Support information

Efficient degradation of MDEA-containing wastewater over Pd-based catalyst via catalytic wet air oxidation process: supports, conditions and kinetics

Longbin Deng,[a ‡] Lin Zhang,[a ‡] Jun Zhao,[a] Zongjian Liu,[ab] Haiyan Wang,[a]* Qun Cui[a]*

[1]College of Chemical Engineering, Nanjing Tech University, Nanjing 211816, China

[2]Research Institute of Sinopec Yangzi Petrochemical, Nanjing 210047, China

*Corresponding author: haiyanwang@njtech.edu.cn

cuiqun@njtech.edu.cn

‡ These authors contributed equally to this work.

Main reagents: N-methyldiethanolamine(≥99.0 wt%), Sodium bicarbonate (≥99.8 wt%),Sodium carbonate (≥99.5 wt%), Sodium sulfate (≥99.0 wt%) and Sodium thiosulfate(≥99.0 wt%), Formic acid (≥99.0 wt%), Phosphoric acid（≥85 wt%）and Acetic acid(≥99.8 wt%) were all purchased from Aladdin Reagent Co., Ltd., Shanghai, China.

Stability of catalyst：

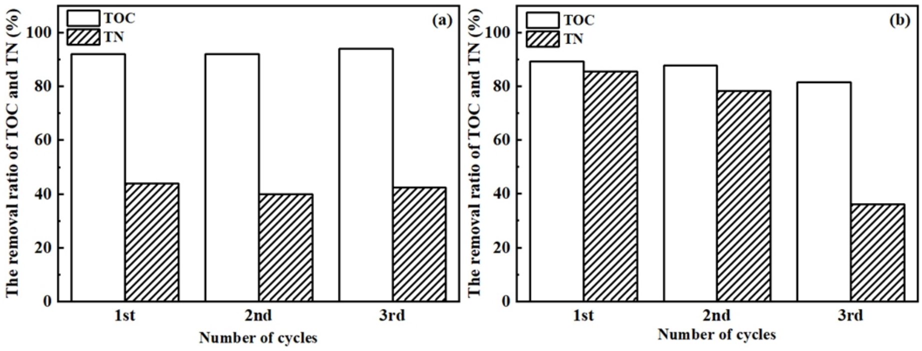

Fig. S1 The stability of Pd/CeO_2-ZrO_2 (a) and Pd/AC (b) in CWAO process.

(Reaction conditions: temperature of 200°C, O_2 pressure of 1.4 MPa, catalyst loading of 3.33 g/L and reaction time of 120 min)

As shown in Fig. S1, after three cycles, the removal rates of TOC and TN are maintained at about 90% and 43%, Pd/CeO_2-ZrO_2 has good stability without significant reduction, while the removal rates TOC and TN on Pd/AC decreased from 89% and 85% to 81% and 39%, decreased by about 10% and 49%, respectively. The inactivation of Pd/AC may be due to the gradual blockage in the micropores of the AC during the recycling process.

Carbon deposition on the surface area was also one of the reasons for the deactivation of Pd/CeO_2-ZrO_2 and Pd/AC catalyst. The TG-DTG of fresh and used Pd/CeO_2-ZrO_2 and Pd/AC was performed. The results were shown in Fig. S2.

