Supporting Information

$(Pd\text{-}CuCl_2)/\gamma\text{-}Al_2O_3$: a high-performance catalyst for carbonylation of methyl nitrite to dimethyl carbonate

Dong-Mei Lv,[a,b] Zhong-Ning Xu,*[a] Si-Yan Peng,[a] Zhi-Qiao Wang,[a] Qing-Song Chen,[a] Yumin Chen,[a] Guo-Cong Guo*[a]

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

[b] *Key Laboratory of Coal to Ethylene Glycol and Its Related Technology, Chinese Academy of Sciences, Fuzhou, Fujian 350002, P. R. China*

** To whom correspondence should be addressed: E-mail: gcguo@fjirsm.ac.cn, znxu@fjirsm.ac.cn; Fax: +86-591-83714946; Tel: +86-591-83512502*

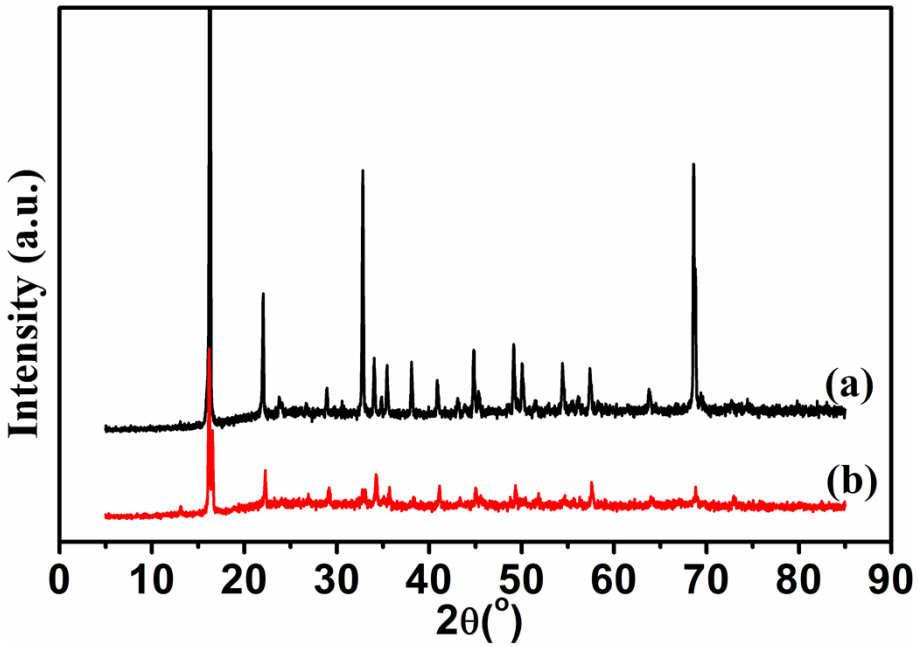

Fig. S1. XRD patterns of (a) $CuCl_2$ and (b) (Pd-$CuCl_2$)/γ-Al_2O_3 catalyst.

