# Ozone catalytic oxidation for ammonia removal from simulated air at room temperature

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## Supplementary data

### Specific quantification methods of NO, $NO_2$ and $N_2$

The mass signal of a given molecule (M) at *m/z* ($I^{\mathrm{M}}_{m/z}$) could be obtained by eqn. S(1):

$$I^{\mathrm{M}}_{m/z} = \eta_{m/z} \cdot C_{\mathrm{M}} \cdot \sigma_{\mathrm{M}} \cdot \beta^{\mathrm{M}}_{m/z} \qquad \text{S(1)}$$

where $\eta_{m/z}$ is the detection constant of the mass spectrometer at *m/z*; $C_{\mathrm{M}}$ is the concentration of M; $\sigma_{\mathrm{M}}$ is the total ionization cross section for M at 70 eV (the electron beam energy used in our mass spectrometer ionizer); $\beta^{\mathrm{M}}_{m/z}$ is the ratio of the partial ionization cross section of M generating the ion fragment with *m/z* to its total ionization cross section at 70 eV. $\sigma_{\mathrm{M}}$ could be acquired from the website of National Institute of Standards and Technology (NIST)[1] and $\beta^{\mathrm{M}}_{m/z}$ could be obtained from our

MS software.

The mass signals at $m/z$ = 44 and 46 ($I_{44}$ and $I_{46}$), derived from single contributor, are attributed to $N_2O$ and $NO_2$, respectively,

$$I_{44} = \eta_{44} \cdot C_{\mathrm{N_2O}} \cdot \sigma_{\mathrm{N_2O}} \cdot \beta_{44}^{\mathrm{N_2O}} \tag{S(2)}$$

$$I_{46} = \eta_{46} \cdot C_{\mathrm{NO_2}} \cdot \sigma_{\mathrm{NO_2}} \cdot \beta_{46}^{\mathrm{NO_2}} \tag{S(3)}$$

However, the mass signal at $m/z$ = 30 ($I_{30}$) derives from the contributions of $N_2O$, $NO_2$ and NO, being the sum of $I_{30}^{\mathrm{N_2O}}$, $I_{30}^{\mathrm{NO_2}}$ and $I_{30}^{\mathrm{NO}}$,

$$I_{30} = I_{30}^{\mathrm{N_2O}} + I_{30}^{\mathrm{NO_2}} + I_{30}^{\mathrm{NO}} \tag{S(4)}$$

Their individual contributions, $I_{30}^{\mathrm{N_2O}}$, $I_{30}^{\mathrm{NO_2}}$ and $I_{30}^{\mathrm{NO}}$, can be expressed as follows:

$$I_{30}^{\mathrm{N_2O}} = \eta_{30} \cdot C_{\mathrm{N_2O}} \cdot \sigma_{\mathrm{N_2O}} \cdot \beta_{30}^{\mathrm{N_2O}} \tag{S(5)}$$

$$I_{30}^{\mathrm{NO_2}} = \eta_{30} \cdot C_{\mathrm{NO_2}} \cdot \sigma_{\mathrm{NO_2}} \cdot \beta_{30}^{\mathrm{NO_2}} \tag{S(6)}$$

$$I_{30}^{\mathrm{NO}} = \eta_{30} \cdot C_{\mathrm{NO}} \cdot \sigma_{\mathrm{NO}} \cdot \beta_{30}^{\mathrm{NO}} \tag{S(7)}$$

