Enhanced Methyl Nitrite Carbonylation to Dimethyl Carbonate via Fully Exposed Palladium Cluster Catalysts

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Experimental section

Chemicals

Palladium(II) chloride tetraammine monohydrate ($[Pd(NH_3)_4]Cl_2 \cdot H_2O$; 99.9%) was purchased from Heowns Opde Technologies, Ltd., Tianjin. Zirconium dioxide (ZrO_2; 99.99%), and ammonia solution ($NH_3 \cdot H_2O$; 25-28%) were purchased from Aladdin. All chemicals were used without further purification.

Synthesis of Pd/ZrO_2

The catalysts with palladium loading lower than 1 wt.% were prepared via strong electrostatic adsorption (SEA) method.[1] Firstly, 2 g ZrO_2 were dispersed in 200 mL of deionized water through vigorous stirring for a duration of 10 minutes, resulting in a well-dispersed suspension. Then an appropriate amount of $[Pd(NH_3)_4]Cl_2 \cdot H_2O$ was dissolved in 40 mL of deionized water, and homogenized using a homogenizer for 10 minutes to obtain a clear and transparent solution. The amount of $[Pd(NH_3)_4]Cl_2 \cdot H_2O$ depends on the desired palladium loading in the different catalysts, which in our study were 0.1 wt.%, 0.2 wt.%, 0.5 wt.%, and 1 wt.% respectively. The suspension of ZrO_2 and solution of $[Pd(NH_3)_4]Cl_2 \cdot H_2O$ were adjusted to a pH of 10 using ammonia solution. After adjusting the value of pH, the suspension and solution were sonicated for 1 h. The solution of $[Pd(NH_3)_4]Cl_2 \cdot H_2O$ was added dropwise to the ZrO_2 suspension under vigorous stirring within one hour. The mixture was vigorously stirred at room temperature over night. Finally, The powder was separated via filtration and washed several times with deionized water. All samples were dried at 60 °C overnight, and calcined in a tube furnace at 350 °C in air for 210 min.[1]

The catalyst with a Pd loading of 2 wt.% was prepared using the incipient wetness impregnation method. An appropriate amount of $[Pd(NH_3)_4]Cl_2 \cdot H_2O$ was dissolved in 1 mL of deionized water and then uniformly dripped onto 2 g of dried ZrO_2 powder. The drying and calcination steps were identical to those employed for other catalysts.

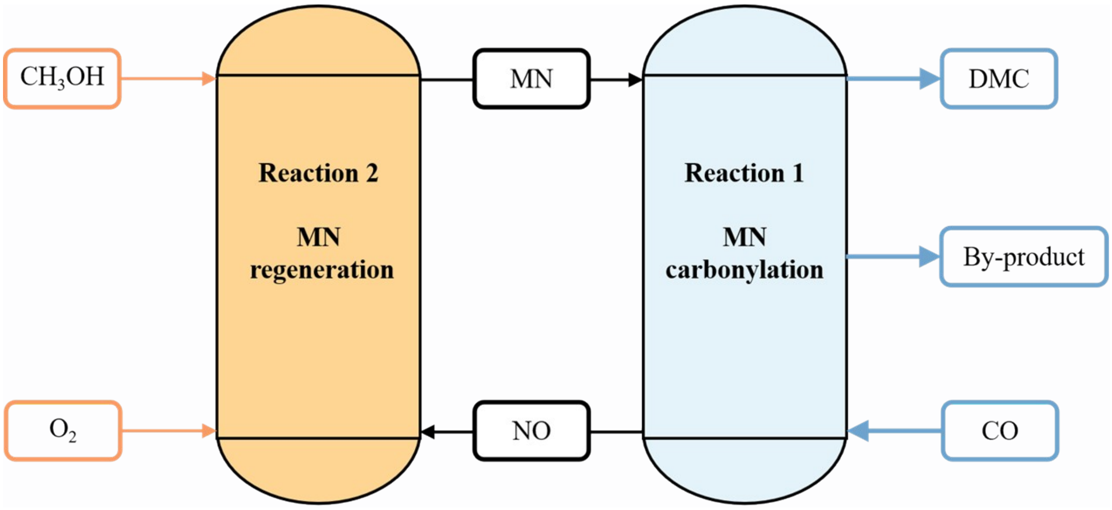
Characterization

The Pd loading was determined using inductively coupled plasma optical emission spectroscopy (ICP-OES) (Agilent 5110 ICP-OES). The Pd dispersion was determined by CO titration performed on a Chemisorption apparatus (Micromeritics AutoChem 2930) equipped with a thermal conductivity detector (TCD).

