

## Supporting Information

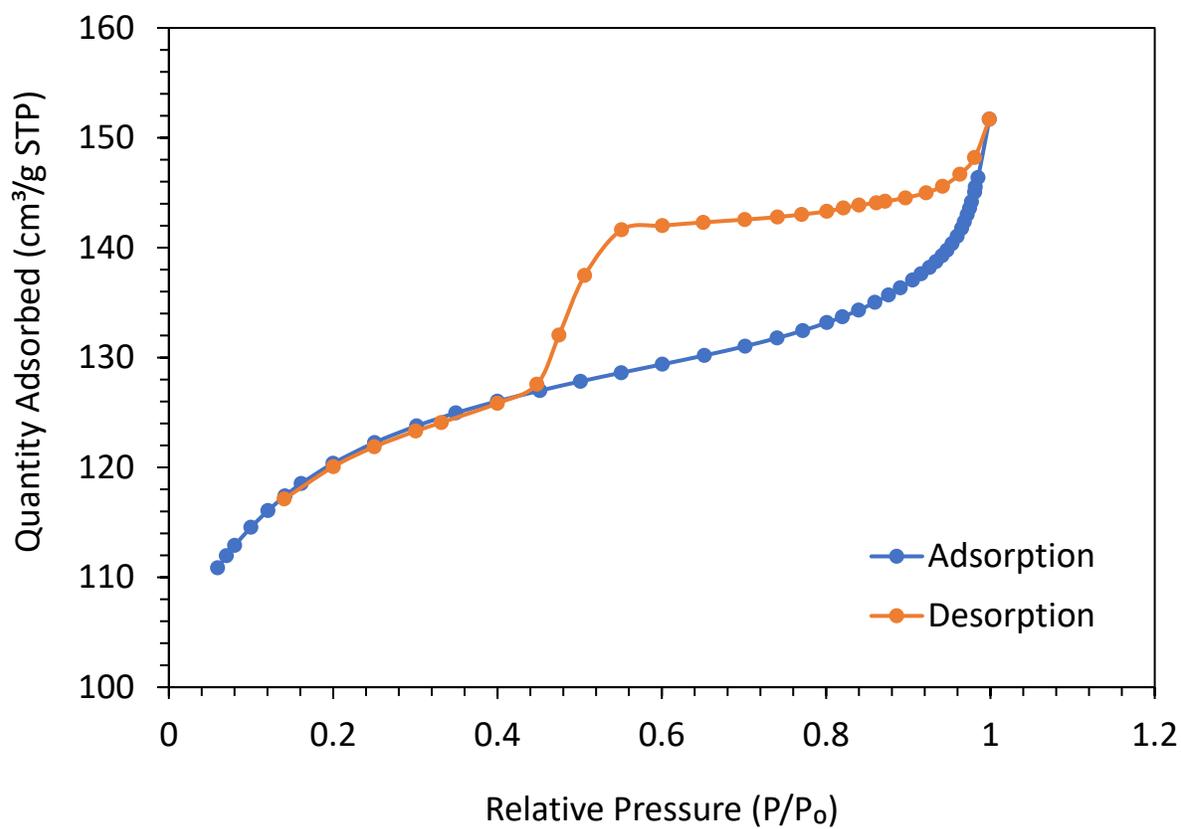


Fig S1: Nitrogen sorption analysis of as-synthesized 2wt.% Fe-ZSM-5.