According to eqns. S(2) and S(5), we can get

$$I_{30}^{\mathrm{N_2O}} = \frac{\eta_{30}}{\eta_{44}} \cdot \frac{\beta_{30}^{\mathrm{N_2O}}}{\beta_{44}^{\mathrm{N_2O}}} \cdot I_{44} \tag{S(8)}$$

where $\frac{\eta_{30}}{\eta_{44}} \approx \left(\frac{30}{44}\right)^{-0.5} = 1.21$, $\beta_{30}^{\mathrm{N_2O}} = 19\%$, $\beta_{44}^{\mathrm{N_2O}} = 62\%$, thereby

$$I_{30}^{\mathrm{N_2O}} = 0.37 \cdot I_{44} \tag{S(9)}$$

Similarly, according to eqns. S(3) and S(6), eqn. S(10) was obtained

$$I_{30}^{\mathrm{NO_2}} = 3.35 \cdot I_{46} \tag{S(10)}$$

Therefore, based on eqns. S(4), S(9) and S(10), $I_{30}^{\mathrm{NO}}$ was obtained:

$$I_{30}^{\mathrm{NO}} = I_{30} - (0.37 \cdot I_{44}) - (3.35 \cdot I_{46}) \tag{S(11)}$$

According to eqns. S(2) and S(7), we can get

$$C_{NO} = \frac{\eta_{44}}{\eta_{30}} \cdot \frac{\sigma_{N_2O}}{\sigma_{NO}} \cdot \frac{\beta_{44}^{N_2O}}{\beta_{30}^{NO}} \cdot \frac{I_{30}^{NO}}{I_{44}} \cdot C_{N_2O} \qquad \text{S(12)}$$

where $\frac{\eta_{44}}{\eta_{30}} \approx \left(\frac{44}{30}\right)^{-0.5} = 0.83$, $\sigma_{N_2O} = 3.7\times10^{-16}\,\text{cm}^2$, $\sigma_{NO} = 2.8\times10^{-16}\,\text{cm}^2$, $\beta_{44}^{N_2O} = 62\%$, $\beta_{30}^{NO} = 88\%$, eqn. S(12) could be simplified as

$$C_{NO} = 0.76 \cdot C_{N_2O} \cdot \frac{I_{30}^{NO}}{I_{44}} \qquad \text{S(13)}$$

Substituting eqn. S(11) into eqn. S(13),

$$C_{NO} = 0.76 \cdot C_{N_2O} \cdot \left(\frac{I_{30}}{I_{44}} - 0.37 - 3.35 \cdot \frac{I_{46}}{I_{44}}\right) \qquad \text{S(14)}$$

where $C_{N_2O}$ and $I_{30}$, $I_{44}$ & $I_{46}$ could be simultaneously acquired by the FT-IR spectrometer and mass spectrometer; therefore, $C_{NO}$ could be obtained from eqn. S(14).

Similarly, the expressions of $C_{NO_2}$ and $C_{N_2}$ were yielded:

$$C_{NO_2} = 3.03 \cdot C_{N_2O} \cdot \frac{I_{46}}{I_{44}} \qquad \text{S(15)}$$

$$C_{N_2} = 0.79 \cdot C_{N_2O} \cdot \left(\frac{I_{28}}{I_{44}} - 0.14\right) \qquad \text{S(16)}$$

For all the reactions to be discussed below, the outlet gaseous products were on-line analyzed by the FT-IR spectrometer and the mass spectrometer.

## Reference

[1] NIST, http://webbook.nist.gov/chemistry/form-ser.html, (accessed June 2014).

**Fig. S1.** OZCO measurements of gaseous $NH_3$ over AgMn/HZ catalyst to verify the reliability of $N_2$ selectivity derived from eqn. (5). Time courses for (a) $NH_3$ conversion, (b) $N_2O$ concentration, (c) MS signals, (d) $N_2$ concentration and (e) $N_2$ and $N_2O$ selectivities during OZCO of gaseous $NH_3$. The $N_2$ selectivity was derived from the direct measurement (eqn. (6)). Conditions: 0.2 g of AgMn/HZ catalyst, 500 SCCM of total flow rate with 1000 ppmv of $NH_3$ and 500 ppmv of $O_3$, 20 vol.% of $O_2$ and Ar balanced.

