Electronic Supplementary Material (ESI) for Dalton Transactions.

Crucial size effect on dicarbonylation of acetylene over Pd/CsHPMo heterogeneous catalysts

Wei Xuemei[a,b,c], Wang Kai[a,b], Wu Guofeng[d], Yu Guoqi[a,b], Shen Hualiang[a,b], Cai Tao[a,b], Luo Yanjuan[a,b], Shang Tianbo[a,b], Chen Xinzhi[c,*], Shen Runpu[a,b,*], Hu Bin[e,*]

[a]*College of Chemistry and Chemical Engineering, Shaoxing University, Shaoxing, 312000, China*

[b]*Zhejiang Engineering Research Center of Fat-soluble Vitamin, Shaoxing University, Shaoxing, 312000, China*

[c]*College of Chemical and Biological Engineering, Zhejiang University, Hangzhou, 310027, China.*

[d]*Zhejiang Medicine Co Ltd, Shaoxing 312000, PR China*

[e]*State Key Laboratory for Oxo Synthesis and Selective Oxidation Lanzhou Institute of Chemical Physics, Chinese Academy of Sciences Lanzhou 730000, China*

* To whom correspondence should be addressed.

E-mail: xzchen@zju.edu.cn, srunpu@usx.edu.cn, hcom@licp.cas.cn

Tel.: 0575-86024773

Text S*. EXPERIMENTAL SECTION

Text S1. Catalysts preparation

Text S1.1. The preparation of CsHPMo

Quantitative (1.9 g) commercial Keggin phosphonolybonic acid ($H_3PMo_{12}O_{40}$, 1 mmol) was dissolved in 20 mL deionized water and fully stirred to obtain a golden clarified solution. After stirring for 30 minutes, bright yellow emulsion was obtained by adding the measured $CsNO_3$ (1 g, 5 mmol). The precipitate was obtained after gentrification (8000 r/min, 1 minute), fully washed, vacuum dried overnight at 80 ℃, and the resulting block was ground into powder, then named CsHPMo.

Text S1.2. Controllable preparation of Pd (2.3-6.7 nm) particle size

Pd nanoparticles with various particle sizes, ranging from 2.3 nm to 6.7 nm, were prepared as follows: 40 mg PVP (K29-32, average molecular weight 58000) was dissolved in 2 mL glycol, oil bath 160 ℃ and stirring for 10 min. Na_2PdCl_4 glycol solution (1 mL, 16 mg/mL) was injected into the above liquids, and keep for 1 hour. After quenching by ice bath, Pd was fully washed with acetone and distilled water until no PVP was attached in TEM image. Pd samples were evenly dispersed in 10 mL ethanol solution (ultrasonic treatment for 30 minutes) for use.

The synthesis for 2.3 nm Pd nanoparticles added 1600 mg PVP, 3.4 nm Pd nanoparticles added 200 mg PVP, 6.7 nm Pd nanoparticles added 200 mg PVP and 80 mg Na_2PdCl_4.

