Supporting Information

Enhanced Stability of Pd/ZnO Catalyst for CO Oxidative Coupling to Dimethyl Oxalate: Effect of Mg²⁺ Doping

Si-Yan Peng,^{†,‡} Zhong-Ning Xu,^{*†,‡} Qing-Song Chen,[†] Zhi-Qiao Wang,[†] Dong-Mei Lv,[†] Jing Sun,[†] Yumin Chen,[†] and Guo-Cong Guo^{*†}

[†]State Key Laboratory of Structural Chemistry, Fujian Institute of Research on the Structure of Matter, Chinese Academy of Sciences, Fuzhou, Fujian 350002, People's Republic of China [‡]Key Laboratory of Coal to Ethylene Glycol and Its Related Technology, Chinese Academy of Sciences, Fuzhou, Fujian 350002, People's Republic of China

*Address correspondence to gcguo@fjirsm.ac.cn and znxu@fjirsm.ac.cn

1. Reactions of coal to ethylene glycol

$$C + H_2O \longrightarrow CO + H_2$$

$$CO + H_2 \xrightarrow{\text{separating}} \begin{cases} CO + H_2 \text{ (small amount)} \\ H_2 \text{ (pure)} \end{cases}$$

$$CO + H_2 \text{ (small amount)} \xrightarrow{\text{catalyst}} CO \text{ (pure)}$$

$$2CO + 2CH_3ONO \xrightarrow{\text{catalyst}} (COOCH_3)_2 + 2NO$$

$$2NO + 0.5O_2 \longrightarrow N_2O_3$$

$$N_2O_3 + 2CH_3OH \longrightarrow 2CH_3ONO + H_2O \end{cases}$$

$$(COOCH_3)_2 + 4H_2 \xrightarrow{\text{catalyst}} (CH_2OH)_2 + 2CH_3OH \quad (3)$$

$$2C + 2H_2 + H_2O + 0.5O_2 \longrightarrow (CH_2OH)_2$$

$$Coal + Water + Air \longrightarrow Ethylene glycol \end{cases} \text{ overall reaction}$$

Figure S1. The reactions of coal to ethylene glycol.

Coal to ethylene glycol contains three main steps: 1) elimination small amount of hydrogen gas in CO separated from coal-derived synthesis gas; 2) CO oxidative coupling to DMO; 3) hydrogenation of DMO to ethylene glycol. The overall reaction means only coal, water and air are consumed to synthesize ethylene glycol, implying that coal to ethylene glycol is a green and atomic economy technology.

2. Sample characterization

catalysts	Pd loading (wt%)	conversion of CO (%)	selectivity to DMO (%)	STY of DMO ^{b} (g L ^{-1} h ^{-1})
Pd/ZnO	0.5	67	98	1454
Pd/Mg–ZnO	0.5	68	98	1476
Pd/MgO ^c	0.5	63	97	1353
$Pd/\alpha - Al_2O_3^{d}$	0.5	56	94	1166
Industrial catalyst	2	34	95	750

 Table S1. Catalytic Performances for CO Oxidative Coupling to DMO over Different

 Catalysts ^a

^{*a*} Reaction conditions: 200 mg of catalyst, 3000 h^{-1} of gas hourly space velocity (GHSV), reactants CO/CH₃ONO volume ratio 1.4, 0.1 MPa, 130 °C.

^{*b*} STY represents the space-time yield, grams of DMO per liter of catalyst per hour (g L⁻¹ h⁻¹). ^{*c*, *d*} The catalytic performances of the Pd/MgO and Pd/ α –Al₂O₃ catalysts were reported in the literature [*Catal. Sci. Technol.* **2014**, *4*, 1925–1930].



Figure S2. Gas chromatogram of the products from CO oxidative coupling to DMO over the Pd/ZnO catalyst at 140 °C.



Figure S3. Conversion of CO (\blacksquare) and selectivity to DMO (\bullet) of the Pd/Mg–ZnO catalysts with different Pd loadings for CO oxidative coupling to DMO at 130 °C.

A series of Pd/Mg–ZnO catalysts with different Pd loadings have been synthesized in order to investigate the influence of Pd loading. According to Figure S3, when the Pd loading is lower than 0.5 wt%, the conversion of CO increases dramatically with the increase of Pd loading. However, when the Pd loading is higher than 0.5 wt%, the conversion of CO does not increase due to the nearly complete consumption of methyl nitrite under the reaction conditions (reactants CO/CH₃ONO volume ratio 1.4, 0.1 MPa, 130 °C). Thus, the Pd loading of 0.5 wt% is optimal form practical and economical viewpoints.



Figure S4. XRD patterns of the Mg^{2+} -doped and un-doped ZHC precursors. Vertical bars at the bottom denote the standard data for zinc hydroxide carbonate [Zn₄CO₃(OH)₆·H₂O] (JCPDS, No. 11-0287).



Figure S5. TGA curves of the Mg^{2+} -doped and un-doped ZHC precursors.



Figure S6. SEM images of (a, b) the ZHC precursor, and (c, d) the ZnO support. Panel d represent the enlarged image of the rectangle in panel c.



Figure S7. SEM images of the fresh Pd/ZnO catalyst with (a) low magnification and (b) high magnification; SEM images of the used Pd/ZnO catalyst after 100 h evaluation with (c) low magnification and (d) high magnification.



Figure S8. SEM images of the fresh Pd/Mg–ZnO catalyst with (a) low magnification and (b) high magnification; SEM images of the used Pd/Mg–ZnO catalyst after 100 h evaluation with (c) low magnification and (d) high magnification.

