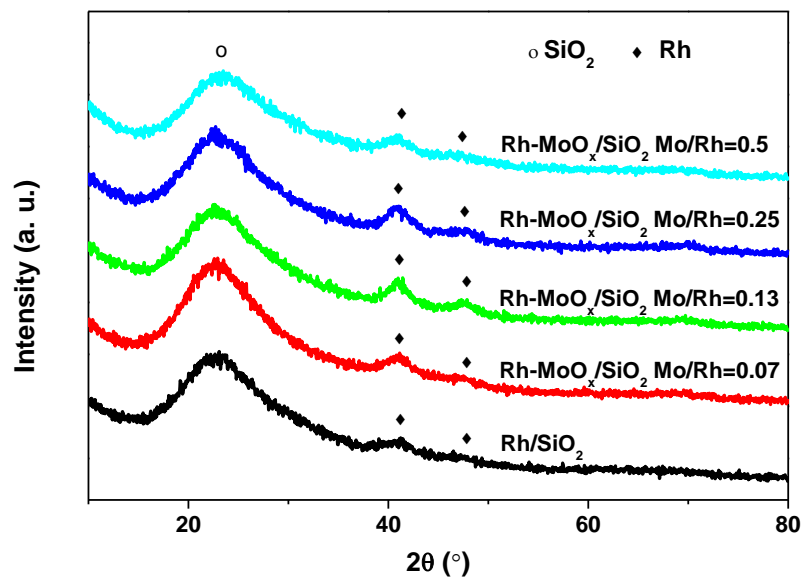
To check the chemical stability of the 4% Rh-MoO<sub>x</sub>/SiO<sub>2</sub> (Mo/Rh = 0.13) catalyst, the Rh and Mo concentration in the liquid product from the aqueous phase hydrogenation of acetic acid were determined by a Thermo IRIS Intrepid II XSP Inductively Coupled Plasma Optical Emission Spectrometer (ICP-OES). From the results shown in Table S6, no Rh was identified in the liquid product, indicating the Rh species is stable under the investigated condition. There is only very small amount of Mo (1.8 ppm) detected in the initial sample after 6 h reaction. With the further increasing of reaction time, no Mo species was identified in the liquid samples. The good chemical stability of the 4% Rh-MoO<sub>x</sub>/SiO<sub>2</sub> (Mo/Rh = 0.13) catalyst is another

reason for its stable performance for the hydrogenation of acetic acid under the investigated conditions.

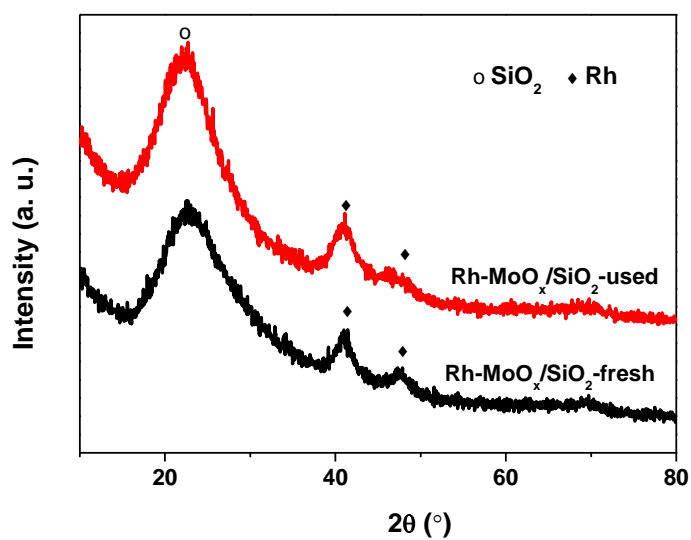


**Figure S1.** Acetic acid conversion and ethanol yield over 4% Rh-MoO<sub>x</sub>/SiO<sub>2</sub> (Mo/Rh = 0.13) catalyst as the function of reaction time. Reaction conditions: 353 K, 6 MPa, 0.5 g catalyst, 10 % acetic acid aqueous solution flow rate 0.08 mL min<sup>-1</sup>, H<sub>2</sub> flow rate 60 mL min<sup>-1</sup>.

