Supporting Information

Thermal degradation of defective high-surface-area UiO-66 in different gaseous environments

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BET Measurement

BET measurement was calculated from the linear region of the isotherms for each sample i.e. Points fitted on the linear isotherm up to relative pressures (p/p°) of 0.09, 0.08, 0.08, 0.06 for the samples having no heat treatment, oxidative heat treatment, reductive heat treatment and inert heat treatment respectively.

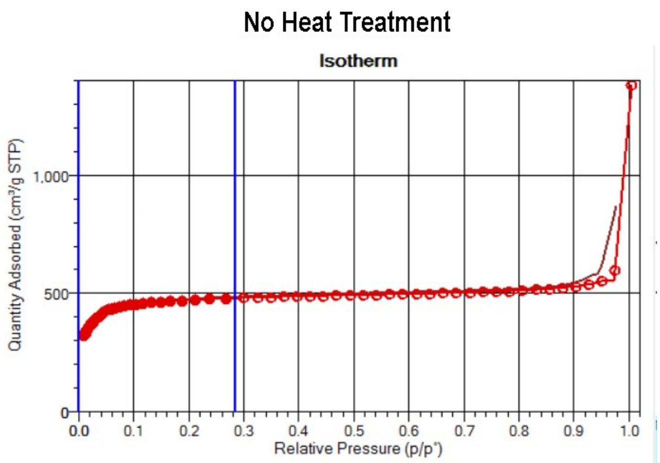

Figure 1 Isotherm for BET surface area of the UiO-66 sample without heat treatment.

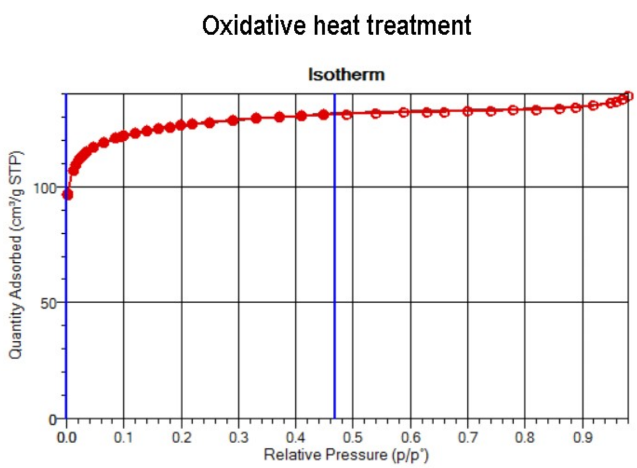

Figure 2 Isotherm for BET surface area of the UiO-66 sample after oxidative heat treatment.

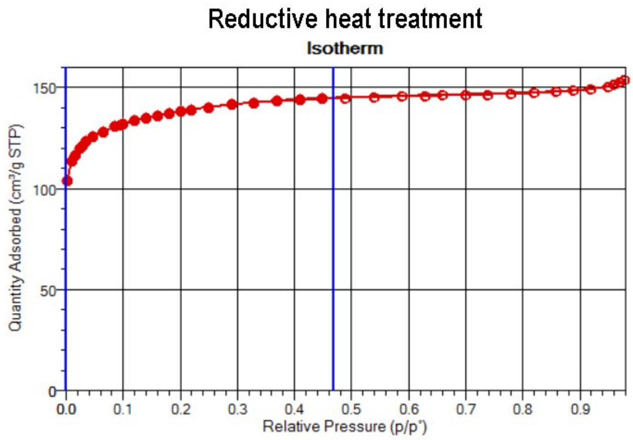

Figure 3 Isotherm for BET surface area of the UiO-66 sample after reductive heat treatment.

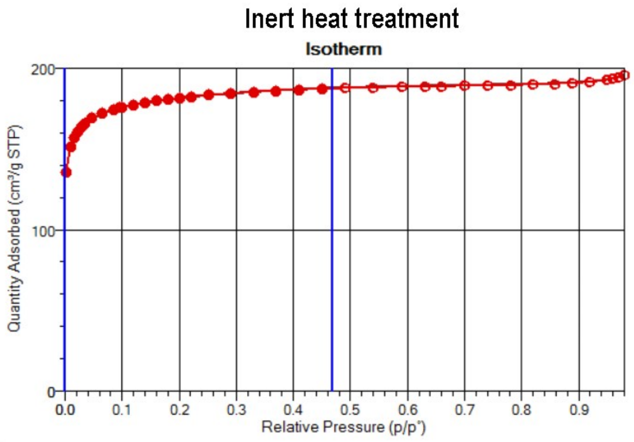

Figure 4 Isotherm for BET surface area of the UiO-66 sample after inert heat treatment.

