

Mechanism of Dimethyl Sulfide Oxidation by Hydrogen Peroxide with Niobium Oxyhydroxide Heterogeneous Catalyst

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INTRODUCTION

Experimental studies have shown that niobium oxyhydroxide (NbO₂OH) acts as support and active phase in various reactions to form highly oxidizing groups on its surface when in contact with H₂O₂.¹ However, reactions on surfaces are generally poorly understood by the difficulty to characterize unequivocally the structure of the adsorbed species and transition states (TS). In this respect, the computational chemistry methods have much to contribute. Thus, in this theoretical study, we have investigated the dimethyl sulfide (DMS) oxidation mechanism by H₂O₂ on the surface of NbO₂OH in order to better understand this catalytic process, since there is no computational study reported in the literature up to date.

METHODS

Equilibrium geometries and harmonic frequencies calculations have been obtained using the X3LYP functional with the SBKJC+P(d) basis set and ECP. More reliable single point energy calculations and solvation free energy using the SMD solvation model have been done at X3LYP/SVP+diff level. The potential of mean force (W(r)) has been calculated according to eq. (1), in order to predict relative rates among different reaction pathways.

$$W(r) = E_g + \Delta G_{\text{solv}} \quad (1)$$

RESULTS AND DISCUSSION

Fig. 1 shows that the catalytic route occurs in two steps: In the first one, the Nb atom of the catalyst surface is attacked nucleophilically by H₂O₂, via TS2a heptacoordinated, leading to the formation of hydroperoxo groups (HO–O–Nb). In the second step, these hydroperoxo groups formed on the surface promote the DMS oxidation (Fig. 2). The oxidation mechanism is similar to a nucleophilic substitution process on the oxygen of the peroxide group, with niobium acting as a Lewis acid and the oxygen of the Nb–O–Nb group as a

Brønsted base in the proton capture. At the end of this heterolytic process, the catalyst is regenerated and a new catalytic cycle starts.

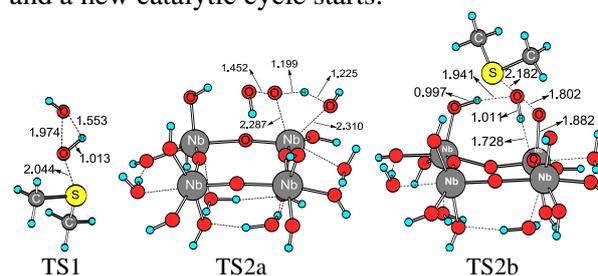


Figure 1. Uncatalyzed (TS1) and catalyzed (TS2a and TS2b) reactions for DMS oxidation by H₂O₂.

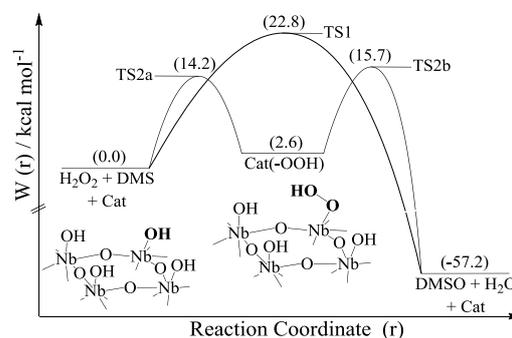


Figure 2. W(r) profile for the DMS oxidation by H₂O₂ catalyzed by NbO₂OH.

CONCLUSIONS

We have found the reaction pathway able to explain the catalytic effect of NbO₂OH on DMS oxidation by H₂O₂. There is formation of a hydroperoxo species on the surface, which is able to act as Lewis base and Brønsted acid, providing a decrease of the activation barrier by -7.1 kcal mol⁻¹ in relation to the free hydrogen peroxide reaction.

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¹ L. C. A. de Oliveira, et al. Appl. Catal. B: Envir., 147, 43, (2014).