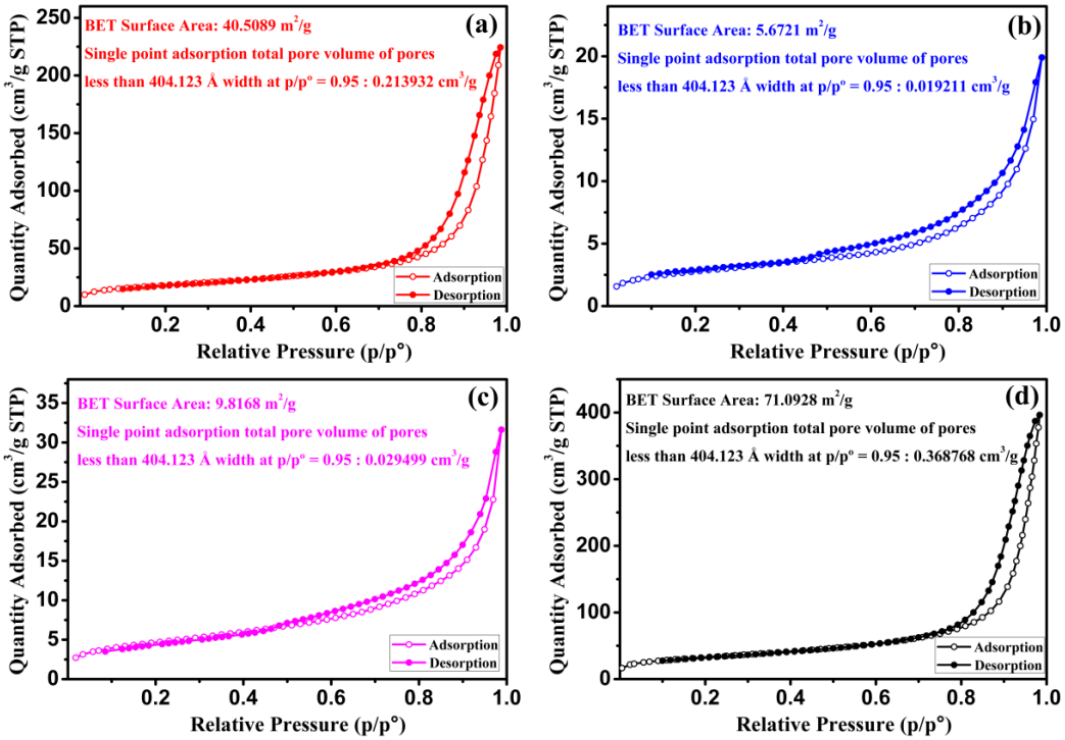

Fig. S2. Nitrogen adsorption-desorption isotherms of (a) (Pd-$CuCl_2$)/γ-Al_2O_3 catalyst, (b) (Pd-$CuCl_2$)/α-Al_2O_3 catalyst, (c) (Pd-$CuCl_2$)/MgO catalyst and (d) Pd/γ-Al_2O_3 catalyst at 77 K.

Table S1. The texture properties of as-synthesized catalysts with different supports.

Catalysts	(Pd-$CuCl_2$)/γ-Al_2O_3	(Pd-$CuCl_2$)/α-Al_2O_3	(Pd-$CuCl_2$)/MgO	Pd/γ-Al_2O_3
S_{BET} (m^2/g)	40.5	5.7	9.8	71.1
Pore volume (cm^3/g)	0.21	0.02	0.03	0.37

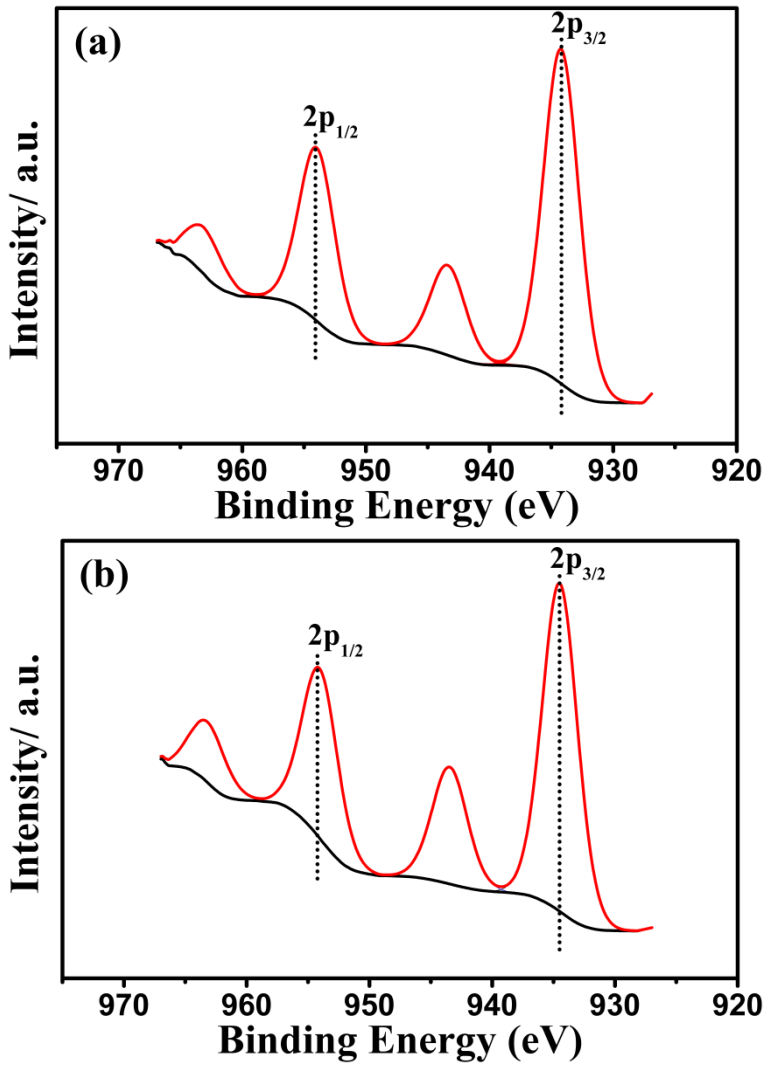

Fig. S3. Cu 2p XPS spectra of (a) fresh and (b) engaged of (Pd-$CuCl_2$)/γ-Al_2O_3 catalysts.