Pore Size Distribution

Horvath-Kawazoe differential pore volume plots for all the samples are given below.

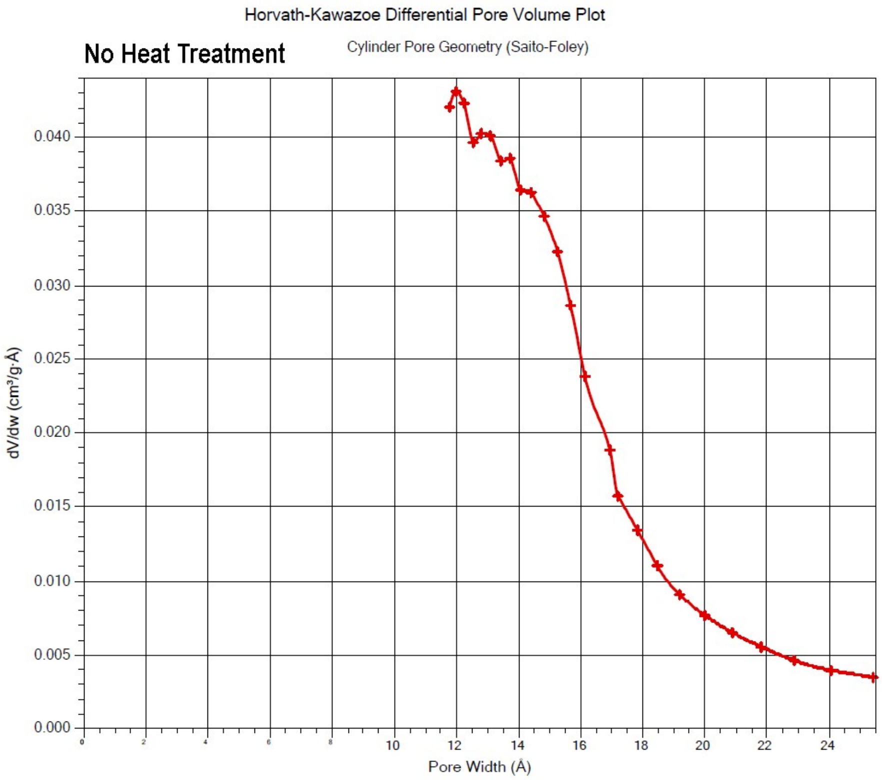

Figure 5 Horvath-Kawazoe differential pore volume plot for the UiO-66 sample without any heat treatment

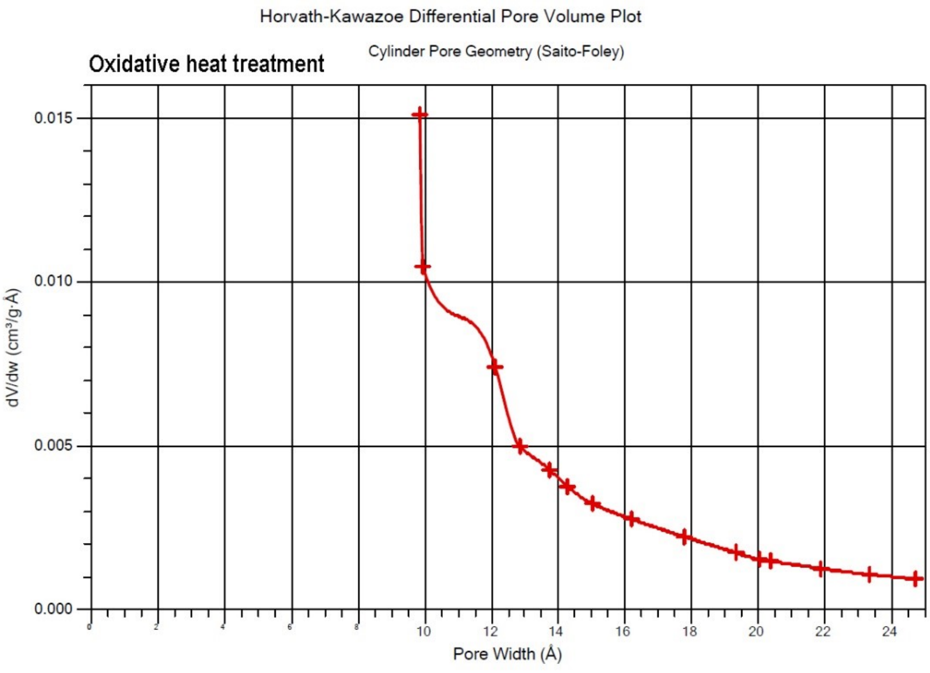

Figure 6 Horvath-Kawazoe differential pore volume plot for the UiO-66 sample afteroxidative heat treatment