CO-probe diffuse reflectance infrared Fourier transform spectroscopy (CO-DRIFTS) was performed on FEI iS50 Fourier Transform Infrared Spectrometer with the MCT/A detector. All catalysts were pretreated identically by 150 °C reduction in 10% H_2/Ar (30 sccm) for 1 h. After cooling to the 30 ℃, 10% CO/Ar flow (40 sccm) was introduced into cell for 20 min to achieve saturation adsorption. Then the gaseous CO and physically adsorbed CO were removed by Ar flow (30 sccm) purging for 30 min.

AC-HAADF-STEM data was collected by field-emission transmission electron microscope (Thermo Scientific Talos F200X). XRD was detected by X-Ray Diffractometer (Rigaku D/MAX 2500VB+/PC) using Cu K_{α} (40kV, 200mA) radiation over a 2θ range of 10−80 ° at a scan rate of 0.2 °/step and a scan time of 2 s/step.

carbonylation of methyl nitrite (MN) to dimethyl carbonate (DMC)



Scheme S1. Schematic diagram of MN to DMC

As shown in Scheme S1, the carbonylation of MN to DMC mainly consists of two reaction. The first reaction is the the carbonylation of MN to produce DMC and the second reaction is the regeneration of MN by reaction between methanol, recycled NO and oxygen. The entire reaction process itself only consumes methanol, oxygen, and CO, and produces DMC and water, making it an environmentally friendly and highly atom-economical reaction. Our study focus on the reaction 1 which needs Pd-based catalyst and has three kinds of by-product.[2,3]

Reactivity measurements

The reaction was evaluated under the following conditions: mixture of 0.5 g catalyst and 2 mL SiO_2 (20-40 mesh), $CO/MN/N_2/Ar = 3/10/28/26$, $GHSV = 8000 \cdot mL \cdot g_{cat}^{-1} \cdot h^{-1}$, p = 1 atm, T = 110 °C.

The calculation method for reaction performance evaluation

The quantification of reactants and products is performed by online gas chromatography (Fuli Instrument GC9790 Plus) . The inorganic components CO, Ar, and N_2 are analyzed by a TCD (thermal conductivity detector), and the organic components MN, DMC, (dimethyl oxalate) DMO,(methyl formate) MF, (dimethoxymethane) DMM, and (methanol) ME are analyzed by an FID (flame ionization detector).

In addition to the main reaction producing DMC (Eq. 1), there are three side reactions that occur concurrently.

$$2CH_3ONO + CO \rightarrow (CH_3O)_2CO + 2NO \qquad \text{main reaction} \qquad (1)$$

$$2\ CH_3ONO + 2\ CO \rightarrow (COOCH_3)_2 + 2\ NO \qquad \text{side reaction-1} \qquad (2)$$

$$4\ CH_3ONO \rightarrow CHOOCH_3 + 2\ CH_3OH + 4\ NO \qquad \text{side reaction-2} \qquad (3)$$

$$2\ CH_3ONO + CH_3OH \rightarrow (CH_3O)_2CH_2 + H_2O + 2\ NO \qquad \text{side reaction-3} \qquad (4)$$

The main reaction (Eq. 1) to produce DMC and side reaction (Eq. 2) to produce DMO takes place on the palladium sites. On the other hand, the side reactions (Eq. 3,4) to produce MF and DMM proceed on the acid sites of the support. The byproduct ME is generated along with MF and is consumed during the formation of DMM, therefore, the selectivity of ME is combined with that of MF. Therefore, the conversion of CO and MN, selectivity of DMC, DMO, MF and DMM based on MN reactant, and selectivity of DMC and DMO based on CO reactant were calculated according to the following equations.

$$V_{tatal} = V_{Ar} / (A_{Ar} / f_{Ar}) \qquad (5)$$

$$V_x = V_{tatal} \times (A_x / f_x) \qquad (6)$$

V_x represents the volumetric flow rate of substance x under standard conditions, A_x represents the peak area of substance x on the corresponding detector, and f_x represents the calibration factor. Ar is used as the standard because its total flow rate remains constant during the reaction process. Therefore, the total flow rate of the system can be calculated based on Ar as the reference, and then the partial flow rates of all other components can be calculated according to the Sub - volume law.