### MDA reactivity evaluation of As-synthesized Fe-ZSM-5

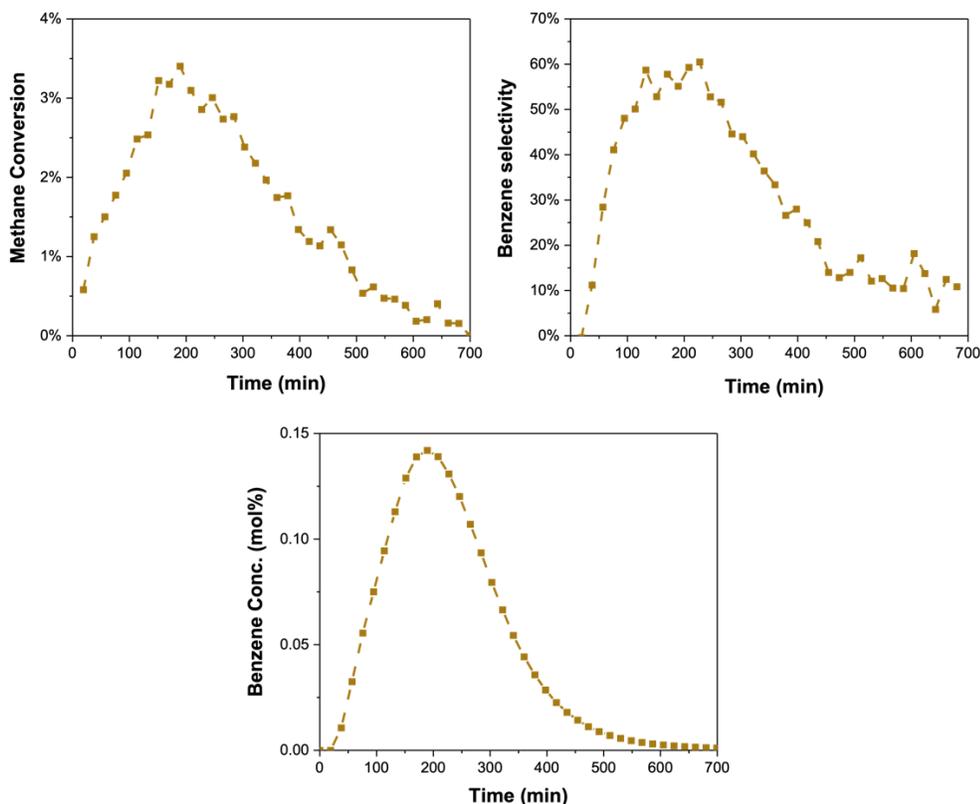


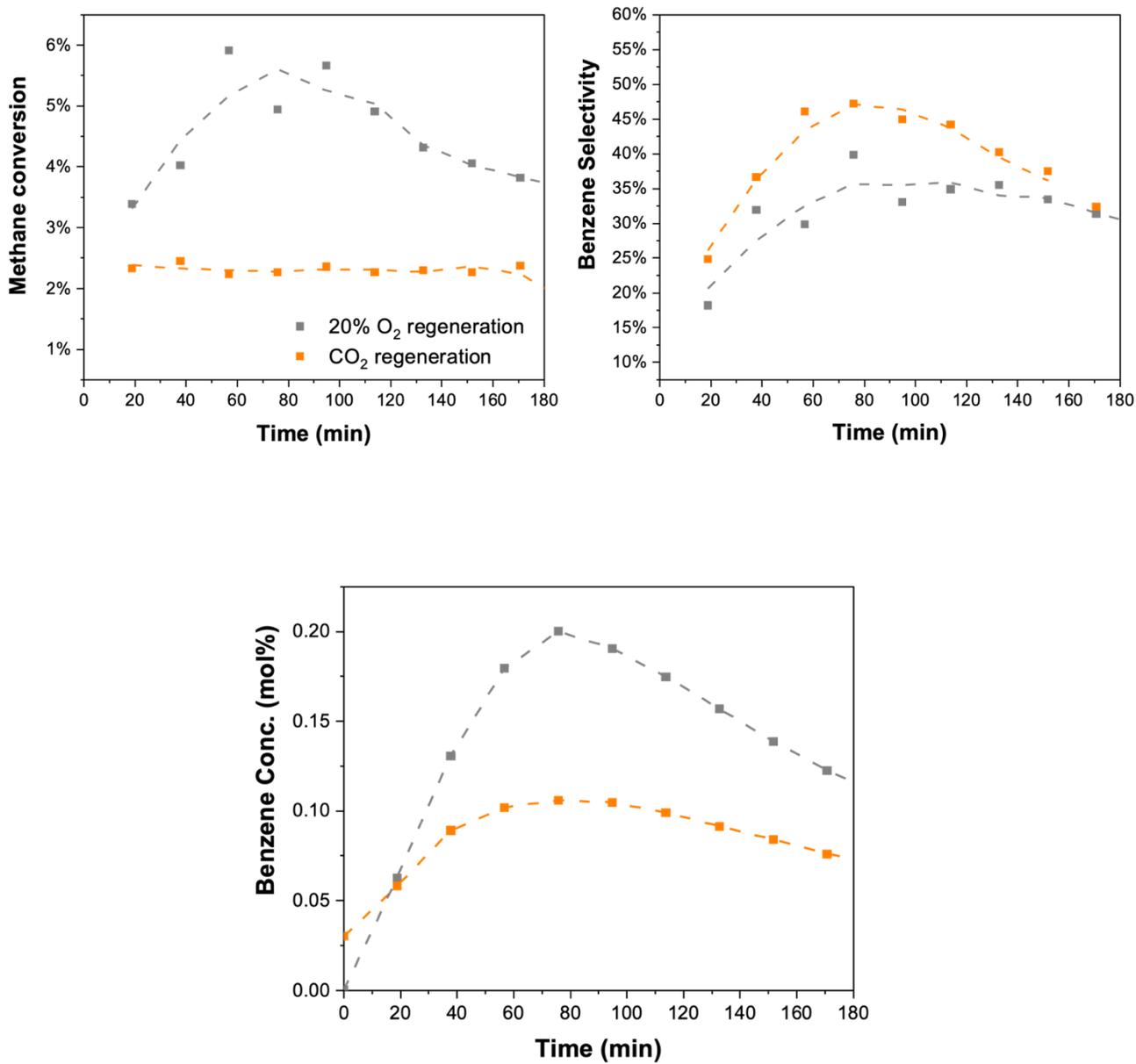
Figure S2 MDA reactivity evaluation of as-synthesized Fe-ZSM-5: methane conversion (top left), benzene selectivity (top right), and benzene concentration (bottom) versus time-on-stream. Reaction conditions: 700C with 50% CH<sub>4</sub> in Ar, at WHSV of 3744 cc/g/hr.

