

# Synthesis of methyl glycolate by hydrogenation of dimethyl oxalate with P modified Co/SiO<sub>2</sub> catalyst

Zailang Zhuang,<sup>†a</sup> Yihui Li,<sup>†b</sup> Fang Chen,<sup>d</sup> Xingkun Chen,<sup>\*a</sup> Zheng Li,<sup>a</sup> Shiyi Wang,<sup>a</sup> Xuepeng Wang,<sup>a</sup>  
Hejun Zhu,<sup>b</sup> Yuan Tan,<sup>a</sup> Yunjie Ding,<sup>\*a,b,c</sup>

<sup>a</sup> Hangzhou Institute of Advanced studies, Zhejiang Normal University, 1108 Gengwen Road, Hangzhou 311231, China. cxklnd@zjnu.cn;

<sup>b</sup> Dalian National Laboratory for Clean Energy, Dalian Institute of Chemical Physics, Chinese Academy of Sciences, 457 Zhongshan Road, Dalian 116023, China. dyj@dicp.ac.cn ;

<sup>c</sup> The State Key Laboratory of Catalysis, Dalian Institute of Chemical Physics, Chinese Academy of Sciences, 457 Zhongshan Road, Dalian 116023, China.

<sup>d</sup> Central Research Institute of China Chemical Science and Technology Co., Ltd., Beijing 100083, China.

<sup>†</sup>Equal contribution.

## 1. Experimental

### 1.1 Materials

### 1.2 Catalyst preparation

The Co/SiO<sub>2</sub> and CoXP/SiO<sub>2</sub> catalysts (20 wt.% Co, X= mol ratio of Co and P) were prepared using the classic volumetric impregnation.

Firstly, the 20 wt.%Co/SiO<sub>2</sub> was prepared. The cobalt nitrate solution with a specific amount of CoNO<sub>3</sub>·6H<sub>2</sub>O was added into the fumed silica (AEROSIL 300). After stirring, the sample was kept at room temperature for 8 h, then dried at 383K for 8 h and eventually calcined at 723K for 4 h. The obtained powder is named as 20Co/SiO<sub>2</sub>.

Then, CoXP/SiO<sub>2</sub> catalysts were prepared by impregnating 20Co/SiO<sub>2</sub> with NH<sub>4</sub>H<sub>2</sub>PO<sub>4</sub> aqueous solution. At first, a certain amount of NH<sub>4</sub>H<sub>2</sub>PO<sub>4</sub> is added in the water. Then, the NH<sub>4</sub>H<sub>2</sub>PO<sub>4</sub> solution was added into the 20Co/SiO<sub>2</sub> sample. After keeping at room temperature for 8 h and drying at 383K for 8 h, the obtained sample was calcined at 723K for 4 h. For comparison, the catalyst with different phosphorus content was synthesized by changing the loading amount of NH<sub>4</sub>H<sub>2</sub>PO<sub>4</sub>. These catalysts are labeled as 20CoXP/SiO<sub>2</sub>, where X represents the molar ratio of cobalt-phosphorus, 20 represents the cobalt loading.

For the catalyst characterization, all the catalysts were reduced at 923K for 3 h in 5% H<sub>2</sub>/Ar (V/V) atmosphere and after cooling down to room temperature at N<sub>2</sub> atmosphere, the catalyst was passivated in 0.5% O<sub>2</sub>/N<sub>2</sub> flow for 2 h.

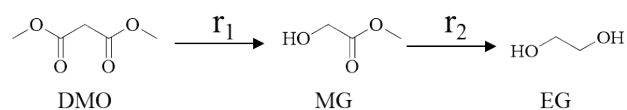
### 1.3 Catalytic tests

The catalytic performance of the synthetic material was evaluated in a stainless steel fixed-bed reactor (inner diameter, 10.0 mm; length, 660 mm) equipped with thermocouples and mass flow controllers to control the reaction temperature and hydrogen flow. Typically, 1.0 g of catalyst is placed in the center of the reactor. Before the reaction, the catalyst was in-situ reduced by hydrogen

flow at 923K for 3 h. After the reactor temperature was cooling down to the reaction temperature and reaction pressure was adjusted to the set point, the methanol solution (10 wt %) of DMO was pumped into the reactor from the top of the reactor along with hydrogen (flow rate: 160mL/min). After passing through the reactor and a cold trap, the product became two phases in a separator. The liquid products were drained periodically from the gas–liquid separator and analyzed by an Agilent 7890B chromatograph equipped with an HP-FFAP capillary column (30 m×0.32 mm×0.25 μm) and a flame ionization detector (FID).