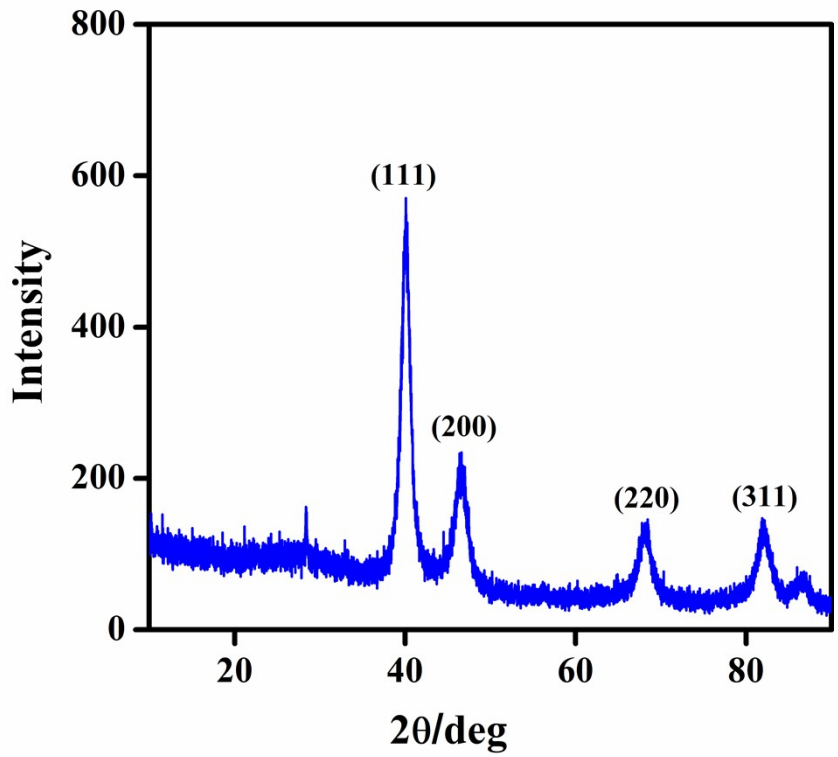


Fig. S1 The XRD patterns of the as-synthesized 5.4Pd nanoparticles.

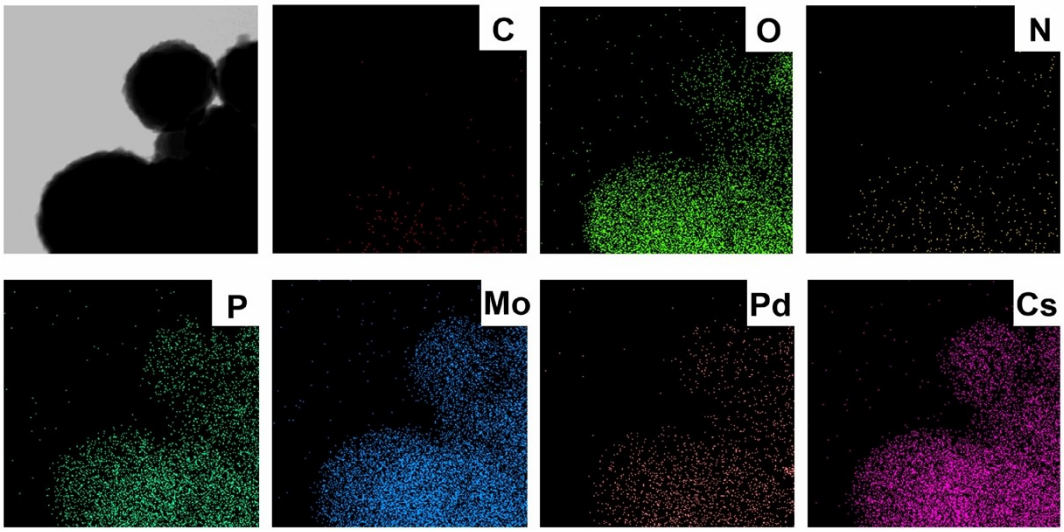


Fig. S2 EDX elemental mapping of C, O, N, P, Mo, Pd and Cs elements for 5.0Pd/CsHPMo catalyst.

