Electronic Supplementary Information (ESI)

Multi-scale promoting effects of lead for palladium catalyzed aerobic oxidative coupling of methylacrolein with methanol

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Experimental

1. Characterization

XRD patterns were measured with a Rigaku SmartLab diffractometer using Cu K_α radiation at 45 kV and 200 mA. XPS measurements were conducted on an ESCALAB 250Xi electron spectrometer using 300 W Al K_α X-ray source and the binding energies were referenced with C 1s at 284.6 eV. X-ray microprobe analysis was performed using a JAX-8230 equipment with an emission current of 17.3 μA and an accelerate voltage of 20.0 kV. Samples used for X-ray microprobe measurements were prepared by embedding suitable amounts of catalyst powders in a resin and then polishing the obtained slides. ICP-AES data were acquired with an ICPE-9000 spectrometer. Chemical and physical sorption experiments were carried out using AutochemII 2920 and ASAP 2020 HD88 instruments, respectively. TEM images were taken on a JEM-2100 microscope operated at 200 kV. *In situ* FTIR spectra were collected at ambient temperature with a Bruker Equinox 55 spectrometer equipped with a mercury cadmium telluride (MCT) detector and operated at a resolution of 4 cm^{-1}. Before measurements, the sample was pretreated in H_2 at 400 °C for 1 h and then maintained at 400 °C for another 1 h in Ar. After cooling to ambient temperature, the probing gas CO was introduced. All FTIR spectra were acquired under steady-state conditions.

2. Catalyst preparation

Alumina microspheres (BET surface area: 240 m^2 g^{-1}, diameter: 60 μm) were provided by local suppliers. $Pb(NO_3)_2$, $PdCl_2$ and NaCl were purchased from Sigma Aldrich and all of them were used as received without further purification. In the first step, Pb_n/alumina composite supporters (n=0, 1, 2, 5, 8, 10 and 20 wt%) were prepared by the incipient wetness impregnation method with a required amount of $Pb(NO_3)_2$ solution and alumina microspheres. The resulting slurry was dried at 80 °C overnight under vacuum and then calcinated in air at 550 °C for 3 h. In the second step, Pd_mPb_n/alumina catalysts with variety of composites were prepared by immersing Pb_n/alumina composite supporters into a Na_2PdCl_4 solution followed by hydrazine reduction at 90 °C for 4 h. After filtration, washed with water and dried at 80 °C overnight under vacuum, Pd_mPb_n/alumina catalysts were obtained.

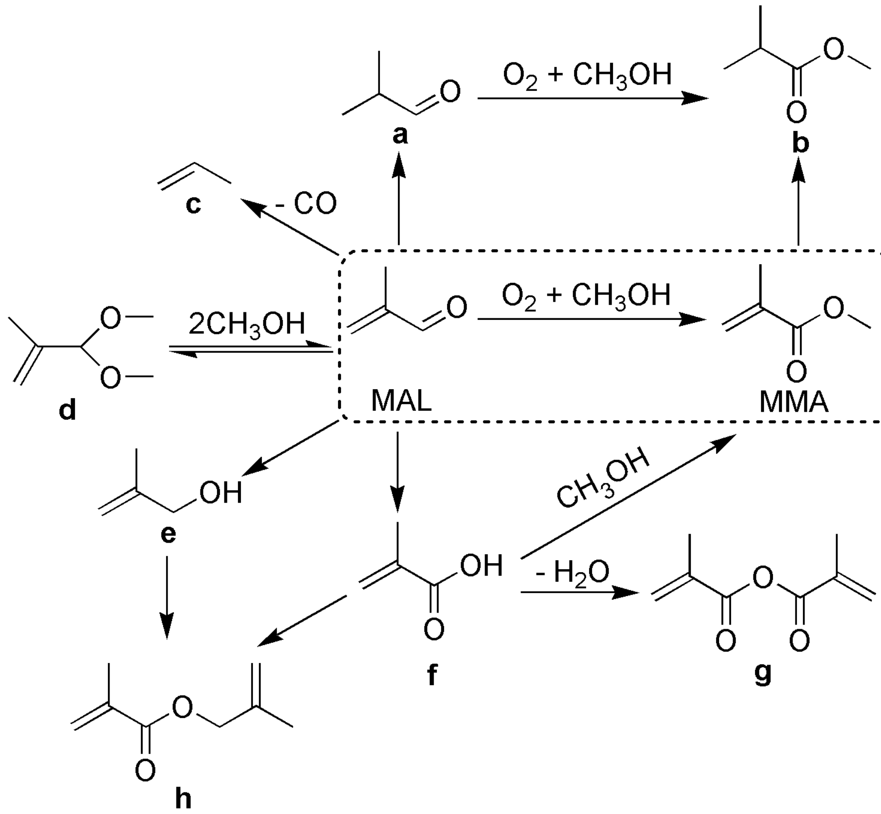
3. Aerobic oxidative coupling of methylacrolein with methanol

