

Supporting information

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FT-IR analysis

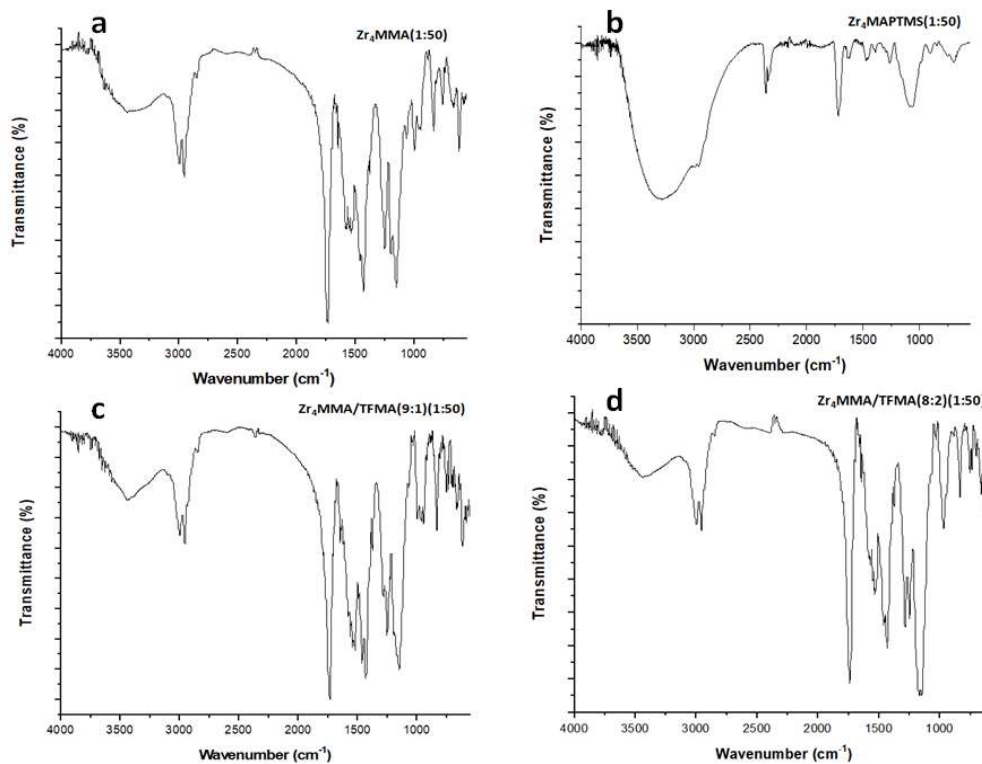


Figure S1. FT-IR spectra of the samples: a) $\text{Zr}_4\text{MMA}(1:50)$, b) $\text{Zr}_4\text{MAPTMS}(1:50)$, c) $\text{Zr}_4\text{MMA}/\text{TFMA}(9:1)(1:50)$, d) $\text{Zr}_4\text{MMA}/\text{TFMA}(8:2)(1:50)$.

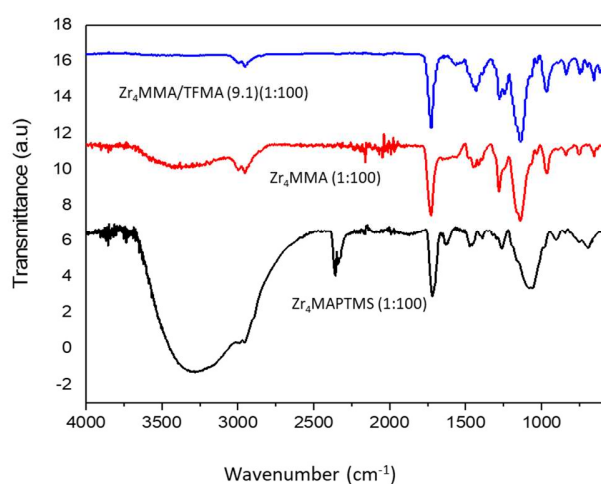


Figure S2. Full scale of the spectra reported in Figure 2.

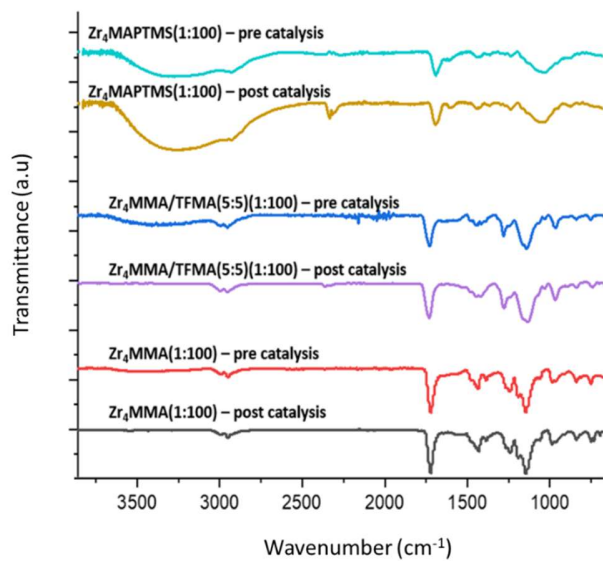


Figure S3. FT-IR analysis of Zr₄MMA(1:100), Zr₄MMA/TFMA(5:5)(1:100) and Zr₄MAPTMS(1:100) before and after catalysis.