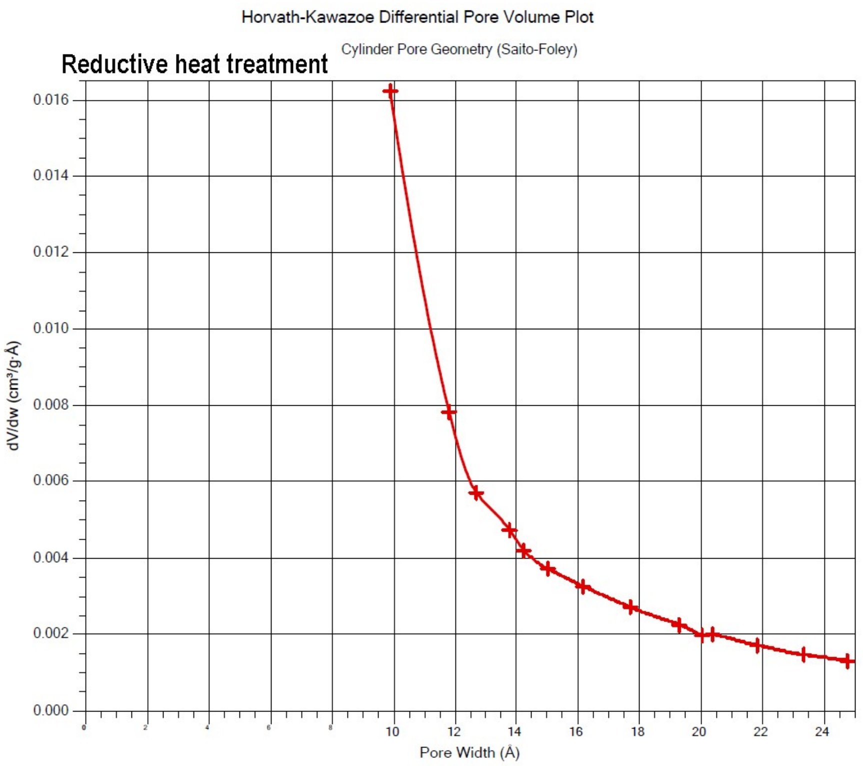

Figure 7 Horvath-Kawazoe differential pore volume plot for the UiO-66 sample after reductive heat treatment

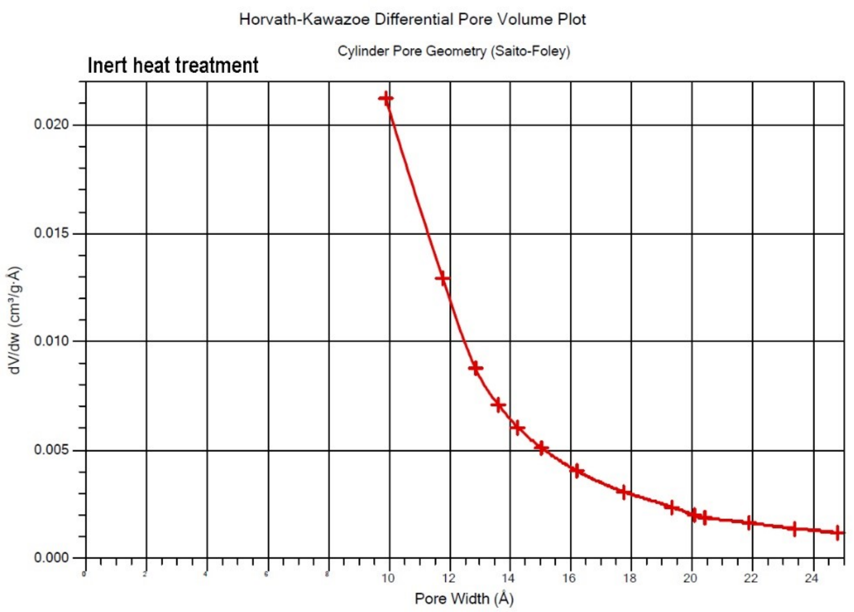

Figure 8 Horvath-Kawazoe differential pore volume plot for the UiO-66 sample after inert heat treatment

Thermogravimetric analysis

The TG curves taken under inert, reductive and oxidative conditions are presented below, the % loss of mass in various steps is mentioned for each curve.