Figure S2 shows the MDA reactivity performance of the as-synthesized Fe-ZSM-5 sample in terms of methane conversion, benzene selectivity, and concentration.

Deng et al. investigated the impact of Fe speciation on MDA reactivity performance by analyzing samples with controlled iron speciation synthesized via different pathways (wet impregnation, ion exchange, and isomorphous substitution)<sup>1</sup>. The study revealed that aggregated iron oxide clusters were beneficial for accelerating the activation period since aggregated iron oxide clusters are more easily carburized than

atomically dispersed iron in the framework, which requires transformation into aggregated iron oxide before being reduced and carburized into the active phase.

Consistent with this finding, samples regenerated at higher temperatures (510°C and 700°C; see Figure 5, main manuscript) show shorter induction time and higher methane conversion than that of the as-synthesized sample (Figure S1), attributed to the greater amount of Fe clusters. The sample regenerated at 425°C shows lower methane conversion than the as-synthesized sample, attributed to the presence of hard coke on the metal site which is not oxidized at this temperature, as discussed in detail in the manuscript. Regeneration treatment was found to have a negligible impact on benzene selectivity, consistent with the previous study.



**Figure S3 Comparison of MDA reactivity performance (conversion, benzene selectivity and benzene concentration) of a spent 2wt.%Fe-ZSM-5 catalyst regenerated using CO<sub>2</sub> (orange curves) and 20% O<sub>2</sub> (in Ar; grey curves), respectively**

Impact of the regeneration process was studied by comparing the MDA reactivity of a spent Fe-ZSM-5 catalyst regenerated using CO<sub>2</sub> and 20% O<sub>2</sub> in Ar. The spent catalyst had been deactivated in MDA over a 200-minute period, and regenerated by exposing the spent sample to 25 SCCM of CO<sub>2</sub> or 20% O<sub>2</sub> in Ar at 800°C for 30 minutes. The regenerated catalysts were then tested for MDA reaction. The catalyst regenerated with CO<sub>2</sub> showed a lower methane conversion in comparison to the oxygen-regenerated catalyst, while maintaining similar benzene selectivity. The lower methane conversion is attributed to the incomplete elimination of coke specifically at the metal site. In contrast, the comparable benzene selectivity indicates efficient removal of coke at the Bronsted acid sites (BAS) through CO<sub>2</sub> oxidation. This suggests the formation of an H-rich, soft coke on the Bronsted acid sites which can be oxidized using the milder oxidant CO<sub>2</sub>.