**Fig. S2.** $NH_3$ concentrations of HZ, Ag/HZ, Mn/HZ and AgMn/HZ catalysts during TPD measurements after 90-min OZCO of gaseous $NH_3$. OZCO conditions: 0.1 g of catalysts, feed gas of 250 SCCM, containing 530 ppmv of $NH_3$, 450 ppmv of $O_3$, 20 vol.% of $O_2$ and balanced by $N_2$. TPD conditions: 0.03 g of the used catalysts, 100 SCCM of He, 10 ℃·min$^{-1}$.

**Fig. S3.** MS signals of (a) HZ, (b) Ag/HZ, (c) Mn/HZ and (d) AgMn/HZ catalysts during TPD measurements after 90-min OZCO of gaseous $NH_3$. OZCO and TPD conditions are the same as those in **Fig. S2.**

**Fig. S4.** $NH_3$ concentrations of (a) HZ and (b) Ag/HZ catalysts during TPD measurements after 30-min OZCO of adsorbed $NH_3$. $NH_3$ adsorption conditions: 0.1 g of catalysts, 540 ppmv of $NH_3$ for 25-min adsorption; OZCO conditions: a feed gas of 250 SCCM containing 450 ppmv of $O_3$, 20 vol.% of $O_2$ and balanced by He. TPD conditions: 0.03 g of the used catalysts, 100 SCCM of He, 10 ℃·min$^{-1}$.

**Fig. S5.** MS signals of (a) HZ, (b) Ag/HZ, (c) Mn/HZ and (d) AgMn/HZ catalysts during TPD measurements after 30-min OZCO of adsorbed $NH_3$. $NH_3$ adsorption, OZCO and TPD conditions are the same as those in **Fig. S4.**