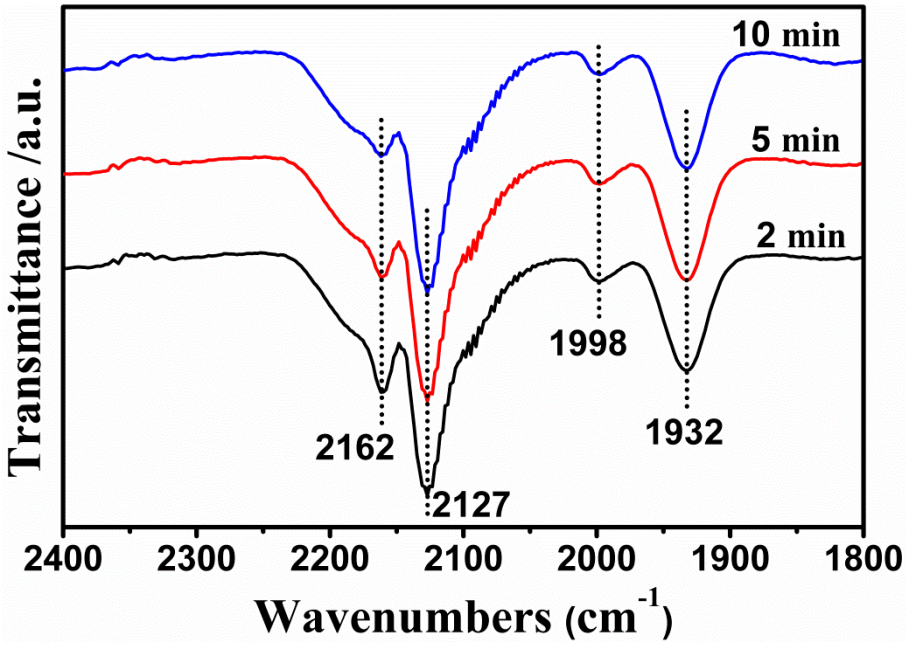

Fig. S4. *In situ* DRIR spectra of CO on (Pd-$CuCl_2$)/γ-Al_2O_3 catalyst at 120 °C, range from 2400 cm^{-1} to 1800 cm^{-1}.

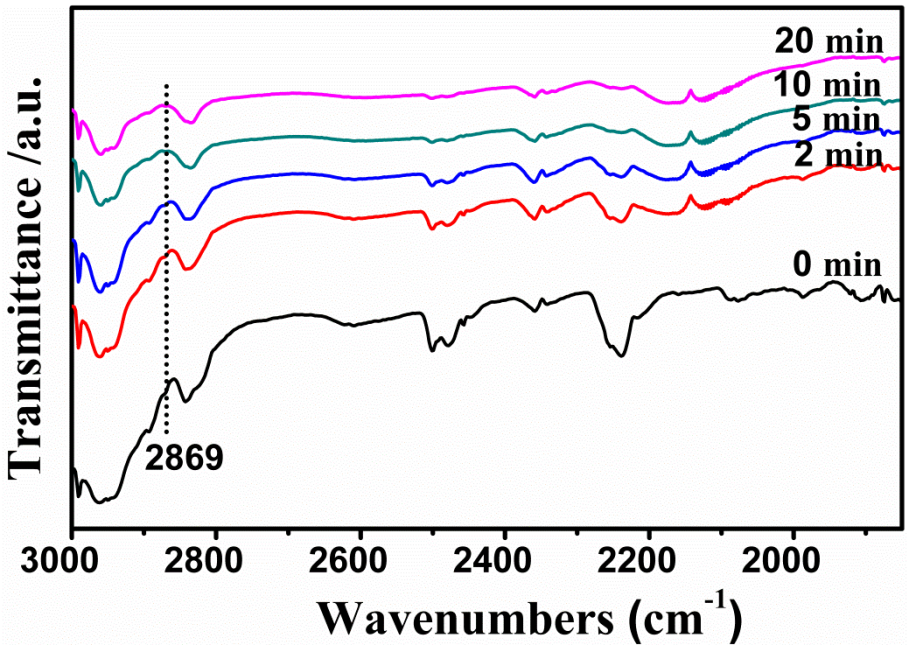

Fig. S5. *In situ* DRIR spectra of CO and MN on (Pd-$CuCl_2$)/γ-Al_2O_3 catalyst at 120 °C, range from 3000 to 1850 cm^{-1}.