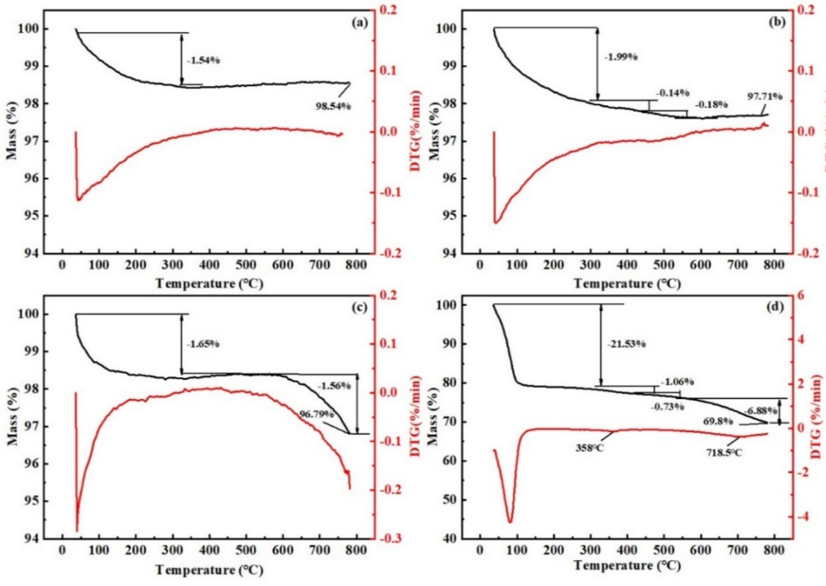

Fig. S2 TG-DTG analysis of Pd/CeO_2-ZrO_2 and Pd/AC before and after CWAO reaction.

(a)Fresh Pd/CeO_2-ZrO_2, (b)Spent Pd/CeO_2-ZrO_2, (c)Fresh Pd/AC, (d)Spent Pd/AC

As shown in Fig. S2, fresh Pd/CeO_2-ZrO_2 has only one weight loss segment with the weight loss is 1.54% at 40-800°C, corresponding to the surface water. Spent Pd/CeO_2-ZrO_2 has two weight loss segments at 40-300°C and 300-500°C, which correspond to the removal of surface water (the weight loss of 1.99%) and combustion of carbon deposition (the weight loss of 0.32%). Fresh Pd/AC has two weight loss segments at 40-300°C and 500-800°C, corresponding to the removal of surface water (the weight loss of 1.65%) and the high temperature loss of support AC (the weight loss of 1.56%). Spent Pd/AC has three weight loss segments, including the removal of surface water at 40-300°C (the weight loss of 21.53%), and the removal of carbon on the catalyst surface area at 300-500°C (the weight loss of 1.79%), the loss of support AC itself and the removal of carbon from catalyst surface area (the weight loss of 6.88%) at 500-800°C. Compared with Pd/CeO_2-ZrO_2, surface carbon deposition of Pd/AC is easier to occur because its lower surface oxygen activity and oxygen content, which is difficult to further oxidize the intermediate substances degraded by MDEA and form carbon deposition to cover the active sites.

O_2-TPD：

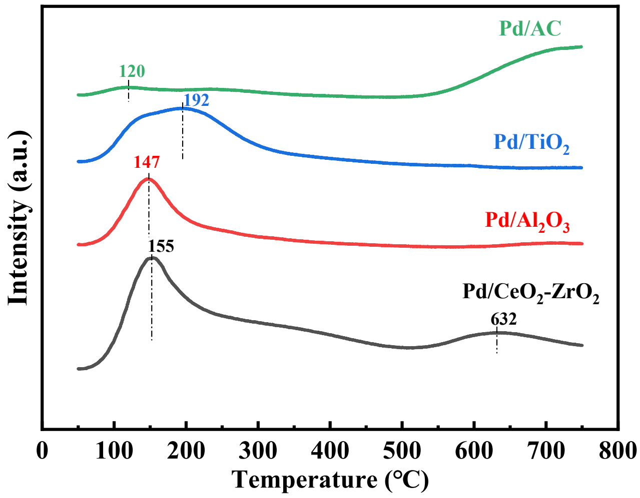

Fig. S3 O_2-TPD patternes of Pd/CeO_2-ZrO_2, Pd/TiO_2, Pd/Al_2O_3 and Pd/AC.

Table S1 Chemical adsorbed oxygen relative content of surface calculated by O_2-TPD peak area

Catalyst	Peak area (＜300°C)	Chemical adsorbed oxygen relative content of surface (%)
Pd/CeO_2-ZrO_2	136113	100
Pd/Al_2O_3	76877	56.5
Pd/TiO_2	58074	42.7
Pd/AC	13253	9.7

Surface chemical adsorbed oxygen relative content calculated by every peak area of catalyst accounts for the peak area of Pd/CeO_2-ZrO_2

Distribution of products:

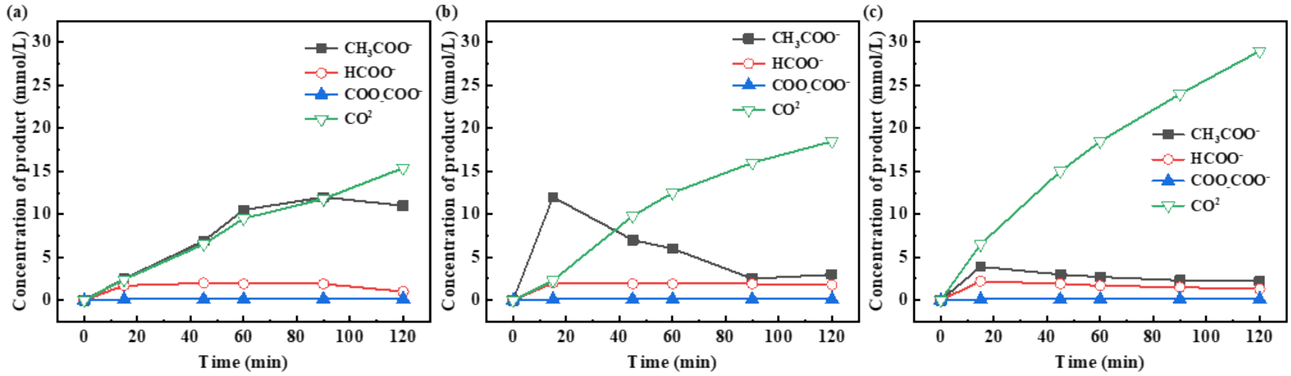

Fig. S4 The distribution of C-containing products during WAO at 200°C (a), 210°C (b) and 220°C (c) within120 min (Catalyst loading of 4.67 g/L, Oxygen partial pressure of 3 MPa, and Initial MDEA concentration of 1000 mg/L)