Raman mapping

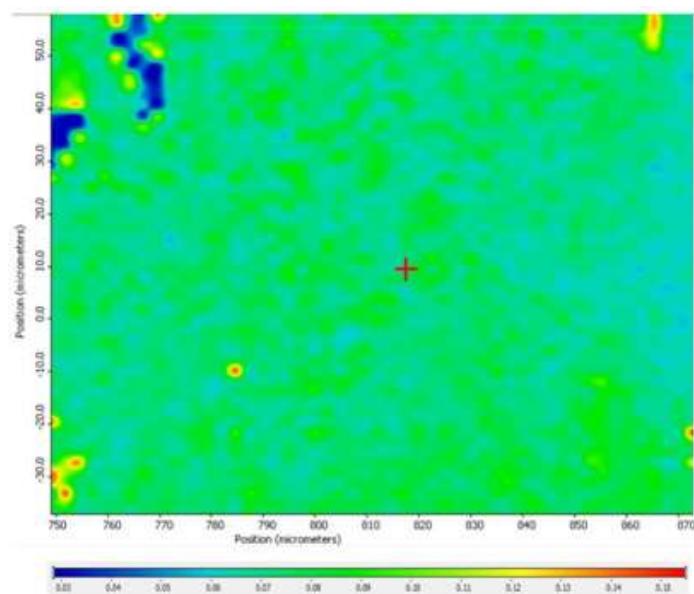


Figure S4. Raman mapping of Zr₄MMA(1:100), collected in a region of 150 x 200 μm and with a power of 8 mW.

