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Supplementary Information for

Highly selective hydrogenation of α, β-unsaturated aldehydes by Pt catalysts supported on Fe-based layered double hydroxides and derived mixed metal oxides

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1. Chemicals

Hexachloroplatinic acid (H₂PtCl₆·6H₂O, 99.9%) was purchased from Aldrich Co. Ltd. The cinnamaldehyde (98%) was purchased from Aike Chemical Reagent Co. Ltd (Chengdu, China). Other chemicals were analytical grade and not further purified prior to using. Distilled deionized water was utilized through the experiments. The purity of hydrogen is 99.9%.

2. Catalysts preparation

MFe-MMO (N=Co, Ni, Mg, Zn) support was derived from a MAI-LDH precursor. NAI-LDH LDH precursor was synthesized using the homogeneous precipitation method. A mixed solution of 0.1 M MCl₂ and 0.05 M FeCl₃, and 0.5 M urea was transferred to an autoclave and hydrothermally treated at 110 °C for 12 h. The precipitate was filtered, washed, dried at 60 °C in vacuum and transformed into MAI-MMO support after calcination at 450 °C for 4 h.

The Pt catalyst was prepared using a reduction-deposition method. The support was impregnated in aqueous solution of H_2PtCl_6 at 80 °C for 5 h in a round-bottom flask. Then, 20 mL of 0.1 mol/L NaBH₄ solution was subsequently added dropwise to the flask under vigorous stirring for another 1 h. Afterwards, filter the slurry and wash the solid with water until filtrate is neutral. The solid obtained was dried at 45 °C under vacuum for 12 h before use. The nominal content of Pt in the catalyst was 2 wt.%.

3. Characterization of the as-prepared catalyst

X-ray diffraction (XRD) patterns were measured at room temperature by using a Bruker D8 Advance X-ray diffractometer with the Cu Kα radiation at 40 kV and 30 mA. The surface functional groups in samples were measured by FT-IR using Thermo Scientific Nicolet 380 Spectrometer (USA) with a spectral range from 4000 to 400 cm-1 at a spectral resolution of 4 cm–1 and 32 scans. SEM analysis was carried out using a NoVaTM Nano SEM 430 scanning electron microscope (FEI, USA) at an electron acceleration voltage of 20 kV. Atomic force microscope observed using a Multimode

Nanoscope IIIa controllor (Veeco, USA) in tapping mode. Transmission electron microscopy (TEM) was characterized by a by a FEI Tecnai G20 (USA) with an accelerating voltage of 200 kV. The textural properties of samples were performed by nitrogen sorption isotherms on a Micromeritics ASAP 3020 instrument (USA) at 77 K. The surface area and pore volume were calculated using BET and BJH methods, respectively. XPS was measured with a K-Alpha XPS system (Thermo Fisher Scientific, USA) using a monochromatic Al K α as the excitation source (1486.6 eV).

4. Typical procedure for hydrogenation reaction

The hydrogenation reactions of CAL were carried out in a stainless autoclave reactor with a 50 mL Teflon sleeve. In a typical procedure, 0.1 g catalyst was dispersed in 19 mL ethanol and then 8.2 mmol CAL was added into solution. The reactor was sealed, purging with H_2 for 3 times respectively and then pressurized to 2.0 MPa. The reaction was conducted at 60 °C with a stirring speed of 750 rpm for 2 h. The reaction mixture was analyzed by Shimadzu GC-2010 gas chromatograph with a flame ionization detector (FID) system.

5. The reaction pathway and main products



Fig. S1 The reaction pathway and main products for hydrogenation of CAL.



Fig. S2 The reaction pathway and main products for hydrogenation of cirtal.

6. XPS spectrum for the the as-prepared catalyst



Fig. S3 XPS survey spectrum for (a) Pt/ZnFe-LDH, (b) Pt/ZnFe-MMO, (c)Pt/NiFe-LDH, and (d)Pt/NiFe-MMO



Fig. S4. XPS spectrum of (A) C1s and (B) Fe2p in the (a) Pt/ZnFe-LDH, (b) Pt/ZnFe-MMO, (c) Pt/NiFe-LDH, and (d) Pt/NiFe-MMO, respectively.

7. Effects reaction time on the hydrogenation performance



Fig. S5 Effects reaction time (a) on CAL hydrogenation performance with the Pt/ZnFe-LDH catalyst and (b) on citral hydrogenation performance over the Pt/NiFe-LDH catalyst.



Fig. S6 Recycling use of the Pt/ZnFe-LDH in the hydrogenation of CAL (Reaction conditions: 8.2 mmol CAL, 19.0 mL C_2H_5OH , 0.1 g catalyst, 60 °C, 2.0 MPa, 2 h).



Fig. S7 Recycling use of the Pt/NiFe-LDH in the hydrogenation of citral (Reaction conditions: 5.8 mmol Citral, 19.0 mL C_2H_5OH , 70 °C, 2.0 MPa, 0.1 g catalyst, 2 h.

9. The effect of support on catalytic performance in the hydrogenation of citral

Catalysts	Conv. (%)	Sele. (%)			
		Citronellal	DOL	Citronellol	UALC
Pt/MgFe-LDH	8.7	9.3	0.0	1.4	89.3
Pt/MgFe-MMO	21.5	6.9	0.0	2.6	90.5
Pt/CoFe-LDH	9.1	8.3	0.0	9.2	82.5
Pt/CoFe-MMO	49.2	6.3	0.0	8.8	84.9

Table S1 The effect of support on catalytic performance in the hydrogenation of citral