

Aerobic Epoxidation of Olefins Catalyzed by the Cobalt-Based Metal Organic Framework STA-12(Co)

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Abstract

The Co-based metal organic framework STA-12(Co) exhibited high catalytic activity in the epoxidation of aromatic olefins by molecular oxygen in DMF. High dispersion and simultaneously a high loading of Co allowed using significantly smaller absolute catalyst amounts compared to Co-modified zeolites often employed for this reaction. Various additives influenced the heterogeneous catalytic reaction which was further studied *in situ* by EPR and EXAFS.

Metal organic frameworks (MOFs) are increasingly used as heterogeneous catalysts but they often exhibit only moderate activity compared to established catalysts [1]. We assessed the potential of STA-12(Co) as a catalyst in the aerobic epoxidation of styrene, (*E*)- and (*Z*)-stilbene in DMF. The MOF features chains of octahedral Co with one coordination site available for catalysis. The micropores in the MOF are relatively large being in the range of 1 nm (Figure 1). The catalyst

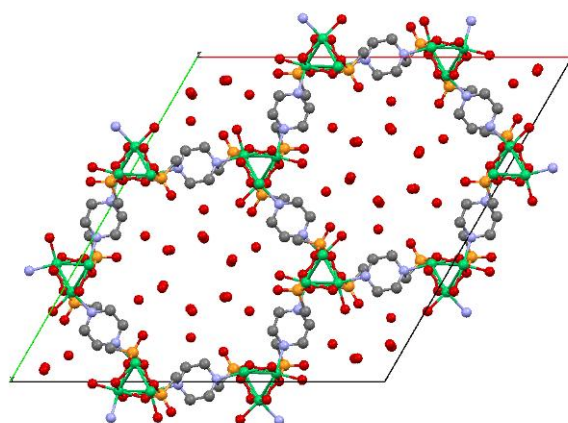


Figure 1. View along the c-axis of the unit cell of the analogous STA-12(Ni) [2]. The micropores are filled with water (red spheres).

showed higher activity and selectivity compared to zeolite catalysts frequently described in the literature. Due to the higher metal loading two orders of magnitude lower absolute catalyst amounts were sufficient to achieve similar conversions.

Leaching of Co was low and the reaction proceeded mainly heterogeneously. Only minor deactivation of the catalyst was observed. Consistently, EXAFS, XRD and SEM data taken before and after the reaction suggested no degradation of the MOF

catalyst. The substrate conversion was accompanied by the formation of peroxides and overstoichiometric amounts of DMF oxidation products indicating the role of the solvent to be that of a sacrificial reductant [3]. Amines formed from DMF could deactivate the catalyst. This underlines the importance of a free Co coordination site.

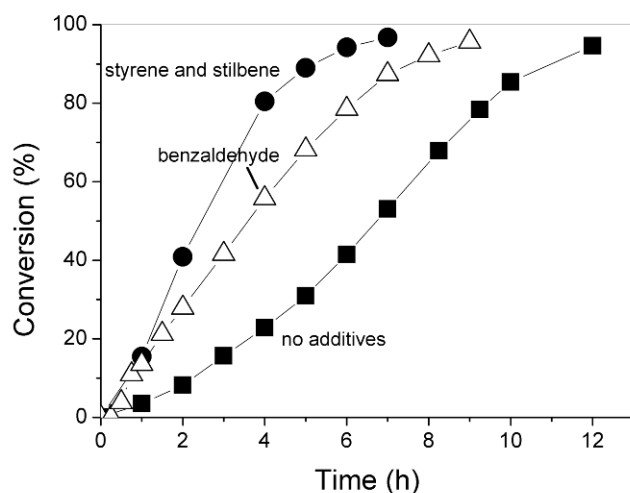


Figure 2. Effect of styrene (2 mmol) or benzaldehyde (0.2 mmol) addition on the (*E*)-stilbene conversion. Reaction conditions: 2.0 mmol (*E*)-stilbene, 100 mg biphenyl, 30 mL DMF, 50 mL min⁻¹ O₂, 2.0 mg STA-12(Co), 100 °C.

The catalytic epoxidation using the MOF exhibited an induction phase which was shorter for styrene than for stilbene isomers. Consequently, epoxidation of stilbene was enhanced by co-epoxidizing styrene, although the substrate-to-catalyst ratio was twice as high. This could be traced back to the activating effect of benzaldehyde being the major byproduct in styrene epoxidation (Figure 2).

In accordance with the literature the reaction was suppressed by a radical scavenger. However, radical initiators had no effect on the reaction. EPR measured under reaction conditions could not identify free organic radicals. Based on parameter studies and further catalytic tests a preliminary, simplified reaction mechanism was proposed including oxygen-transfer to the olefin after activation at the Co centers and subsequent regeneration of the active site by solvent oxidation.

In summary, the Co-based MOF STA-12(Co) was found to be a highly active and selective catalyst for the heterogeneous epoxidation of olefins by molecular oxygen using DMF as a solvent.

References

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