Supporting Information For

Synthesis of $Co_{1.5}PW_{12}O_{40}$ and Its Catalytic Performance of Converting Methanol to Ethylene

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1. Characterization

X-ray powder diffraction was acquired on Rigaku Dmax 2200 diffractometer with graphite monochromatized Cu Kα radiation (λ=0.154178nm) at 40kV and 30mA. The sample was scanned from 3° to 70° at a rate of 4°/min. The crystallite sizes of the particles were calculated from the XRD peaks using the Scherrer equation.

$Co_{1.5}PW_{12}O_{40}$ catalyst was characterized by Scanning Electron Microscope (SEM), performed on a Hitachi S-4800 equipped with an energy dispersive X-ray detector at 10.0 kV under high vacuum. The energy dispersion spectra (EDS) were also recorded.

Thermogravimetric and differential thermalgravimetric analysis (TG-DTA) were performed on a Perkin-Elmer SII Pyris Diamond TG/DTA thermal analyzer. TG analyses were carried out over a range of 30 to 600℃ under a high-purity N_2 flow with a controlled heating rate of 10℃/min.

Identification of reaction products was measured by GCMS-QP2010 Plus equipped with a capillary column of Rxi-5ms (5% diphenyl /95% dimethyl polysiloxane) and an electron bombardment ion source (EI).

Temperature programmed desorption (TPD) was measured on Quantachrom Chem-BET 3000 apparatus to determine the surface acid-base properties of catalysts. Before adsorption experiments, 20 mg of the samples were pretreated at 300℃ in a quartz U-tube in an nitrogen flow with a flow rate of 100 mL per minute for 1h to remove absorbed water. Upon cooling to room temperature, the samples were saturated with 10%NH_3/90%N_2 for 30min. Then the physical adsorbed NH_3 was removed by streaming with 30%N_2/70% He for 2h under a flow rate of 60mL/min. The samples were then heated up to 550℃ at a heating rate of 8℃/min in N_2/He under a flow rate of 50mL/min.

2. Results

Table S1 shows the crystalline data of $Co_{1.5}PW_{12}O_{40}$ in details. In a unit cell, the largest interplanar spacing (D) is 9.90 nm and the smallest interplanar spacing (D) is 3.08 nm. Also from the XRD data, it can be found that the crystallite size ranges from 10.5 to 29.9nm and the average grain size is 20.5nm.

The morphologies of $H_3PW_{12}O_{40}$ and $Co_{1.5}PW_{12}O_{40}$ were examined by SEM. As shown in **Fig. S1a**, $H_3PW_{12}O_{40}$ consists of blocky particles. As **Fig.S1b** shows, particles of $Co_{1.5}PW_{12}O_{40}$ appear as needles with obviously layered structure. The introduction of cobalt yields $Co_{1.5}PW_{12}O_{40}$ crystal particles with a longer and thinner morphology.

Fig. S2 shows the energy dispersion spectra of $Co_{1.5}PW_{12}O_{40}$, and the data are listed in **Table S2** accordingly. In order to guarantee the accuracy of the test, the surface scanning was performed at low magnification. As shown in **Table S2**, the atomic contents of P, Co, W and O are 1.86%, 2.86%, 22.05% and 73.23% in turns. In calculation, the molecular formula is $Co_{1.538}P_1W_{11.855}O_{39.371}$ which is in very good consistent with the theoretical value.

As shown in **Fig. S3**, two weight loss steps can be observed in the TG profile. The first weight loss at temperatures of 30～180℃ can be attributed to desorption of adsorbed water. The second weight loss between 410℃ and 520℃ corresponds to the decomposition of $Co_{1.5}PW_{12}O_{40}$ catalyst. Consequently, the catalyst is thermally stable

from 180℃ to 410℃ indicating that the catalyst can be used at the said temperature range. From the profile of DTG, maximum weight loss rates locate at 72℃ and 497℃, respectively.

The conversion products from methanol were analyzed by GC-MS method. **Fig. S4** shows the chromatograms of the products obtained at 250℃. The structures annotated onto the chromatograms are peak identifications in comparison with the mass spectra of those in the NIST database. Retention times of 1.321, 1.391 and 1.416min are ethylene, dimethyl ether and methanol in their turns.

