

FIRST-PRINCIPLES KINETIC MONTE CARLO STUDY OF BIOMASS CONVERSION OVER SUPPORTED METAL OXIDE CATALYST

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Abstract

Ruthenium supported on titania (Ru/TiO₂) is a promising catalyst for hydrodeoxygenation (HDO) of bio-oil to fuels and chemicals. We performed grid-based first-principles kinetic Monte Carlo (kMC) simulations to explain the reduction and hydroxylation behavior of metal oxide and supported metal oxide catalysts under a H₂/H₂O atmosphere and qualitatively reproduce experimental results from XPS and inertial mass measurement. Our kMC results also explain the experimentally observed effect of co-feeding water on the activity and selectivity when hydrotreating phenolic compounds. In general, our multiscale kinetic model discriminates metal, oxide and interfacial activities, and assigns a dominant catalytic role to each component on supported metal oxide catalysts under different reaction and surface conditions.

Keywords

Biofuels (Energy), Catalysis and Hydrocarbons, Multiscale Modeling

Introduction

Catalytic upgrade of bio-oil to fuels and chemicals requires the selective reduction of its 10-40 wt% oxygen content. Ruthenium supported on titania (Ru/TiO₂) has evolved as one of the better performing catalysts for such hydrodeoxygenation (HDO) processes. Commonly proposed HDO mechanisms on oxide containing materials invoke oxygen vacancy sites as catalytically active sites, but the mechanism of their formation and detailed description of active sites at the interface of Ru/TiO₂ is still lacking. Omotoso *et al.* (2017) found a positive linear relation between toluene formation rate from *m*-cresol and Ru perimeter length for Ru/TiO₂ catalyst supporting the placement of active sites at the interface. They also reported that water partial pressure plays a significant role in increasing the toluene formation rate for low loading Ru/TiO₂ catalysts (0.5 wt% and 3.5 wt% Ru), which may be attributed to a proton-assisted HDO mechanism. Here, we combine density functional theory (DFT) and kMC simulations to investigate reduction and hydroxylation

properties of rutile TiO₂(110) in the presence and absence of Ru nanoparticles, as well as *m*-cresol HDO reactions, with particular focus on the Ru/TiO₂ interface.

Method

While DFT can provide energetic information on atomistic processes, it is not sufficient to predict the interplay of these elementary steps and the observable kinetics of a complex reaction network under different reaction conditions. To address this question, we use first-principles kinetic Monte Carlo (kMC) simulations, a multiscale modeling approach that extends atomic-scale energetic information obtained from DFT to realistic time and length scales, to investigate the HDO reactions of *m*-cresol over TiO₂(110) in the presence and absence of Ru. A key advantage of kMC over more traditional microkinetic modeling is that it explicitly considers correlations, fluctuations, and spatial distributions of the chemicals on

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catalyst surface as illustrated by Reuter and Scheffler (2006).

Results and Discussion

Lateral interactions of adsorbates are important factors that govern surface structures and rates of elementary events as shown in the work by Mei *et al.* (2006). To eliminate the strong effect of Lewis acid-base pairs on adsorbate-adsorbate interactions as illustrated by Metiu *et al.* (2012), we extract pairwise interaction parameters from a series of co-adsorbed configurations that do not exhibit any electronic artifacts on rutile TiO₂(110).

Our kMC results show that the presence of Ru nanoparticles dramatically increases the reduction rate of the TiO₂(110) surface and HDO rate attributed to H spillover and a facile, heterolytic H₂ cleavage pathway across the Ru/TiO₂ interface as shown in Figure 1. We also qualitatively reproduce experimental results as conducted by Ketteler *et al.* (2007) for water adsorption on TiO₂(110). Notably, we show that the final surface termination of TiO₂(110) upon exposure to water depends on the initial vacancy concentration, while the same equilibrated surface termination is found for any initial condition when Ru nanoparticles are present. Under HDO reaction conditions over Ru/TiO₂, a coverage transition occurs at around 550 K. Consequently, two kinetic regimes at low and high temperature emerge as demonstrated by the Arrhenius plot in Figure 2(a). By varying the water partial pressure, a maximum turn over frequency (TOF) was found at 0.7 bar of water partial pressure as shown in Figure 2(b). It is interesting to note that, even though the reaction of adsorbed *m*-cresol on Ru with a vacancy at the interface has the lowest activation barrier of 0.62 eV and is the most exothermic C-O scission pathway ($\Delta E_{rxn}^0 = -2.12$ eV), the presence of added water in the feed impedes this reaction pathway by rapid water dissociation on vacancies, resulting in two hydroxyl groups. Alternatively, proton-assisted HDO reactions may occur at the interface.

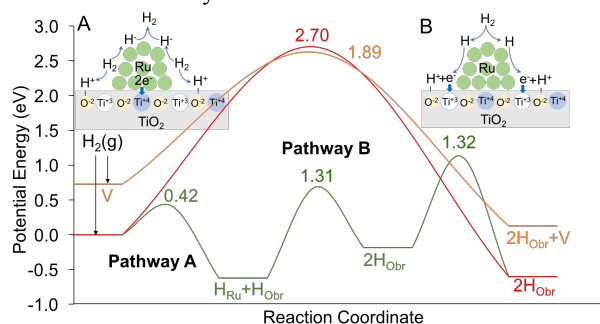


Figure 1. Potential energy diagram for TiO₂ reduction pathways: (A) Heterolytic H₂ activation; (B) spillover. Subscripts indicate different active sites: ruthenium (Ru) and oxygen bridge sites (O_{br}) at the interface.

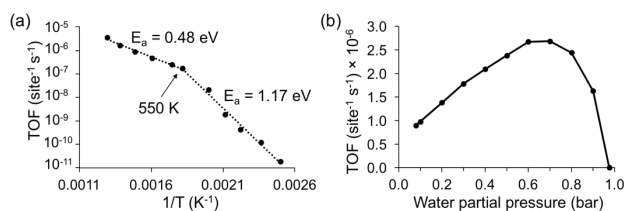


Figure 2. (a) Arrhenius plot for *m*-cresol HDO on Ru/TiO₂. (b) Turnover frequency dependence of the water partial pressure for *m*-cresol HDO on Ru/TiO₂.

Conclusion

Overall, our detailed simulation is capable of capturing coverage effects and mechanistic changes in response to variations in temperature or feed composition, including the addition of water to the feed. To our knowledge, there exist no comparable model with the ability to discriminate between metal, oxide and interfacial activity, and assign a dominant catalytic role to each component. This unprecedented insight into the fundamental processes that govern the activity of supported metal catalysts may pave the road to the design of next generation catalysts.

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