Pd_2Pb_8/alumina catalyst (2.5 g, 0.25 mol% Pd), methylacrolein (0.18 mol), methanol (1.44 mol) and $Mg(OH)_2$ (0.15 g) were added to a 100 mL autoclave sequentially. After filling the autoclave with 0.3

MPa of oxygen, the reaction was stirred at 80 °C for 2 h with the oxygen flow rate of 20 mL min^{-1}. After cooling to ambient temperature, the reaction mixture (1 mL) and ethanol (0.2 mL) (the internal standard) were mixed together. The obtained sample was directly subjected to GC analysis. Conversion and yield were measured by GC-FID (Agilent 6890 equipped with DB-624 capillary column). Qualitative analysis of esters and byproducts was made by GC-MS and identified by comparison with authentic samples. Aerobic oxidative coupling of other aldehydes to corresponding esters was carried out in a similar way. The reproducibility for each experiment was repeated for three times.

Table S1 Textural parameters of typical samples and adsorption capacity of carbon dioxide

Sample	BET surface area (m^2 g^{-1})	Total pore volume (cm^3 g^{-1})	CO_2 desorption (μmol g^{-1})	CO_2 desorption (μmol m^{-2})
Pd_2/alumina	254	0.43	30.68	0.12
Pd_2Pb_8/alumina	234	0.39	13.25	0.06
alumina	241	0.47	7.13	0.03
Pb_1/alumina	217	0.43	10.54	0.05
Pb_2/alumina	219	0.40	11.29	0.05
Pb_5/alumina	222	0.43	13.58	0.06
Pb_8/alumina	224	0.46	16.65	0.07
Pb_{10}/alumina	194	0.38	19.63	0.10
Pb_{20}/alumina	183	0.37	19.65	0.11
MgO-alumina	172	0.45	28.07	0.16



Scheme S1 Reaction network of aerobic oxidative coupling of methylacrolein with methanol.

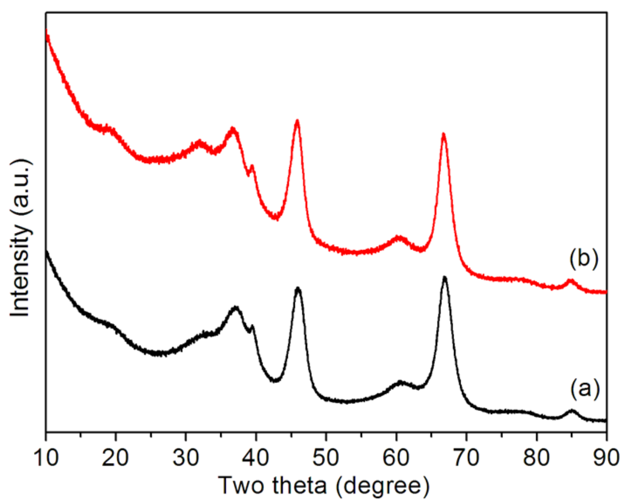


Fig. S1 XRD patterns of (a) alumina and (b) Pb_8/alumina.