As shown in **Fig. S5**, methanol conversion is kept almost at a level of 100% with ethylene selectivity at an extremely high value. It can also be seen that the complete transformation from methanol to ethylene is achieved within 6 h. It should be noted that the product is very clean without any other by-product when using $Co_{1.5}PW_{12}O_{40}$ as catalyst. To our best knowledge, this is the best result compared to reported literatures.

CAPTIONS:

Table S1 X-ray Diffraction Data of $Co_{1.5}PW_{12}O_{40}$

Table S2 Energy Dispersion Spectra of $Co_{1.5}PW_{12}O_{40}$

Fig. S1 Scanning Electron Microscope **(**SEM) images of (a) $H_3PW_{12}O_{40}$ (b) $Co_{1.5}PW_{12}O_{40}$

Fig. S2 Energy Dispersion Spectra of $Co_{1.5}PW_{12}O_{40}$

Fig. S3 Thermogravimetric and differential thermalgravimetric analysis (TG-DTA) of $Co_{1.5}PW_{12}O_{40}$ catalyst

Fig. S4 GC–MS chromatogram of reaction products over Methanol-To-Ethylene reaction at 250℃

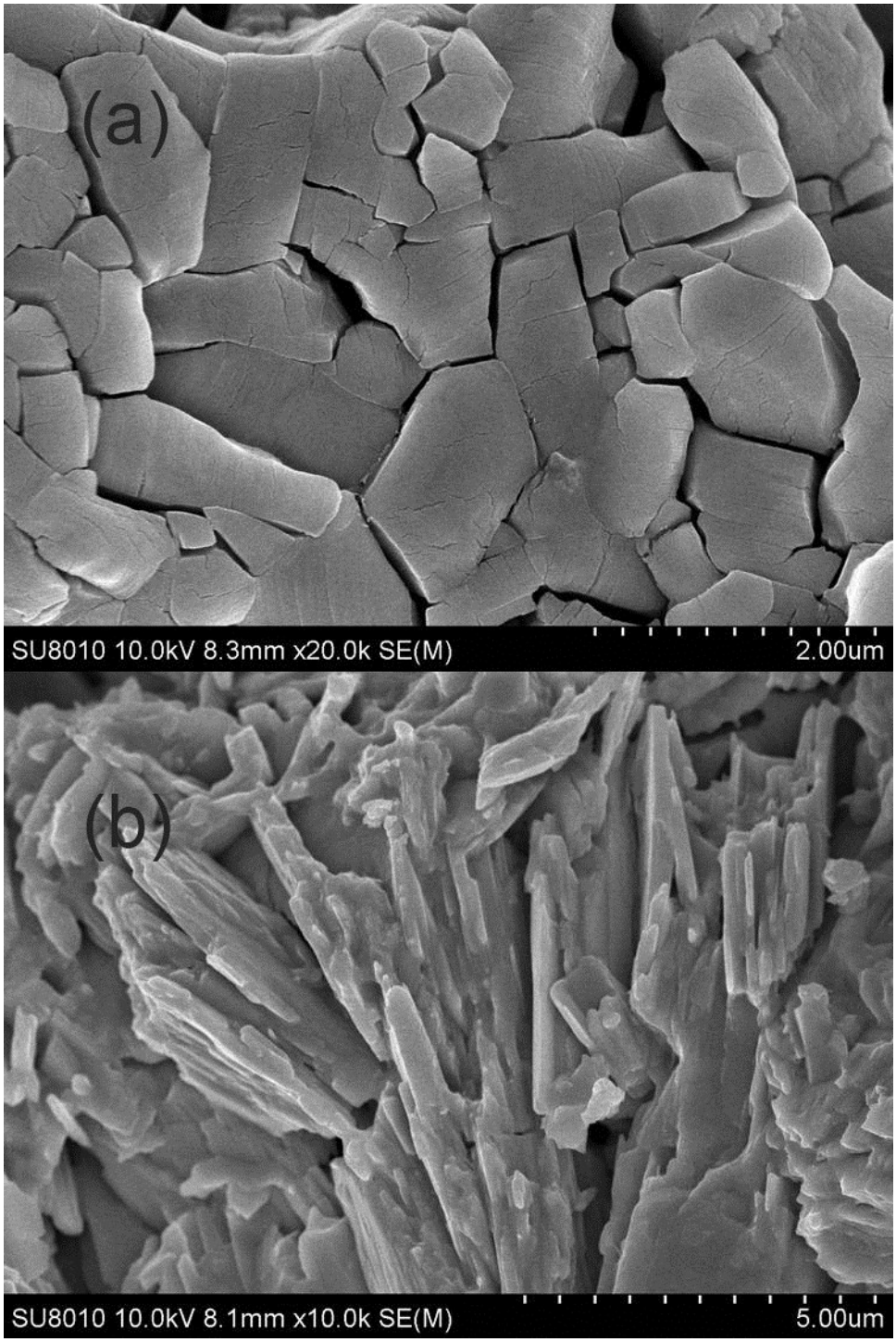
Fig. S5 Catalytic performance of $Co_{1.5}PW_{12}O_{40}$ as a function of time on stream (reaction temperature 300℃, reaction pressure 0.1MPa, methanol WHSV is $1.5h^{-1}$, carrier gas He is 60mL/min)

