Using Microkinetic Analysis to Search for Novel Anhydrous Formaldehyde Production Catalysts

Han-Jung Li,^a Adam C. Lausche,^a Andrew A. Peterson,^b Heine A. Hansen,^c Felix Studt,^a and Thomas Bligaard^{a*}

^a SUNCAT Center for Interface Science and Catalysis, SLAC National Accelerator Laboratory, 2575 Sand Hill Road, Menlo Park, CA 94025, USA and Department of Chemical Engineering, Stanford University, Stanford, CA 94305, USA

^b School of Engineering, Brown University, Providence, RI 02912, USA

^c Department of Energy Conversion and Storage, Technical University of Denmark, Frederiksborgvej 399, DK-4000, Denmark

* Corresponding author: bligaard@stanford.edu, phone: +1 (650) 926-2716

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Abstract

Direct dehydrogenation of methanol to produce anhydrous formaldehyde is investigated using periodic density functional theory (DFT) and combining the microkinetic model to estimate rates and selectivities on stepped (211) surfaces under a desired reaction condition. Binding energies of reaction intermediates and transition state energies for each elementary reaction can be accurately scaled with CHO and OH binding energies as the only descriptors. Based on these two descriptors, a steady-state microkinetic model is constructed with a piecewise adsorbate-adsorbate interactions model that explicitly includes the effects of adsorbate coverage on the rates and selectivities as well as the volcano plots are obtained. Our results show that most of the stepped (211) pure-metallic surfaces such as Au, Pt, Pd, Rh, Ru, Ni, Fe, and Co are located in a region of low activity and selectivity towards CH_2O production due to higher rate for CH_2O dehydrogenation than CH_2O desorption. The selectivities toward CH_2O production on Zn, Cu, and Ag surfaces are located on the boundary between the high and low selectivity regions. To find suitable catalysts for anhydrous CH_2O production, a large number of A_3B -type transition metal alloys are screened based on their predicted rates and selectivities, as well as their estimated stabilities and prices. We finally propose several promising candidates for the dehydrogenation of CH_3OH .

1. Introduction

Formaldehyde (CH₂O) production from methanol is of considerable interest because CH₂O is an important intermediate in the production of a large number of industrial chemicals, such as plastics, resins, and explosives [1]. Recently, anhydrous CH₂O has gained increased attention because of its important applications, such as the production of high polymeric polyoxymethylene, solid CH₂O, polyacetal resin, agricultural chemicals, and medical intermediates [2]. Generally, CH₂O can be obtained from oxidative or non-oxidative methanol dehydrogenation by the following processes [3]:

The majority of CH₂O production is at present achieved through the catalytic partial oxidation of methanol in air over an Fe₂O₃–MoO₃ or silver catalyst, which produces 40% CH₂O in aqueous solution [4]. However, in this process a significant fraction of the reactant stream is wasted in producing by-products: large amounts of H₂O, CO, and dimethyl ether, as well as small amounts of CO₂ and formic acid [5]. This is further complicated by the formation of an azeotrope, which makes it costly to remove H₂O from the aqueous CH₂O product stream [6]. Non-oxidative dehydrogenation of CH₃OH, therefore, represents one strategy to not only produce anhydrous CH₂O but also to potentially reduce the waste of CH₃OH [4].

Ruf et al. experimentally reported that without any catalyst, methanol could dehydrogenate to anhydrous CH₂O at a very high temperature, 1173K, with a CH₂O yield being less than 20% and only 43% selective towards formaldehyde [7]. Anhydrous CH₂O production from non-oxidative CH₃OH dehydrogenation has been investigated on bulk and supported Ag, Zn, Cu, and Au catalysts [8-16], however, these catalysts were shown to deactivate a few hours. For instance, experimental work by Yamamoto et al. reported that, a P-promoted CuO/SiO₂ catalyst with 50% CH₃OH conversion and 80% CH₂O selectivity, was partially deactivated over the course of 4 h, possibly due to sintering [9]. Ren et al. also showed that although a AgO/SiO₂/MgO/Al₂O₃ catalyst could yield 100% CH₃OH conversion and 100% CH₂O selectivity at 873 K, the overall conversion decreased to 10% after only a few hours because of the reduction of the active AgO phase to inactive Ag [12]. Similarly, the non-oxidative CH₃OH dehydrogenation processes have also been reported with 62% CH₂O selectivity on mica- or zeolite-supported ZnO catalysts, where CH₂O production rates decreased with time due to the reduction of active ZnO to inactive Zn metal [17,18]. Generally, the reductive environment inherent to CH₃OH dehydrogenation causes oxygen-containing catalysts to deactivate quickly [5];

therefore, a highly capable catalyst for the dehydrogenation of CH_3OH is needed.