SEM characterizations of the fresh and used catalysts have been carried out. As shown in Figures S7 and S8, the SEM images of the fresh Pd/ZnO and Pd/Mg–ZnO catalysts indicate that the flower-like structures of supports have been destroyed after vigorous magnetic stirring for 18 h during the process of catalysts preparation. However, the porous nanosheets are retained, and the morphologies and microstructures of the used Pd/ZnO and Pd/Mg–ZnO catalysts after 100 h evaluation are similar as those of the fresh catalysts.

samples	ZnO	fresh Pd/ZnO	used Pd/ZnO ^a	Mg–ZnO	fresh Pd/Mg–ZnO	used Pd/Mg–ZnO ^b
S_{BET}^{c} (m ² /g)	17.463	15.415	14.307	20.128	26.239	23.110
Pore volume (cm ³ /g)	0.039	0.043	0.043	0.100	0.103	0.088

Table S2. BET Surface Area and Pore Volume of Different Samples

^a Used Pd/ZnO: the used Pd/ZnO catalyst after 100 h evaluation

^b Used Pd/Mg–ZnO: the used Pd/Mg–ZnO catalyst after 100 h evaluation

^{*c*} S_{BET}: BET surface area of samples

The BET surface area and pore volume of different samples are shown in Table S2. It is obvious to find that both the BET surface area and pore volume of Mg^{2+} doped samples are higher than those of undoped samples, implying that the doping of Mg^{2+} ions can improve the BET surface area and pore volume.

catalysts	fresh	used	fresh	used
	Pd/Mg–ZnO	Pd/Mg–ZnO ^a	Pd/ZnO	Pd/ZnO ^b
Pd dispersion	26.0	21.5	20.7	7.0
(%)	20.9	21.3		
Pd surface area	0.60	0.49	0.46	0.16
(m ² /g-catalyst)	0.00	0.48		

Table S3. The Dispersion and Surface Area of Pd for the Fresh and Used Pd/Mg–ZnO and Pd/ZnO Catalysts Obtained from CO Pulse Chemisorption

^a used Pd/Mg–ZnO: the used Pd/Mg–ZnO catalyst after 100 h evaluation

^b used Pd/ZnO: the used Pd/ZnO catalyst after 100 h evaluation

CO pulse chemisorption can provide valuable information about the dispersion and surface area of Pd. We have performed CO pulse chemisorption experiments over the fresh and used Pd/Mg–ZnO and Pd/ZnO catalysts. As shown in Table S3, the dispersion of Pd for the fresh Pd/Mg–ZnO catalyst is 26.9% and the surface area of Pd is 0.60 m²/g, which are higher than those (21.5% and 0.48 m²/g) for the used Pd/Mg–ZnO catalyst. While the dispersion of Pd for the fresh Pd/ZnO catalyst is 20.7% and the surface area of Pd is 0.46 m²/g, which are much higher than those (7.0% and 0.16 m²/g) for the used Pd/ZnO catalyst. Thus, the drops in the dispersion and surface area of Pd for the Pd/Mg–ZnO catalyst after 100 h evaluation are much less than those for the Pd/ZnO catalyst. It further demonstrates that the doping of Mg²⁺ ions can effectively restrain the sintering of active Pd nanoparticles; retard the growth of Pd nanoparticles; and thus enhance the catalytic stability.



Figure S9. XRD patterns of the fresh (a) Pd/Mg–ZnO and (b) Pd/ZnO catalysts; and the used (c) Pd/Mg–ZnO and (d) Pd/ZnO catalysts after 100 h evaluation. Vertical bars at the bottom denote the standard data for a hexagonal wurtzite structure of ZnO (JCPDS, No. 65-3411). Asterisks "*" denote the diffraction peak of Pd.



Figure S10. Pd 3d XPS spectra of the Pd/Mg–ZnO and Pd/ZnO catalysts after Ar⁺ etching.

In order to demonstrate the partial oxidation of the surfaces of Pd nanoparticles in air, both catalysts were further treated with Ar^+ etching. The Pd 3d XPS spectra after Ar^+ etching (Figure S10) show a Gaussian distribution, and the XPS results reveal that the oxidation state of Pd in the Pd/Mg–ZnO and Pd/ZnO catalysts after Ar^+ etching is Pd(0). Moreover, the 0.4 eV shift of the binding energies of Pd 3d between the Pd/Mg–ZnO and Pd/ZnO catalysts after Ar^+ etching is also observable, which further demonstrates the electron transfer from support to Pd nanoparticles.



Figure S11. H₂-TPR profiles of the calcined PdO/Mg–ZnO and PdO/ZnO samples.

The H₂-TPR experiments were carried out in the range of -50 to 300 °C to explore the redox behavior of PdO species. As shown in Figure S11, one sharp H₂ consumption peak over the calcined PdO/ZnO and PdO/Mg–ZnO samples appears at -0.5 and -5.5 °C due to the reduction of PdO, respectively. There are another slight negative peaks followed by the reduction peak of PdO, respectively, which are attributed to the decomposition of palladium hydride. It should be noted that the reduction peak center shifts toward lower temperature by 5 °C after the doping of Mg²⁺ ions, implying that the PdO species in the PdO/Mg–ZnO sample are more easily reduced in comparison with the PdO/ZnO sample, which derives from the relatively lower charge of Pd in the PdO species in PdO/Mg–ZnO sample due to the electron transfer from support to PdO species. Therefore, the electron transfer in the Pd/Mg–ZnO catalyst has been further proved by the results of H₂-TPR characterization.