Table S1 X-ray Diffraction Data of $Co_{1.5}PW_{12}O_{40}$

Catalyst	2 Theta	FWHM	D(nm)	Crystallite(nm)
$Co_{1.5}PW_{12}O_{40}$	8.925	0.284	9.900	29.9
	18.03	0.358	4.915	23.4
	20.15	0.579	4.404	14.1
	27.24	0.345	3.271	24.8
	28.73	0.788	3.084	10.5

Table S2 Energy Dispersion Spectra of $Co_{1.5}PW_{12}O_{40}$

Element	**Mass (%)**	**Atom (%)**
O K	21.50	73.23
P K	1.06	1.86
Co K	3.09	2.86
W M	74.35	22.05
Total	100.00	
Molecular Formula	$Co_{1.538}P_1W_{11.855}O_{39.37}$	
	[1]	



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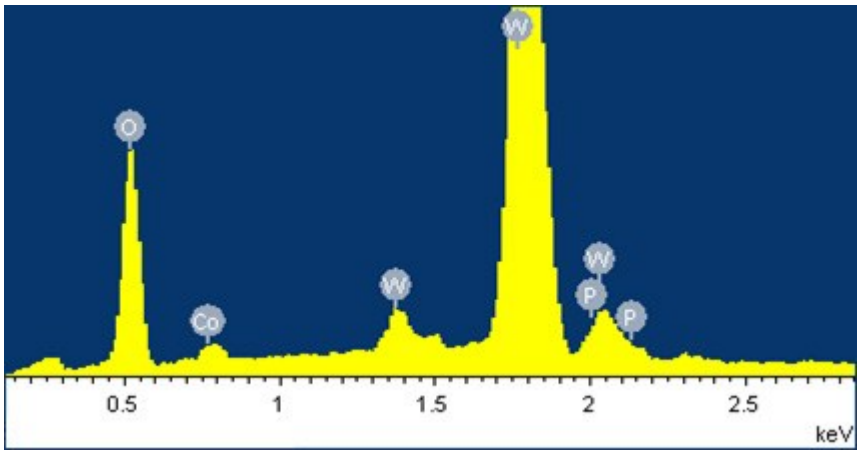

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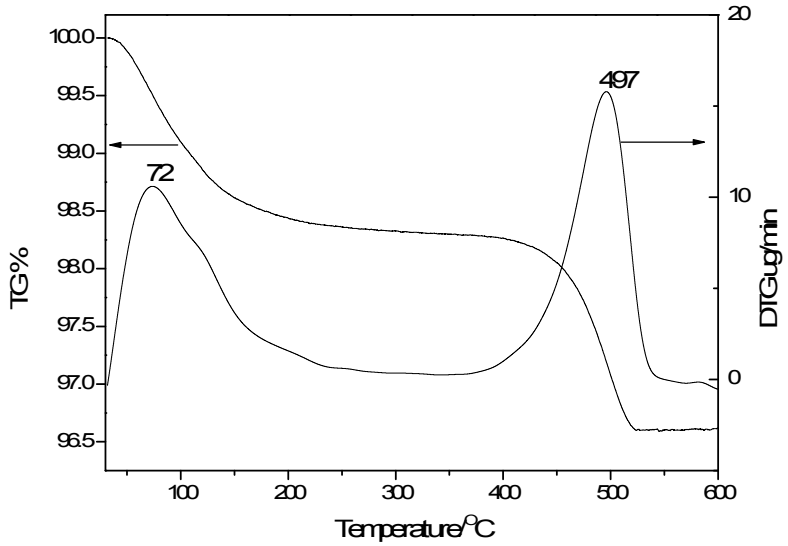


