Electronic Supplementary Information

SnO_2-isolated Pt_3Sn alloy on reduced graphene oxides: an efficient catalyst for selective hydrogenation of C=O in unsaturated aldehydes

Juanjuan Shi,[a] Mengyuan Zhang,[a] Weichen Du,[a] Wensheng Ning[b] and Zhaoyin Hou*[a]

[a] *Key Lab of Applied Chemistry of Zhejiang Province, Department of Chemistry, Zhejiang University, Hangzhou 310028, PR China. Tel./Fax: +86 571 88273283; E-mail: zyhou@zju.edu.cn*

[b] *State Key Laboratory Breeding Base of Green Chemistry-Synthesis Technology, Zhejiang University of Technology, Hangzhou 310032; E-mail: ningwensheng@zjut.edu.cn*

1. Experimental section

1.1 Synthesis of SnO_2/rGO hybrid

Graphene oxides (GO) was prepared by a modified Hummers method.[1] GO (0.25g C) and controlled amount of $SnCl_2\cdot 2H_2O$ were first dispersed in benzyl alcohol (100 mL) under stirring, the mixture was sonicated for 1 h and then heated in microwave oven (Sineo, MAS-II, 600 W, 2.45 GHz) at 185 °C for 6 minutes. The solid products were isolated by filtration and washed with ethanol and a large amount of water until free of Cl^-, and finally dried in a vacuum oven at 40 °C for 10 h.

1.2 Synthesis of Pt_3Sn/SnO_2/rGO catalyst

The above prepared SnO_2/rGO nanocomposite was added to a solution of H_2PtCl_6 in ethylene glycol (EG, 40.0 mL), and this solution was stirred for 30 minutes. The pH of above suspension was adjusted to 8.0 with 0.5 M

NaOH/EG. And then, the suspension was subjected to microwave irradiation for 5 minutes at 140 ºC, the final solid was recovered by centrifugation, washed with ethanol and dried in a vacuum oven at 40 ºC for 10 h.

1.3 Synthesis of Pt/rGO catalyst

As reference, Pt/rGO was also synthesized in similar method as above. GO (0.25g C) was first dispersed in benzyl alcohol (100 mL) under stirring, the mixture was sonicated for 1 h and then heated in microwave oven (Sineo, MAS-II, 600 W, 2.45 GHz) at 185 ºC for 6 minutes. The solid products (rGO) were isolated by filtration and washed with ethanol and a large amount of water, and finally dried in a vacuum oven at 40 ºC for 10 h. The rGO and controlled amount of H_2PtCl_6 solution were dispersed in EG (40.0 mL), and this solution was stirred for 30 minutes. The pH of above suspension was adjusted to 8.0 with 0.5 M NaOH/EG. And then, the suspension was subjected to microwave irradiation for 5 minutes at 140 ºC, the final solid was recovered by centrifugation, washed with ethanol and dried in a vacuum oven at 40 ºC for 10 h. Pt contents in the prepared Pt_3Sn/SnO_2/rGO and Pt/rGO were checked *via* inductively coupled plasma-atomic emission spectroscopy (ICP, Plasma-Spec-II spectrometer).

1.4 Characterization

X-ray diffraction (XRD) patterns were recorded on a diffractometer (RIGAKU D/MAX 255/PC) at 40 kV and 100 mA with Cu Kα radiation (λ=1.5406 Å). The crystalline size of Pt, SnO_2 or Pt_3Sn alloy was estimated using Scherrer's equation. Scanning transmission electron microscopy (STEM) and high angle annular dark field (HAADF) imaging were utilized to observe the image of individual particle at atomic resolution with an aberration corrected JEOL 2200FS (S)TEM operating at 300 kV, in addition with the capability of taking X-ray energy dispersive spectrometer (EDS) spectra from individual particles larger than 1 nm. X-ray photoelectron spectra (XPS) were recorded on a Perkin-Elmer PHI ESCA System. X-ray source was Mg standard anode (1253.6 eV) at 12 kV and 300 W.

1.5 Catalytic reactions

Selective hydrogenation of unsaturated aldehydes was performed in a 100 mL stainless steel autoclave with a Teflon inner layer. In a typical procedure, a certain amount of catalyst was first dispersed in 20.0 mL ethanol, and then a varying amount of substrates was added under stirring. After sealing the reactor, the air content was quickly purged by flushing with H_2 for several times. The autoclave was then heated to certain temperature and the reaction mixture was stirred (at 1000 rpm) with a magnetic stirrer (MAG-NEO, RV-06M, Japan). After reaction, solid catalyst was separated by centrifugation and products were analyzed by gas chromatograph (HP 5890, USA) with a 30 m capillary column (HP-5) using a flame ionization detector. And all products were confirmed by GC-MS (Agilent 6890-5973N). For each successive use, the catalyst was washed with ethanol three times to remove the products, followed by drying at 40 °C for 6 h.