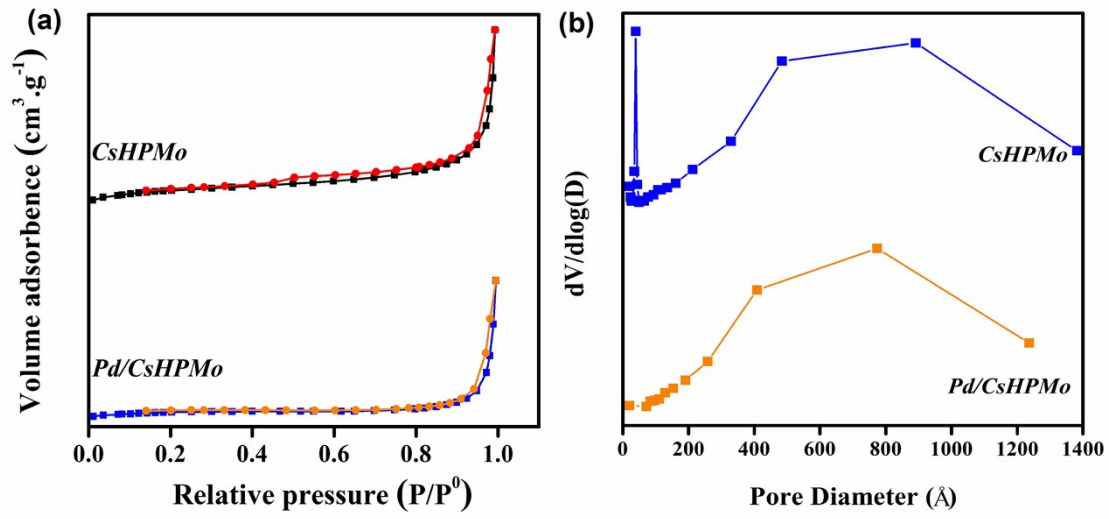


Fig. S3 Nitrogen adsorption/desorption isotherms (a) and aperture profile of BJH of CsHPMo support and 5.4Pd/CsHPMo catalyst.

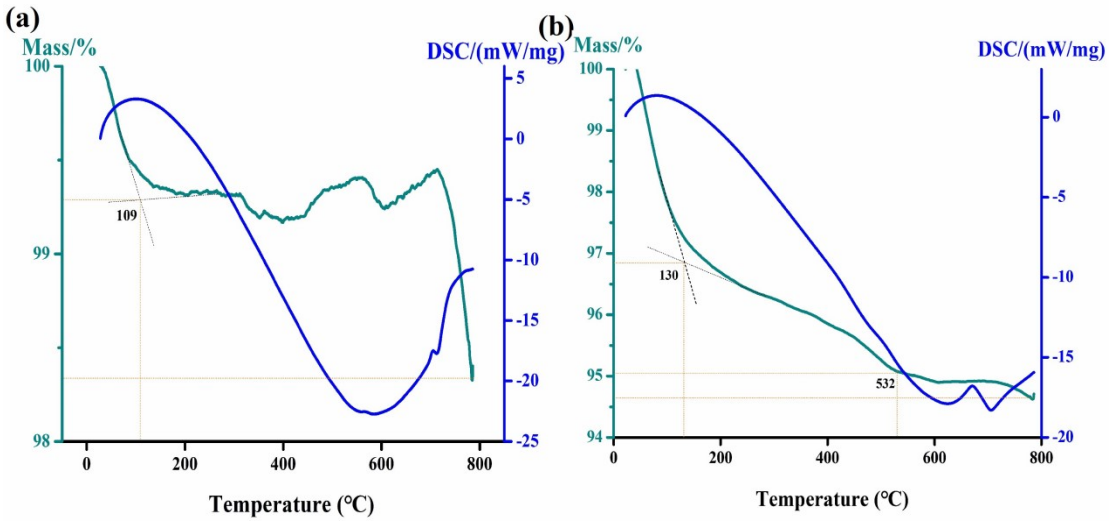


Fig. S4 TGA curves of pure CsHPMo support (a) and 5.0Pd/CsHPMo catalyst (b) under N_2 atmosphere with a ramp rate of 5 °C/min.

Thermo gravimetric analysis (TGA) was carried out in N_2 to determine the thermostability of as-synthesized catalyst (Fig. S4). The TGA curve noted that the structure of the two materials has good thermal stability, with a weight loss of only 1.7% (Fig. S4a) and 5.3% (Fig. S4b) for CsHPMo and 5.0Pd/CsHPMo, respectively. The weight loss below 200 °C mainly caused by the loss of adsorbed water.