# Fig. S1

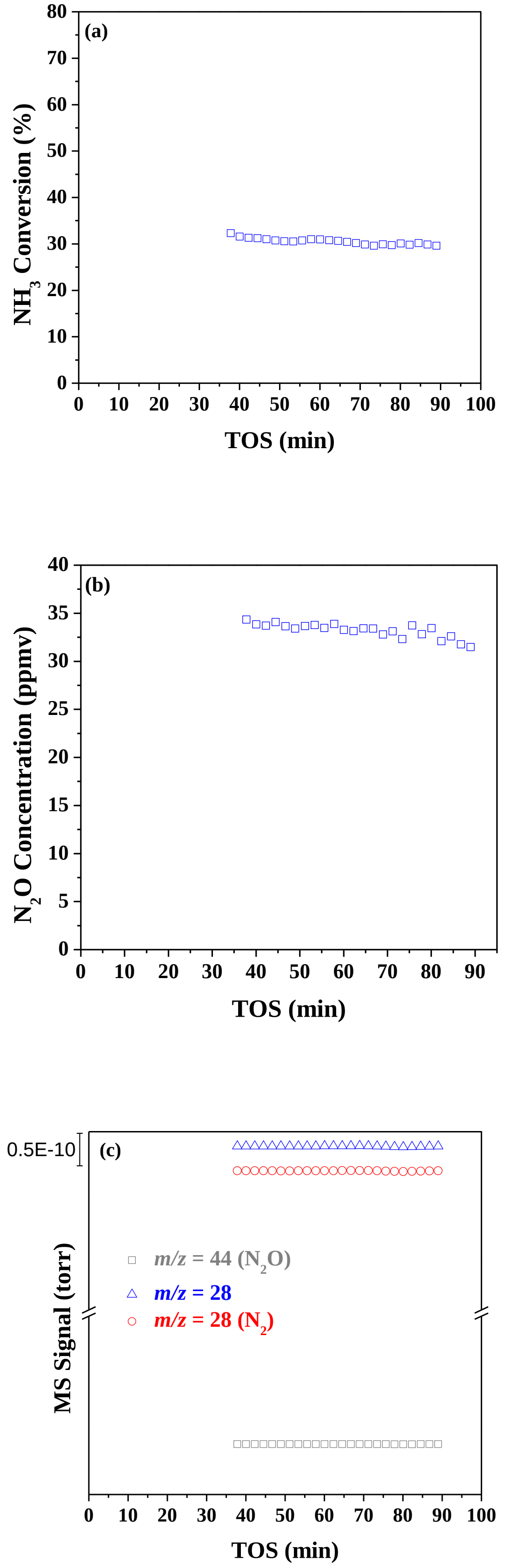

(a)
NH3 Conversion (%)
0
10
20
30
40
50
60
70
80
TOS (min)
0
10
20
30
40
50
60
70
80
90
100
(b)
N2O Concentration (ppmv)
0
5
10
15
20
25
30
35
40
TOS (min)
0
10
20
30
40
50
60
70
80
90
(c)
MS Signal (torr)
0.5E-10
□ m/z = 44 (N2O)
△ m/z = 28
○ m/z = 28 (N2)
TOS (min)
0
10
20
30
40
50
60
70
80
90
100

**Fig. S1**

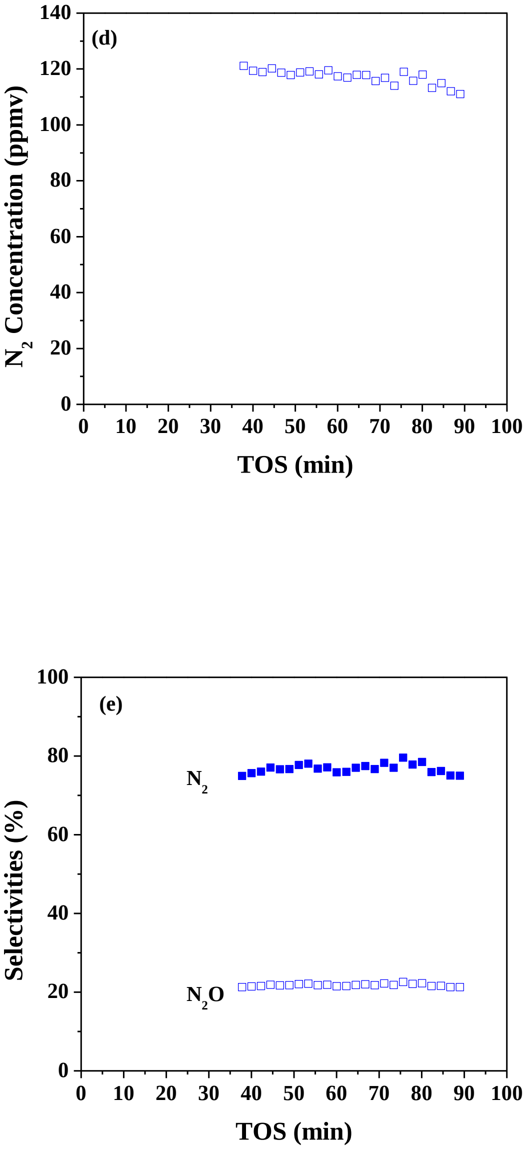

(d)
N$_2$ Concentration (ppmv)
0
20
40
60
80
100
120
140
TOS (min)
0
10
20
30
40
50
60
70
80
90
100
(e)
N$_2$
N$_2$O
Selectivities (%)
0
20
40
60
80
100
TOS (min)
0
10
20
30
40
50
60
70
80
90
100