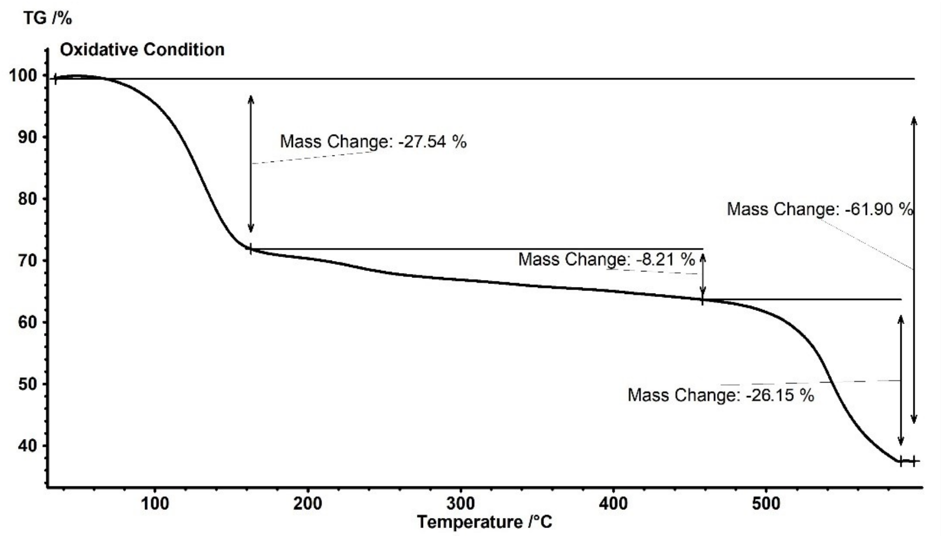

Figure 9 TG Curve of the UiO-66 sample under oxidative condition. The mass loss % of each step is mentioned.

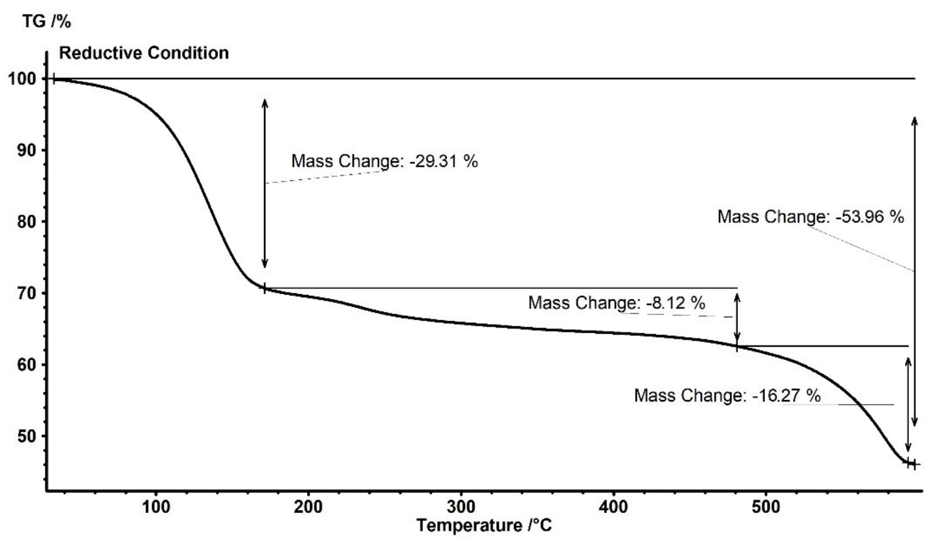

Figure 10 TG Curve of the UiO-66 sample under reductive condition. The mass loss % of each step is mentioned.

