Supporting Information

Mechanochemical Synthesis of High-surface-area Pd/α-Al$_2$O$_3$ Catalyst for CO Oxidative Coupling to Dimethyl Oxalate Reaction

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Table S1. Band areas of bridging OH and terminal OH from FTIR spectra

Supports	A $_{terminal\ OH}$	A $_{bridging\ OH}$
Al$_2$O$_3$-B	13.94	8.33
Al$_2$O$_3$-B400	15.06	5.14
Al$_2$O$_3$-B600	10.82	3.95
Al$_2$O$_3$-B800	8.96	1.58

The peaks located at 3741 cm^{-1} and 3719 cm^{-1} were ascribed to terminal hydroxyls bonded to octahedral Al ions and the band centered at 3680 cm^{-1} was assigned to a bridging OH over an octahedrally coordinated Al ion. Band areas of bridging OH and terminal OH were calculated by integrating the peaks in 3695-3660 cm^{-1} and 3770-3695 cm^{-1} in Figure 2 (a) respectively.

Table S2 Weight loss and OH amount of the Al_2O_3-Bx supports from TG results

Supports	Region A [a] (%)	Region B [b] (%)	Region C [c] (%)	OH amount [d] (mmol/g)
Al_2O_3-B	2.87	3.82	1.04	1.16
Al_2O_3-B400	0.74	1.04	1.01	1.12
Al_2O_3-B600	0.57	0.79	0.45	0.50
Al_2O_3-B800	0.42	0.62	0.40	0.44

[a] Weight loss in 40-150 °C region, [b] weight loss in 150-500 °C region and [c] weight loss in 500-1000 °C region measured by thermogravimetric analysis. [d] The amount of OH was calculated based on weight loss in region C (J. Mater. Chem., 1999, 9, 549-553.) using the formulas: OH amount (mmol/g) = $2 \times \dfrac{m_C}{M_{H_2O}}$. m_C stands for weight loss in region C and M_{H_2O} is the molar mass of H_2O (g/mol).

As we all know, FTIR is a technique sensitive to surface group while TG results reflect weight loss of the whole sample. The two characterizations complement each other. As suggested, we have integrated the peaks of bridging hydroxyls and terminal hydroxyls in FTIR and listed the peak area in Table S1. In TG results, the weight loss at 400 °C mainly came from interlayer water removing. In FTIR results, after

calcination at 400°C the bridging hydroxyls decreased and terminal hydroxyls increased slightly. This is probably due to a small number of terminal hydroxyls generated during dehydration. The total amount of surface hydroxyls decreased slightly. When the temperature increased to above 500 °C, the weight loss was due to hydroxyls dehydration in TG and the amount of hydroxyls decreased gradually. With calcination temperature increase, the amount of bridging hydroxyls and terminal hydroxyls both decreased gradually.

Table S3 Amount of acid sites of the Al_2O_3-Bx supports from NH_3-TPD-MS results

Supports	Amount of acid sites (μmol NH_3/g)		
	Weak acid sites [a]	Strong acid sites [b]	Total
Al_2O_3-B	2.58	4.32	6.90
Al_2O_3-B400	3.22	2.96	6.18
Al_2O_3-B600	2.98	1.01	3.99
Al_2O_3-B800	0.93	0.59	1.52

[a,b] Amount of weak and strong acid sites were calculated by integrating the NH_3 desorption peaks in 100-300 °C region and 450-700 °C region in Figure 3 and calibrated by NH_3-pulse.