TGA analysis

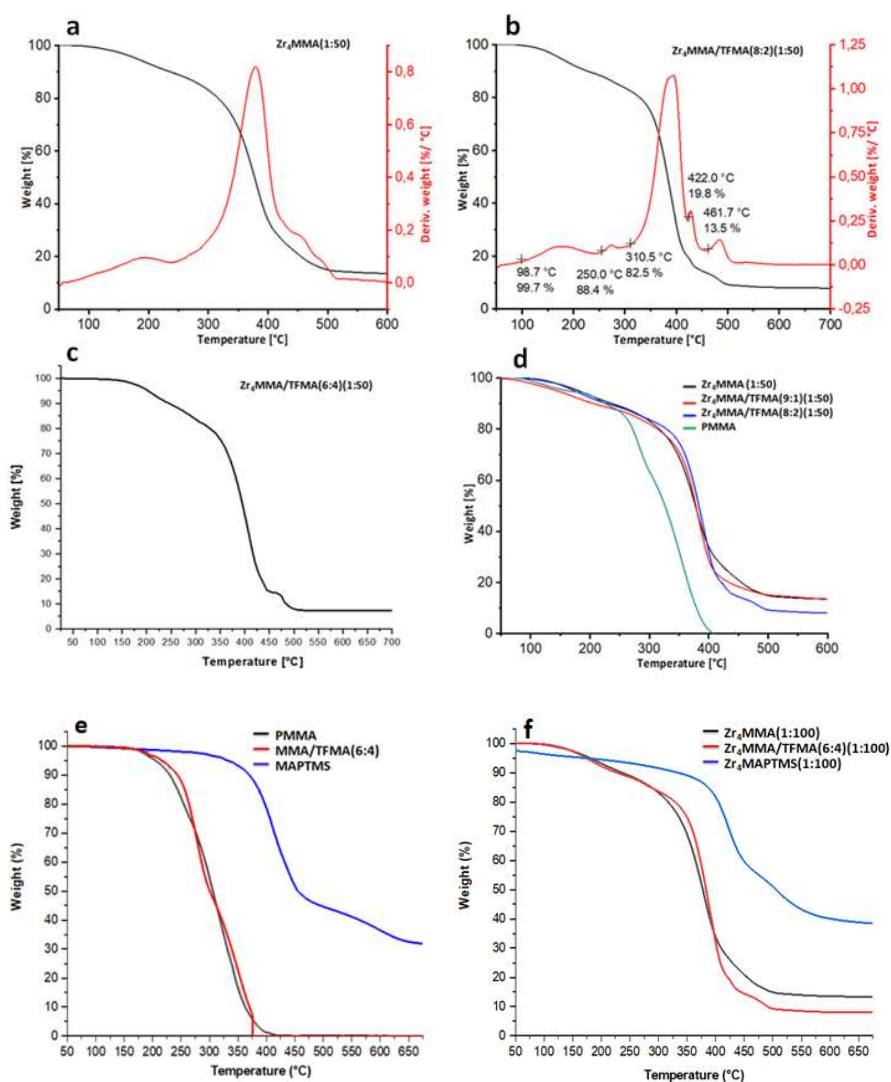


Figure S5. TGA analyses of the samples: a) $\text{Zr}_4\text{MMA}(1:50)$, b) $\text{Zr}_4\text{MMA}/\text{TFMA}(8:2)(1:50)$, c) $\text{Zr}_4\text{MMA}(6:4)(1:50)$, d) comparison between three polymers, $\text{Zr}_4\text{MMA}(1:50)$, $\text{Zr}_4\text{MMA}/\text{TFMA}(9:1)(1:50)$ and $\text{Zr}_4\text{MMA}/\text{TFMA}(8:2)(1:50)$ and PMMA, e) comparison between three blanks, PMMA, MMA/TFMA (6:4) and MAPTMS, f) comparison between three polymers, $\text{Zr}_4\text{MMA}(1:100)$, $\text{Zr}_4\text{MMA}/\text{TFMA}(6:4)(1:100)$ and $\text{Zr}_4\text{MAPTMS}(1:100)$, whose calculations are reported in Table 2. The TGA were collected with a ramp of $10^\circ\text{C}/\text{min}$ from room temperature (25°C) up to 900°C , under air flow.

Catalytic tests

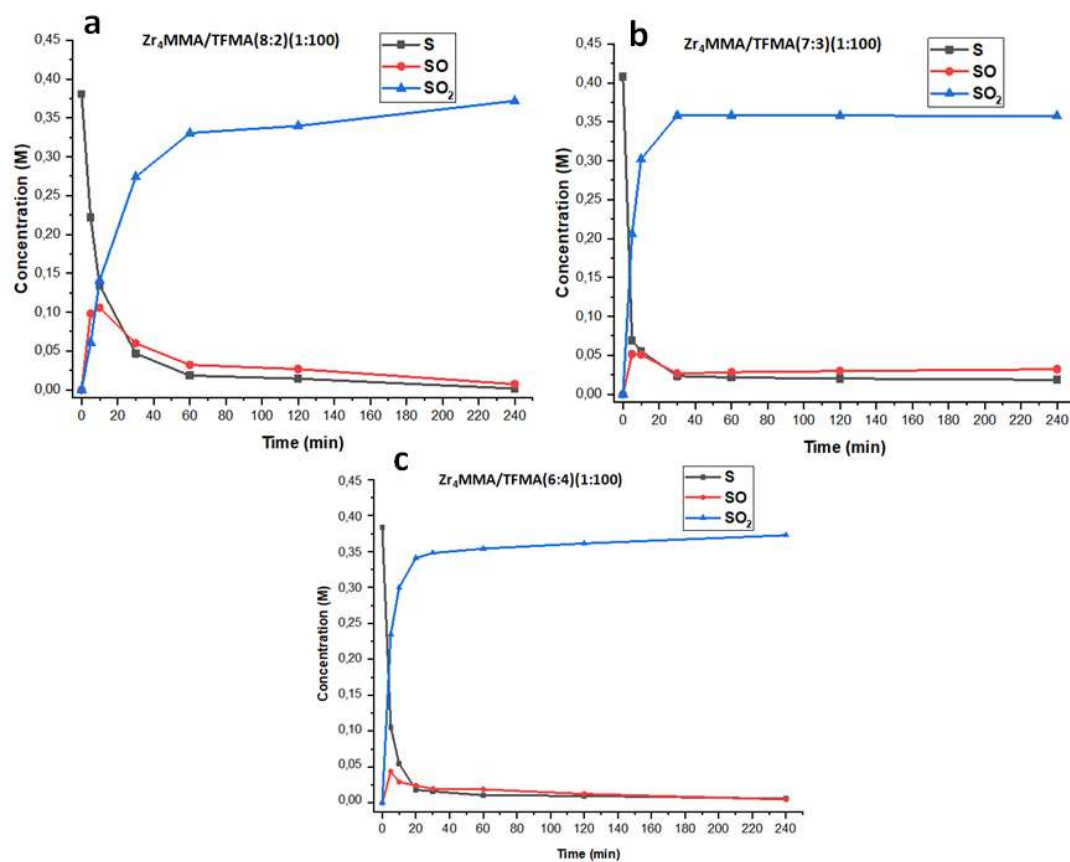


Figure S6. Catalytic tests on the following hybrids: a) Zr₄MMA/TFMA(8:2)(1:100), b) Zr₄MMA/TFMA(7:3)(1:100), c) Zr₄MMA/TFMA(6:4)(1:100). The tests were performed under diluted conditions: 0.40 M sulphide, 0.81 M H₂O₂ in 2.2 mL of ACN.