2. Results and discussion

2.1 XRD

Fig. S1 shows the X-ray diffraction (XRD) patterns of SnO_2/rGO, Pt_3Sn/SnO_2/rGO and Pt/rGO. In the diffraction spectrum of SnO_2/rGO (Fig. S1a), the peaks at 26.4, 33.9, 52.0 and 65.7 ° were assigned to the (110), (101), (211) and (301) planes of SnO_2 (JCPDS 41–1445),[2] respectively, confirming that the as-prepared SnO_2 NPs were well crystallized. For the face-centered-cubic (fcc) crystalline Pt (Fig. S1c) (JCPDS 04–0802), the (111), (200) and (220) peaks were present at 39.8, 46.2 and 67.5 °, respectively. The XRD peaks (Fig. S1b) matched with the fcc Pt_3Sn standard (JCPDS 35–1360), and shifted to the lower diffraction angles compared with that of monometallic Pt, indicating that alloying Pt with Sn resulted in a crystal lattice expansion in Pt_3Sn NPs.[3] However, the weak peaks at 33.8 and 52.0 ° were identified as the (101) and (211) diffraction signals of SnO_2. The loading amount of Pt is lower in Pt/rGO (17.2%, Table S1) than that in Pt_3Sn/SnO_2/rGO (19.8%, Table S1). It was demonstrated that the presence of SnO_2 played an important role in anchoring Pt_3Sn NPs. The (220) peak of Pt or Pt_3Sn and SnO_2 (101) peak were obtained in the XRD pattern and used for calculation of mean crystallite sizes of Pt or Pt_3Sn and SnO_2, respectively.

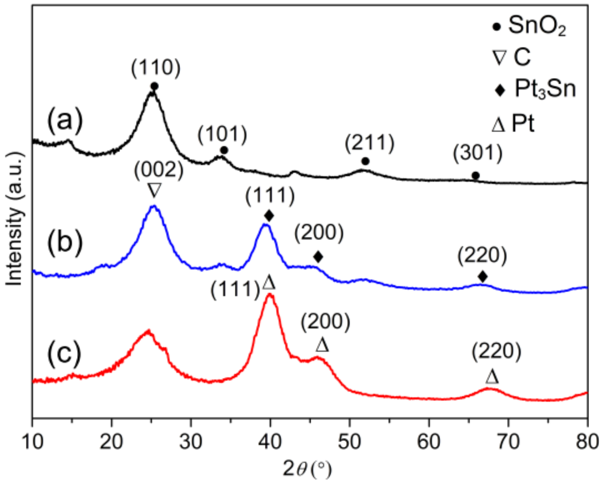

Fig. S1 XRD patterns of (a) SnO_2/rGO, (b) Pt_3Sn/SnO_2/rGO and (c) Pt/rGO.

Table S1 The structure of Pt/rGO and Pt_3Sn/SnO_2/rGO derived from XRD and TEM analysis.

Catalysts	Pt loading wt% [a]	Sn/Pt [b]	Particle size of SnO_2 (nm)		Particle size of Pt (nm)	
			XRD	TEM	XRD	TEM
Pt/rGO	17.2	-	-	-	2.6	2.8
SnO_2/rGO	-	-	5.4	5.9	-	-
Pt_3Sn/SnO_2/rGO	19.8	1.7	5.3	5.7	0.9	1.1

[a] The controlled Pt loading amount was 20 mass percent with respect to C.

[b] Molar Sn/Pt ratio was estimated by ICP-AES.

2.2 TEM images

Fig. S2a shows TEM image of SnO_2/rGO nanohybrid, SnO_2 NPs were uniformly **dispersed** on the surface of rGO sheets, and the average particle size of SnO_2 NPs was 5.9 nm. A HRTEM image of SnO_2/rGO nanohybrid (Fig. S2b) displayed the lattice spacing of about 0.335, 0.262, 0.237 and 0.212 nm, corresponding to the (110), (101), (200), and (210) crystal planes of tetragonal SnO_2, respectively. Large amount of highly dispersed, unique sized Pt NPs (~2.8 nm) were also detected on the surface of few-layered rGO sheets in Pt/rGO (Fig. S2c). The TEM image of Pt_3Sn/SnO_2/rGO (Fig. S2d) displayed the rGO sheets were covered by Pt_3Sn and SnO_2 NPs, and the average crystallite size of Pt_3Sn and SnO_2 NPs were 1.1 and 5.7 nm, respectively.

