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Understanding trends in hydrodeoxygenation reactivity of metal and bimetallic alloy catalysts from ethanol reaction on stepped surface

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ABSTRACT

Platform molecules obtained from biomass are often found enriched with oxygen and require a suitable deoxygenation process for their conversion into high value chemicals and fuels. In this study, a combined density functional theory (DFT) and microkinetic model (MKM) based approach was utilized to understand the catalytic activity and selectivity trends observed for the hydrodeoxygenation (HDO) reactions of biomass-derived platform molecules on supported metal catalysts. This understanding was developed on modeling the C—O cleavage reaction of ethanol molecule over the stepped (2 1 1) surface of the metal catalysts using both carbon and oxygen binding energies as the descriptors. The two descriptor MKM showed that the activity for ethanol conversion to ethane at 523 K for a range of metal catalysts follows the order; Co > Ru > Ir > Rh > Ni > Fe > Pt > Pd > Cu > Re > Ag > Au. In general, as observed in the experiments of previous reports, the C—C cleavage in ethanol to produce methane shows higher turnover frequencies (TOFs) with negligible ethane formation. In contrast, since the focus of the MKM developed here was on the stepped surfaces, significant conversion towards the formation of ethane was calculated. The selectivity towards the HDO product was further improved on reducing the reaction temperature to 373 K. A range of metal catalysts viz. Cu, Pt, Rh, Ir, Ru, Ni and Co was observed to yield ethane selectively at 373 K, albeit with significantly reduced conversion. While the shift in selectivity towards the HDO product was at the expense of catalyst reactivity, general conclusions on the design of a selective metal HDO catalyst were drawn, further extending it to the design of a bimetallic alloy. In the screening of metal alloys, three specific catalysts (Co_3Ni, Co_3Fe and Ni_3Fe) were observed to show the maximum turnover of ethane ($10^{-3}\ s^{-1}$) with high selectivity. More specifically, the MKM developed for both metal and bimetallic catalysts provided insights into the reactivity trends observed in recent experimental HDO studies on biomass-derived model phenolic compounds.

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1. Introduction

HDO reactions are an important class of deoxygenation methods employed for catalytic transformation of platform molecules, obtained from biomass [1–4]. As compared to the C—C hydrogenolysis reaction, C—O bond cleavage in HDO helps in retaining the carbon chain length, while removing the unwanted oxygen. Ethanol, being the smallest molecule containing a single bond C—O and C—C, is an ideal system to study the trends in metal catalyzed HDO reactions vis-à-vis to C—C and C—O hydrogenolysis. Both theoretical and experimental attempts have been made in the past to study HDO in ethanol [5,6]. However, these attempts showed limited success in drawing comparison between C—C and C—O hydrogenolysis, since turnover frequencies (TOFs) higher by two orders of magnitude were reported for the formation of C—C scission product (CH_4 and CO) as compared to the C—O scission product (C_2H_6) [5]. Owing to the predominant formation of methane, kinetic modeling efforts were entirely focused on understanding the reaction on majority (1 1 1) sites leading to C—C cleavage [5,6]. For example, the kinetic model utilized by Mavrikakis et al. had explained the trends in C—C cleavage on the (1 1 1) surface of six metals: Cu, Pt, Pd, Ir, Rh, and Ru as a function of the carbon binding energy [5]. Similarly, DFT based study by Shan and Guo showed that the most probable decomposition pathway for ethanol on Pd(1 1 1) and Rh(1 1 1) involves C—C bond scission [7,8].

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Being a minor product, the trend in ethane formation from ethanol was difficult to discuss and thus predicting the trend of HDO reactions in biomass-derived molecules remained an elusive approach.

Herein an attempt is made to study the trend in HDO reaction while screening metal catalysts for ethanol decomposition in presence of hydrogen. The study showed significant success due to two important modifications as compared to previous attempts. First, the kinetic model was developed on the (2 1 1) surface, which is known to be more reactive as compared to the (1 1 1) surface [9,10]. Second, since HDO reactions involve an optimum balance between the strength of carbon and oxygen binding with the metal surface [4], a microkinetic model (MKM) using both carbon and oxygen binding energies as the descriptor was employed to explain catalyst activity and selectivity towards the HDO product. In the development of the MKM, no assumptions were made for any favored bond scission (C—C, C—O, C—H or O—H). Since transition metals show varying reactivity for the cleavage of different bonds, reaction routes with five different possibilities of initial bond-scission in ethanol were included in the model.

