Supporting Information

Lewis Acid Sites in MOFs Supports Promoting the Catalytic Activity and Selectivity for CO Esterification to Dimethyl Carbonate

Yu-Ping Xu,[a,b] Zhi-Qiao Wang,[b] Hong-Zi Tan,[b] Kai-Qiang Jing,[b] Zhong-Ning Xu,[b*] Guo-Cong Guo[b*]

[a] *College of Chemistry and Materials Science, Fujian Normal University, Fuzhou, Fujian 350007, P. R. China.*

[b] *State Key Laboratory of Structural Chemistry, Fujian Institute of Research on the Structural of Matter, Chinese Academy of Sciences, Fuzhou, Fujian 350002, P. R. China.*

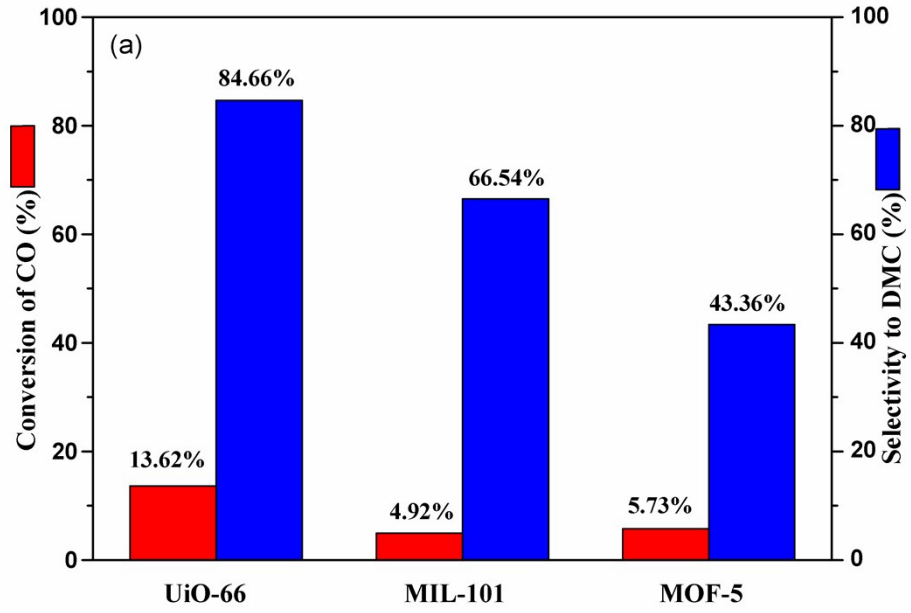
† Dedicated to Professor Jin-Shun Huang on the occasion of his 80th birthday.

[*] *To whom correspondence should be addressed: E-mail: gcguo@fjirsm.ac.cn; znxu@fjirsm.ac.cn*

Table S1. The conversion of CO and selectivity to DMC over Pd(II)/MOFs catalysts (Pd(II)/UiO-66, Pd(II)/MIL-101 and Pd(II)/MOF-5) for CO esterification to DMC.

Entry	Catalysts	CO conversion (%)	[b] DMC selectivity (%)	[c] WTY of DMC ($g \cdot kg_{cat.}^{-1} \cdot h^{-1}$)
1	Pd(II)/UiO-66 (Zr)	87.92%	98.47%	1653
2	Pd(II)/MIL-101 (Cr)	47.03%	72.04%	647
3	Pd(II)/MOF-5 (Zn)	68.26%	24.25%	316

[a] Reaction conditions: 200 mg catalyst, weight hour space velocity (WHSV) = 2500 $L \cdot kg_{cat.}^{-1} \cdot h^{-1}$, CO : CH_3ONO : Ar : N_2 = 19 : 45: 3 : 33 (volume), 393 K, 0.1 MPa. [b] Selectivity to DMC based on CO. [c] WTY represents the weight-time yield, grams of DMC per kilograms of the catalyst per hour ($g \cdot kg_{cat.}^{-1} \cdot h^{-1}$).