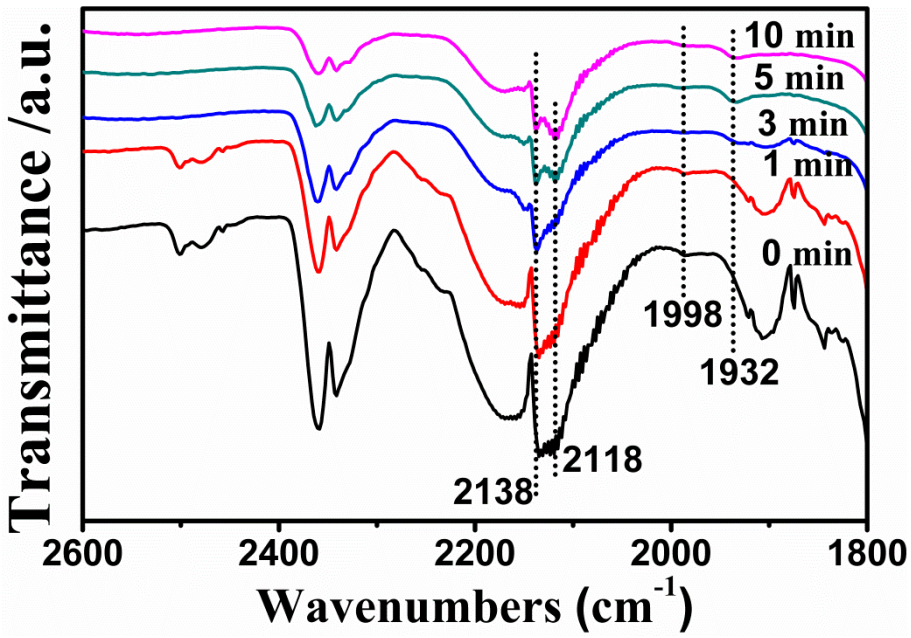

Fig. S6. *In situ* DRIR spectra of the reaction between CO and MN after sweeping by N_2 over (Pd-$CuCl_2$)/γ-Al_2O_3 catalyst at 120 °C, range from 2600 to 1800 cm^{-1}.

The *in situ* DRIR spectra of the reaction between CO and MN over (Pd-$CuCl_2$)/γ-Al_2O_3 catalyst after sweeping by N_2 are shown in Fig. S6. The small peaks appeared at 1998 and 1932 cm^{-1} are assigned to adsorbed CO on metallic Pd(0) in bridge (Pd_2–CO). The large peaks at 2118 and 2138 cm^{-1} (not the bimodal peaks of CO in gas) have been detected, which can be ascribed to the C–O stretching vibrations of CO adsorbed on Pd(II). According to the results of *in situ* DRIR experiments, most of CO are adsorbed on Pd(II), while only a few of CO are adsorbed on Pd(0) during the reaction process of CO and MN, which is consistent with the results of XPS characterization.