**Fig. S2**

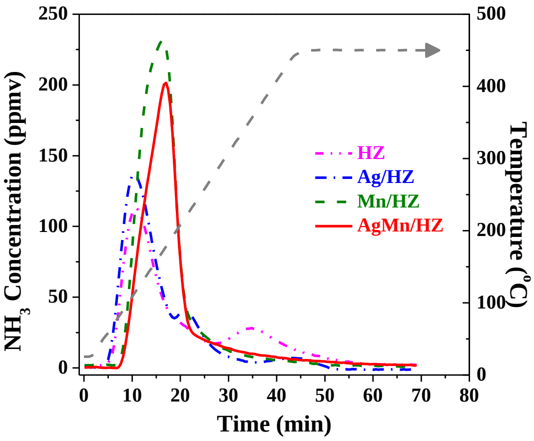
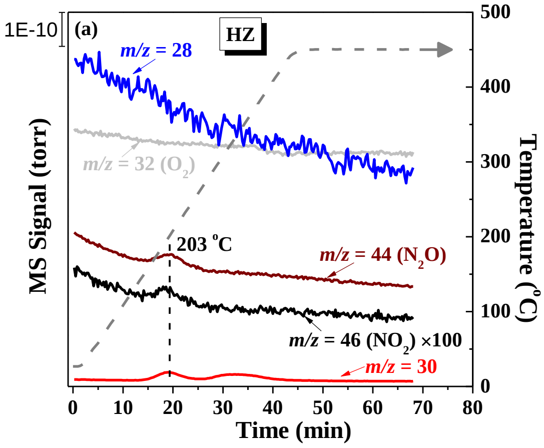
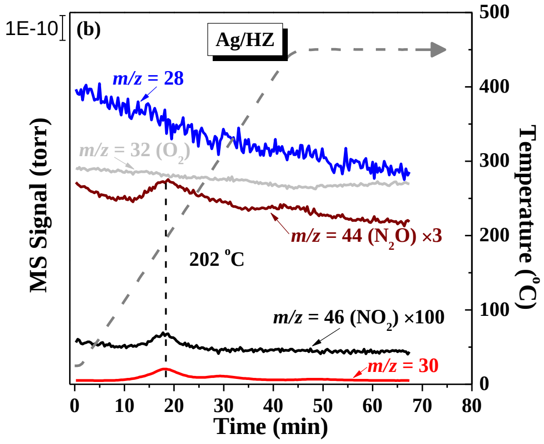
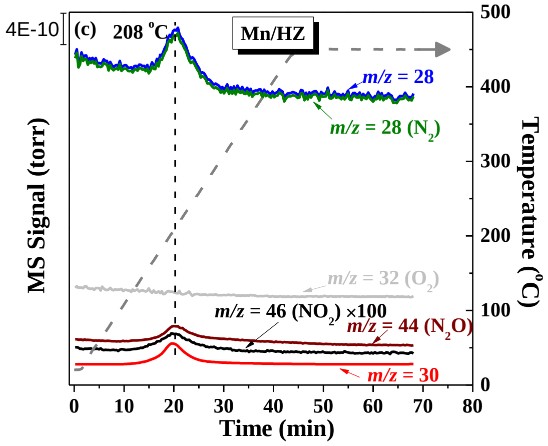

HZ
Ag/HZ
Mn/HZ
AgMn/HZ
NH3 Concentration (ppmv)
Temperature (°C)
Time (min)
0
50
100
150
200
250
0
100
200
300
400
500
0
10
20
30
40
50
60
70
80

**Fig. S3**


1E-10
(a)
HZ
m/z = 28
m/z = 32 (O2)
203 °C
m/z = 44 (N2O)
m/z = 46 (NO2) ×100
m/z = 30
MS Signal (torr)
Temperature (°C)
Time (min)
0
10
20
30
40
50
60
70
80
0
100
200
300
400
500


1E-10
(b)
Ag/HZ
m/z = 28
m/z = 32 (O2)
m/z = 44 (N2O) ×3
202 °C
m/z = 46 (NO2) ×100
m/z = 30
MS Signal (torr)
Temperature (°C)
Time (min)
0
10
20
30
40
50
60
70
80
0
100
200
300
400
500

# Fig. S3


4E-10
(c)
208 °C
Mn/HZ
m/z = 28
m/z = 28 (N2)
m/z = 32 (O2)
m/z = 46 (NO2) ×100
m/z = 44 (N2O)
m/z = 30
MS Signal (torr)
Temperature (°C)
500
400
300
200
100
0
0
10
20
30
40
50
60
70
80
Time (min)