Fig. S3 Thermogravimetric and differential thermalgravimetric analysis (TG-DTA) of $Co_{1.5}PW_{12}O_{40}$ catalyst

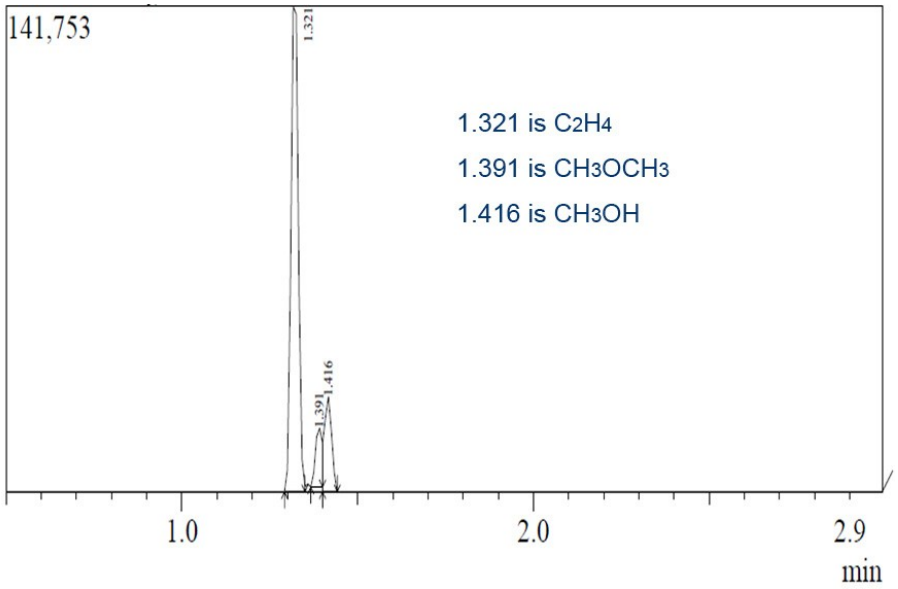
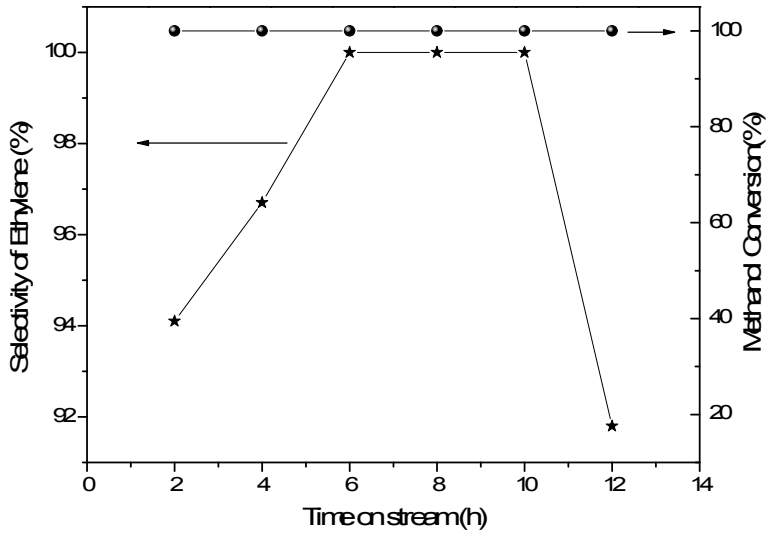


Fig. S4 GC–MS chromatogram of reaction products over Methanol-To-Ethylene reaction at 250℃



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