

Mechanisms of hydrogen peroxide activation over Ti(IV) and Nb(V) single-site catalysts: Insights from model studies on polyoxometalates

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Ti(IV) and Nb(V) single site catalysts have attracted much recent attention due to their ability to catalyze selectively oxidations with the green oxidant hydrogen peroxide. However, their catalytic performance differs significantly in terms of activity, chemo- and regioselectivity [1-3]. In this lecture, we present our recent works directed toward understanding of the mechanisms of H₂O₂ activation over Ti(IV) and Nb(V). Ti- and Nb-substituted tungstates of the Lindqvist structure [M(L)W₅O₁₈]ⁿ⁻ (MW₅, M = Ti and Nb) have been employed as tractable molecular models to gain insights into the structure and reactivity of Ti and Nb peroxo species using UV-vis, FT-IR, Raman, ⁹³Nb, ¹⁷O and ¹⁸³W NMR spectroscopic techniques and DFT calculations [4,5]. For both metals, peroxo form 'HMO₂' is more stable than hydroperoxo form 'MOOH', but 'MOOH' is more reactive than 'HMO₂' toward epoxidation of alkenes. The superior heterolytic pathway selectivity observed for Nb catalysts can be explained by a combination of two main factors: 1) a lower energy barrier for the oxygen atom transfer from 'NbOOH' to the C=C bond leading to epoxide and 2) a lower activity of Nb in homolytic H₂O₂ decomposition. The size of M and the flexibility of its coordination environment affect the oxygen transfer mechanism. For a rigid Ti(IV) environment, β-oxygen transfer from Ti(η¹-OOH) is favored over α-oxygen transfer. The larger size of Nb(V) enables formation of a 7-coordinated Nb(η²-OOH) species for which α-oxygen transfer is energetically preferable over β-oxygen transfer. The different oxygen transfer mechanisms may account for different regioselectivities observed in heterogeneous Ti- and Nb-catalyzed epoxidations.

References:

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