X-ray absorption spectroscopy

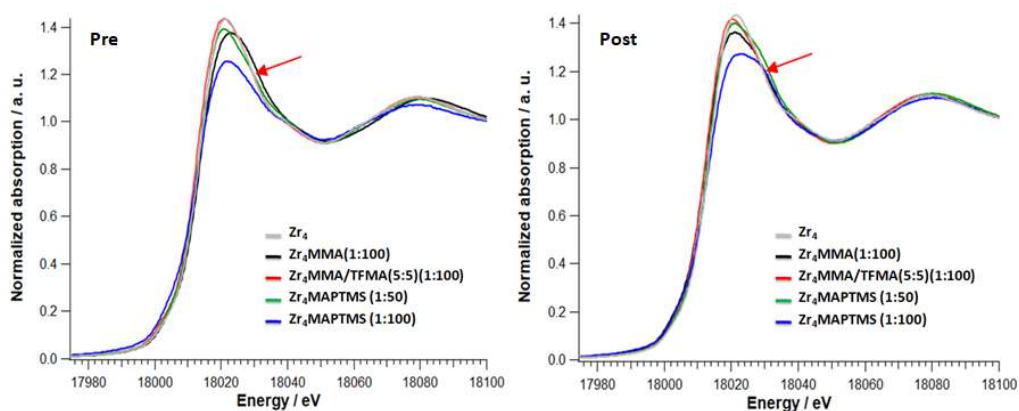


Figure S7. Zr K-edge XANES spectra of samples before (left) and after (right) catalysis. The arrows indicate the isosbestic point.

Recycles tests

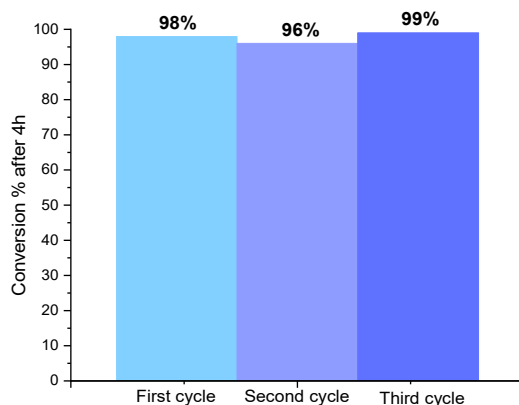


Figure S8. Recycles tests on the best synthesised heterogeneous catalysts $Zr_3MMA/TFMA(5:5)(1:100)$: after the first cycle a conversion of 98% can be observed and a conversion of 96% and 99% after the second and the third catalytic recycles can be pointed out, highlighting the high stability of the samples even after tree catalytic cycles. The tests were performed for 4 hours under the same diluted conditions of 0.40 M sulphide, 0.81 M H_2O_2 in 2.2 mL of ACN, by recycling the catalyst.