The catalyst stability was tested at the following conditions: reaction temperature was 513K, the reaction pressure was 2.5 MPa with the hydrogen follow rate controlled at 160 mL/min.

The kinetics analysis experiment was carried out with the DMO conversion below 5% by changing the DMO liquid hourly space velocity. The temperature was controlled between 200-240 °C. The kinetic law equation was defined as below:



$$\ln k_1 = \ln A_1 - E_{a1}/RT$$

$$\ln k_2 = \ln A_2 - E_{a2}/RT$$

#### 1.4. Characterization

XRD measurements were performed to analyze the structure and crystallinity of the CoXP/SiO<sub>2</sub> catalyst. The XRD pattern was obtained using Rigaku Ultra IV ACS Applied Materials & Interfaces Research Article u K $\alpha$  radiation ( $\lambda = 0.1542$  nm) at 35 kV and 25 mA in the 2 $\theta$  scan range of 10–90°, the scan rate is 10° min<sup>-1</sup>.

Transmission electron microscope (TEM) measurement was performed on Tecnai G2 F30 (FEI, USA). Before measurement, the sample was evenly dispersed in ethanol and then placed on a copper mesh. Scanning electron microscope (SEM) measurements were performed on Hitachi S-4800 (Japan) with an accelerating voltage of 3.0 kV.

Nitrogen adsorption-desorption isotherms was conducted at -196 °C on a Quantachrome Autosorb-3B instrument. Before adsorption-desorption, vacuum the sample at 100°C for at least 6 hours. The specific surface area (SSA) is calculated from the adsorption branch by the Brunauer-Emmett-Teller method in the relative pressure range of 0.05 to 0.25.

The actual P loading amount of the catalyst was quantitatively determined by inductively coupled plasma atomic emission spectrometry (ICP-AES) on the Thermo IRIS Intrepid IIXSP ICP spectrometer.

The superficial chemical composition was determined by X-ray Photoelectron Spectroscopy (XPS). The analyses were performed in an ultra-high vacuum (UHV) surface analysis station using an electron spectrometer equipped with a hemispherical analyzer PHOIBOS 150, an X-ray cannon XR-50 of double anode using Al K $\alpha$  non-monochromatic radiation (1486.6 eV). The anode was operated at 10 kV and 10 mA. General spectra and high-resolution spectra were recorded with a pass energy of 50 and 20 eV, respectively. The binding energy displacement that occurs due to

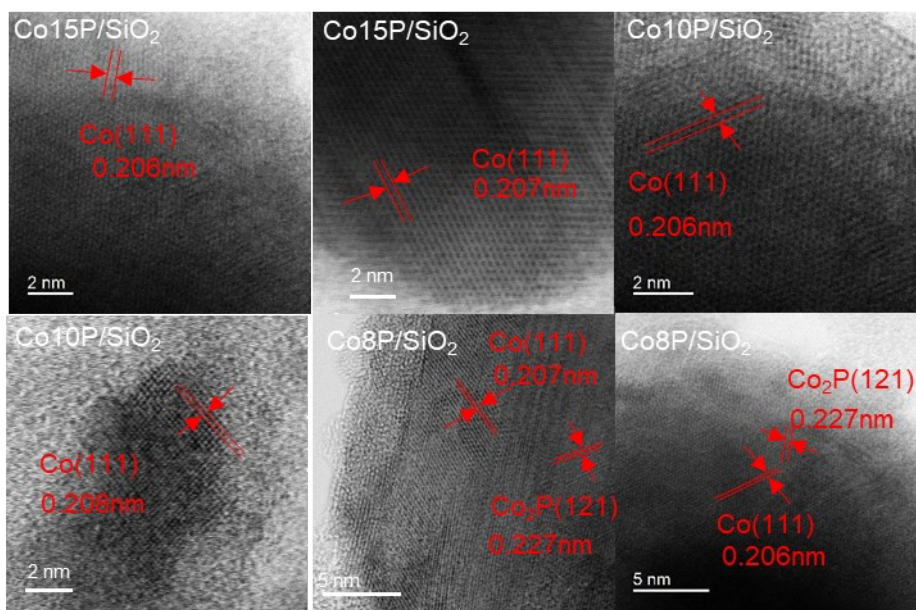
surface charges was corrected by an internal reference (C1s binding energy at 284.8 eV). The spectra were corrected by subtracting the background using the Shirley method and adjusted using Casa XPS software version 2.3.14. The composition was calculated using Co 2p and P 2p core levels. The samples were analyzed after heating at 500 °C. The sample went through chambers under successively growing vacuum: pre-chamber ( $10^{-3}$ mbar), intermediate chamber ( $10^{-6}$ – $10^{-9}$ mbar) and UHV chamber ( $< 3 \times 10^{-9}$ mbar).

