Supporting Information

Highly Efficient Polyoxometalate-based Catalysts for Clean-Gasoline Synthesis

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1. Experimental

1.1. Catalyst preparation

1.1.1. Preparation of Co/Al_2O_3 FTS catalyst

The Al_2O_3 (SCCA-5/200) support was provided by SASOL company. Co/Al_2O_3catalyst was obtained using incipient wetness impregnation of cobalt nitrate hexahydrate solutions in water. Then the catalyst precursor was evaporated for 3 hours, dried at 100°C for 10 hours, and calcined in air at 350°C for 3 hours. The cobalt loading in the samples was 10 wt%.

1.1.2. Preparation of CsPW catalyst

An appropriate amount of $CsNO_3$, $H_3PW_{12}O_{40}$ with molar ratios of 2.5 : 1 was ground with ball milling for 0.5 hours and then the solid powder was calcined at 300°C in flowing air for 2 hours.

1.1.3. Preparation of bifunctional catalyst

The bifunctional catalyst P-F was prepared by mechanically mixing FTS catalyst Co/Al_2O_3 and POMs catalyst CsPW. The weight of CsPW in the P-F catalyst was 5%, 10%, 20%, 50%.

1.2. Catalysts characterization

Powder X-ray diffraction (XRD) measurements were performed with a RigakuD/Max-RBX-ray diffractometer with Cu $K\alpha$ radiation. BET surface areas were determined by N_2adsorption-desorption isotherm measurements at -196^oC (Auto-sorb-ZQ-MP, Quantachrome, USA). The specific surface was calculated from the adsorption branch of the isotherm by BET method, while pore volume and pore size distributions were calculated from desorption branch of the isotherm by BJH method. Reduction mechanism and reduction extent of bifunctional catalyst were assessed by H_2-TPR (Micromeritics Auto Chem II 2920). The catalytic products were analyzed by a GC (ShimadzuGC2014).

1.3. Fischer-Tropsch synthesis test

The Fischer-Tropsch synthesis was carried out in a stainless steel fixed bed reactor (i.d. 12mm, length 600 mm). A quantity of 1.0 g bifunctional catalyst (60-80 mesh) diluted with silica sand (60-80 mesh) was loaded into the isothermal region of the reactor tube for all reaction tests. Prior to each test, the catalyst was reduced *in situ* under flowing H_2 (100 ml/min) at 300^oC for 2h at 2MPa. After reduction, the temperature of the reactor was lowered to 200^oC under flow of H_2, and a flow of a mixture of H_2, CO and N_2 (H_2: CO: N_2 volume ratio of 2:1, N_2 as internal standard for chromatography) was established through the reactor. The temperature was raised up to 250^oC at a rate of 1^oC min^{-1}. The temperature in the catalytic bed was controlled by two thermocouples connected to independent PID controllers. The finally reaction conditions were 2.0MPa, SV = 3000h^{-1}, and the reaction temperature was 250^oC.

The tail gas was analyzed by gas chromatography using a TDX-01 column (2.0 m×3.00 mm) with TCD and FID detectors. The liquid products were determined by gas chromatography with a HP-1 column (30.0m×0.32mm×1.00μm) and an FID detector.