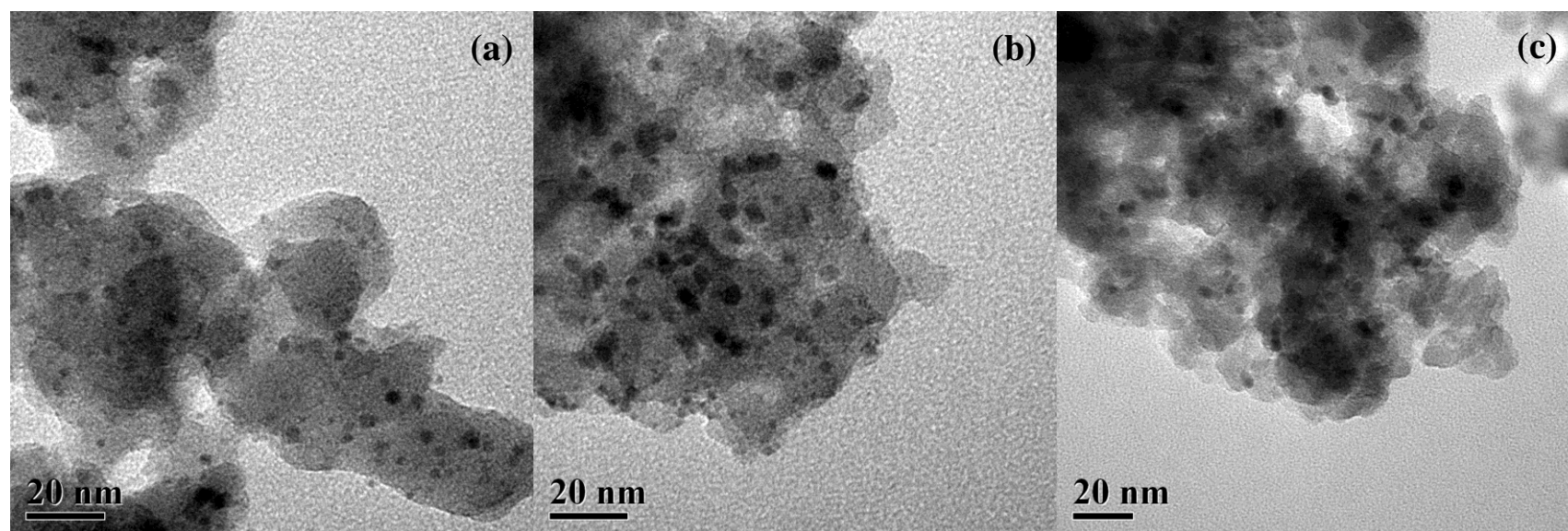




**Figure S2.** XRD patterns of the 4% Rh/SiO<sub>2</sub> and 4% Rh-MoO<sub>x</sub>/SiO<sub>2</sub> catalysts.



**Figure S3.** XRD patterns of the fresh and used 4% Rh-MoO<sub>x</sub>/SiO<sub>2</sub> (Mo/Rh = 0.13) catalysts.



**Figure S4.** TEM images of the 4% Rh/SiO<sub>2</sub> (a), fresh (b) and used (c) 4% Rh-MoO<sub>x</sub>/SiO<sub>2</sub> (Mo/Rh = 0.13) catalysts.

**Table S1.** Carbon yield and selectivity of gas phase products from the hydrogenation of levulinic acid or GVL over different catalysts. Reaction conditions: 353 K, 6 MPa, 2.0 g catalyst, 10 % levulinic acid (or GVL) aqueous solution flow rate 0.08 mL min<sup>-1</sup>, H<sub>2</sub> flow rate 60 mL min<sup>-1</sup>.