**Table S1** Physicochemical properties of different Co based catalysts

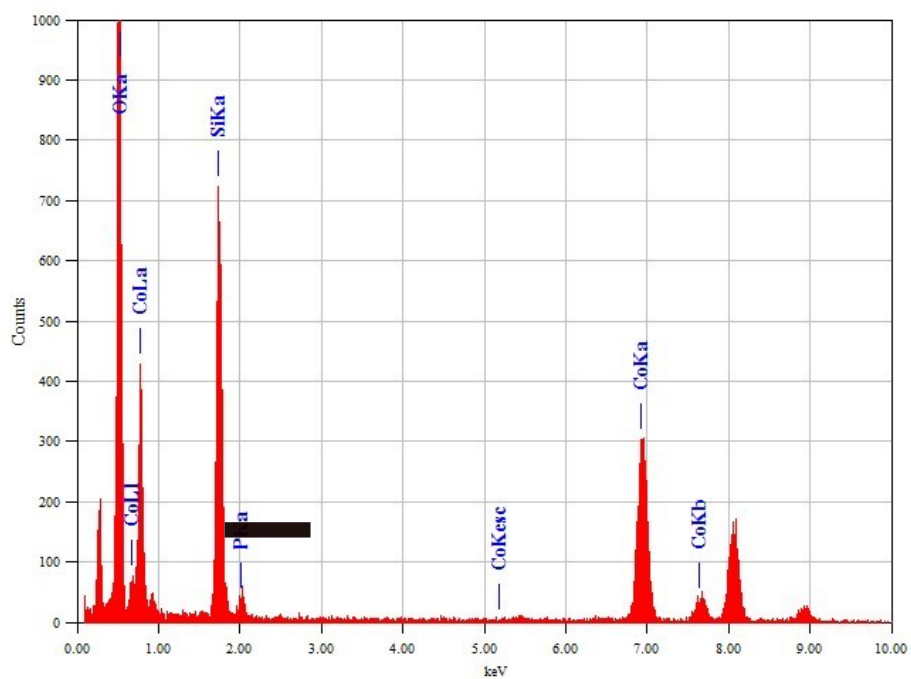
Catalysts	V <sub>pore</sub> (cm <sup>3</sup> .g <sup>-1</sup> )	S <sub>BET</sub> (m <sup>2</sup> .g <sup>-1</sup> )	D <sub>pore</sub> (nm)	Co* Wt %	P* Wt %	Co:P(atom/atom)		TOF <sub>(Co)</sub> /h <sup>-1</sup>
						XPS	ICP	
Co1P/SiO <sub>2</sub>	0.85	135	9.04	16.9	7.83	0.70	1.13	0.181
Co3P/SiO <sub>2</sub>	0.65	156	9.11	19.5	3.44	1.98	2.98	0.231
Co6P/SiO <sub>2</sub>	0.75	161	9.07	20.6	1.63	5.58	6.64	0.258
Co8P/SiO <sub>2</sub>	0.81	165	9.01	20.4	1.06	6.90	10.1	0.288
Co10P/SiO <sub>2</sub>	0.76	175	9.05	21.3	0.89	7.63	12.6	0.237
Co15P/SiO <sub>2</sub>	0.77	184	9.07	22.7	0.69	11.7	17.3	0.202
Co/SiO <sub>2</sub>	1.13	211	8.98	19.6	0	/	/	0.067