SEM-EDX measurements

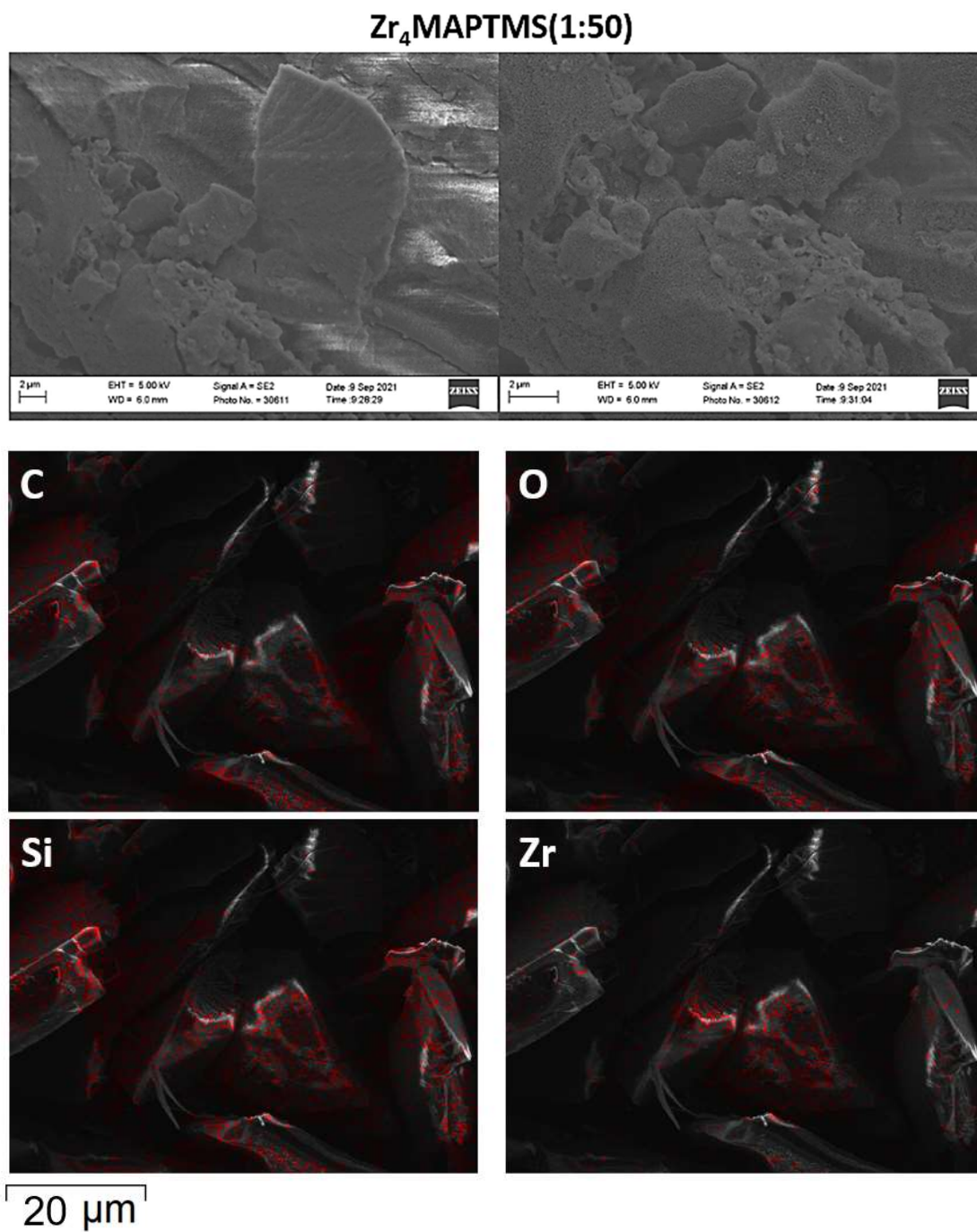


Figure S9: SEM-EDX measurements of Zr₄MAPTMS(1:50).