Although the non-oxidative dehydrogenation of CH_3OH attracts considerable interest because of the significant market for anhydrous formaldehyde, currently available catalysts are still unsatisfactory. Previous work by Lausche et al. combined density functional theory calculations with microkinetic modeling to provide a framework for understanding the trends in activity and selectivity for methanol dehydrogenation on stepped (211) sites of transition metal surfaces [19]. Generally, the more open surfaces are more active, which has been shown to give a reasonable correlation with experiments in a number of previous studies. In the present work, we have employed the same strategies to study anhydrous CH_2O production. However, in order to accurately scale large intermediates such as CH_2OH , CHOH , and CH_2O , we use the binding energies of CHO (E_{CHO}) and OH (E_{OH}) as descriptors rather than the binding energies of C (E_{C}) and O (E_{O}). In addition, we have considered adsorbate-adsorbate interactions using a piecewise model, previously reported by Khan et al. [20], to take into account the effects of adsorbate coverage on the rates and selectivities. One promising possibility is to use bimetallic alloys as catalysts, which have unique physical and chemical properties that differ from those of the pure metals. We have thus used our microkinetic model based on the pure metals to screen a large number of transition metal alloys based on their predicted rates and selectivities, as well as their estimated stabilities and prices. Finally we propose several candidates for the dehydrogenation of CH_3OH .

2. Methods

2.1 Density Functional Theory Calculations

All the binding energies of surface intermediates and transition states for the $\text{Ag}(211)$, $\text{Cu}(211)$, $\text{Pd}(211)$, $\text{Pt}(211)$, and $\text{Rh}(211)$ surfaces were taken from previously published works [19] and *CatApp* [21,22]. All other electronic structure calculations were performed using the DACAPO [23] plane wave code using the RPBE exchange-correlation functional [24]. We note here that RPBE yields similar energies for all intermediates involved in this study when compared to BEEF-vdW [25,26], a functional that specifically treats vdW interactions [27]. Face-centered cubic surfaces ($\text{Fcc}(211)$) were modeled by nine-layer slabs with a unit cell size of (1×3) . An energy cutoff of 340 and a density cutoff 500 eV were used, and a Monkhorst-Pack k-point grid of density $4 \times 4 \times 1$ was used to sample the Brillouin zones.

2.2 Microkinetic Modeling

In this work, the adsorption energies of C_xH_yO intermediates and transition states can be scaled linearly with the adsorption energies of CHO^* and/or OH^* , and the details of scaling relations for intermediates and transition states are described in the section 1 and 2 of the supplementary information, along with the fitting parameters of all the scaling relations. All the parameters of the microkinetic model were performed as described in Section 3 of the supplementary information. The steady-state numerical solutions to the microkinetic model were obtained assuming a 0.1% approach to equilibrium (95% CH_3OH , 1% CH_2O , 1% CO , and 3% H_2) at 823 K and 1 bar to achieve reasonable rates and simulate reactor operation under differential conditions [28].

A piecewise adsorbate-adsorbate interaction model was included in the microkinetic model, which was previously reported by Khan et al. [20]. The adsorbate-adsorbate interaction effects were calculated by calculating the change in adsorption energy at various coverages. At the stepped (211) surface coverages above the threshold coverage, $\theta^0 = 0.5$ ML, adsorption energies of adsorbates decreased linearly, while the change in the adsorption energy was negligible for surface coverages below this value, similar to results described elsewhere [29,30]. As described in reference [29], three different adsorption sites, step (s), four-fold (f), and terrace (t) were included in a stepped (211) surface. All of the intermediates in this work preferentially adsorbed at the step site over the other sites. In addition, the presence of under coordinated sites such as the step sites have been shown to be particularly important for catalytic activity of the metal nanoparticles for different catalytic processes [31]. Therefore, we performed an interaction model, which assumed that all reaction intermediates were preferentially adsorbed at step sites and are present in negligible amounts at the other sites. Further details of the adsorbate-adsorbate interaction model and the linear scaling parameters used in this work are shown in section 4 of the supplementary information.