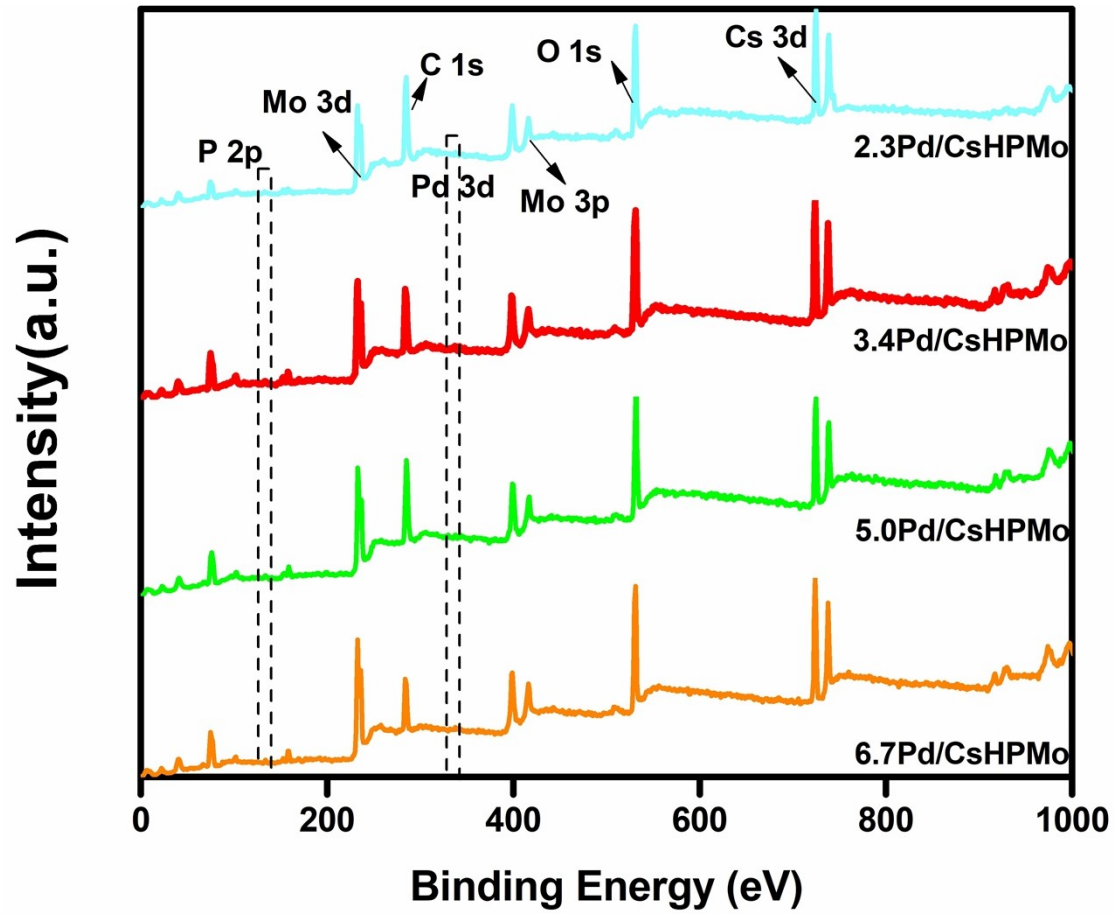
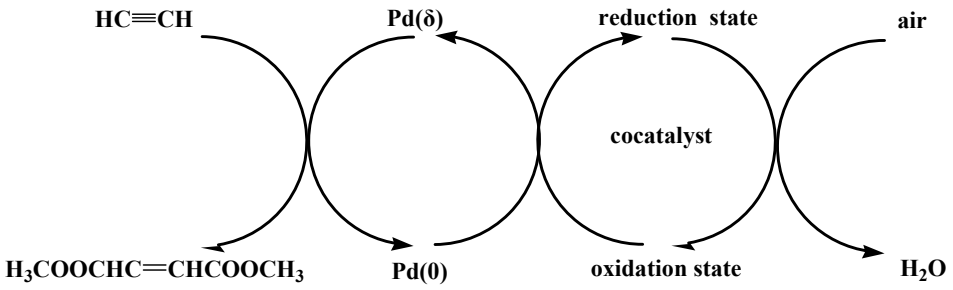


Fig. S5 The XPS spectra of the (2.3~6.7)Pd/CsHPMo catalysts.



Scheme S1. The specific $Pd^{\delta+}$-Pd^{0}-$Pd^{\delta+}$ catalytic reaction process.