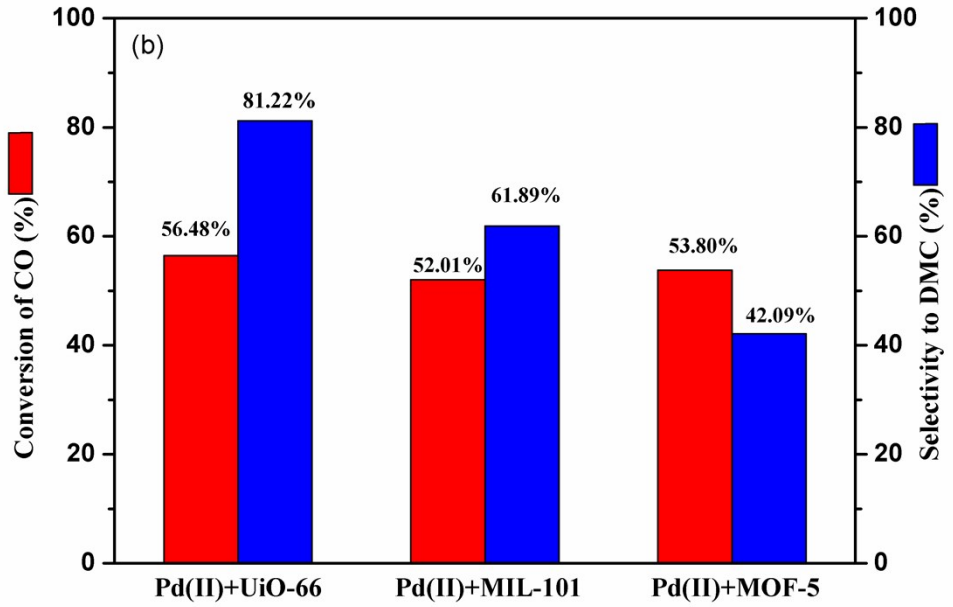


Fig. S1 The conversion of CO and selectivity to DMC over pure MOFs (UiO-66, MIL-101 and MOF-5) and (b) physical mixture of MOFs and $Pd(OAc)_2$ for CO esterification to DMC after 2 hours.