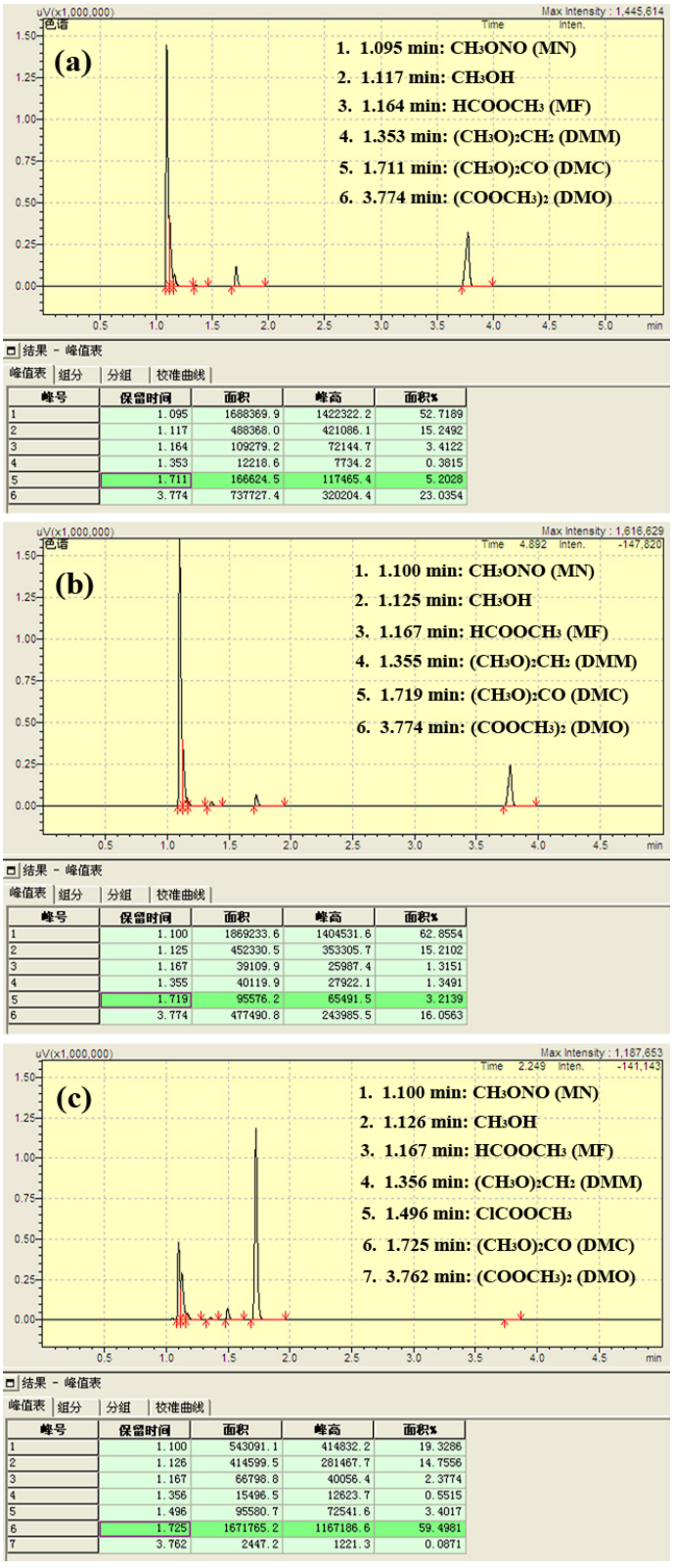

Fig. S7. GC diagrams on FID of methyl nitrite and organic products over (a) Pd/γ-Al_2O_3 catalyst, (b) (Pd-$CuSO_4$)/γ-Al_2O_3 catalyst and (c) (Pd-$CuCl_2$)/γ-Al_2O_3 catalyst at 0.1 MPa and 120 °C.

The organic products over as-synthesized catalysts are methanol, methyl formate (MF), dimethoxymethane (DMM), DMC and dimethyl oxalate (DMO). The products of methanol, MF, and DMM come from the decomposition of methyl nitrite (MN) [reactions (1) and (2) shown as follows]. The products of DMC [reaction (3) shown as follows] and DMO [reaction (4) shown as follows] come from the carbonylation of MN. The selectivity to DMC is calculated based on CO. Thus, the byproduct based on CO of as-synthesized catalysts is only DMO. The selectivities to DMC over Pd/γ-Al_2O_3 and (Pd-$CuSO_4$)/γ-Al_2O_3 catalysts not containing Cl^- are much lower than that over (Pd-$CuCl_2$)/γ-Al_2O_3 catalyst containing Cl^-, which can be directly observed in GC diagrams (Fig. S7).

$$4CH_3ONO \xrightarrow{catalyst} 2CH_3OH + \underset{(MF)}{HCOOCH_3} + 4NO \quad (1)$$

$$2CH_3ONO + CH_3OH \xrightarrow{catalyst} \underset{(DMM)}{(CH_3O)_2CH_2} + 2NO + H_2O \quad (2)$$

$$CO + 2CH_3ONO \xrightarrow{catalyst} \underset{(DMC)}{(CH_3O)_2CO} + 2NO \quad (3)$$

$$2CO + 2CH_3ONO \xrightarrow{catalyst} \underset{(DMO)}{(COOCH_3)_2} + 2NO \quad (4)$$