Table S1 Relative content of different components

Sample	Pd		Mo		Cs		Mo-O-Mo (Cont.%)	Mo-O-P
	$3d_{3/2}$	$3d_{5/2}$	$3d_{3/2}$	$3d_{5/2}$	$3d_{3/2}$	$3d_{5/2}$		
2.3Pd /CsHPMo	343.3	338.0	236.1	233.0	738.3	724.2	530.5 63.2%	531.8
3.4Pd /CsHPMo	343.4	338.0	236.2	233.1	738.2	724.2	530.7 62.0%	532.1
5.0Pd /CsHPMo	343.4	338.0	236.1	232.9	738.3	724.3	530.7 59.5%	532.1
6.7Pd /CsHPMo	343.4	338.2	236.3	233.2	738.2	724.3	530.8 75.6%	532.1

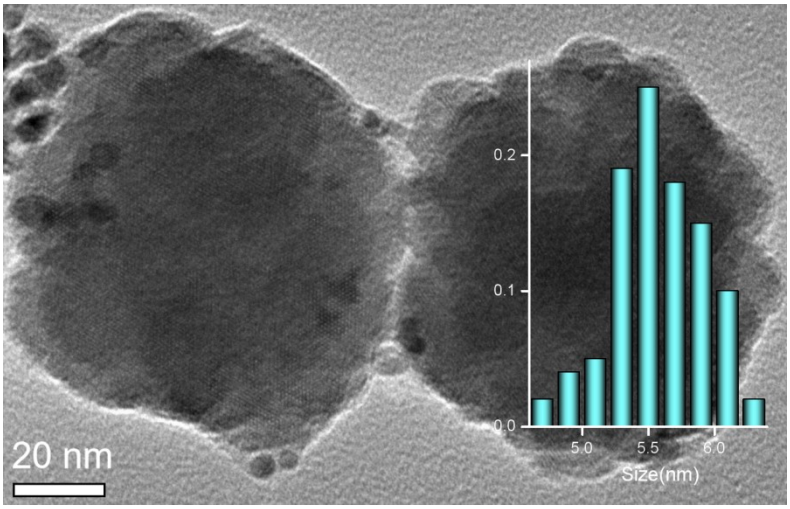


Fig. S6 TEM image of the spent 5.0Pd/CsHPMo catalyst and the histogram of Pd particle size distribution (*inset*).

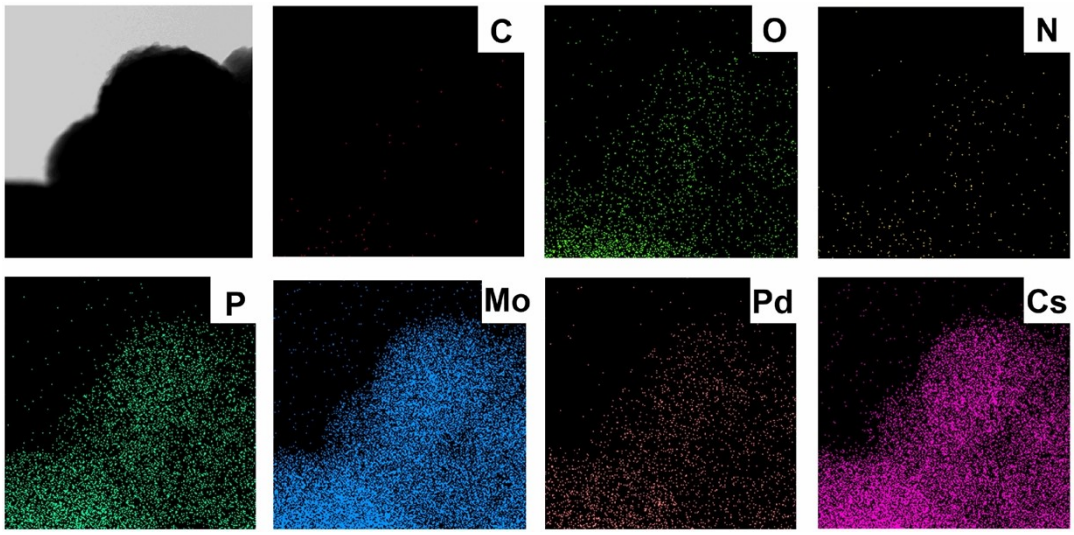


Fig. S7 EDX elemental mapping of C, O, N, P, Mo, Pd and Cs elements for spent 5.0Pd/CsHPMo catalyst.