Importance of the reactivity of step sites has been recently elucidated in the DFT calculations on the HDO of phenol to benzene and cyclohexane, wherein Rh(2 1 1) was calculated to be more active than Rh(1 1 1) for C—O bond cleavage [11]. An attempt was made by Mavrikakis and co-workers to include the effect of step sites for explaining ethanol decomposition, however; the reaction energetics and corresponding rates of elementary steps on the step sites were extrapolated only from the (1 1 1) surfaces [5]. The higher reactivity of step sites is well known to play a crucial role in ethanol synthesis from syngas [12–14]. Therefore, it can be hypothesized that the trends in HDO of biomass-derived molecules may be explained by studying trends of HDO in ethanol on the stepped surface, which establishes the goal of this study. Moreover, the volcano plots, using the dual descriptor model, are expected to provide a rational design of a bimetallic catalyst to obtain high product yield in a HDO reaction. Following the principle of interpolation, the reactivity of a monometallic catalyst may be improved to approach the theoretical Sabatier maxima by alloying with another monometallic catalyst. For example, CO hydrogenation forming methane and water gives higher turnover on NiFe formed upon alloying Fe with Ni catalyst compared to pure Fe and Ni catalysts [15]. To the best of our knowledge, screening of bimetallic catalysts for ethanol reaction in presence of hydrogen is not discussed before. In an earlier attempt to predict trends of HDO selectivity for transition metals, Studt and co-workers have developed a MKM for ethylene glycol reaction, however; the model included only NiPt bimetallic alloy catalyst in the discussion, where Pt was indeed an expensive metal [4]. Thus, by providing a more comprehensive modeling approach by analyzing the reactivity of stepped surface for C—O scission in ethanol, the study aims to draw important conclusions on the reactivity of a wide range of both metal and bimetallic catalysts for HDO.

2. Methodology

The kinetic model was designed for the (2 1 1) surface of transition metals – Ag, Au, Pd, Pt, Ir, Cu, Ni, Co, Fe, Ru and Rh using the descriptor based analysis platform in CatMAP [16], developed at the Stanford University. The code utilizes mean field microkinetic approach, wherein steady-state solutions of the governing differential equations of the model were obtained using a multi-dimensional Newton's root finding method from the python mpmath library. Owing to the small size of hydrogen molecule, which enables adsorption at any site, two different adsorption sites were used in the model – one for all the adsorbates and the other for hydrogen so that hydrogen adsorption does not compete with the other adsorbates. The ratio of hydrogen sites and step sites was considered to be 1. In order to understand the sensitivity towards this ratio, other ratios (0.5, 0.1 and 0.01) were tried and the results were observed to be insensitive (Fig. SI-4). Fixed entropy gas and frozen adsorbate approximations were used for running the MKM. These solutions were obtained for reaction conditions at T = 523 K and 373 K, P = 2 bar, 50% H_2 and 50% CH_3CH_2OH. In this model, the adsorption and transition state energies are scaled with the binding energies of carbon and oxygen. More details of the MKM methodology developed by the Norskov's group is available in the previously reported work [17,18].

The energetics for most of the species used in the development of MKM were obtained from previous studies [13,14,19] on DFT calculations performed on transition state metals. Since energies of all the reaction intermediates were not available in the literature, adsorption energies of CHOH over Cu, Pd, Pt and Rh, CH_3CH_2 over Pd and CH_3CH_2O over Cu, Pd, Pt, and Rh (2 1 1) step surfaces were calculated using the periodic, plane-wave DFT code as implemented in Vienna Ab initio Simulation Package (VASP) [20]. Geometries of the intermediates adsorbed on the respective metal surfaces are shown in Fig. SI-5. The exchange–correlation energies were calculated by the Revised Perdew-Burke-Ernzerhof (RPBE) parameterization of the Generalized Gradient Approximation (GGA) [21]. The core electrons were defined using Ultrasoft pseudopotentials [22]. Kohn–Sham one-electron valence states were expanded using a plane wave basis set truncated to a cutoff energy of 396 eV. The surface Brillouin zone was sampled using a $3 \times 6 \times 1$ Monkhorst–Pack grid. The energy and force convergence criteria for the structure optimization were set to 1×10^{-4} eV and 0.05 eV/Å respectively. The (2 1 1) surface of Cu, Pd, Pt, and Rh was modeled as four-layer slab, with a vacuum of 15 Å between successive slabs. The lattice parameters of the unit cell are given in Table SI-1. A 3×3 supercell for metal (2 1 1) surfaces was used for the calculations. All adsorbates and the top two layers were allowed to relax, while the remaining two bottom layers were kept fixed to their bulk positions. The energy of the species was referenced with respect to hydrogen, water and methane. For all the metals, an error bar of 0.2 eV was considered for carbon and oxygen binding energies [23]. Transition state scaling relations were employed to determine the energy of the activated complex by correlating it to the energy of the corresponding dissociated state [24,25]. These relations correlate the transition state energy to the final state energy of the reaction step, incorporating both the geometric and electronic effect.

3. Results and discussion

Ethanol decomposition may begin with the initial α-H, O—H, β-H, C—O or C—C bond dissociation of the molecule opening into several different mechanistic routes as shown in Fig. 1, leading to the production of methane, carbon monoxide, methanol, water and ethane. In the MKM developed, different reaction pathways (details of elementary steps available in SI) were explored and the model was solved for the steady state condition. As compared to a Langmuir-Hinshelwood type model, in the MKM, none of the reaction steps were assumed to be rate-determining. Similarly, the model assumes no species on the surface as the most abundant reaction intermediate, or the surface to be nearly empty. From the input reaction energetics data, the model builds adsorption energy relationships as given by Abild-Pedersen et al. [26] and Jones et al. [27], to calculate the energetics of all the reaction intermediaries in terms of the MKM descriptors, E_C and E_O (binding energies of C and O respectively). Using these relationships, the model computed TOFs of reaction products with respect to the MKM descriptors, thereby reducing the descriptor space to two variables.

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