3. Results and discussions

3.1 Microkinetic Modeling

The 13 elementary steps for the CH_3OH dehydrogenation process are shown below:

The free energy diagram for CH_3OH dehydrogenation to CH_2O , CO , and H_2 on a stepped $\text{Cu}(211)$ surface is depicted in Fig. 1. From the free energy diagram, there are two possible reaction pathways for CH_3OH dehydrogenation: through the O–H bond scission of CH_3OH to form a CH_3O intermediate or through the C–H bond scission of CH_3OH to form a CH_2OH intermediate in the first step.

Fig. 1. Free energy diagram for CH_3OH dehydrogenation to CH_2O , CO , and H_2 on a $\text{Cu}(211)$ surface. Reaction conditions are: $T = 823 \text{ K}$, $P = 1 \text{ bar}$, with a gas composition of 95% CH_3OH , 1% CH_2O , 1% CO and 3% H_2 .

The volcano plots for calculated turnover frequencies (TOFs) for CH_3OH decomposition starting from O–H or C–H bond scissions of CH_3OH are shown in Fig. 2. These plots are shown without (a and b) and with (c and d) adsorbate-adsorbate interactions. Comparing the volcano plots of O–H (Fig. 2(c)) and C–H (Fig. 2(d)) bond scission rates, we found that the rate of O–H bond scission was ca. 3 ~ 4 orders of magnitude greater than C–H bond scission on a stepped $\text{Cu}(211)$ surface, in agreement with previous theoretical work [32,33]. The other transition metals in the volcano plots, materials such as Ag, Zn, Co,

Ru, Ni, and Fe, are predicted to proceed through an initial O–H bond scission, while materials such as Pd and Pt prefer to proceed through an initial C–H bond scission. On Rh and Au, the first dehydrogenation of CH₃OH competitively proceeds through O–H or C–H bond cleavages. These results are consistent with previous theoretical studies [34–37], which have investigated the reaction pathways for CH₃OH dehydrogenation.

Comparing the TOFs of CH₃O–H bond scissions without (Fig. 2(a)) and with (Fig. 2(c)) the inclusion of adsorbate–adsorbate interactions, it was found that the maximum TOFs and the trend do not change after the interactions are included. The shape of the volcano with adsorbate–adsorbate interactions is different from the counterpart without interactions in that the former one becomes broad in the strong-binding region of E_{OH} (E_{OH} < -1 eV) due to the change of CH₃O* coverage (see Fig. 3(b) and (e)). With the inclusion of adsorbate–adsorbate interactions, the decreased coverage of CH₃O* produces an increased coverage of surface free sites, which can help the dissociation process; the shape of the volcano for TOFs of CH₃O–H bond scissions, accordingly, becomes broad in this area.

Fig. 2. Calculated turnover frequencies (TOFs) for CH₃OH decomposition through CH₃O–H and H–CH₂OH bond scissions without (a and b) and with (c and d) the inclusion of adsorbate–adsorbate interactions as a function of CHO (E_{CHO}) and OH (E_{OH})

binding energies. E_{CHO} and E_{OH} for the (211) surfaces of selected transition metals are depicted along with error bars that indicate an estimated error of 0.2 eV for E_{CHO} and E_{OH} . Reaction conditions are 823 K and 1 bar with a gas composition of 95% CH_3OH , 1% CH_2O , 1% CO , and 3% H_2 .

Similarly, as can be seen from the TOFs for $\text{H}-\text{CH}_2\text{OH}$ bond scissions without (Fig. 2(b)) and with (Fig. 2(d)) the inclusion of adsorbate–adsorbate interactions, the position of the TOF maximum and the trend is essentially unchanged after the interactions are included. Again, the shape of the volcano with interactions becomes broad in the region of CHO binding energy around $-0.5 \sim 0.5$ eV compared to the volcano without interactions, which is due to the change in CO^* (Fig. 3(a) and (d)) coverage. The inclusion of adsorbate–adsorbate interactions decreases the coverages of CO^* (around $E_{\text{CHO}} = -0.5 \sim 0.5$ eV), which results in an increased coverage of surface free sites and cause $\text{H}-\text{CH}_2\text{OH}$ bond scission to be dominant.