Entry	Catalyst	Mo/M atomic ratio (M: Rh, Ir, Pt, Pd, Ru)	Carbon yield of gas phase products from the hydrogenation of levulinic acid (%) <sup>a</sup>	Selectivity (%)					
				CO <sub>2</sub>	Methane	Ethane	Propane	Butane	Pentane
1	4%Rh/SiO <sub>2</sub>	0	0.7	0	57.5	0	0	9.6	32.9
2	4%Rh-MoO <sub>x</sub> /SiO <sub>2</sub>	0.07	3.6	0	34.4	0	0	0.1	75.5
3	4%Rh-MoO <sub>x</sub> /SiO <sub>2</sub>	0.13	8.2	0	11.9	0	0	1.6	86.5
4	4%Rh-MoO <sub>x</sub> /SiO <sub>2</sub>	0.25	1.9	0	18.4	0	0	2.8	78.8
5	4%Rh-MoO <sub>x</sub> /SiO <sub>2</sub>	0.50	0.6	0	28.0	17.3	0	2.9	51.8
6	MoO <sub>x</sub> /SiO <sub>2</sub>	—	0	0	0	0	0	0	0
7	4%Rh/SiO <sub>2</sub> + MoO <sub>x</sub> /SiO <sub>2</sub> <sup>b</sup>	0.13	0.4	0	56.3	0	0	8.4	35.3
8	4%Ir-MoO <sub>x</sub> /SiO <sub>2</sub>	0.13	8.6	0	12.3	0	0	0.1	87.6
9	4%Pt-MoO <sub>x</sub> /SiO <sub>2</sub>	0.13	0.3	0	100	0	0	0	0
10	4%Ru-MoO <sub>x</sub> /SiO <sub>2</sub>	0.13	0.6	0	57.9	0	0	0	42.1
11	4%Pd-MoO <sub>x</sub> /SiO <sub>2</sub>	0.13	0.2	0	25.8	0	0	74.2	0
12 <sup>c</sup>	4%Rh-MoO <sub>x</sub> /SiO <sub>2</sub>	0.13	0.9	0	15.6	0	0	6.2	78.2
13 <sup>c</sup>	4%Rh-MoO <sub>x</sub> /SiO <sub>2</sub>	0.13	0.2	0	20.3	0	0	31.4	48.3
14 <sup>d</sup>	4%Rh-MoO <sub>x</sub> /SiO <sub>2</sub>	0.13	0.2	0	46.4	0	0	13.5	40.1

a: Carbon yield of gas phase products (%) = Sum of carbon detected from the gas phase products in unit time/Carbon fed into the reactor in unit time × 100%.

b: 4%Rh/SiO<sub>2</sub> + MoO<sub>x</sub>/SiO<sub>2</sub> means the physical mixture of the 4%Rh/SiO<sub>2</sub> and MoO<sub>x</sub>/SiO<sub>2</sub> at the mass ratio of 1:1.

c: Experiment 12 and 13 were carried out with 0.5 g and 0.2g 4%Rh-MoO<sub>x</sub>/SiO<sub>2</sub> (Mo/Rh =0.13) catalyst, respectively.

d: Experiment 14 was carried out with 10% GVL aqueous solution.

**Table S2.** Carbon yield and selectivity of gas phase products from the hydrogenation of different biomass derived carboxylic acids over the 4%Rh-MoO<sub>x</sub>/SiO<sub>2</sub> (Mo/Rh = 0.13) catalyst. Reaction conditions: 353 K, 6 MPa, 2.0 g catalyst, 10% carboxylic acid aqueous solutions flow rate 0.08 mL min<sup>-1</sup>, H<sub>2</sub> flow rate 60 mL min<sup>-1</sup>.

Reactant	Carbon yield of gas phase product from the hydrogenation of different acids (%) <sup>a</sup>	Selectivity (%)			
		Methane	Ethane	Propane	Butane
Propanoic acid	11.9	1.4	3.1	95.5	0
Butanoic acid	6.0	1.7	0	4.5	93.8
Lactic acid	3.6	4.6	4.1	91.3	0
Malonic acid	1.9	42.6	9.8	47.6	0
Succinic acid <sup>b</sup>	1.1	13.7	1.1	6.0	79.1

a: Carbon yield of gas phase products (%) = Sum of carbon detected from the gas phase products in unit time/Carbon fed into the reactor in unit time × 100%.

b: 5% aqueous solution of succinic acid was used as feedstock.

**Table S3.** Results of the aqueous phase hydrogenation of levulinic acid over 4%Rh-MoO<sub>x</sub>/SiO<sub>2</sub> (Mo/Rh = 0.13) catalyst as the function of reaction time. Reaction conditions: 353 K, 6 MPa, 2.0 g catalyst, 10 % levulinic acid aqueous solution flow rate 0.08 mL min<sup>-1</sup>, H<sub>2</sub> flow rate 60 mL min<sup>-1</sup>.