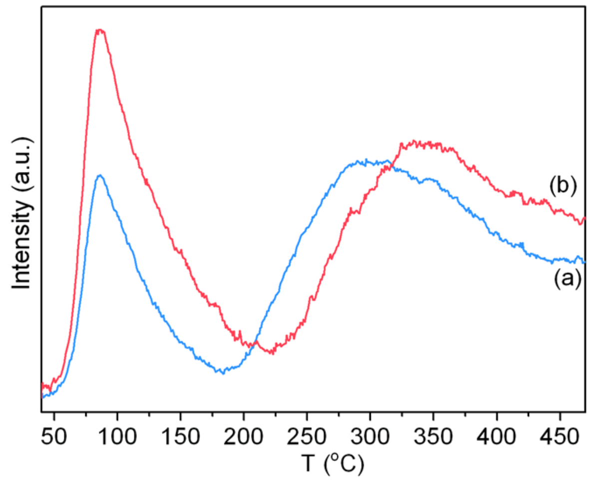


Fig. S2 CO_2-TPD profiles of (a) alumina and (b) Pb_8/alumina.

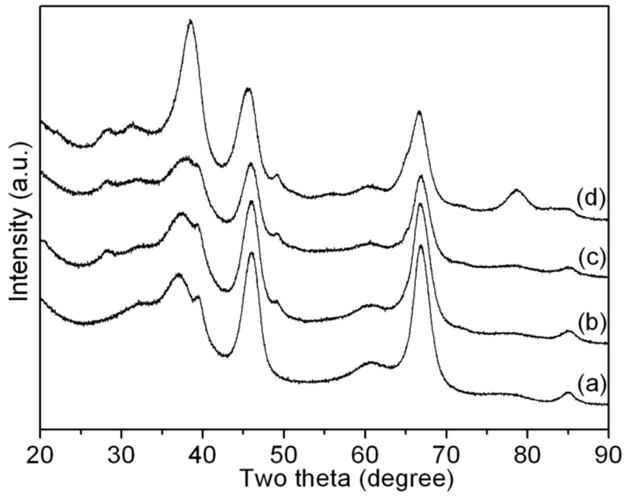


Fig. S3 XRD patterns of (a) alumina, (b) Pd_2/alumina, (c) Pd_2Pb_8/alumina and (d) $Pd_5Pb_5Mg_2$/alumina.

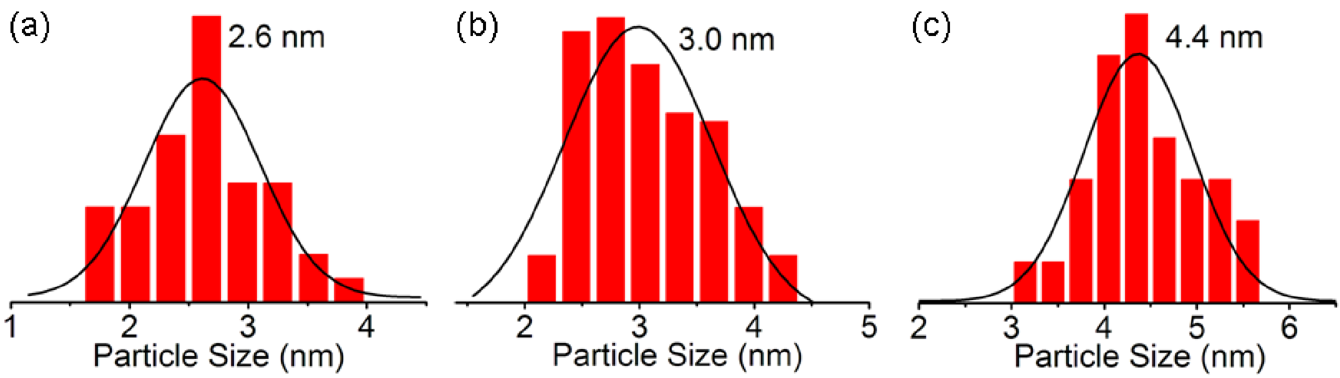


Fig. S4 Pd-Pb bimetallic nanoparticle size distributions of (a) Pd_2/alumina, (b) Pd_2Pb_8/alumina and (c) $Pd_5Pb_5Mg_2$/alumina.

