Active Pd(II) Complexes: Enhancing Catalytic Activity by Ligand Effect for Carbonylation of Methyl Nitrite to Dimethyl Carbonate

Hong-Zi Tan,[ab] Zhi-Qiao Wang,*[ab] Zhong-Ning Xu,*[ab] Jing Sun,[a] Zhe-Ning Chen,[a] Qing-Song Chen,[a] Yumin Chen,[a] and 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.

Table S1. The comparison of activity and selectivity over Pd(II)/NaY and Pd(0)/NaY catalysts

Catalysts	Pd(II) samples			Pd(0) samples		
	C1	**C2**	**C3**	**C4**	**C5**	**C6**
Conversion of CO (%)	60.1	56.1	53.9	52.1	46.8	39.6
Sel_{DMC} (%)	99.9	99.8	99.5	33.3	21.4	29.7
Sel_{DMO} (%)	0.01	0.02	0.05	66.7	78.6	70.3

Reaction conditions: 120 °C, 0.1 MPa, 200 mg catalyst, weight hour space velocity (WHSV) = 1440 $L \cdot kg_{cat.}^{-1} \cdot h^{-1}$, CO: MN: Ar: N_2 = 16.9%: 51.6%: 2.4%: 29.1%.

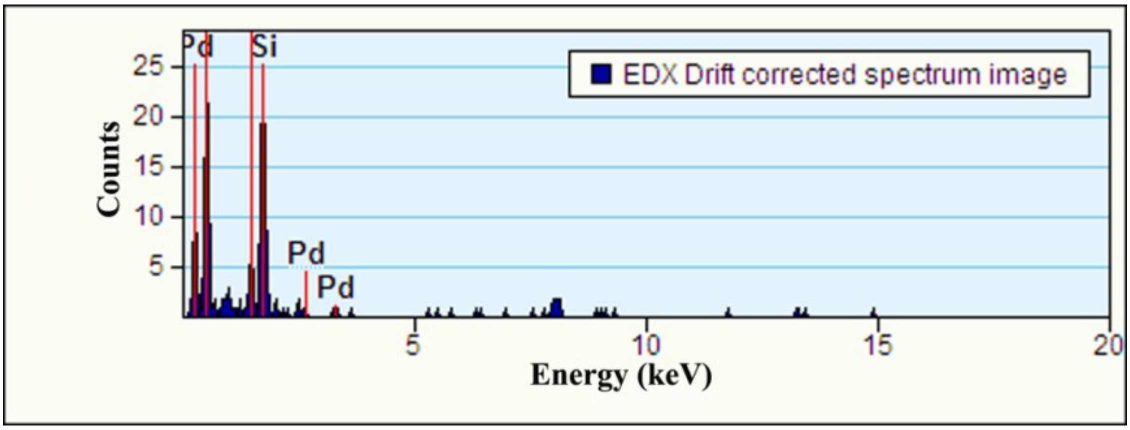

Figure S1. The EDX image of fresh **C1** catalyst.

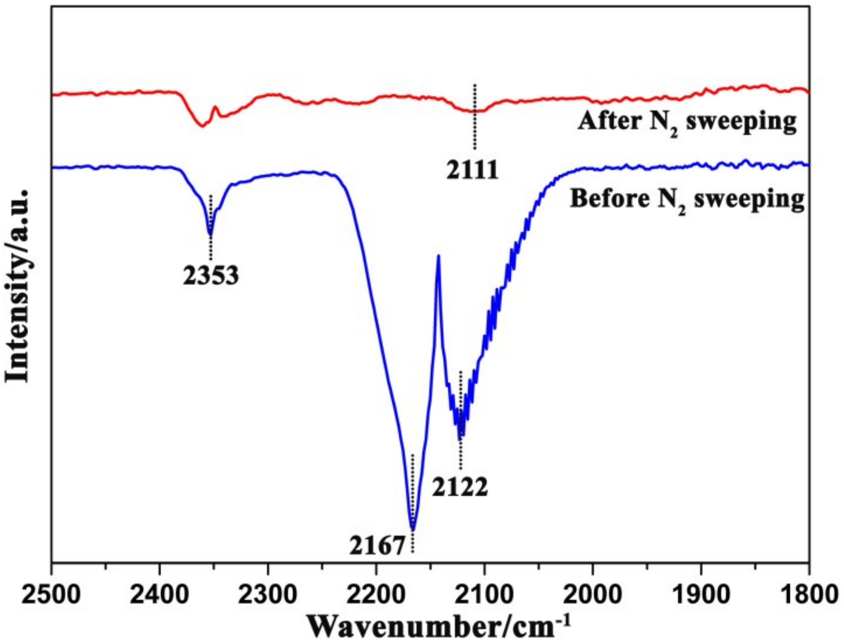

Figure S2. The *in-situ* DRIR spectra of CO adsorption on **C1** catalyst.