Reaction time (h)	Conversion (%)	Selectivity (%) <sup>a</sup>					
		1,4-PeD	2-Peol	1-Peol	GVL	MTHF	Others
6	100	69.7	13.1	2.5	0.5	4.4	9.9
12	100	70.0	13.2	2.6	1.1	4.7	8.5
18	100	69.8	12.9	2.5	1.2	4.7	9.0
24	100	70.5	12.3	2.4	1.5	4.5	8.8
30	100	71.5	12.7	2.4	1.9	4.6	6.9

a: 1,4-PD = 1,4-Pentenediol; 2-Peol = 2-Pentanol; 1-Peol = 1-Pentanol; GVL =  $\gamma$ -valerolactone; MTHF = 2-Methyl-tetrahydrofuran; Others means alkanes and some unidentified products.

**Table S4** The average sizes and dispersion of Rh particles on 4% Rh/SiO<sub>2</sub> and 4% Rh-MoO<sub>x</sub>/SiO<sub>2</sub> catalysts estimated by XRD, TEM and CO chemisorption results.

Catalyst	Average size of Rh particles (nm)		Dispersion of Rh (%) <sup>c</sup>
	XRD <sup>a</sup>	TEM <sup>b</sup>	
Rh/SiO <sub>2</sub>	< 3.5	3.8±0.7	11.5
Rh-MoO <sub>x</sub> /SiO <sub>2</sub> (Mo/Rh = 0.07)	< 3.5	-	11.7
Rh-MoO <sub>x</sub> /SiO <sub>2</sub> (Mo/Rh = 0.13)	3.7	4.3±0.6	8.1
Rh-MoO <sub>x</sub> /SiO <sub>2</sub> (Mo/Rh = 0.25)	3.5	-	7.7
Rh-MoO <sub>x</sub> /SiO <sub>2</sub> (Mo/Rh = 0.5)	< 3.5	-	10.9
Rh-MoO <sub>x</sub> /SiO <sub>2</sub> (Mo/Rh = 0.13)	3.8	4.7±0.6	8.0

after being used for 30 h

a: Average size of Rh particles estimated by Scherrer's equation.

b: Average size of Rh particles estimated by TEM images of different catalysts.

c: The dispersions of Rh were calculated according to CO chemisorption results.

**Table S5** The amount of acid sites over the fresh and used 4% Rh-MoO<sub>x</sub>/SiO<sub>2</sub> (Mo/Rh = 0.13) catalysts measured by NH<sub>3</sub>-TPD.

Catalyst	Amount of acid site (mmol g <sup>-1</sup> )
Fresh 4% Rh-MoO <sub>x</sub> /SiO <sub>2</sub> (Mo/Rh = 0.13)	0.31
Used 4% Rh-MoO <sub>x</sub> /SiO <sub>2</sub> (Mo/Rh = 0.13)	0.11



**Table S6** The concentrations of Rh and Mo in the liquid products from the aqueous hydrogenation of acetic acid over the 4% Rh-MoO<sub>x</sub>/SiO<sub>2</sub> (Mo/Rh = 0.13) catalyst. Reaction conditions: 353 K, 6 MPa, 0.5 g catalyst, 10 % acetic acid aqueous solution flow rate 0.08 mL min<sup>-1</sup>, H<sub>2</sub> flow rate 60 mL min<sup>-1</sup>.

Reaction time (h)	Concentration (ppm)	
	Rh	Mo
6	0	1.8
12	0	0
18	0	0
24	0	0
30	0	0

## References

1. S. Koso, N. Ueda, Y. Shinmi, K. Okumura, T. Kizuka and K. Tomishige, *J. Catal.*, 2009, **267**, 89-92.
2. N. Li and G. W. Huber, *J. Catal.*, 2010, **270**, 48-59.
3. N. Li, G. A. Tompsett, T. Y. Zhang, J. A. Shi, C. E. Wyman and G. W. Huber, *Green Chem.*, 2011, **13**, 91-101.