$$Cov._{CO} = 100\ \% - (V_{DMC} + 2\times V_{DMO}) / V_{CO,\ in} \tag{7}$$

$$Cov._{MN} = 100\ \% - [2\times(V_{DMO} + V_{DMC} + V_{MF}) + 3\times V_{DMM} + V_{ME}] / V_{MN,\ in} \tag{8}$$

$$Sel._{DMC/MN} = 2\times V_{DMC} / [2\times(V_{DMO} + V_{DMC} + V_{DMM}) + 4\times V_{MF}] \times 100\% \tag{9}$$

$$Sel._{DMO/MN} = 2\times V_{DMO} / [2\times(V_{DMO} + V_{DMC} + V_{DMM}) + 4\times V_{MF}] \times 100\% \tag{10}$$

$$Sel._{DMC/MF} = 4\times V_{MF} / [2\times(V_{DMO} + V_{DMC} + V_{DMM}) + 4\times V_{MF}] \times 100\% \tag{11}$$

$$Sel._{DMM/MN} = 2\times V_{DMM} / [2\times(V_{DMO} + V_{DMC} + V_{DMM}) + 4\times V_{MF}] \times 100\% \tag{12}$$

$$Sel._{DMC/CO} = V_{DMC} / (2\times V_{DMO} + V_{DMC}) \times 100\% \tag{13}$$

$$Sel._{DMO/CO} = 2\times V_{DMO} / (2\times V_{DMO} + V_{DMC}) \times 100\% \tag{14}$$

Where $V_{CO,\ in}$, in and $V_{MN,\ in}$ are the volumetric flow rates of CO and MN at the reactor inlet; V_{DMC}, V_{MF}, V_{DMO} and V_{DMM} are the volumetric flow rates of DMC, DMO, MF and DMM at the reactor outlet; Cov. $_{CO}$ and Cov. $_{MN}$ are the conversion rates of CO and MN; Sel. $_{DMC/MN}$, Sel. $_{DMO/MN}$, Sel. $_{MF/MN}$ and Sel. $_{DMM/MN}$ are the MN selectivity of DMC, DMO, MF, DMM; Sel. $_{DMC/CO}$ and Sel. $_{DMO/CO}$ are the CO selectivity of DMC, DMO, respectively.

The space time yield (STY) of DMC was calculated as follows

$$STY = W_{DMC} / m_{cat} = (V_{DMC} / V_M \times M_{DMC}) / m_{cat} \tag{15}$$

$$STY_{nomalized\ to\ Pd} = STY / Pd\ Loading \tag{16}$$

$$STY_{nomalied\ to\ exposed\text{-}Pd} = STY / (Pd\ Loading \times D\%) \tag{17}$$

W_{DMC} represents the mass flow rate of DMC, m_{cat} is the mass of the catalyst, V_M is the standard molar volume, M_{DMC} is the molar mass of DMC, and D% is the dispersion degree of Pd. The STY of other products is similar to that of DMC, and only requires substituting the corresponding volumetric flow rate and molar mass.

The TON calculation within 330 minutes uses a cumulative summation approach. Gas chromatography (GC) completed the analysis every 30 minutes, the obtained STY values being treated as the average over each 30-minute interval. By summing the total DMC production over 330 minutes (150 minutes for Pd_2/ZrO_2 due to its poor selectivity), we obtained a representative TON value, as shown in Eq. (18):

$$TON = \sum_{i=1}^{11} STY_i \left(g_{DMC} \cdot kg_{Pd}^{-1} \cdot h^{-1}\right) \cdot 0.5 \cdot \frac{M_{Pd}}{M_{DMC} \cdot 1000} \tag{18}$$

Kinetic testing method

The kinetic testing was evaluated under the following conditions: mixture of 0.1 g catalyst and 2 mL SiO_2 (20-40 mesh), CO/MN/N_2/Ar = 3/10/28/26 (vol %), A high GHSV of 80000 mL·g_{cat}^{-1}·h^{-1} is used to achieve a lower MN conversion (below 5 %) rate and allow the reaction to proceed within the kinetic control range. When testing the MN reaction orders the feed gas of MN reactant range from 350-880 mmol·g_{cat}^{-1}·h^{-1} and balanced with N_2 to maintain the same GHSV without change CO and Ar. When testing the Arrhenius plot, the temperature settings ranges from 105 ℃ to 115 ℃ without changing other conditions.

Under these conditions, the effects of by-products and NO on the reaction are negligible. Therefore, according to the Law of Mass Action, the formation rate of DMC is related to the concentrations of CO and MN in the following power-law relationship (19).[4,5]

$$r_{DMC} = k\, C_{CO}^{\alpha} \times C_{MN}^{\beta} \tag{19}$$

Here, r_{DMC} represents the molar formation rate of DMC, C_{CO} and C_{MN} are the gas-phase concentrations of CO and MN, α and β are the reaction orders of CO and MN respectively, and k is the reaction rate constant which depends solely on the catalyst and temperature. By taking the logarithm of both sides of the equation (19), we can obtain the following relationship (20). When analyzing the MN series, keeping other conditions constant and only varying the concentration of MN (N_2 balance), plotting ln r_{DMC} against ln C_{MN} will yield a straight line, and the slope of this line represents the reaction order of MN.[4]

$$\ln r_{DMC} = \alpha \ln C_{CO} + \beta \ln C_{MN} + \ln k \tag{20}$$

The activation energy can be obtained by fitting the Arrhenius equation (21).