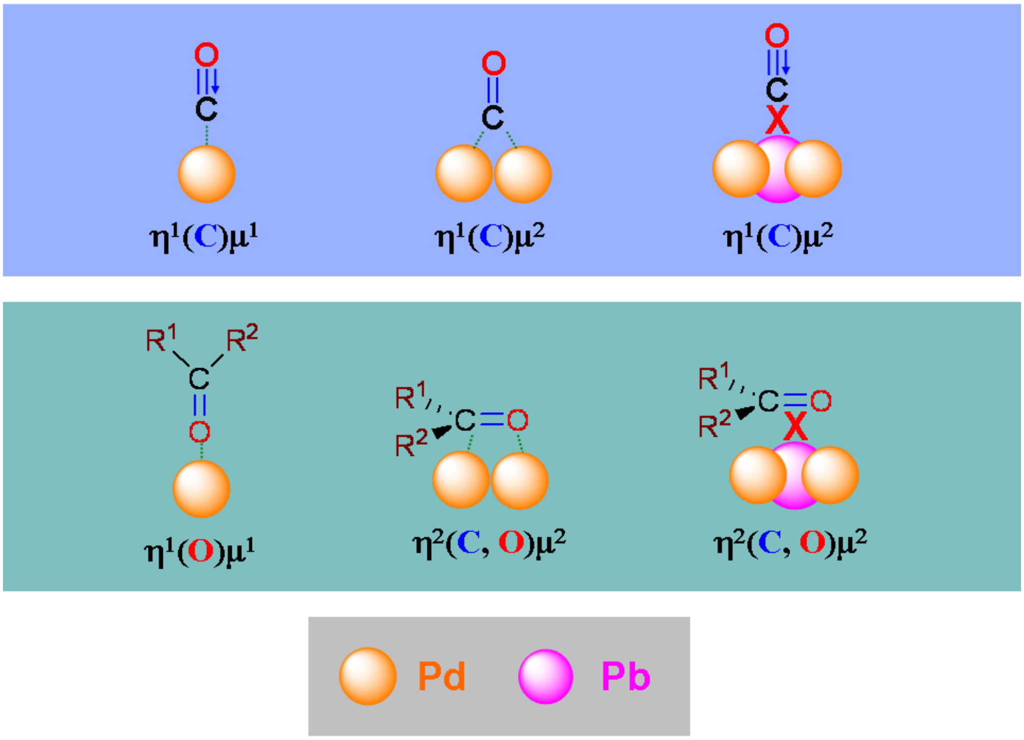


Fig. S5 Adsorption modes of CO and carbonyl on monometallic Pd and bimetallic Pd-Pb nanoparticles.

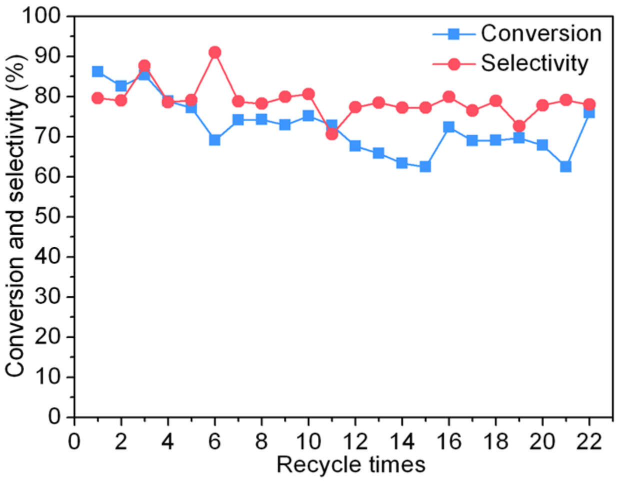


Fig. S6 Recycling tests of the Pd_2Pb_8/alumina catalyst for aerobic oxidative coupling of methylacrolein with methanol (molar ratio 1/8).