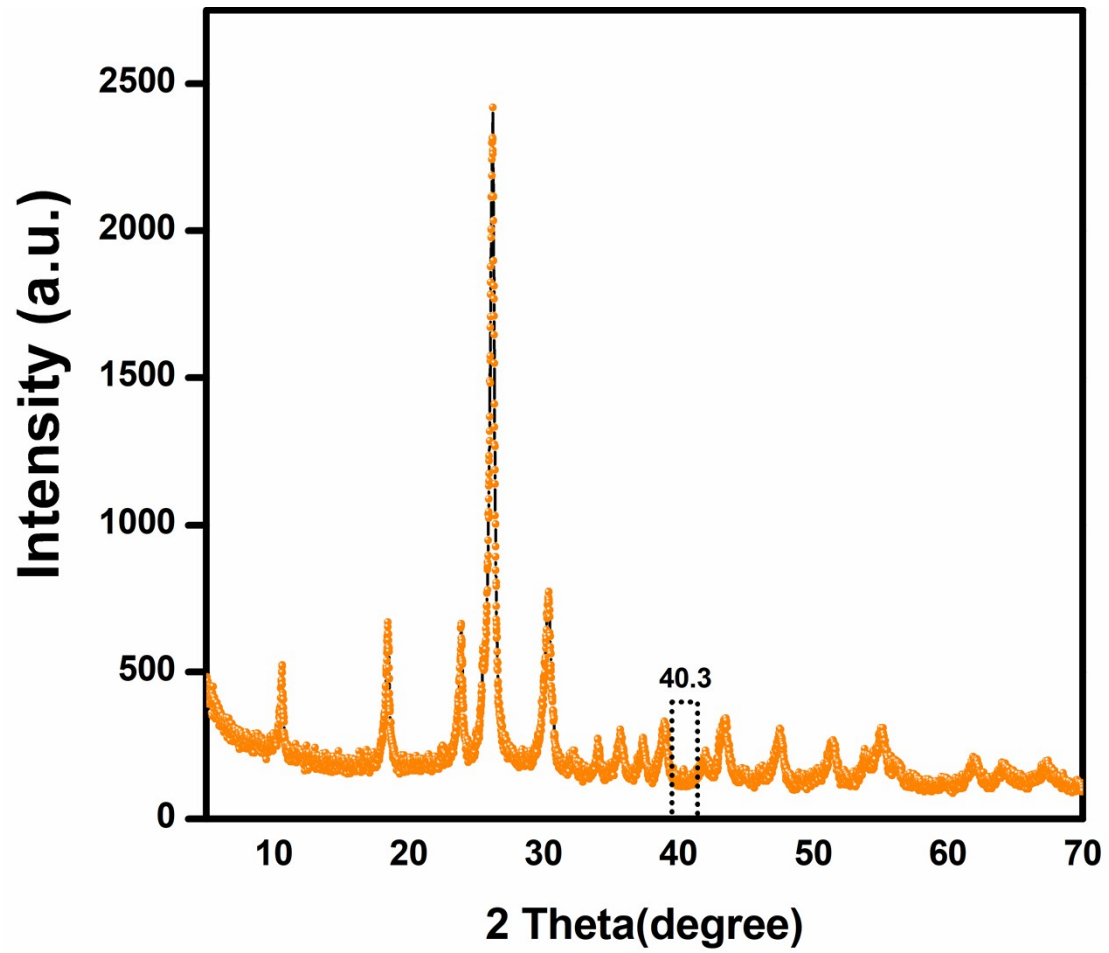


Fig. S8 The XRD patterns of the spent 5.0Pd/CsHPMo catalyst.