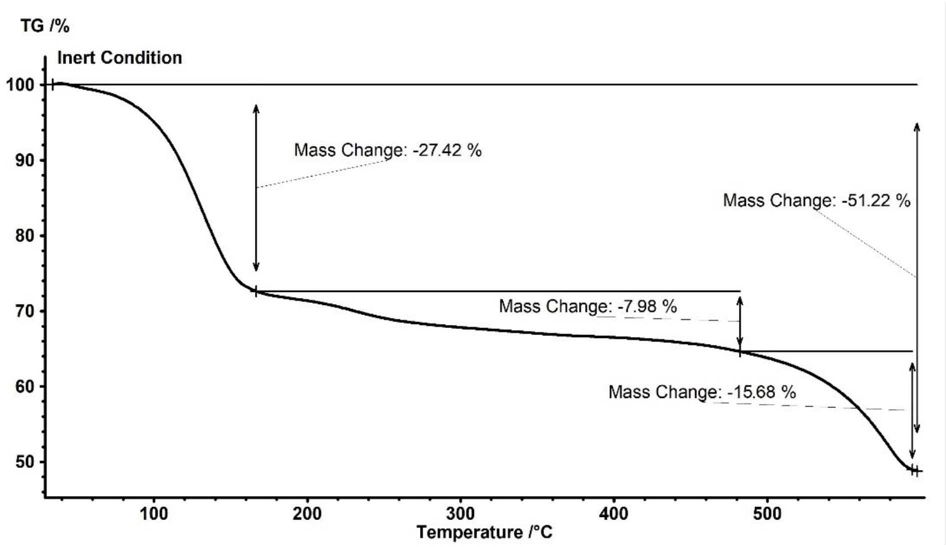

Figure 11 TG Curve of the UiO-66 sample under inert condition. The mass loss % of each step is mentioned.

Calculation of Missing linkers' Defects

Final mass of the product is taken as the mass of $6ZrO_2$.

A Perfect UiO-66 (having no defects) after dehydroxylation has the formula $Zr_6O_6(BDC)_6$

If the final mass % of $6ZrO_2$ is taken as 100 %, the mass% of perfect UiO-66 will be 220%.

The point of TG curve when there is negligible mass loss after dehydroxylation and no heat absorbed/evolved is taken as the mass % of the defect-containing UiO-66 having formula $Zr_6O_{(6+X)}(BDC)_{(6-X)}$.

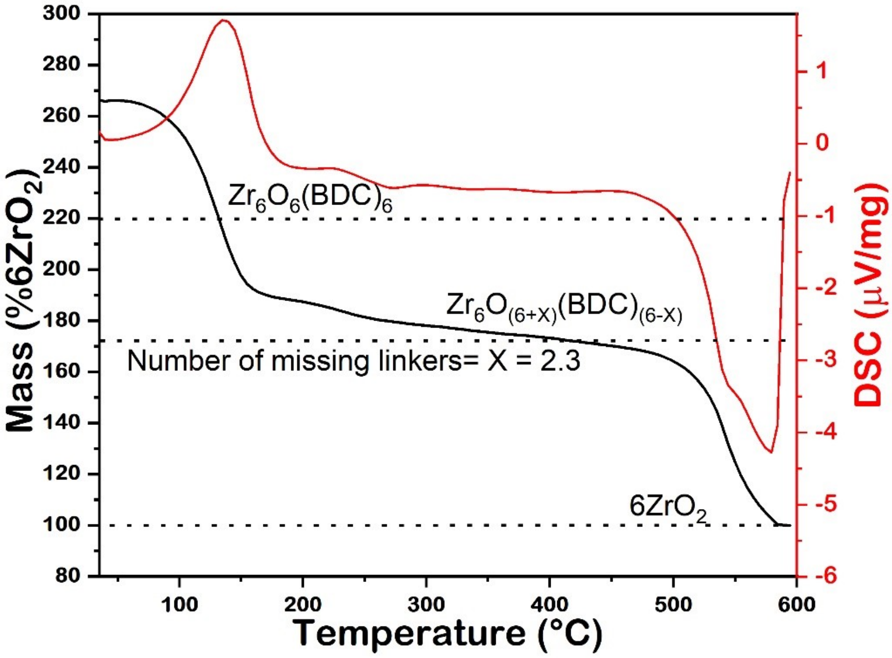

Figure 12 Calculation of number of the missing BDC linkers per hexa-zirconium node. The final mass of $6ZrO_2$ is taken as 100 and the dehydroxylated perfect MOF before thermal decomposition is taken as 220.

The value of x is calculated by the following equation

$$\frac{220}{A} = \frac{1628.2\ (Molar\ mass\ of\ Zr_6O_6(BDC)_6)}{1628.2 - 148x\ (Molar\ mass\ of\ Zr_6O_{(6+x)}(BDC)_{(6-x)})}$$

Solving this equation, we get;

$$x = \frac{1628.2 - 7.4A}{148}$$

X = Number of missing linkers defect per formula unit.

A = value of mass % of defect-containing UiO-66 ($Zr_6O_{(6+X)}(BDC)_{(6-X)}$) on y-axis of TG curve

For A = 173 (our sample), x = 2.35