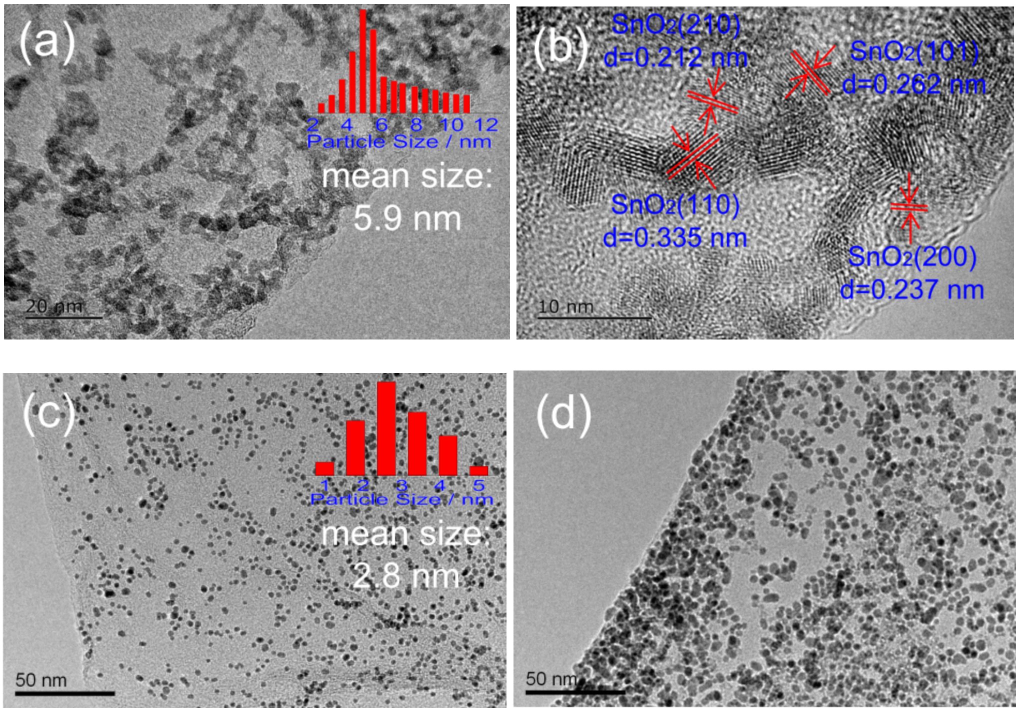

Fig. S2 TEM (a) and HRTEM (b) images of SnO_2-coated rGO (SnO_2/rGO), **TEM images of (c) Pt/rGO and (d) Pt_3Sn/SnO_2/rGO.**

2.3 XPS analysis

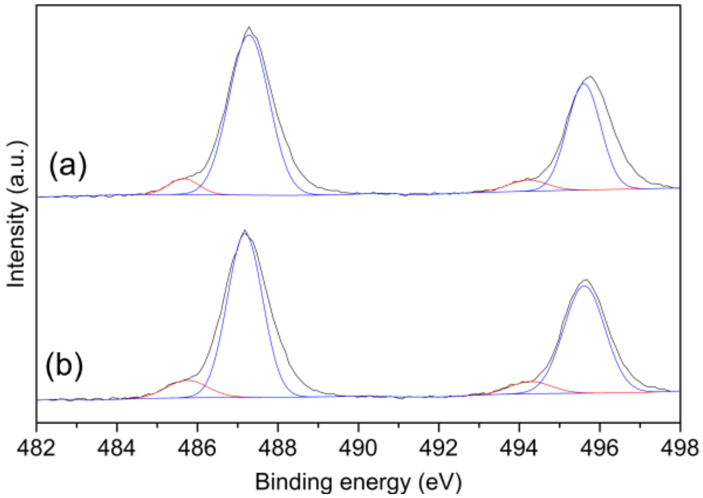

Fig. S3 XPS spectra of Sn 3d in (a) SnO_2/rGO and (b) Pt_3Sn/SnO_2/rGO. (Sn(0) in red, Sn(II, IV) in blue)

Table S2 XPS analysis results of Pt 4f and Sn 3d spectra in the Pt/rGO and Pt_3Sn/SnO_2/rGO.