\*Tested by ICP

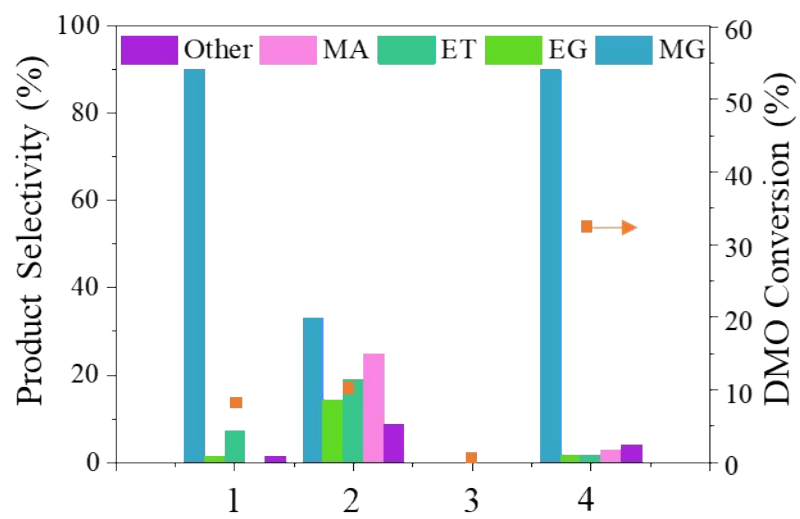
Comparing the molar ratio of Co/P calculated by XPS and ICP, we can see that the content of P element on the surface of the catalyst was much higher than on the whole phase. This was because that the catalyst was prepared by first impregnating Co then subsequently impregnating P.



**Fig. S1** HRTEM micrographs of the catalysts



**Fig. S2** EDS of Co<sub>15</sub>P/SiO<sub>2</sub> catalyst



**Fig. S3** Catalytic performance of different catalysts:  
 1.  $\text{Co}_3(\text{PO}_4)_2/\text{SiO}_2$ ; 2.  $\text{Co}/\text{SiO}_2$ ; 3.  $\text{P}/\text{SiO}_2$ ; 4. Physically mixed  $\text{P}/\text{SiO}_2$  and  $\text{Co}/\text{SiO}_2$ .