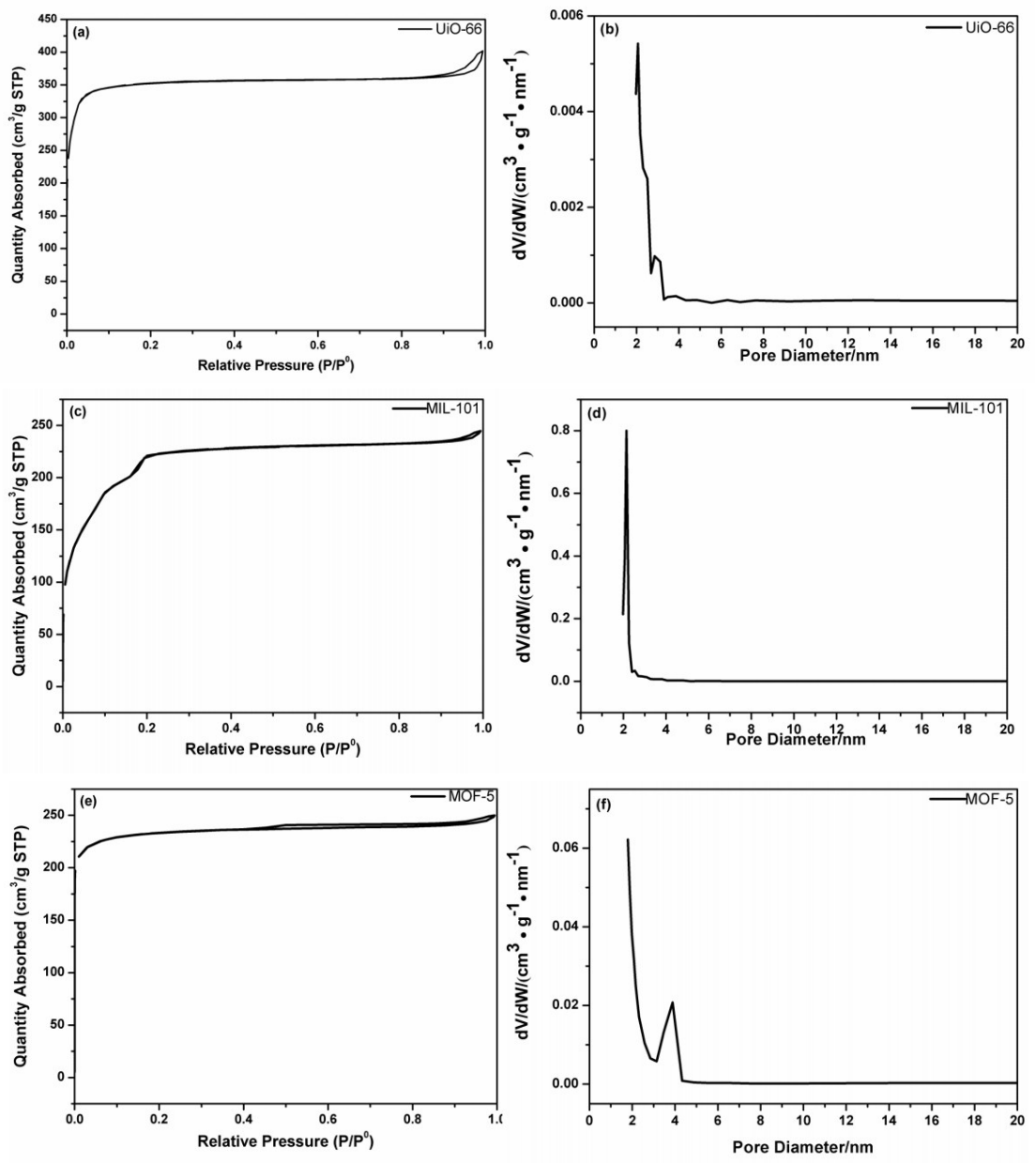


Fig. S2 (a) Nitrogen adsorption-desorption isotherms and (b) BJH desorption average pore size distribution of UiO-66. (c) Nitrogen adsorption-desorption isotherms and (d) BJH desorption average pore size distribution of MIL-101. (e) Nitrogen adsorption-desorption isotherms. (f) BJH desorption average pore size distribution of MOF-5.

