Catalytic Role of Active Sites on Mo-Doped MCM-41 Zeolite for the Aerobic Oxidation of 5-Hydroxymethylfurfural to 2,5-Diformylfuran

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Abstract: On the pores surface of MCM-41, two kinds of $–(SiO)_2Mo(O)_2$ ([Mo-4]) and $–(SiO)_3Mo(OH)(O)$ ([Mo-5]) active sites have been theoretically designed. The aerobic oxidation of 5-hydroxymethylfurfural (HMF) to 2,5-diformylfuran (DFF) includes two main reaction steps, the O–H and C–H bond cleavages of HMF, in which the crucial reaction step is associated with the C–H bond cleavage of $–CH_2–$ group for the first HMF. The –Mo=O group is responsible for the O–H bond activation, and the –OH group is in charge of the C–H bond activation. The [Mo-5] active site behaves the better catalytic reactivity than the [Mo-4] active site.

Keywords: 5-Hydroxymethylfurfural; 2,5-Diformylfuran; MCM-41 Silica; Mo Dopant; QMERA; DMol^3

1. Introduction

Currently, 2,5-diformylfuran (DFF) can be synthesized via the partial oxidation of the primary hydroxyl group without attacking the more reactive α,β-unsaturated aldehyde group from pure HMF. In this sense, especially using clean molecular oxygen as a oxidant, various catalytic systems have been developed. Nevertheless, because of the dominant production of humin and other side-products, all attempts to conduct this reaction in a one-pot process have suffered from low activity or difficulties in separating the product from the reaction solutions. In the light of these premises, the development of highly reactive and reusable heterogeneous catalytic system for the direct DFF production from carbohydrates, including the selective transformation of HMF to DFF, remains a significant challenge to date.

Taking into account the reusability of zeolite and the high catalytic reactivity of Mo active sites, one can speculate that the Mo-containing zeolite should possess good catalytic performance for the DFF synthesis from carbohydrates. Despite the present research situation and existing issues, how the Mo-doping zeolite catalyst behaves the catalytic performance holds elusive.

2. Theoretical

The Mo-doped MCM-41 pore model (Mo-MCM-41) was first generated by replacing a Si atom in $–(SiO)_3Si(OH)$ and $–(SiO)_2Si(OH)_2$ moieties by a Mo atom. Next, to maintain the +6 valence state of Mo atom, in $–(SiO)_2Mo(OH)_2$ moiety, the hydrogen atoms of hydroxyls were deleted, resulting in $–(SiO)_2Mo(O)_2$ active site; In the meantime, in $–(SiO)_3Mo(OH)$ moiety, the oxygen atom may be added to molybdenum atom, leading to $–(SiO)_3Mo(OH)(O)$ active site. Therefore, there are two kinds of Mo active sites on the pores surface, $–(SiO)_2Mo(O)_2$ and $–(SiO)_3Mo(OH)(O)$.

For the geometrical optimization, the forces imposed on each The QMERA module implemented in Materials Studio 7.0 software package was used to perform the hybrid quantum mechanics (QM) and molecular mechanics (MM) calculations, which combines QM/MM forcefield calculations using the ChemShell environment. This QMERA module employs DMol^3 for the description of the QM region and the GULP force field engine for the MM region. For the QM region, the generalized gradient approximation with the Becke exchange plus Perdew correlation functional (GGA-BP) was chosen together with the doubled numerical basis set plus polarization basis sets (DNP), using the Dmol^3 program.

3. Results and discussion

Over both [Mo-4] and [Mo-5] active sites, the whole reaction of 2HMF + $O_2 \rightarrow$ 2DFF + $2H_2O$ is concerned to three successive reaction stages, the oxidation of the first HMF to DFF through consuming the oxygen source of active site, the import of O_2 to form the peroxide, and the oxidation of the second HMF to DFF through expending the oxygen source of O_2. Furthermore, the oxidation of each HMF contains two main reaction steps, the O–H and C–H bond cleavages of HMF, in which the crucial reaction step is associated with the C–H bond cleavage of $–CH_2–$ group for the first HMF.

For the aerobic oxidation of HMF to DFF, the [Mo-5] active site exhibits the best catalytic reactivity among these three kinds of active sites ([Mo-4], [Mo-5], and Mo-HPA). By analysing the activation strain of the C–H bond cleavage of $–CH_2–$ group in HMF moiety, the lowering activation energy from over [Mo-4] to over [Mo-5] originates mainly from the lowering activation strain of catalyst $\Delta E^{\neq}_{\text{strain}}$[Cat], which interrelates positively with the corresponding HOMO-LUMO gap.

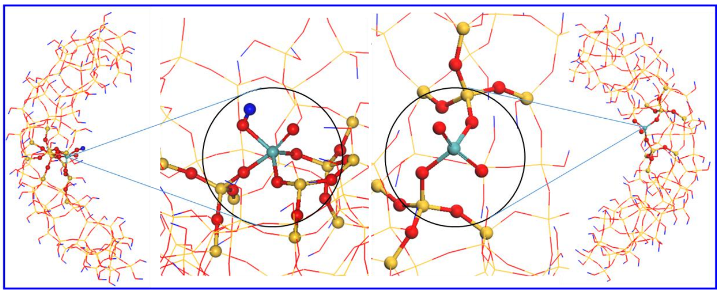

Figure 1. Mo-MCM-41 QM/MM model, where the two kinds of Mo active sites, the five-coordinated $–(SiO)_3Mo(OH)(O)$ (422 atoms) and the four-coordinated $–(SiO)_2Mo(O)_2$ (413 atoms), are shown. Atoms shown in yellow, red, blue and ultramarine represent Si, O, H and Mo atoms, respectively. Spherical atoms are QM atoms, others are MM atoms.

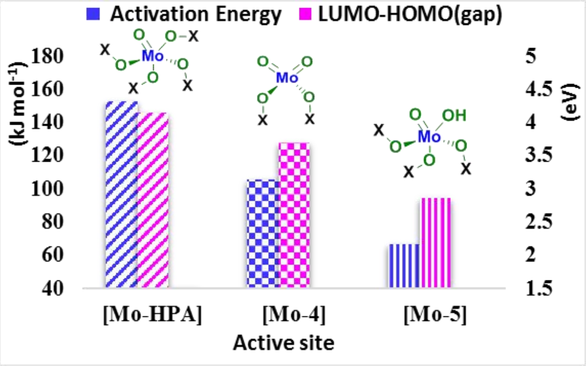

Figure 2. The HOMO-LUMO gap and the corresponding activation energies for the [Mo-HPA], [Mo-4] and [Mo-5] are shown.

4. Conclusions

Over [Mo-4], [Mo-5], and [Mo-HPA] active sites, the –Mo=O group is responsible for the O–H bond activation in HMF, and the –OH group answers for the C–H bond activation in HMF. The [Mo-5] active site exhibits the best catalytic reactivity, because it involves both –Mo=O and –OH groups. Both –Mo=O and –OH groups can synergistically activate both O–H and C–H bonds in HMF. These new insights offer strategies for the design of novel catalyst to activate the C–H and O–H bonds at low temperature with good catalytic performance, especially for some typical platform molecules of biomass.

References

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