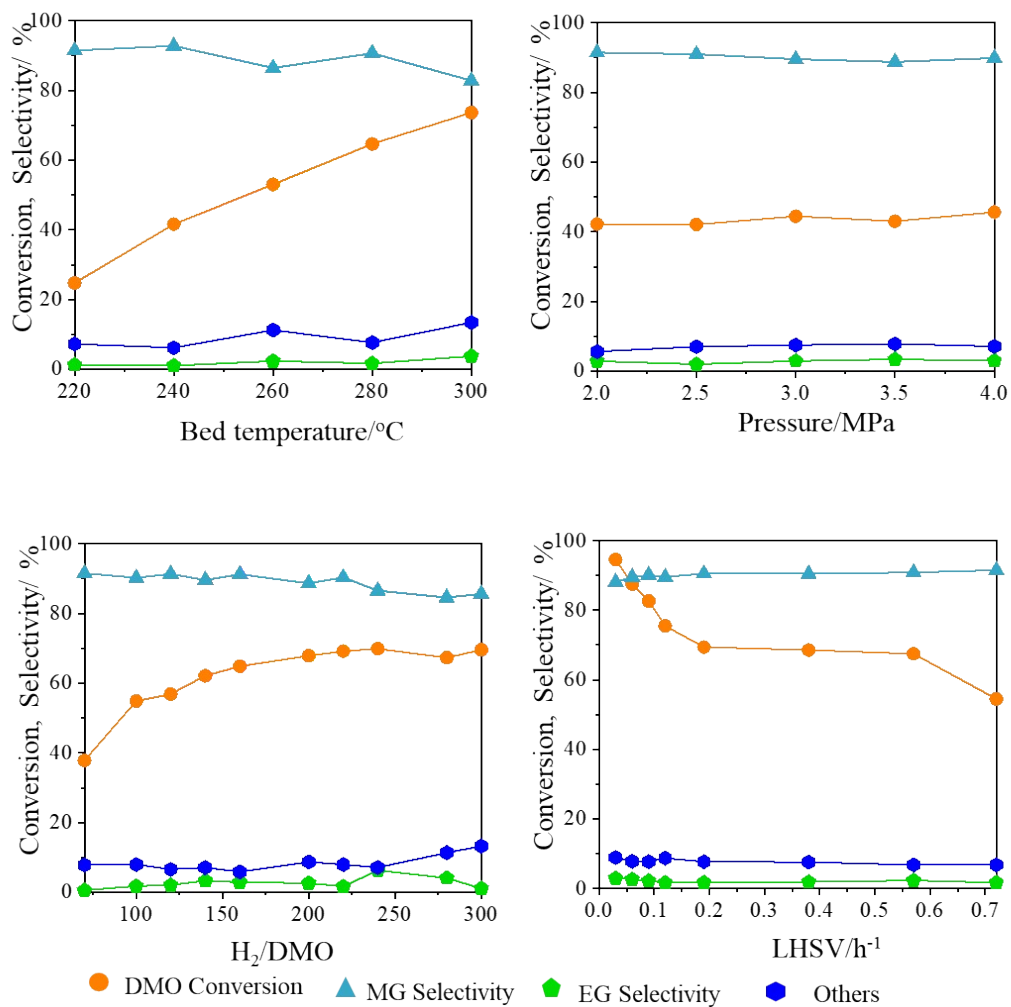
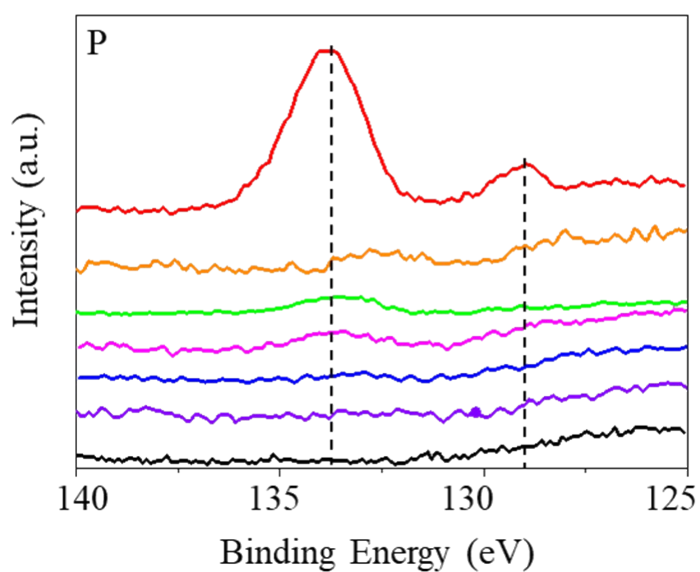