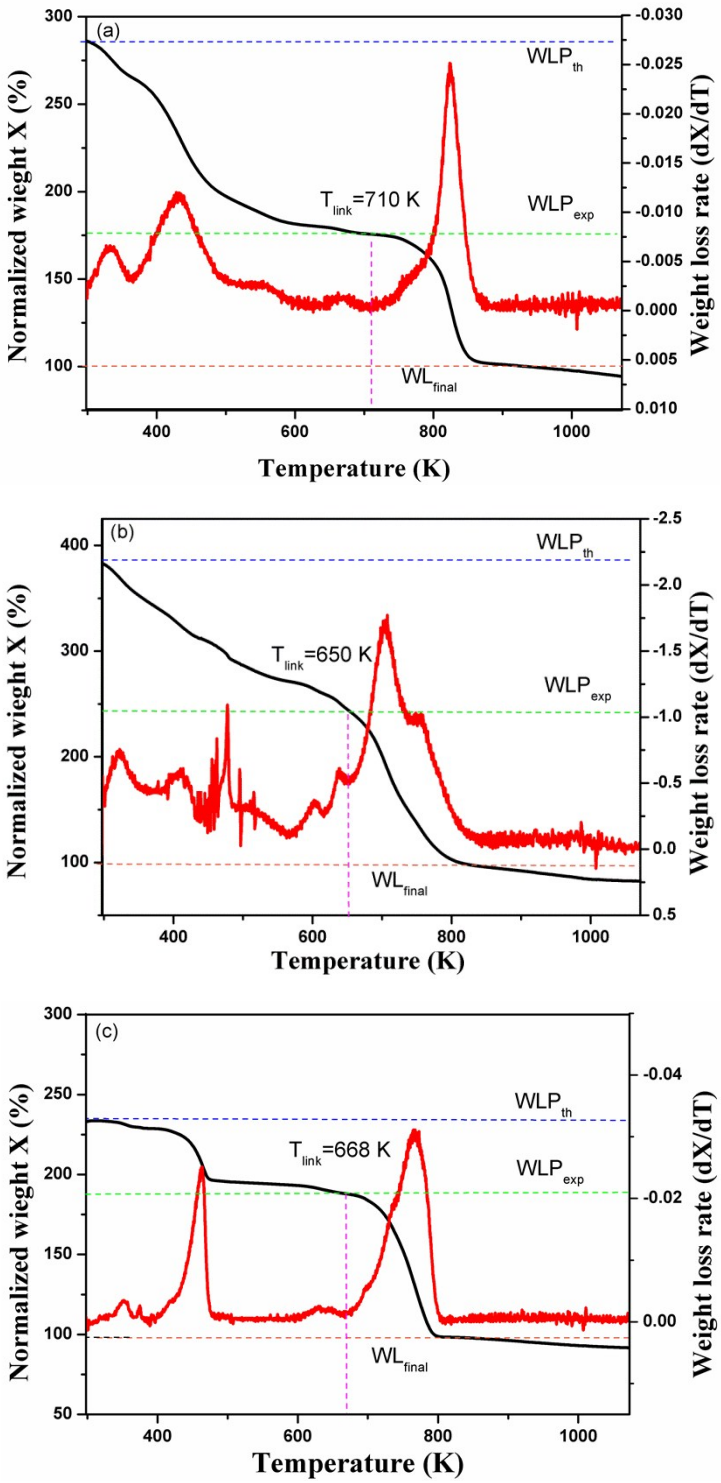


Fig. S3 TGA/DTG profiles of (a) UiO-66, (b) MIL-101 and (c) MOF-5.

Black solid line, left axis TGA curve, Red solid line, right axis DTG curve. WL_{final} (orange dashed line) represents the end of the theoretical TGA weight-loss plateau; WLP_{th} (blue dashed line) represents the start of the theoretical TGA weight-loss plateau; WLP_{exp} (green dashed line) represents the start of the experimental TGA weight-loss plateau; T_{link} (pink dashed line) represents the temperature of the combustion of the linker.

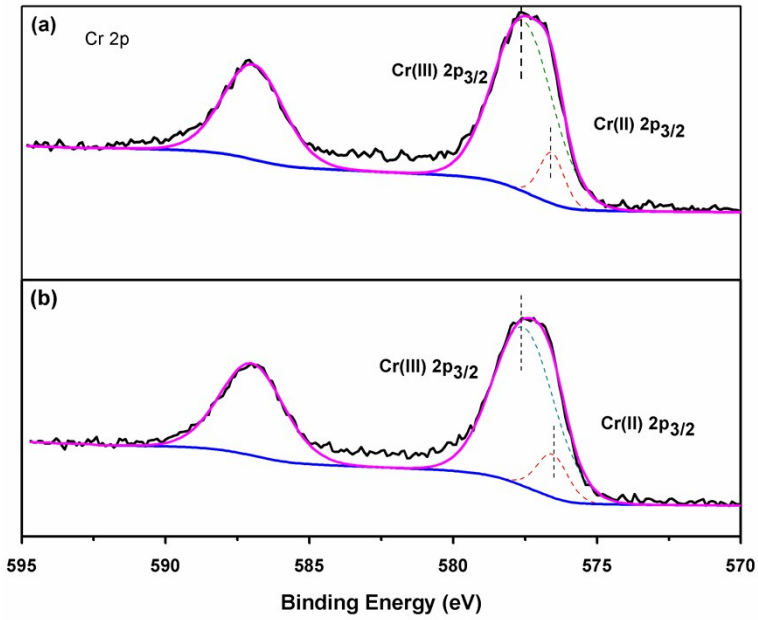


Fig. S4 The XPS spectra of Cr 2p (a) fresh and (b) engaged Pd(II)/MIL-101 catalyst.