$\text{Zr}_4\text{MAPTMS}(1:100)$

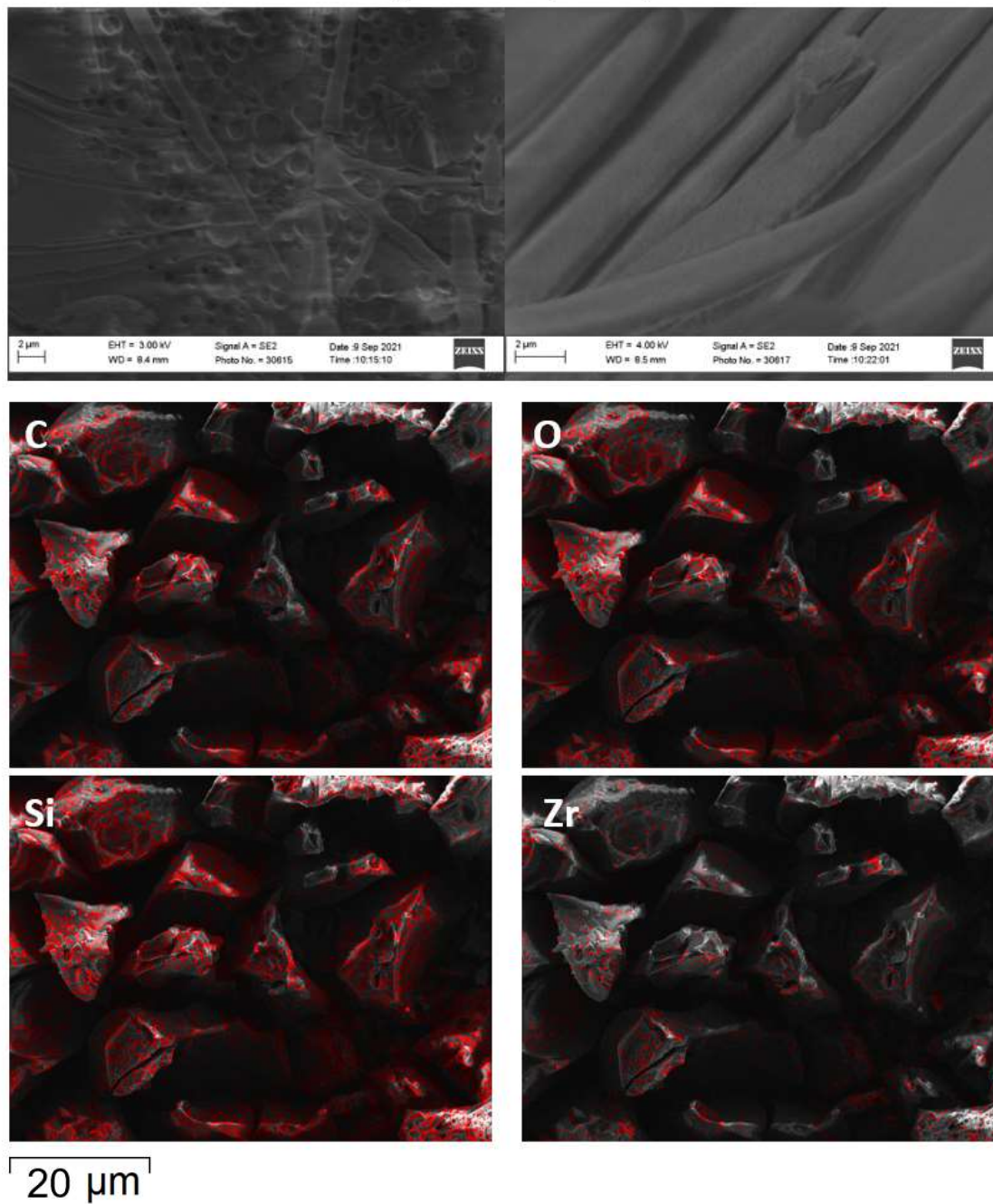
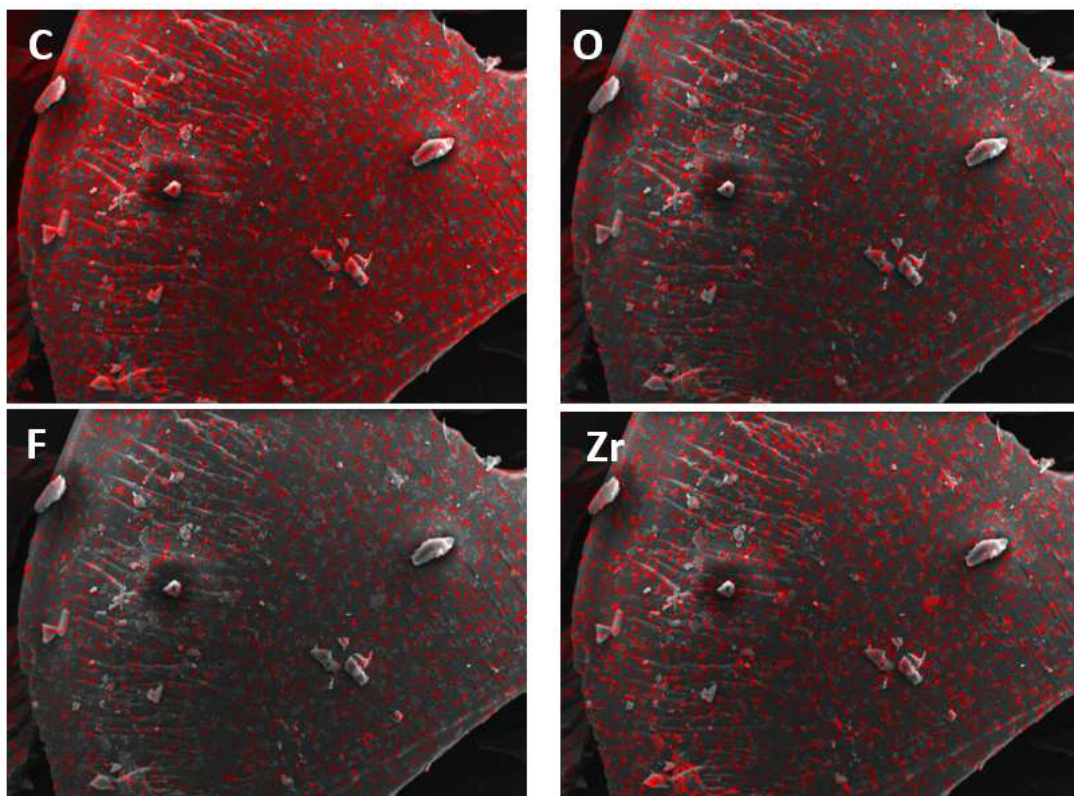
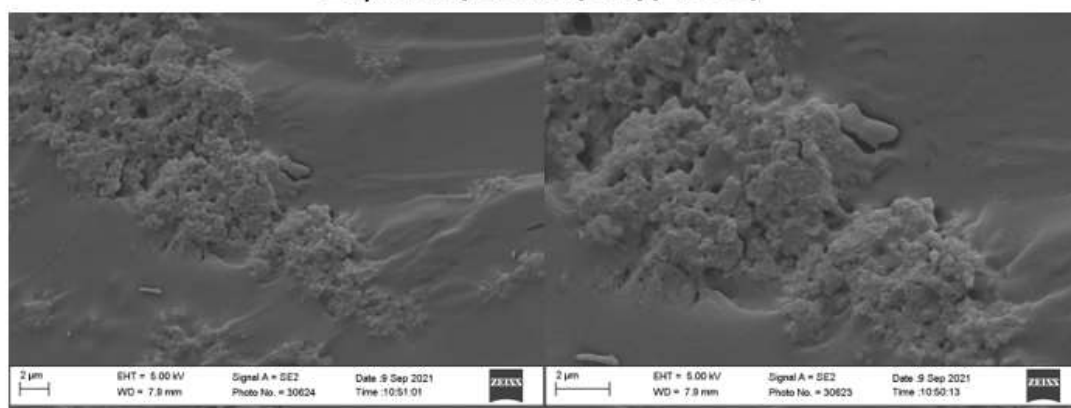


Figure S10: SEM-EDX measurements of $\text{Zr}_4\text{MAPTMS}(1:100)$.