Fig. S4 Optimization of reaction condition

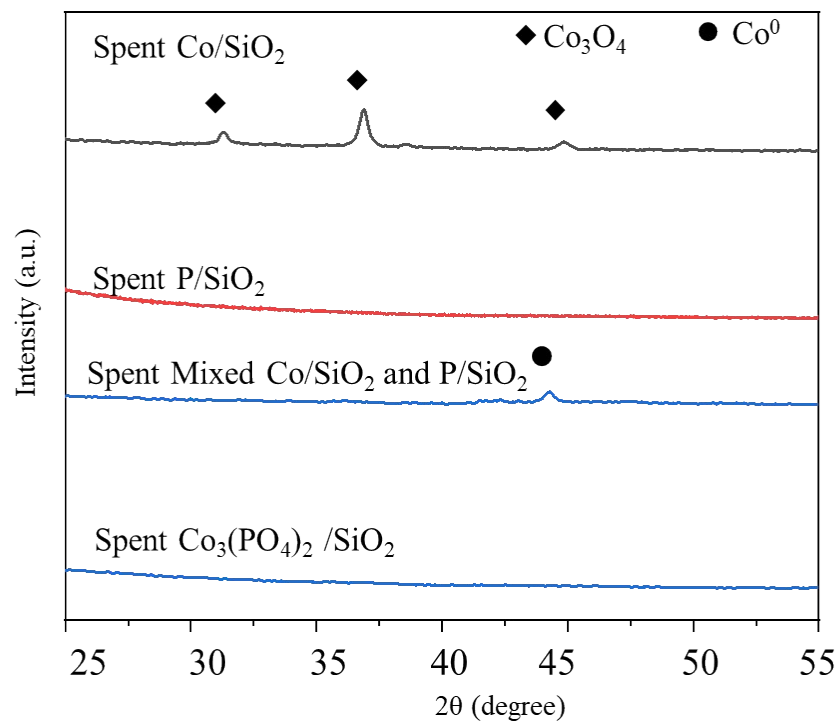


— Co/SiO<sub>2</sub>    — Co1P/SiO<sub>2</sub>    — Co3P/SiO<sub>2</sub>    — Co6P/SiO<sub>2</sub>  
— Co8P/SiO<sub>2</sub>    — Co10P/SiO<sub>2</sub>    — Co15P/SiO<sub>2</sub>



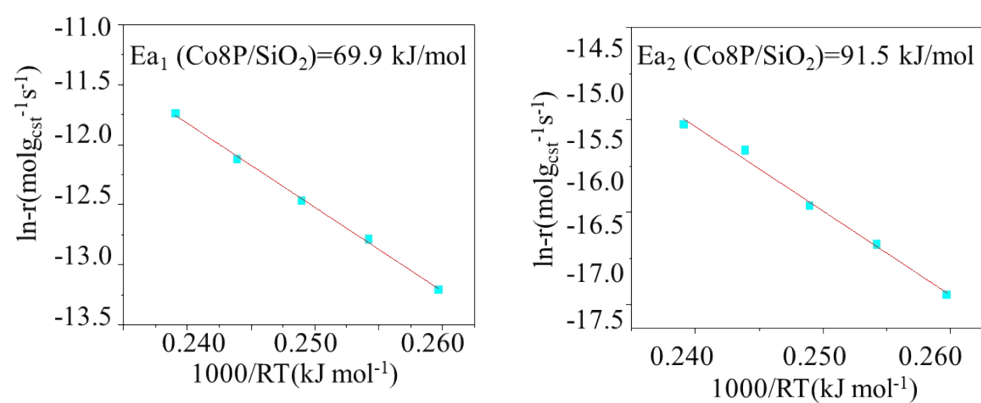
**Fig. S5** P 2p XPS spectra of reduced CoXP/SiO<sub>2</sub> (X=0, 1.0, 3.0, 6.0, 8.0, 10.0, 15.0).

The P 2p core-level spectra of Co1P/SiO<sub>2</sub> show two types of contributions: one at around 129 eV, the fingerprint of P<sup>δ-</sup> ( $0 < \delta < 1$ ) in cobalt phosphides (Co<sub>2</sub>P); and one at 133 eV, assigned to PO<sub>4</sub><sup>3-</sup> or PO<sub>3</sub><sup>3-</sup>.