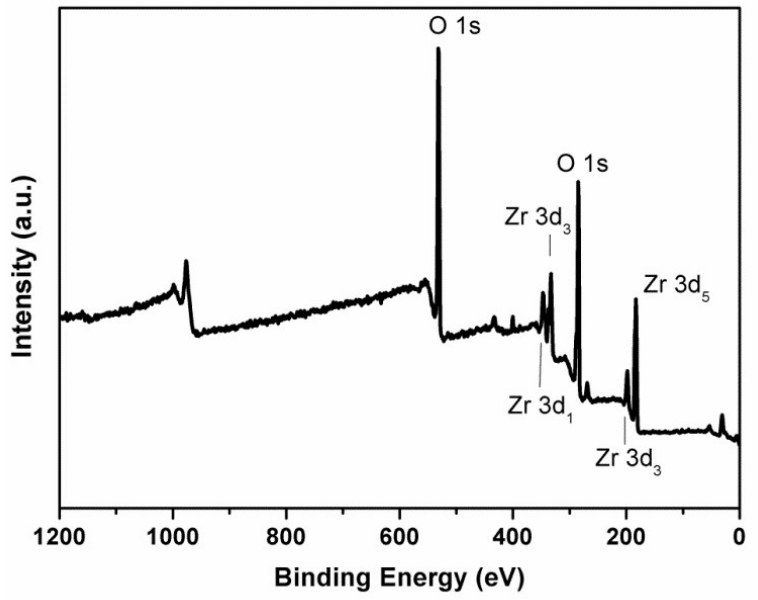


Fig. S5 The wide XPS spectrum of UiO-66.

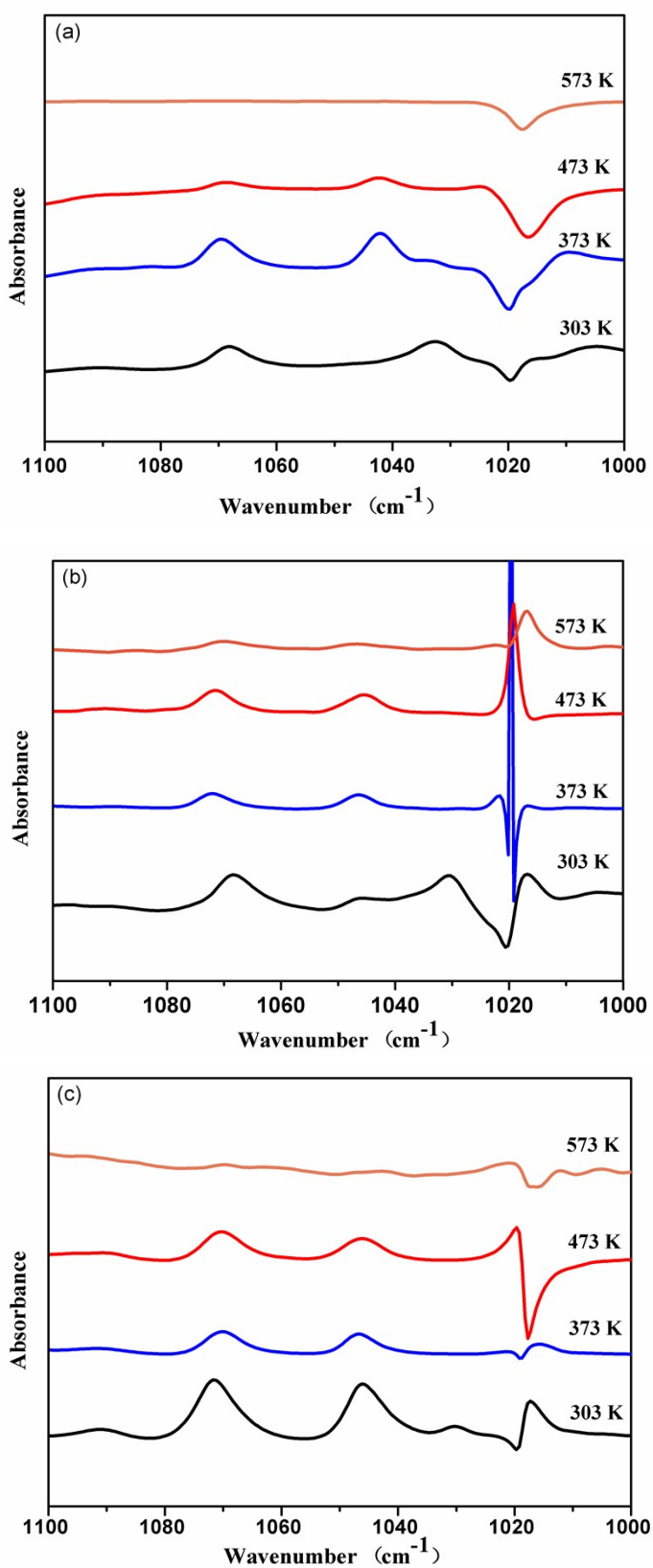


Fig. S6 IR spectra of (a) UiO-66, (b)MIL-101 and (c) MOF-5 after adsorption of pyridine at 303 K followed by vacuum treatment at different temperatures 373 K, 473 K and 573 K.