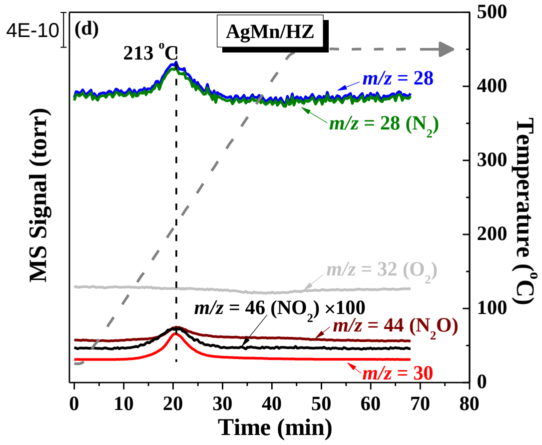

4E-10
(d)
213 °C
AgMn/HZ
m/z = 28
m/z = 28 (N2)
m/z = 32 (O2)
m/z = 46 (NO2) ×100
m/z = 44 (N2O)
m/z = 30
MS Signal (torr)
Temperature (°C)
500
400
300
200
100
0
0
10
20
30
40
50
60
70
80
Time (min)

**Fig. S4**

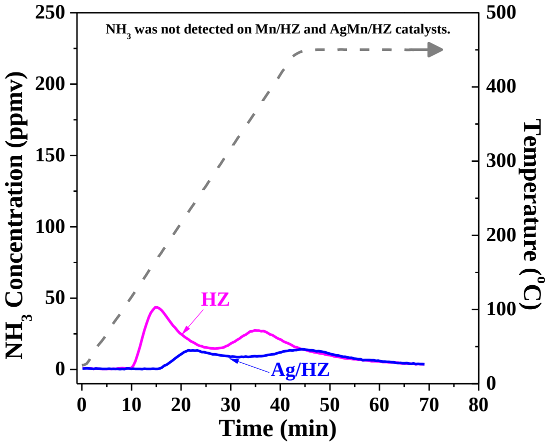

NH$_3$ was not detected on Mn/HZ and AgMn/HZ catalysts.
HZ
Ag/HZ
NH$_3$ Concentration (ppmv)
Temperature ($^0$C)
Time (min)
250
200
150
100
50
0
500
400
300
200
100
0
0
10
20
30
40
50
60
70
80