Zr₄MMA/TFMA(9:1)(1:100)



20 μm

Figure S11: SEM-EDX measurements of Zr₄MMA/TFMA(9:1)(1:100).

Zr₄MMA/TFMA(5:5)(1:100)_pre catalysis

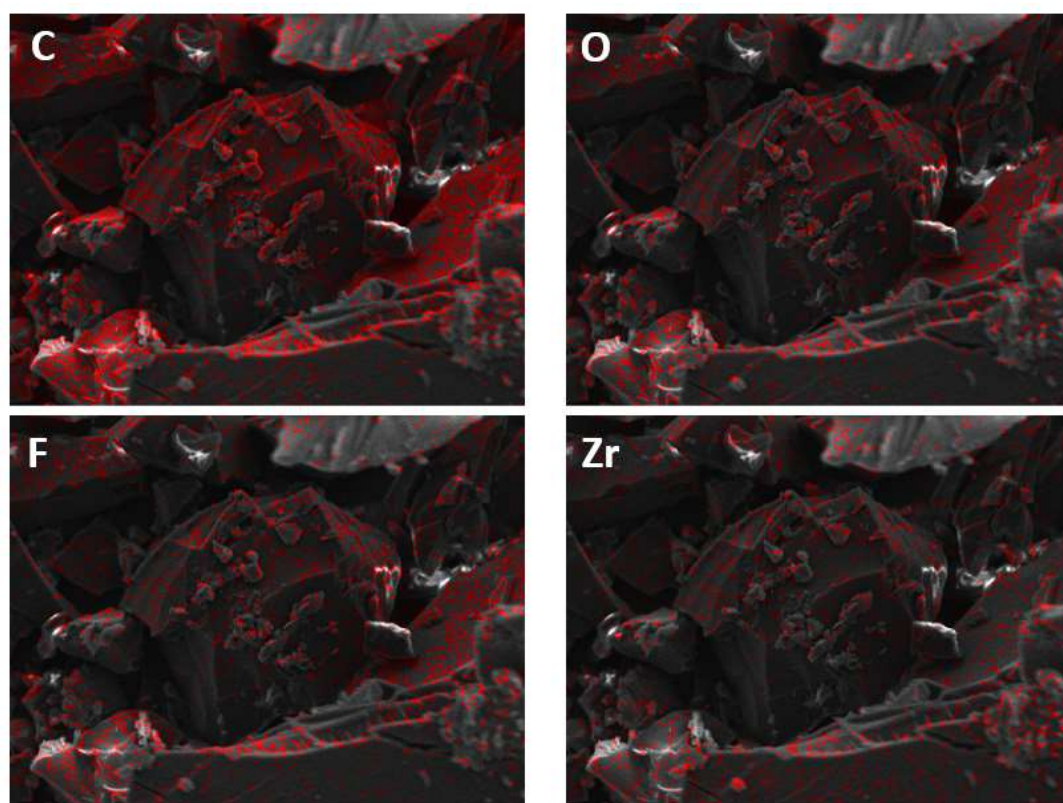
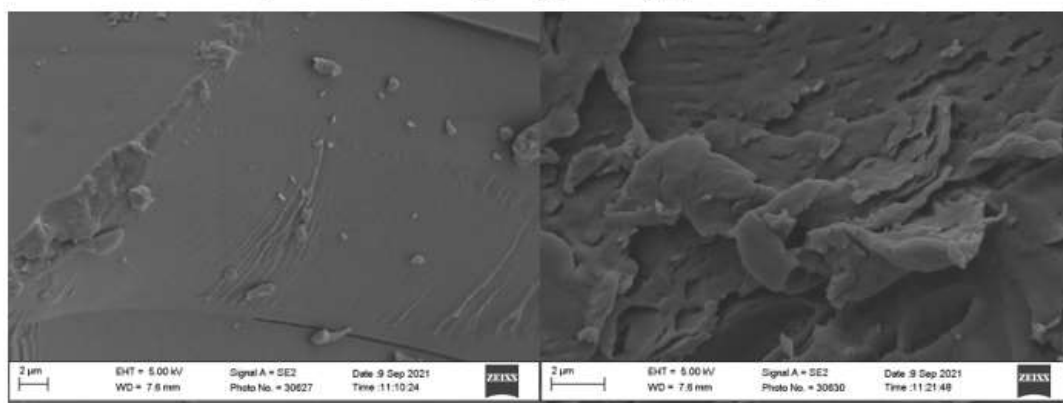


Figure S12: SEM-EDX measurements of Zr₄MMA/TFMA(5:5)(1:100) before the catalysis.