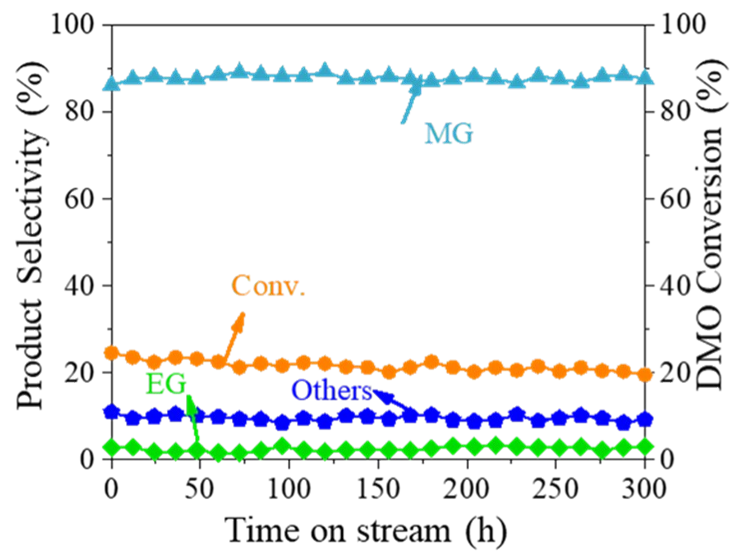


**Fig. S6** XRD spectra of the spent catalysts.

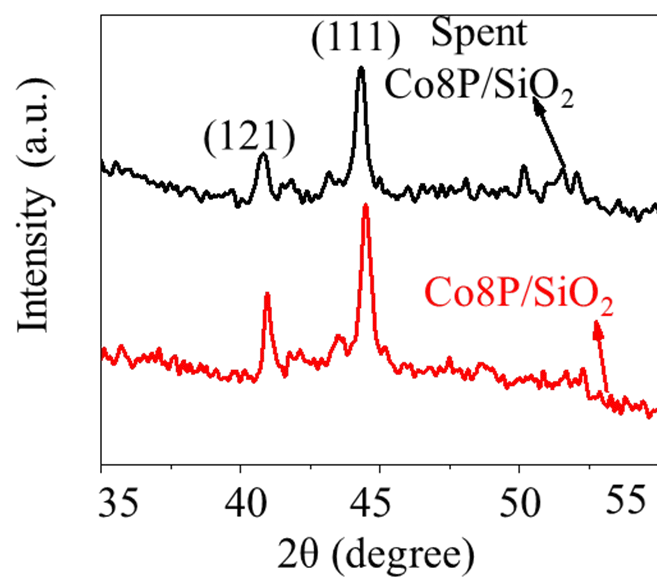
1. Co/SiO<sub>2</sub>; 2. P/SiO<sub>2</sub>; 3. Physically mixed P/SiO<sub>2</sub> and Co/SiO<sub>2</sub>; 4. Co<sub>3</sub>(PO<sub>4</sub>)<sub>2</sub>/SiO<sub>2</sub>.



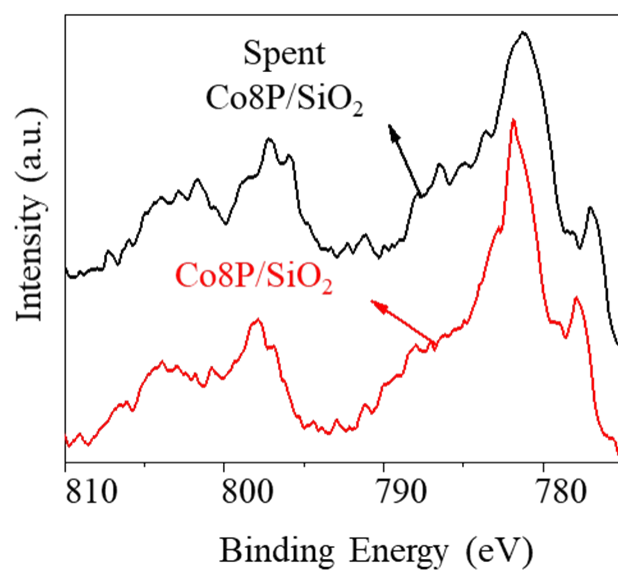
**Fig. S7** Kinetic measurement of Co8P/SiO<sub>2</sub>



**Fig. S8** Stability of the Co<sub>8</sub>P/SiO<sub>2</sub> catalyst. Reaction conditions: P=3 MPa, T=240 °C ,  
H<sub>2</sub>/DMO=160, LHSV=0.28 h<sup>-1</sup>



**Fig. S9** XRD spectra of spent and fresh Co8P/SiO<sub>2</sub>



p

**Fig. S10** XPS spectra of Co 2p of spent and fresh Co8P/SiO<sub>2</sub>