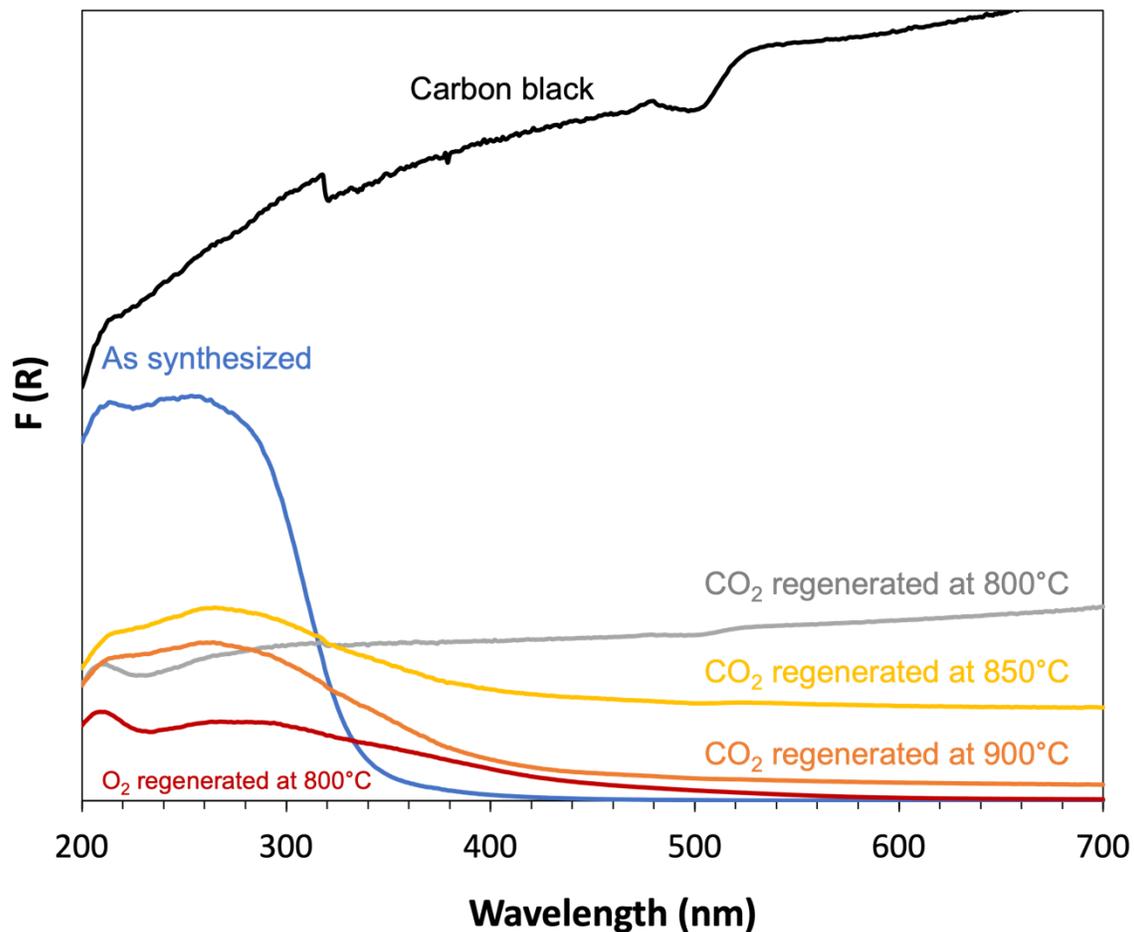


Figure S4 UV-vis analysis of as-synthesized Fe-ZSM-5 catalyst, O<sub>2</sub> regenerated and CO<sub>2</sub> regenerated catalyst, and carbon black (as reference).

UV-Vis spectroscopic analysis was conducted on the as-synthesized Fe-ZSM-5 catalyst, O<sub>2</sub>-regenerated (regenerated at 800°C for 30 min), and CO<sub>2</sub>-regenerated samples to assess the effect of regenerative treatments on metal distribution and efficiency of coke removal during regeneration (Figure S4). For comparison, the UV-Vis spectrum of carbon black is added as well, which shows a broad peak spanning wavelengths from 200 to 700

nm. UV-Vis analysis of the spent, CO<sub>2</sub>-regenerated sample at 800°C reveals a similar broad band, indicating the presence of carbonaceous species, i.e. incomplete coke removal during CO<sub>2</sub> regeneration at 800°C. CO<sub>2</sub> regeneration at higher temperatures of 850°C and 900°C results in increasingly efficient coke removal, as evidenced by the diminishing intensity of this broad carbon band. In contrast, the O<sub>2</sub>-regenerated sample showed complete removal of this broad band, indicating thorough and efficient removal of coke during regeneration.