The predicted TOFs for the production of CH_2O from CH_3OH dehydrogenation with and without the inclusion of interactions are shown in Fig. 4(a) and (d), respectively. The volcano for CH_2O production (Fig. 4(d)) is similar to a lower right portion of the volcano for $\text{CH}_3\text{O}-\text{H}$ bond scission (Fig. 2(c)), indicating that the production of CH_2O primarily proceeds through the $\text{CH}_3\text{O}-\text{H}$ path via a CH_3O intermediate. On the other hand, the volcano for CO production (Fig. 4(e)) is similar to the sum of the volcanoes for $\text{H}-\text{CH}_2\text{OH}$ (Fig. 2(d)) and $\text{CH}_3\text{O}-\text{H}$ bond scissions, which demonstrates that CO production might be a combined contribution from these two paths. Unsurprisingly, the volcano for H_2 production (Fig. 4(f)) corresponds to the sum of the volcanoes for CH_2O and CO production. As shown in Fig. 4(d) ~ (f), the TOFs of CH_2O , CO , and H_2 productions are quite small in the E_{CHO} strong-binding region with $E_{\text{CHO}} = -0.5 \sim -1$ eV, which can be attributed to the surface being almost completely blocked by CO in this area. Besides, Fig. 4(d) illustrates that in the upper left portion of volcano plot, the TOF for CH_2O production is negligible due to CH_2O being adsorbed from gas phase rather than desorbed in this area.

Fig. 3. Coverages of CO*, CH₃O*, and surface free site as a function of E_{CHO} and E_{OH} as obtained from the solutions of the microkinetic model without (a ~ c) and with (d ~ f) the inclusion of adsorbate-adsorbate interactions. E_{CHO} and E_{OH} for the (211) surfaces of selected transition metals are depicted and the error bars indicate an estimated error of 0.2 eV for E_{CHO} and E_{OH} . Reaction conditions are 823 K and 1 bar with a gas composition of 95% CH₃OH, 1% CH₂O, 1% CO, and 3% H₂. Small amounts of coverage for COH* are in left bottom corner of volcano, which is shown in Fig. S2 of the supplementary information.

The predicted selectivity plots toward CH₂O production with the inclusion of adsorbate-adsorbate interactions are given in Fig. 5(d). Selectivity is defined by the rate of CH₂O formation divided by the sum of the rates of CH₂O and CO formation. As shown in Fig. 5(d), most of the stepped (211) metallic surfaces such as Au, Pt, Pd, Rh, Ru, Ni, Fe, and Co are located in the region of low selectivity towards CH₂O, which means that the majority of products are predicted to be CO rather than CH₂O. Inspection of Fig. 5(a) and (b) reveals that Au, Pt, Pd, Rh, Ru, Ni, Fe, and Co, have higher TOFs for CH₂O dehydrogenation compared to CH₂O desorption, which is consistent with the low selectivity toward CH₂O that we found on the corresponding stepped (211) surfaces. These results suggest the intriguing possibility of improving the selectivity towards CH₂O production by tuning the reactivity of the metallic catalyst. Since the selectivities toward CH₂O production on Zn, Cu, and Ag surfaces are located in the boundary between the high and low selectivity regions, we expect that Zn, Cu, and Ag might be better candidates for tuning the reactivity. Two possible strategies are: (1) modifying the electronic structure of the metal by forming bimetallic alloys, or (2) changing the coordination number of metal by using the (111) facet. We demonstrate the first

possibility in the next section, while the latter possibility is explored in a forthcoming work [38].