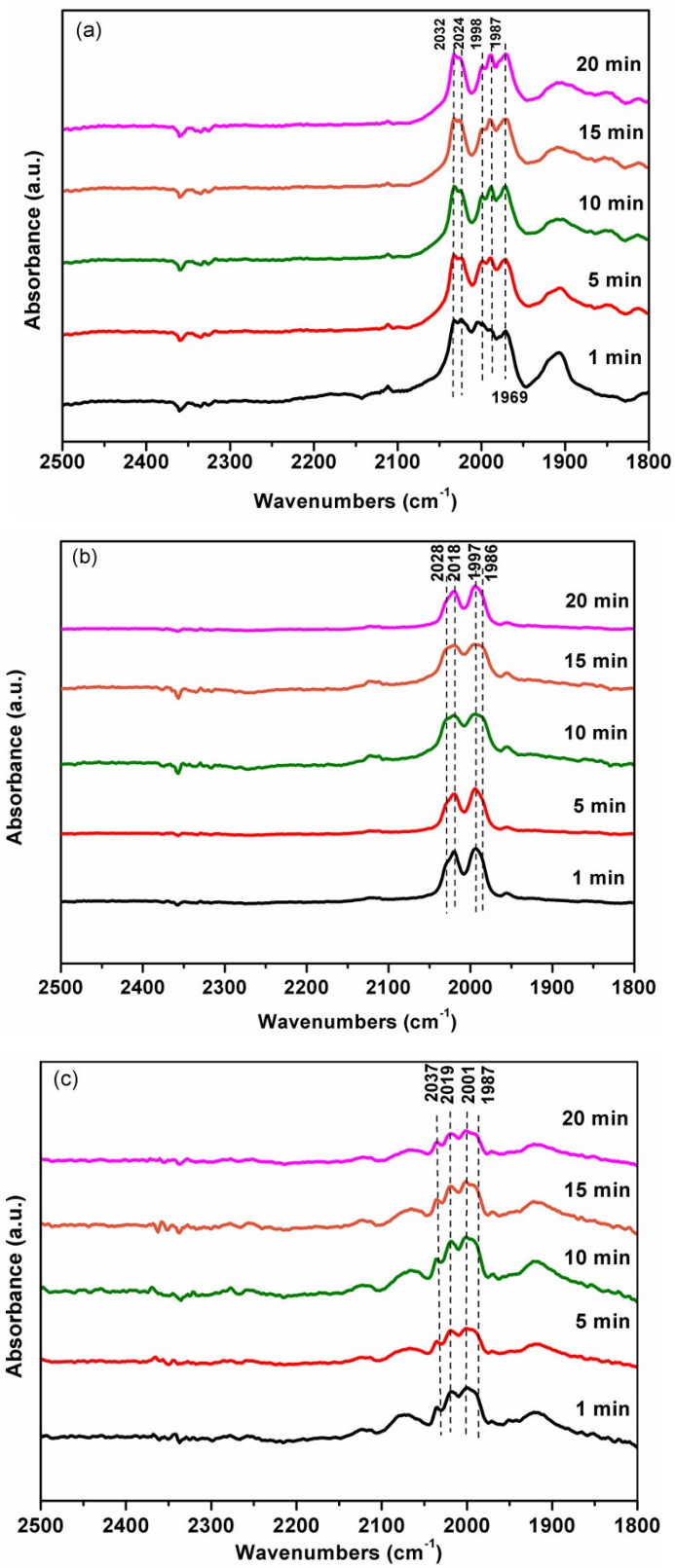


Fig. S7 *In situ* DRIR spectra of CO adsorption on catalysts at 293 K range from 2500 to 1800 cm^{-1} (a) Pd(II)/UiO-66 (b) Pd(II)/MIL-101 and (c) Pd(II)/MOF-5.