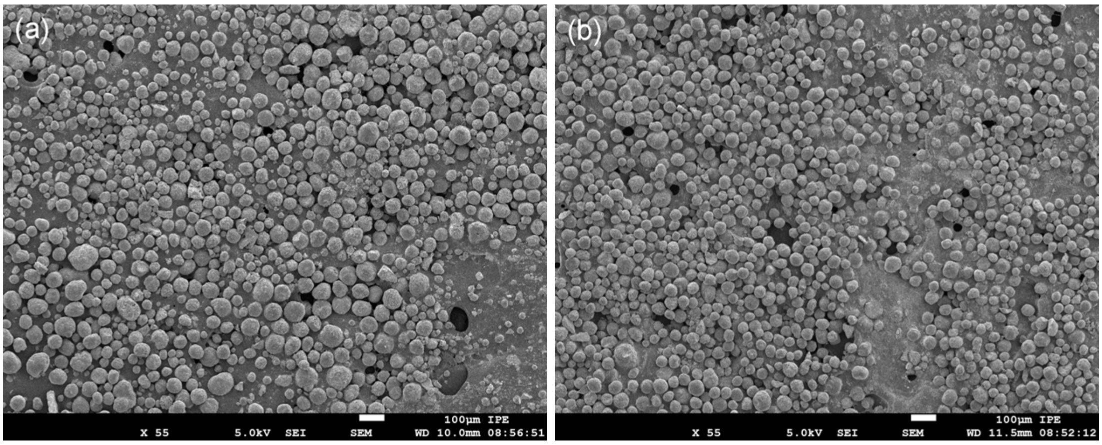


Fig. S7 SEM images of Pd_2Pb_8/alumina catalyst: (a) fresh and (b) used for 22 times.

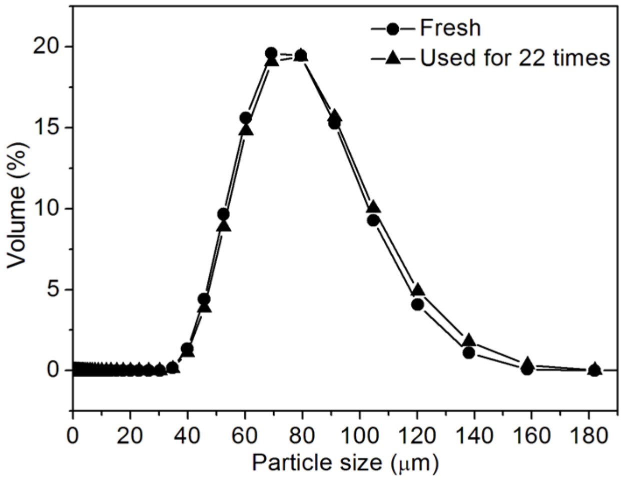


Fig. S8 Particle size distribution of Pd_2Pb_8/alumina measured with the Malvern Mastersizer 2000.

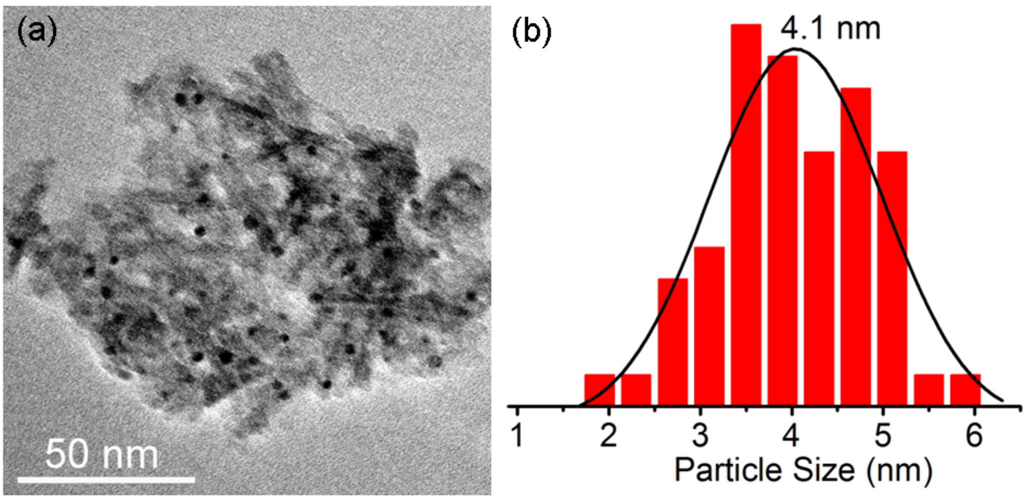


Fig. S9 (a) TEM image of Pd_2Pb_8/alumina catalyst used for 22 times; (b) Pd-Pb bimetallic nanoparticle size distribution of Pd_2Pb_8/alumina used for 22 times.