**Fig. S5**

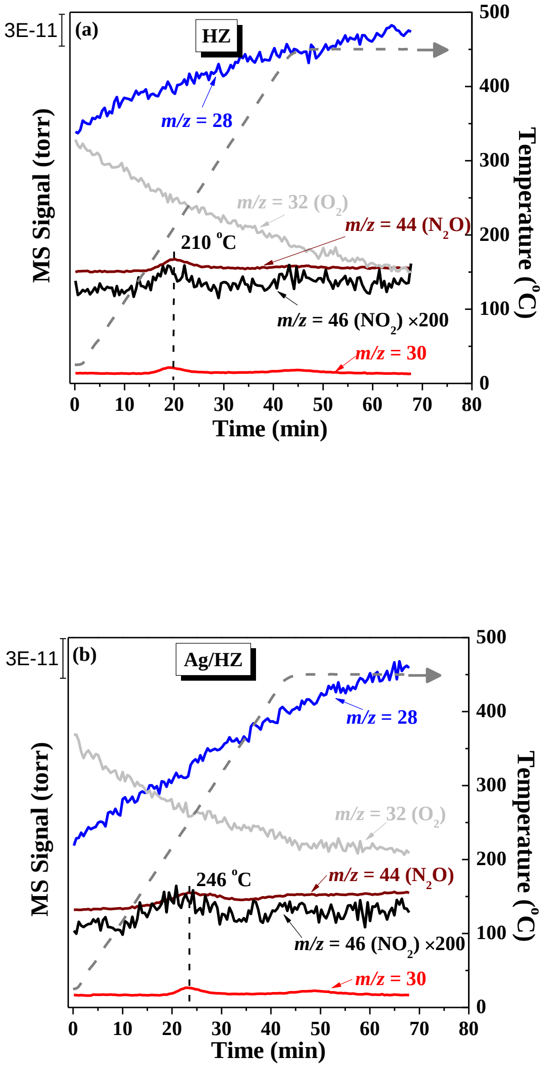
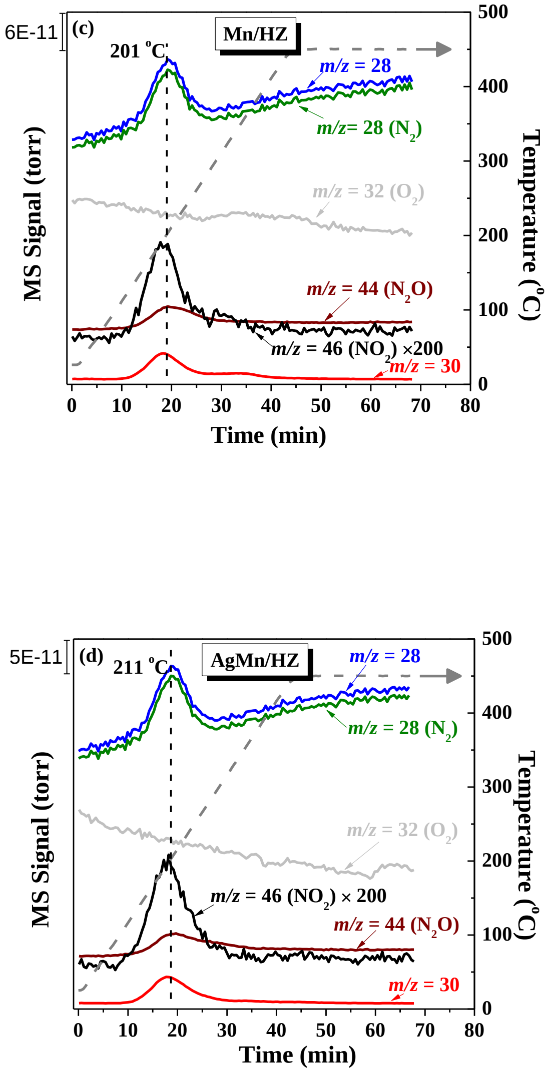

3E-11
(a)
HZ
m/z = 28
m/z = 32 (O₂)
m/z = 44 (N₂O)
210 °C
m/z = 46 (NO₂) ×200
m/z = 30
MS Signal (torr)
Temperature (°C)
0
100
200
300
400
500
0
10
20
30
40
50
60
70
80
Time (min)
3E-11
(b)
Ag/HZ
m/z = 28
m/z = 32 (O₂)
246 °C
m/z = 44 (N₂O)
m/z = 46 (NO₂) ×200
m/z = 30
MS Signal (torr)
Temperature (°C)
0
100
200
300
400
500
0
10
20
30
40
50
60
70
80
Time (min)

**Fig. S5**


6E-11
(c)
Mn/HZ
201 °C
m/z = 28
m/z= 28 (N$_2$)
m/z = 32 (O$_2$)
m/z = 44 (N$_2$O)
m/z = 46 (NO$_2$) ×200
m/z = 30
MS Signal (torr)
Temperature (°C)
0
100
200
300
400
500
0
10
20
30
40
50
60
70
80
Time (min)
5E-11
(d)
211 °C
AgMn/HZ
m/z = 28
m/z = 28 (N$_2$)
m/z = 32 (O$_2$)
m/z = 46 (NO$_2$) × 200
m/z = 44 (N$_2$O)
m/z = 30
MS Signal (torr)
Temperature (°C)
0
100
200
300
400
500
0
10
20
30
40
50
60
70
80
Time (min)