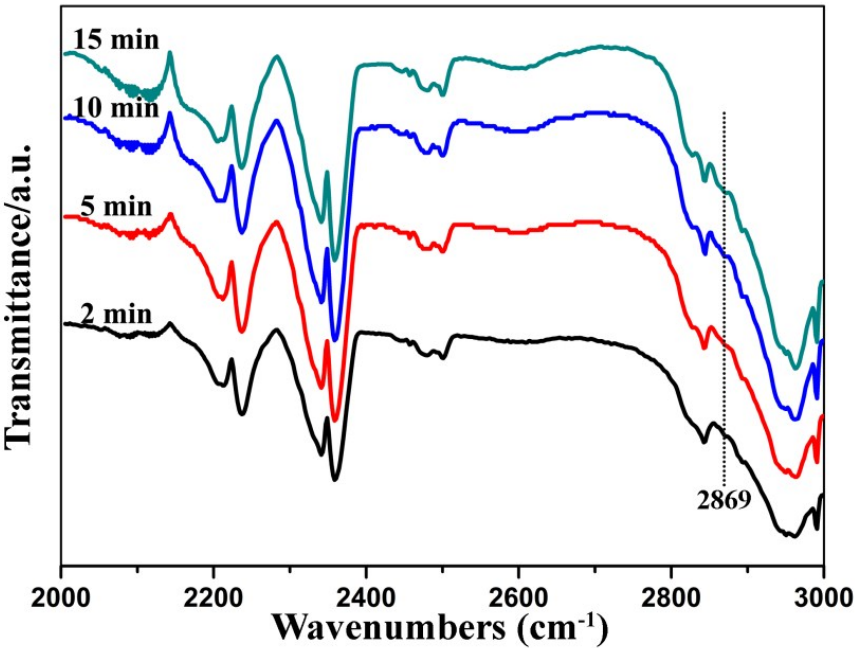

Figure S3. The *in-situ* DRIR spectra of the reaction between CO and MN on **C1** catalyst at 120 °C.

Computational details

All geometry optimizations were performed with the hybrid density functional theory (DFT) at the level of B3LYP.[1-2] The 6-311+G(d, p) all-electron basis sets[3] were employed for the main group elements, and the corresponding basis sets with the Stuttgart/Dresden effective-core potentials (SDD)[4-6] were employed for the transition metal palladium. The subsequent analytical harmonic frequency calculations were performed at the same level of theory to ensure that each geometry corresponds to a true local minimum. All calculations were performed by using the Gaussian 09 suite of program.

1. D. Becke, Density-functional exchange-energy approximation with correct asymptotic-behavior. *Phys. Rev. A* **38**, 3098-3100 (1988).
2. C. T. Lee, W. T. Yang, R. G. Parr, Development of the colle-salvetti correlation-energy formula into a functional of the electron-density. *Phys. Rev. B* **37**, 785-789 (1988).
3. R. Krishnan, J. S. Binkley, R. Seeger, J. A. Pople, Self-consistent molecular-orbital methods .20. Basis set for correlated wave-functions. *J. Chem. Phys.* **72**, 650-654 (1980).
4. G. A. Petersson, A. Bennett, T. G. Tensfeldt, M. A. Allaham, W. A. Shirley, J. Mantzaris, A complete basis set model chemostry .1. The total energies of closed-shell atoms and hydrides of the 1st-row elements. *J. Chem. Phys.* **89**, 2193-2218 (1988).
5. W. Kuchle, M. Dolg, H. Stoll, H. Preuss, Energy-adjusted pseudopotentials for the actinides - parameter sets and test calculations for thorium and thorium monoxide. *J. Chem. Phys.* **100**, 7535-7542 (1994).
6. T. Leininger, A. Nicklass, H. Stoll, M. Dolg, P. Schwerdtfeger, The accuracy of the pseudopotential approximation .2. A comparison of various core sizes for indium pseudopotentials in calculations for spectroscopic constants of InH, InF, and InCl. *J. Chem. Phys.* **105**, 1052-1059 (1996).