$$\ln k = \ln A - Ea / RT \tag{21}$$

where k is rate constant, A the pre-exponential factor, Ea the apparent activation energy, R the gas constant.[6,7]

Table S1. Performance of catalysts

Catalysts	DMC STY (g_{DMC} • kg_{Pd}^{-1} • h^{-1})	DMO STY (g_{DMO} • kg_{Pd}^{-1} • h^{-1})	Sel. $_{DMC/CO}$ (%)
ZrO_2	0	0	--
$Pd_{0.1}/ZrO_2$	237.70	0	100
$Pd_{0.2}/ZrO_2$	502.55	0	100
$Pd_{0.4}/ZrO_2$	723.29	0	100
Pd_1/ZrO_2	418.22	31.84	86.79
Pd_2/ZrO_2	9191.75	29280.98	13.57

Table S2. Pd loading before and after reaction

Catalysts	Pd loading before reaction (wt.%)	Pd loading after reaction (wt.%)
$Pd_{0.1}/ZrO_2$	0.09	0.09
$Pd_{0.2}/ZrO_2$	0.19	0.19
$Pd_{0.4}/ZrO_2$	0.42	0.42
Pd_1/ZrO_2	0.94	0.93
Pd_2/ZrO_2	1.92	1.92

Table S3. TON of DMC formation for all the catalysts

Catalysts	TON*
$Pd_{0.1}/ZrO_2$	1.93
$Pd_{0.2}/ZrO_2$	3.90
$Pd_{0.4}/ZrO_2$	5.09
Pd_1/ZrO_2	2.97
Pd_2/ZrO_2	27.09

*The TON is calculated based on the total reaction yield within 330 minutes, except for Pd_2/ZrO_2, for which the TON is calculated using the total yield within 150 minutes.

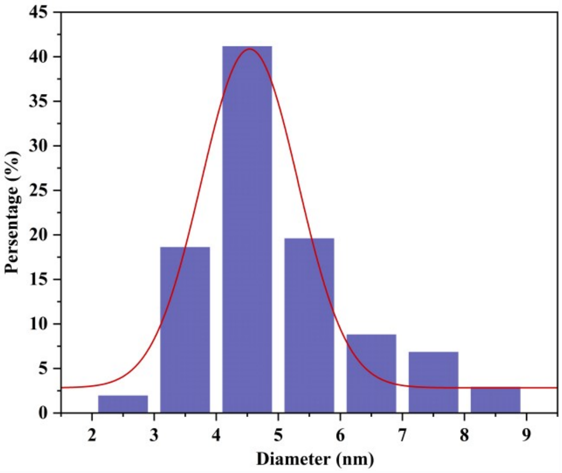


Fig. S1 HAADF-STEM images of particle size distribution histogram of Pd on the Pd_2/ZrO_2

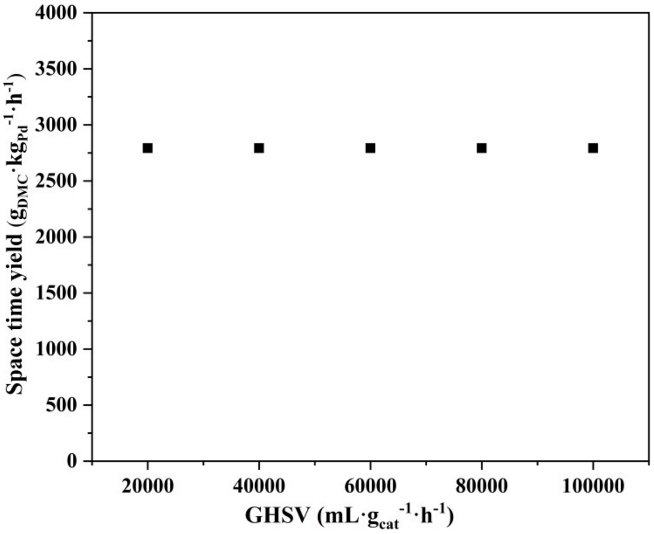


Fig. S2 The mass transfer limitation test was evaluated under the following conditions: mixture of 0.1 g catalyst and 2 mL SiO_2 (20-40 mesh), CO/MN/N_2/Ar = 3/10/28/26 (vol %), GHSV = 20000 ~ 100000·mL·$g_{cat}^{-1}\cdot h^{-1}$, p = 1 atm, T = 110 °C.

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