Electronic Supplementary Information (ESI)

Catalytic ozonation of dichloromethane at low temperature and even room temperature on Mn-loaded catalysts

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Fig. S1. DCM conversion curves at 100 ~ 450 °C of O₂ catalytic oxidation over the samples.

Fig. S2. Stability performance of the M/A-II with O₃/DCM=6 at 20 °C. (conditions: DCM initial concentration = 100 ppm; GHSV ≈ 30000 h⁻¹).
Fig. S3. (a) ~ (e) SEM and (f) ~ (j) EDS mapping images of all catalysts. (a) ~ (e) and (f) ~ (j) correspond to M/A-I, M/A-II, M/T, M/Z-I and M/Z-II in order, respectively.
Fig. S4. TEM images of all catalysts. (a) and (b) correspond to M/A-I, and (c) – (f) correspond to M/A-II, M/T, M/Z-I and M/Z-II, respectively. (Due to the lack of high photographic magnification, the M/A-I data can be roughly FFT measured to a lattice spacing of 2.41 Å, which can correspond to the converted lattice spacing of PDF# 04-0877 for Al₂O₃)
Fig. S5. N\textsubscript{2} adsorption and desorption isotherms and pore size distribution curves of Mn-loaded catalysts.

Fig. S6. Py-IR spectra of M/Z-II, M/T and M/A-II.
Fig. S7. XPS spectrum of S 2p after SO₂ single and both SO₂ and H₂O effect.

Fig. S8. Byproducts concentration of DCM ozone catalytic oxidation on M/A-II with the dynamic effects of SO₂.
Fig. S9. XPS spectrum of Cl 2p after (a) 20 °C stability test (b) 120 °C stability test and (c) 120 °C H₂O effect test; and the Mn 2p₂/₃ after catalytic ozonation on the M/A-II with the effects of (d) SO₂ and (e) simultaneous presence of water vapor and SO₂.
Fig. S10. Carbon/chlorine balance plots for all catalytic reactions in this study. (a) and (b) are the five catalysts carbon balance and chlorine balance from 20 to 120 °C reactions, respectively, corresponding to Fig. 2 (a) ~ (d) in the revised version; (c) is the reaction of changing the initial molar ratio of O<sub>3</sub>/DCM at 120 °C on M/A-II, corresponding to Fig. 2 (e) ~ (f) in the revised version. (d) to (f) are the reactions at 120 °C on M/A-II when SO<sub>2</sub>, water vapor, and both SO<sub>2</sub> and water vapor are introduced.
Fig. S11. By-products of catalytic ozonation of DCM at 20 °C and 120 °C on M/A-II measured by CG-MS after collection in adsorption tubes.

Table S1
Binding energy and species distribution of Mn 2p<sub>2/3</sub> for M/A-II in different reaction environments.

| Catalysts          | Mn<sup>2+</sup> (eV) | Mn<sup>3+</sup> (eV) | Mn<sup>4+</sup> (eV) | Mn<sup>2+</sup>/Mn (%) | Mn<sup>3+</sup>/Mn (%) | Mn<sup>4+</sup>/Mn (%) |
|--------------------|---------------------|---------------------|---------------------|------------------------|------------------------|------------------------|
| Fresh M/A-II       | /                   | 642.68              | 644.43              | /                      | 69.84                  | 30.16                  |
| SO<sub>2</sub> M/A-II | 641.00              | 642.69              | 644.71              | 9.87                   | 60.03                  | 30.09                  |
| SO<sub>2</sub>+H<sub>2</sub>O M/A-II | 641.08              | 642.96              | 644.79              | 7.92                   | 59.36                  | 29.50                  |
Table S2
The specific information on the by-products of the exhaust gas detected by GC-MS after adsorption tube collection.

| No. | Molecular name       | Molecule formula | Molecular structure |
|------|----------------------|------------------|---------------------|
| 1    | Chloropropylene      | C₃H₅Cl           | ![molecule](image)   |
| 2    | Trichloromethane     | CHCl₃            | ![molecule](image)   |
| 3    | Carbon tetrachloride | CCl₄             | ![molecule](image)   |
| 4    | 1,2-dichloroethane   | C₂H₂Cl₂          | ![molecule](image)   |
| 5    | 1,2-dichloropropane  | C₃H₆Cl₂          | ![molecule](image)   |
| 6    | 1,1,2-trichloroethane| C₂H₅Cl₃          | ![molecule](image)   |
| 7    | Tetrachlorethylene   | C₂Cl₄            | ![molecule](image)   |
| 8    | 1,1,2,2-tetrachloroethane | C₂H₂Cl₄   | ![molecule](image)   |

According to Fig. S11, that all experiments have reached the carbon balance within 10% error range. For the chlorine balance, the visible chlorine balance only reaches 60 ~ 80% in the absence of water vapor. When a high concentration of water vapor was introduced, the value of Ratio of Cl\textsubscript{in-out} decreased to nearly zero and the visible chlorine balance was achieved. In addition, the carbon balance deviated from normal in Fig. S11 (a) when reacting on M/T at 20 ~ 60 °C. One reason is that M/T has poor low temperature performance and cannot oxidize DCM to CO\textsubscript{x}, thus generating more byproducts CH\textsubscript{3}OH which may compete with DCM. The second reason is the higher boiling point of CH\textsubscript{3}OH, i.e., CH\textsubscript{3}OH (64.7 °C) > DCM (39.8 °C), which could stay on the surface of M/T and affect the carbon balance. Similarly, in Fig. S11 (d), after the poisoning of M/A-II by the erosion of high concentration of SO\textsubscript{2}, more CH\textsubscript{3}OH production was detected at the same time. Therefore, it could be said that the poisoned M/A-II also had difficulty in resisting the CH\textsubscript{3}OH production and the carbon balance deviated from the normal.