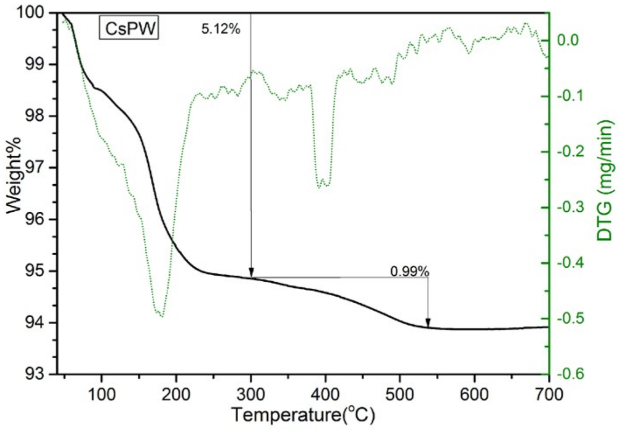

Fig.S1 The TG curve of CsPW catalyst

The thermal behaviors of CsPW catalyst was investigated under air atmosphere by thermogravimetric analysis with a heating rate of 10 K min^{-1} in the temperature range of 303 K to 973 K (Fig.S1). The TG curve exhibits a multistep continuous weight loss process. The weight loss of 5.12% before 573 K corresponds to the loss of lattice and coordinated water molecules. The weight loss of 0.99% from 573 K to 823 K is due to the loss of composition water molecules.