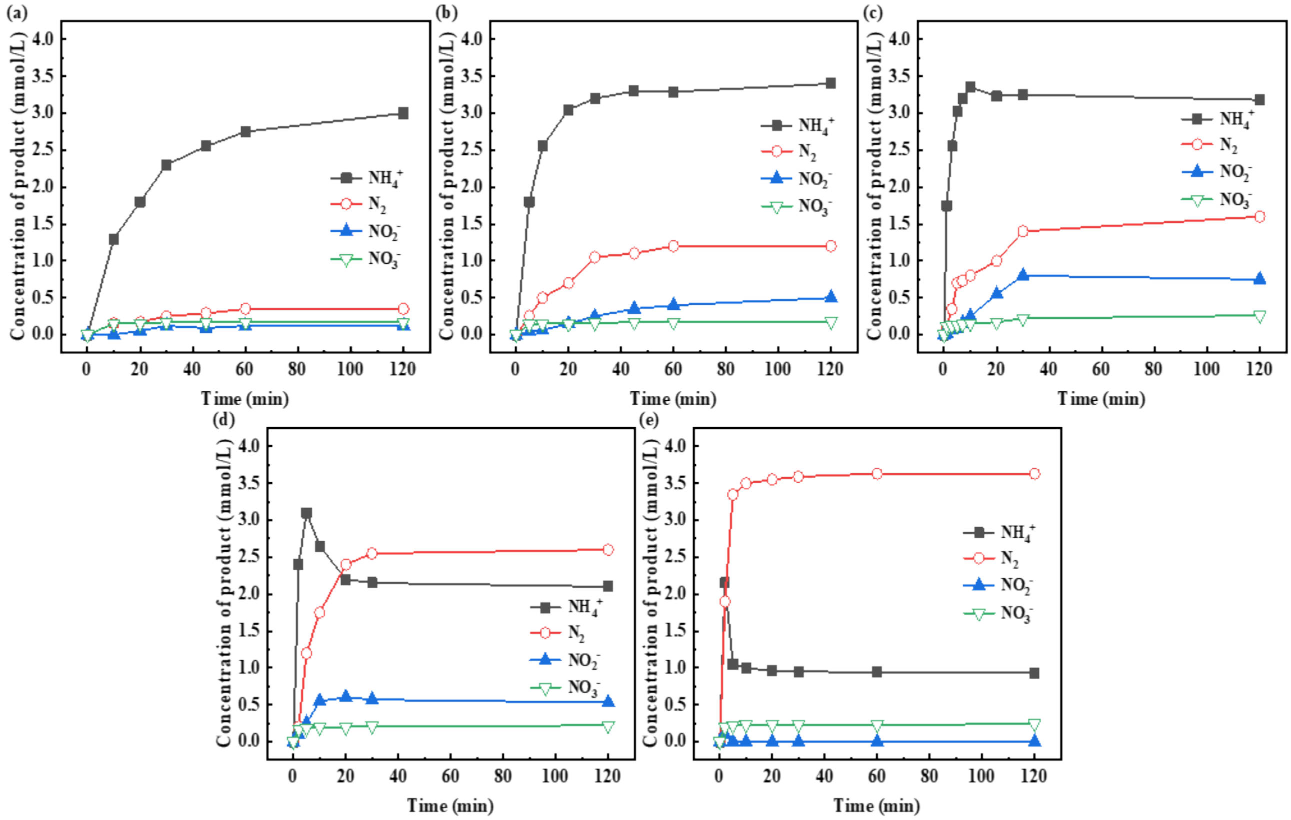

Fig. S5 The distribution of N-containing products during WAO at 200°C (a), 210°C (b) and 220°C (c) within 120 min.

(Catalyst loading of 4.67 g/L, Oxygen partial pressure of 3 MPa, and Initial MDEA concentration of 1000 mg/L)

Reaction kinetics and activation energy:

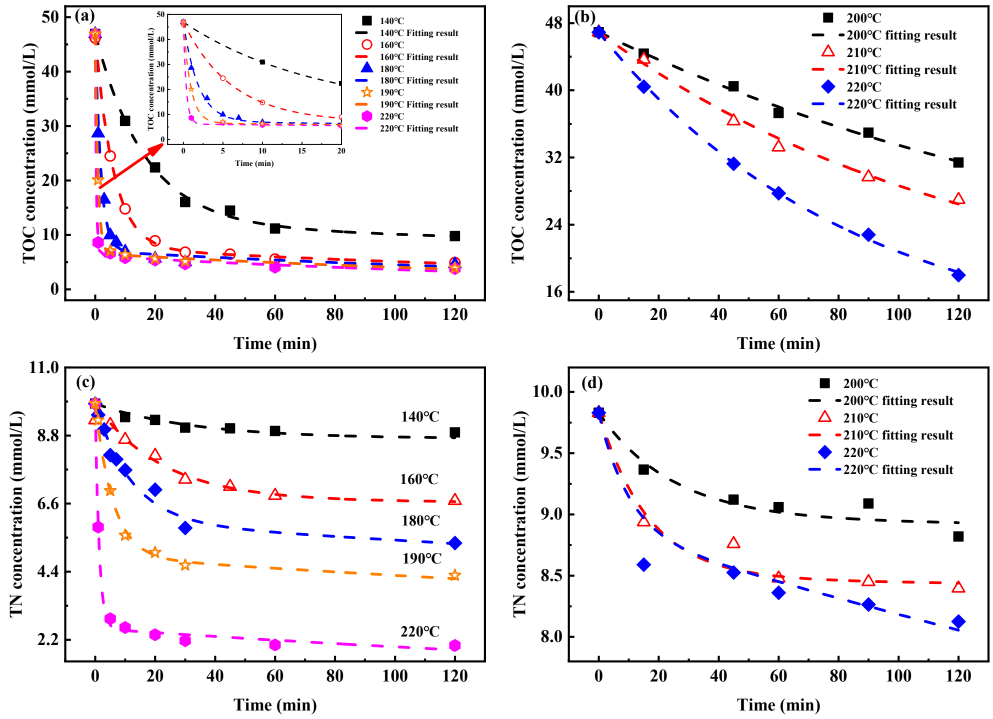

Fig. S6 The kinetic fitting curves of TOC-CWAO, TOC-WAO, TN-CWAO and TN-WAO in MDEA at different temperature.