Zr₄MMA/TFMA(5:5)(1:100)_post catalysis

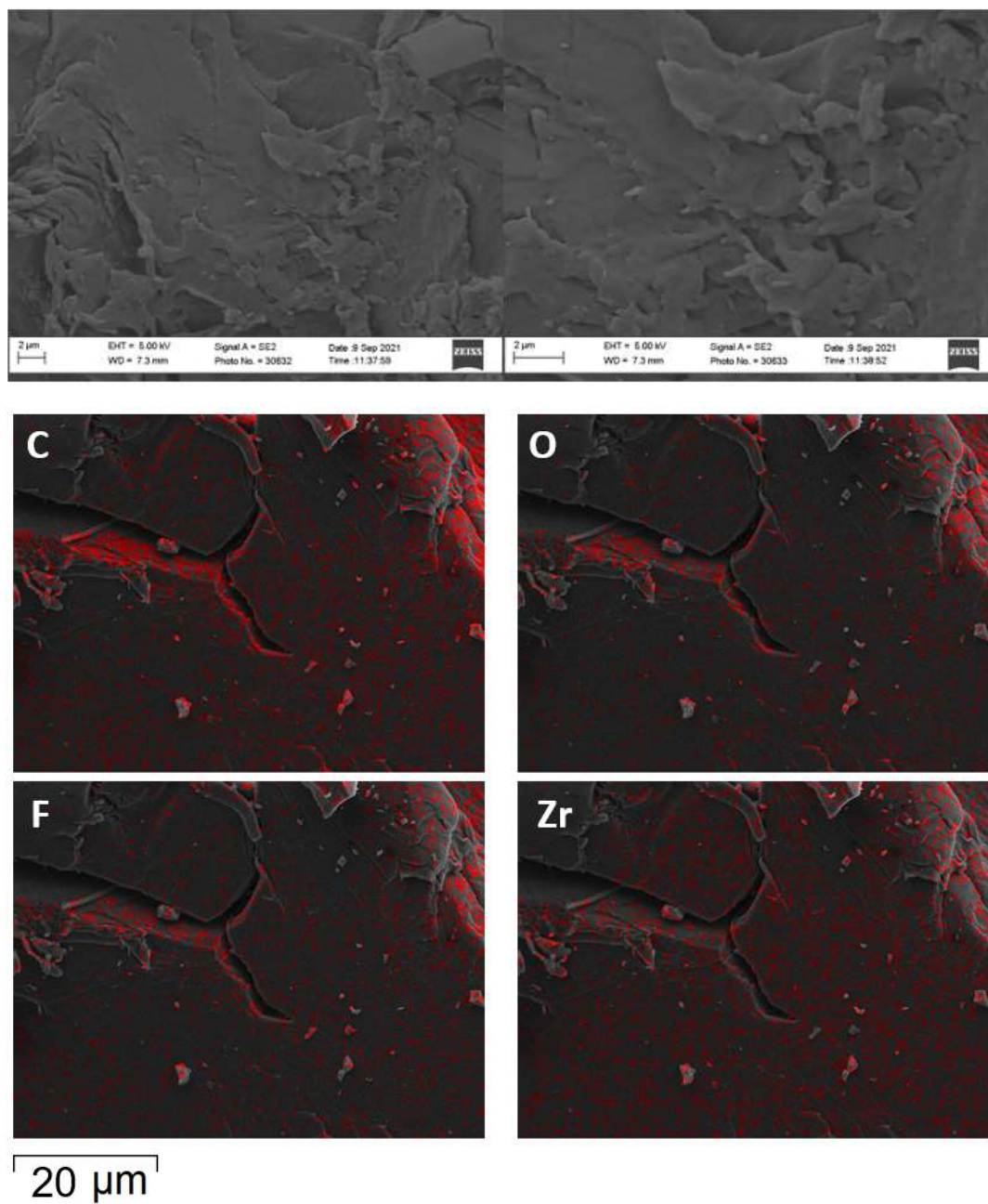


Figure S13: SEM-EDX measurements of Zr₄MMA/TFMA(5:5)(1:100) after the catalysis.

	Zr (% wt.)
Zr4MMA/TFMA(5:5)(1:100)_pre	1,97 ± 0,21
Zr4MMA/TFMA(5:5)(1:100)_post	1,16 ± 0,62

Table S1: Semi-quantitative data from EDX measurements regarding the Zr-content in the Zr₄MMA/TFMA(5:5)(1:100) before and after the catalytic oxidation.