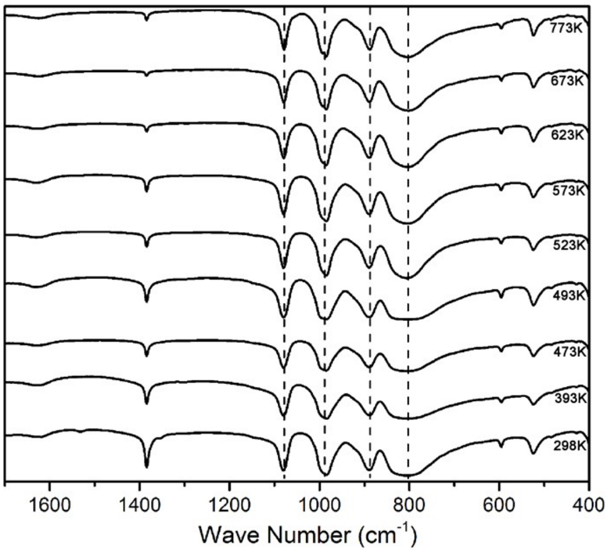

Fig.S2 IR profiles of CsPW with programming temperature

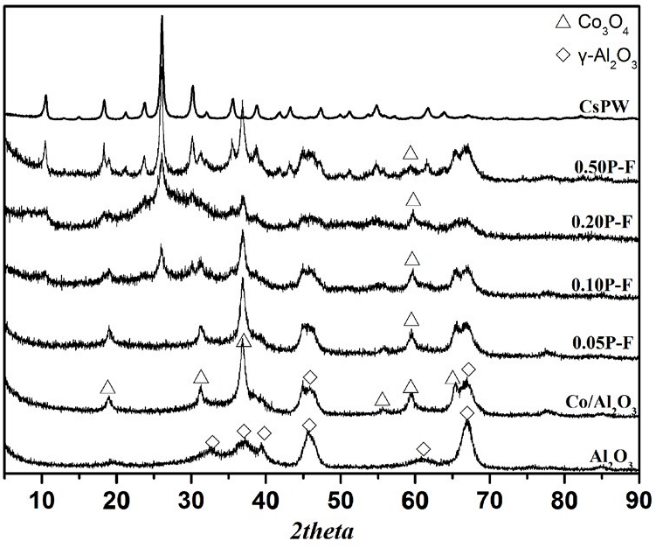

Fig.S3 Powder X-ray diffraction pattern of bifunctional catalysts

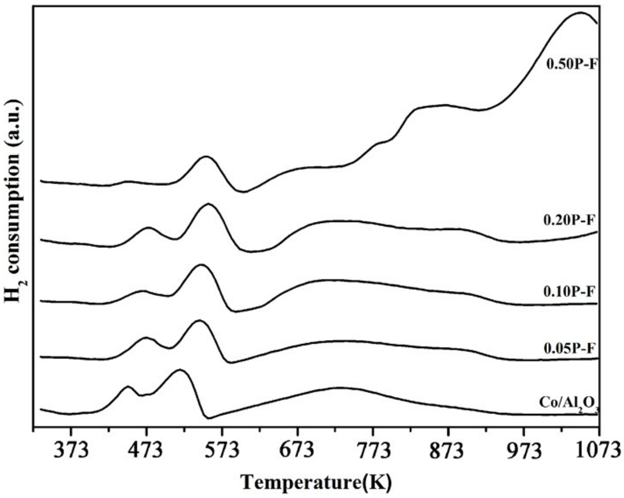

Fig.S4 H_2-TPR profiles of bifunctional catalysts

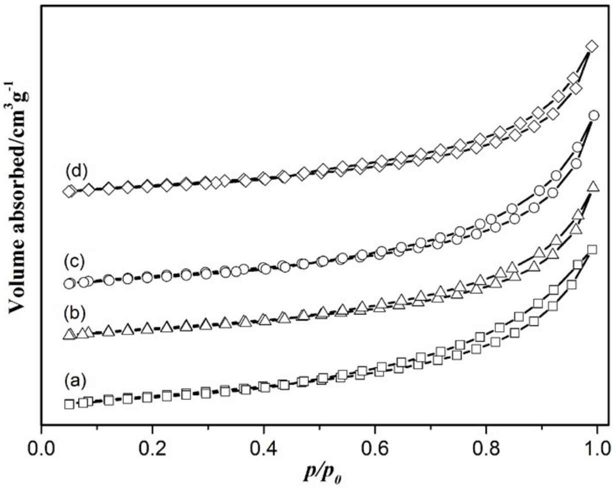

Fig.S5. N_2 adsorption-desorption isotherms of bifunctional catalysts (a) 0.05P-F, (b) 0.1P-F, (c) 0.2P-F, (d) 0.5P-F.

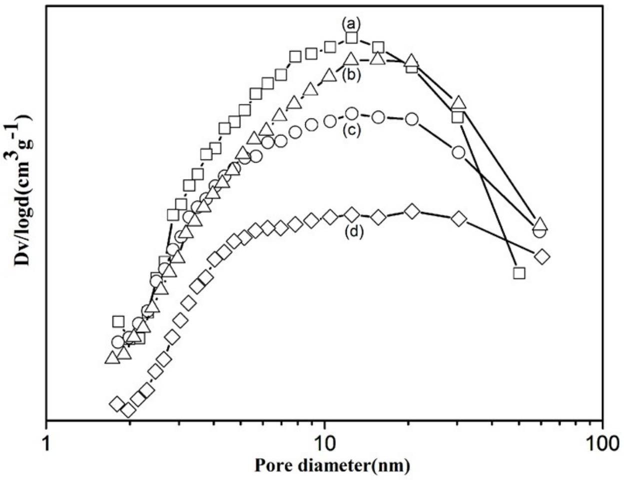

Fig.S6. Pore-size distributions of bifunctional catalysts (a) 0.05P-F, (b) 0.1P-F, (c) 0.2P-F, (d) 0.5P-F.