Catalyst	Content of Pt (wt%)	Relative atomic percentage (%)			
		Pt(0)	Pt(II)	Sn(0)	Sn(II, IV)
Pt/rGO	17.2	65.5	34.5	-	-
SnO_2/rGO	--	-	-	9.6	90.4
Pt_3Sn/SnO_2/rGO	19.8	90.9	9.1	17.8	82.2

2.4 Catalytic activity of Pt_3Sn/SnO_2/rGO

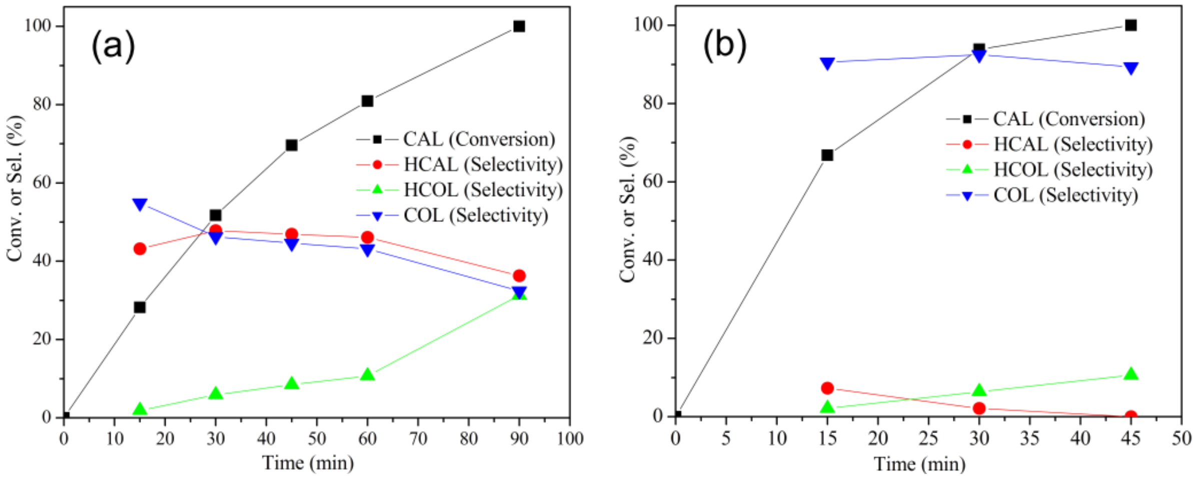

Fig. S4 Time course of CAL hydrogenation over (a) Pt/rGO and (b) Pt_3Sn/SnO_2/rGO.

(Reaction conditions:CAL 8.0 mmol in ethanol (20.0 mL), S/C=654, H_2 2.0 MPa, 70 °C.)

Table S3 Hydrogenation of CAL with various the S/C ratios over Pt_3Sn/SnO_2/rGO [a]

Entry	S/C	Conv. (%)	Sel. (%)		
			HCAL	HCOL	COL
1	327	98.4	0.8	12.4	86.8
2	654	93.9	2.1	5.4	92.5
3	981	69.4	6.1	1.8	92.1
4	1308	42.6	5.6	0.0	94.4

[a] Reaction conditions: CAL 8.0 mmol, ethanol 20.0 mL, 70 °C, 2.0 MPa, 30 min.

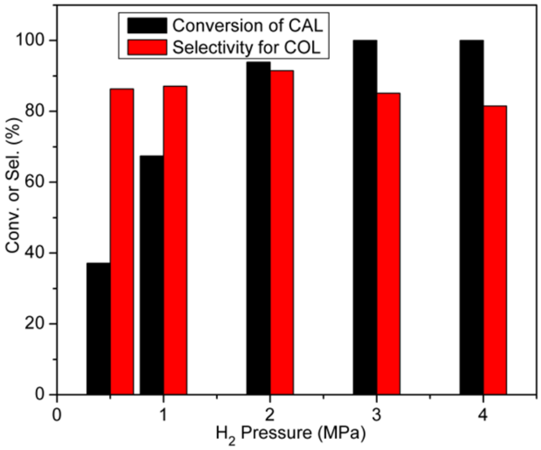

Fig. S5 Hydrogenation of CAL under different reaction H_2 pressure over Pt_3Sn/SnO_2/rGO catalyst.

(Reaction conditions: CAL 8.0 mmol, S/C=654, ethanol 20.0 mL, 70 ºC, 30 min.)

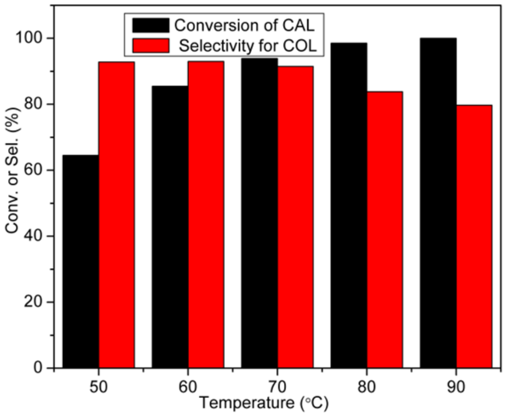

Fig. S6 Hydrogenation of CAL under different reaction temperature over Pt_3Sn/SnO_2/rGO catalyst.

(Reaction conditions: CAL 8.0 mmol, S/C=654, ethanol 20.0 mL, 2.0 MPa, 30 min.)

References

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