Table S4 Catalyst characteristics of Pd/Al$_2$O$_3$-Bx catalysts

Catalysts	D [a] (%)	d_H [b] (nm)	d_T [c] (nm)	Pd [d] (wt.%)
Pd/Al$_2$O$_3$-B	43.2	2.60	2.76	1.05
Pd/Al$_2$O$_3$-B400	36.3	3.08	2.91	1.06
Pd/Al$_2$O$_3$-B600	32.7	3.43	3.17	1.06
Pd/Al$_2$O$_3$-B800	27.3	4.10	3.88	1.02

[a.] Pd dispersion (D) was calculated as: D (%)= $\dfrac{S_f \times \dfrac{V_{ads}}{V_g} \times \dfrac{M_{Pd}}{w} \times 100\%}{}$, where S_f stands for stoichiometry factor (assume H/Pd = 1), V_{ads} represents volume of adsorbed H$_2$ (cm^3/g), V_g stands for molar volume of gas at standard temperature and pressure (22414 cm^3/mol), M_{Pd} represents molecular weight of Pd (g/mol) and w stands for Pd loading in samples (%). [b] The Pd particle size (d_H) determined by H$_2$ chemisorption was calculated as: d_H=1.12/D.; [c] Pd NPs size (d_T) was measured by TEM by counting more than 100 particles in the images and calculated by the formulas:

$$d_T = \frac{\sum n_i \times d_i}{\sum n_i}$$
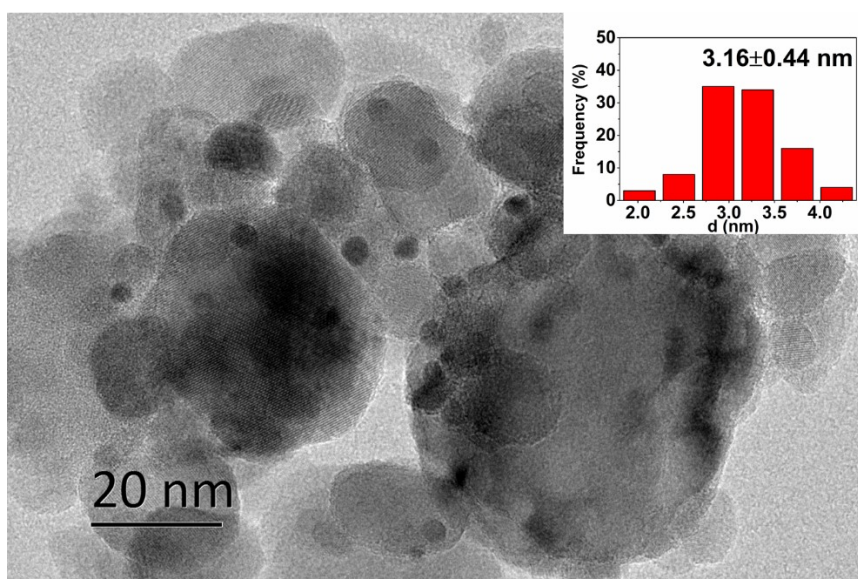
; [d] Pd loading determined by ICP.

Figure S1 Pd/Al$_2$O$_3$-B catalyst after 100 h test

Table S5. Textural properties of Pd/Al$_2$O$_3$-B and Pd/Al$_2$O$_3$-B after 100 h test

Catalysts	S$_{BET}$ (m^2/g)[a]	V$_{Pore}$ (cm^3/g)[b]	D$_{Pore}$ (nm)[c]
Pd/Al$_2$O$_3$-B	65.7	0.16	8.0
Pd/Al$_2$O$_3$-B after 100 h test	62.9	0.16	8.0

[a] S$_{BET}$ represents BET surface area; [b] V$_{Pore}$ represents volume of pores; [c] D$_{Pore}$ represents average pore diameter

Table S6. Product distribution in CO oxidative coupling to DMO reaction on Pd/Al$_2$O$_3$-Bx catalysts

Catalysts	S$_{DMO}$ (%)	S$_{DMC}$ (%)
Pd/Al$_2$O$_3$-B	85.3	14.7
Pd/Al$_2$O$_3$-B400	80.2	19.8
Pd/Al$_2$O$_3$-B600	94.3	5.7
Pd/Al$_2$O$_3$-B800	99.8	0.2

DMO and DMC were products of CO oxidative coupling with MN and methanol and MF were products of MN decomposition. Thus only DMO and DMC were considered in the calculation of CO selectivity.