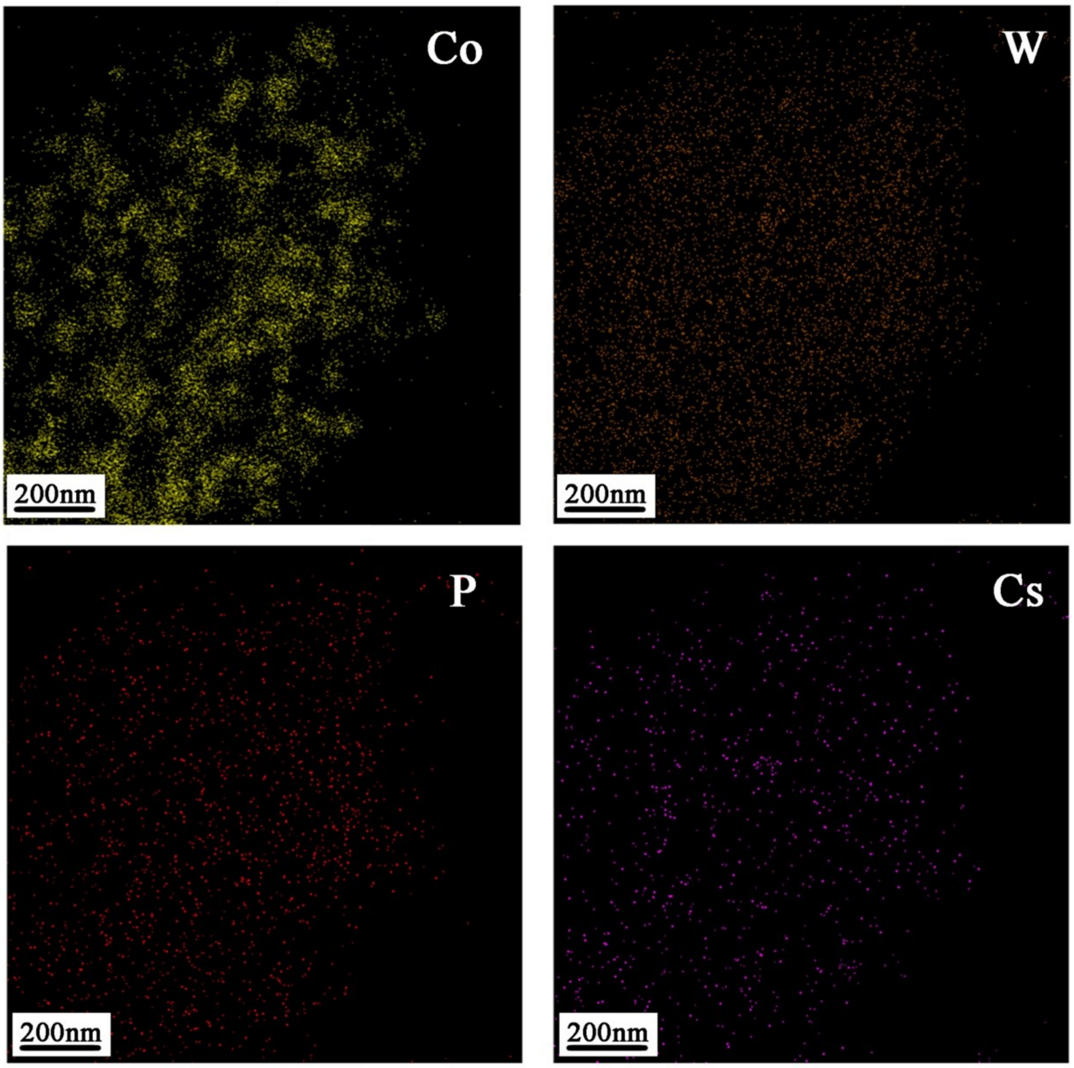

Fig.S7 The mapping of the element Co, P, Cs and W on the 0.2P-F

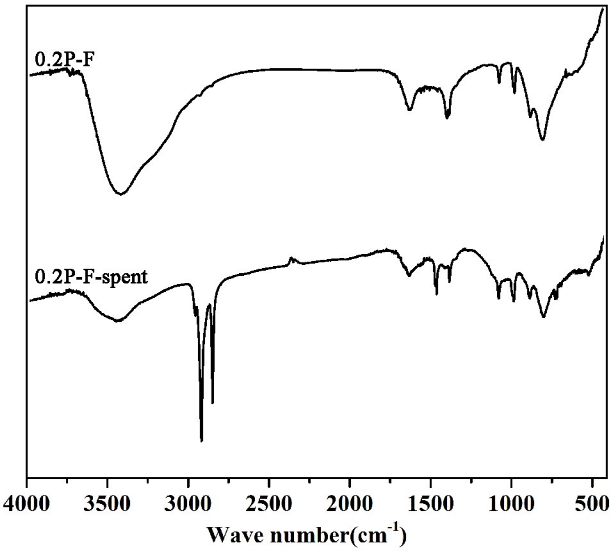

Fig.S8 IR profile of 0.2P-F and the catalyst after reaction 0.2P-F-spent