（a. TOC-CWAO， b. TOC-WAO, c. TN-CWAO, d. TN-WAO）

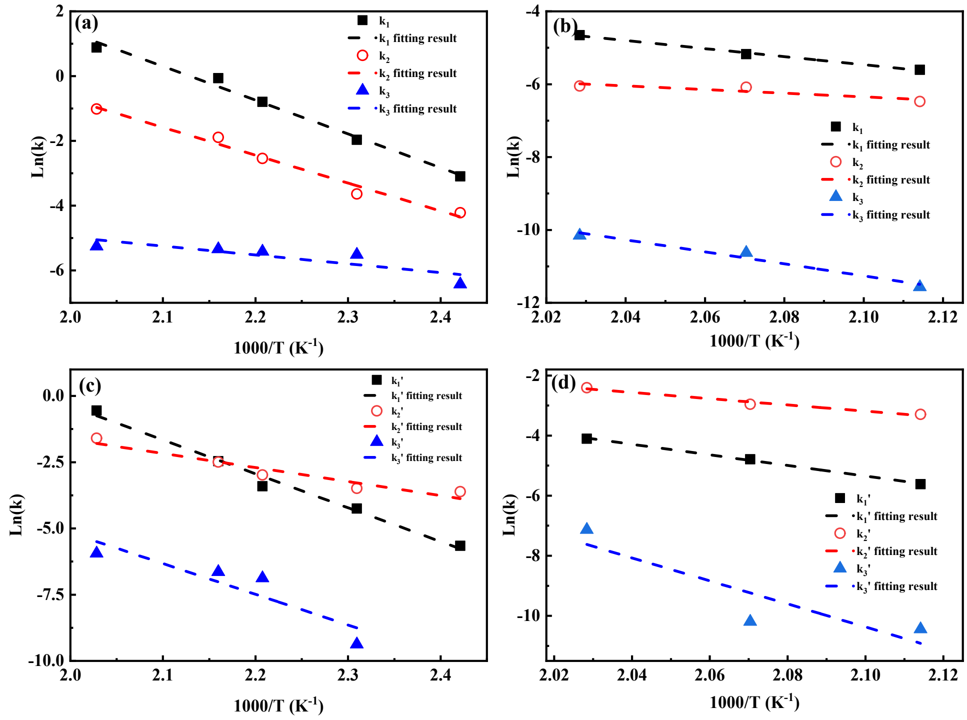

Fig. S7 The activation energy fitting curves of (a)TOC-CWAO, (b)TOC-WAO, (c) TN-CWAO and (d) TN-WAO.

Stability of catalyst:

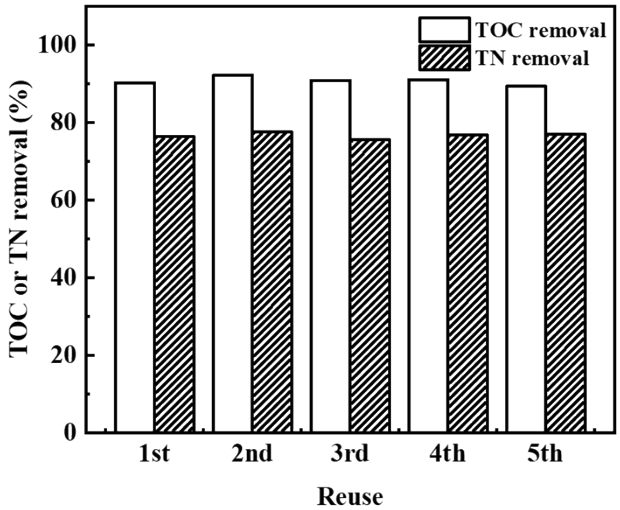

Fig. S8 The stability of Pd/CeO2-ZrO2 in CWAO process.

Pore size distribution:

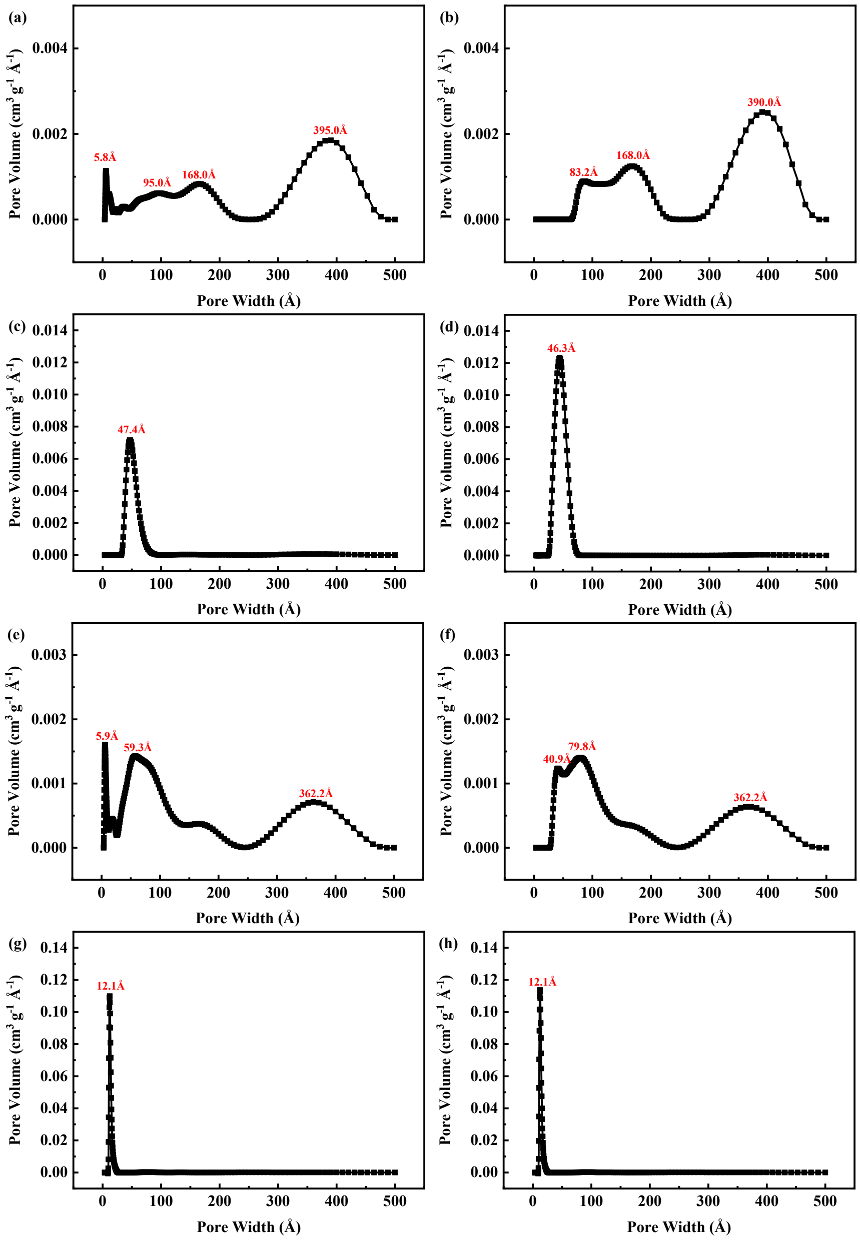

Fig. S9 Pore size distribution of CeO_2-ZrO_2 (a), Pd/CeO_2-ZrO_2 (b), Al_2O_3 (c), Pd/Al_2O_3 (d), TiO_2 (e), Pd/TiO_2 (f), AC (g) and Pd/AC (h).

Comparison table of different catalysts:

Table S2 TOC removal rates of catalyzers reported in the literature and this study

Catalysts	Catalyst loading	Oxygen partial pressure	temperatures	TOC removal rate	References
Pd/CeO_2-ZrO_2	2 wt%	3 MPa	200℃	90%	This study
Pd/AlOH	1 wt%	1.84 MPa	436K	26%	[1]
Pd/AC	9.8 wt%	0.69 MPa	473.15K	85%	[2]
Pd-Pt-Ce/Al_2O_3	4.05 wt%,0.42 wt%,4.58 wt%	1.5 MPa	443K	65%	[3]
Pd/CeO_2-R	1 wt%	/	/	57.5%	[4]
PdO/TiO_2	2 wt%	50 bar	250℃	65%	[5]
Pd-Pt/Al_2O3	10 wt%,1 wt%	1.5 MPa	423K	73%	[6]
Ru/CeO_2-R	1 wt%	3 MPa	220℃	97.6%	[7]

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