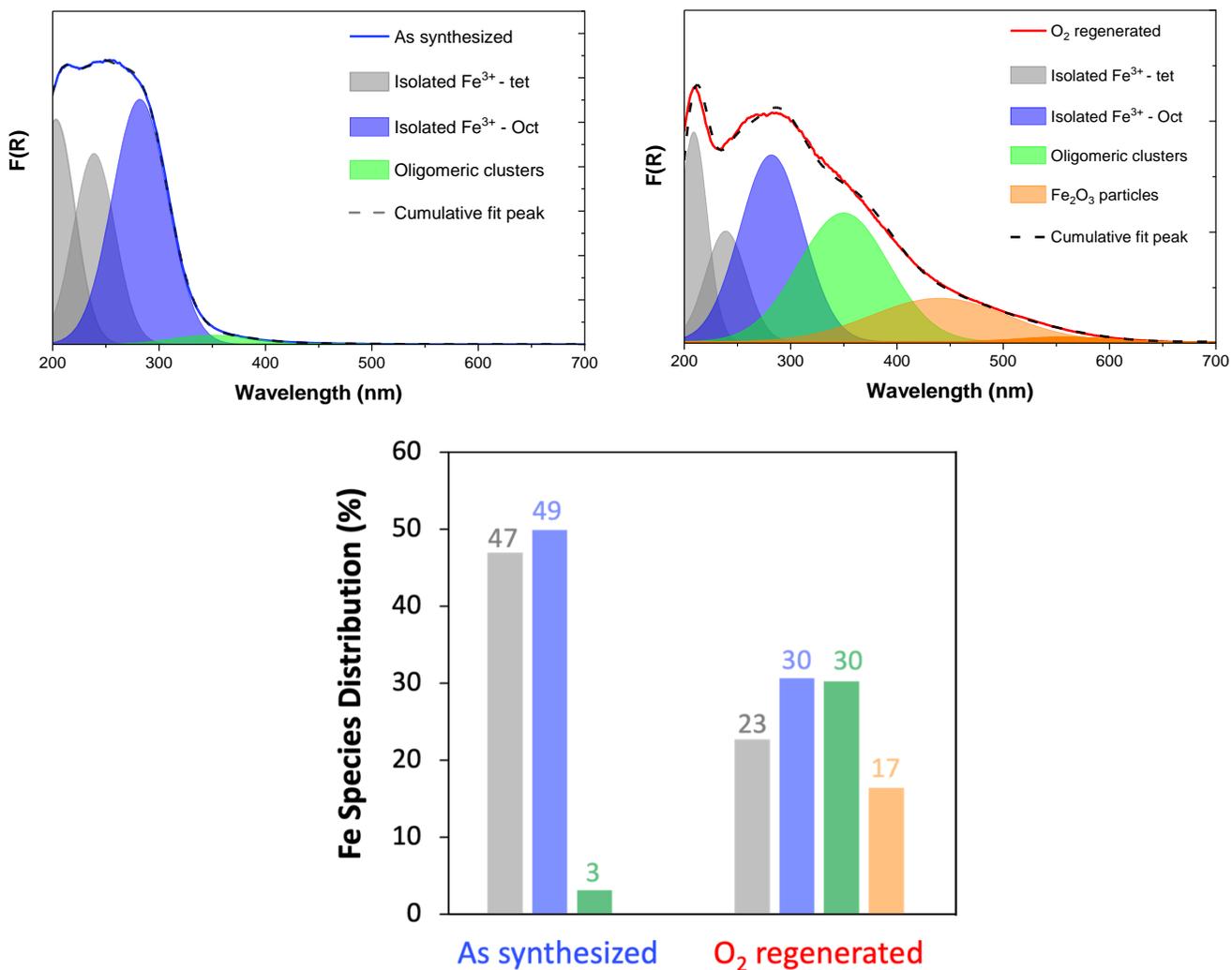


Figure S5 Deconvolution analysis of UV-vis spectra of as-synthesized Fe-ZSM-5 catalyst and O<sub>2</sub> regenerated catalyst to determine Fe species distribution.

Figure S5 shows the deconvolution analysis of the UV-Vis spectra of the as-synthesized and O<sub>2</sub>-regenerated samples to determine the distribution of Fe species. Following regeneration, the UV-Vis spectrum shifts towards longer wavelengths,

indicating Fe aggregation. The deconvolution analysis shows that the O<sub>2</sub>-regenerated sample has a lower amount of isolated Fe<sup>3+</sup> species (gray and blue bars), while the amount of Fe<sub>2</sub>O<sub>3</sub> clusters and nanoparticles (green and orange bars) is higher, confirming the agglomeration. This suggests that Fe bleeds out from the zeolite framework during exothermic O<sub>2</sub> regeneration and subsequently agglomerates into Fe oxide clusters and nanoparticles.

This aligns with the observation of a lower amount of Brønsted acid sites (BAS) in the O<sub>2</sub>-regenerated samples compared to the as-synthesized sample (seen from pyridine FTIR analysis in Figure 6 of the manuscript). This suggests that Fe bleed-out leads to a decrease in BAS, which are active sites for the MDA reaction. These findings indicate damage to the catalyst during O<sub>2</sub> regeneration, consistent with previous reports.