Fig. 4. Calculated TOFs for the production of CH_2O , CO and H_2 from CH_3OH dehydrogenation without (a ~ c) and with (d ~ f) inclusion of adsorbate–adsorbate interactions as a function of E_{CHO} and E_{OH} . E_{CHO} and E_{OH} for the (211) surfaces of selected transition metals are depicted and the error bars indicate an estimated error of 0.2 eV for E_{CHO} and E_{OH} . Reaction conditions are 823 K and 1 bar with a gas composition of 95% CH_3OH , 1% CH_2O , 1% CO , and 3% H_2 .

3.2 Alloy Screening

We have screened a large number of transition metal alloys based on their predicted rates and selectivities from our microkinetic model, estimated their stabilities and prices, and finally propose several candidates for the dehydrogenation of CH_3OH process. Two terminations of the A_3B -type alloy (where A and B are two different transition metals), AA and AB, are considered in the screening process (shown in Fig. S2 of the supplementary information). The estimated formation energies, calculated binding energies of CHO and OH , predicted rates of CH_2O production, and price of considered alloys are summarized in Table S4 of the supplementary information.

Fig. 5. Calculated TOFs for (a) CH_2O production, (b) H–CHO bond scission, and (c) CO production as well as (d) selectivity toward CH_2O production with inclusion of adsorbate-adsorbate interactions as a function of E_{CHO} and E_{OH} . E_{CHO} and E_{OH} for the (211) surfaces of selected transition metals are depicted and the error bars indicate an estimated error of 0.2 eV for E_{CHO} and E_{OH} . Reaction conditions are 823 K and 1 bar with a gas composition of 95% CH_3OH , 1% CH_2O , 1% CO, and 3% H_2 .

3.2.1 Stability filter

As described in reference [39], the stable formation of an intermetallic compound composed of two metallic elements is described by the alloy's formation energy, E_f , which can be defined as:

$$E_f = E_{\text{alloy}} - N_A E_{A(\text{bulk})} - N_B E_{B(\text{bulk})}$$

where E_f is the formation energy, E_{alloy} is the DFT-calculated energy of the metal alloy, N_i and $E_{i(\text{bulk})}$ are the molar ratios and the DFT calculated energies, respectively, of the individual metal, i . According to this definition, the more negative the value, the more stable the alloy. For the purposes of the present analysis, only alloys with formation energy less than 0 eV per unit cell were considered to be potentially stable (approximately 440 alloys). The estimated formation energies are listed in Table S4 of the supplementary information.

3.2.2 Activity and selectivity filters

As we have shown, the binding energies of CHO and OH are valid descriptors for predicting the reaction rate and selectivity for anhydrous CH₂O production. The binding energies of CHO and OH on these thermodynamically stable stepped (211) alloys were also calculated using DFT and given in Table S4 of the supplementary information. Now we proceed to screen these stable transition metal alloys based on the established volcano from microkinetic modeling, illustrated in Fig. 6(a). As shown in Fig. 6(a), the alloys can be divided into two categories based on both activity and selectivity: (1) the alloys with the turnover frequencies of CH₂O production smaller than 10⁻¹ s⁻¹ or the selectivity toward CH₂O smaller than 0.7 (denoted with a black circle); (2) the alloys with the turnover frequencies of CH₂O production larger than 10⁻¹ s⁻¹ and the selectivity toward CH₂O larger than 0.7 (denoted with a white star). After filtering by activity and selectivity, approximately 90 alloys (denoted by white stars) are predicted to be the suitable catalysts for anhydrous CH₂O production. These approximately 90 alloys further are screened by price in next section.

Fig. 6. Alloys screening from activity, selectivity, and costs with adsorbate-adsorbate interactions: (a) Alloys are divided into two categories based on both activity and selectivity: (1) alloys with low activity or selectivity (TOFs < 10⁻¹ s⁻¹ or selectivity < 0.7, black circle) and (2) alloys with high activity and selectivity (TOFs ≥ 10⁻¹ s⁻¹ and selectivity ≥ 0.7, white star); (b) alloys are divided into two categories based on the material costs of their component metals: (1) expensive alloys (cost ≥ \$2000 kg⁻¹, black star) and (2) inexpensive alloys (cost < \$2000 kg⁻¹, yellow star). The volcanoes for the production of CH₂O under reaction conditions are 823 K and 1 bar with a gas composition of 95% CH₃OH, 1% CH₂O, 1% CO, and 3% H₂.

3.2.3 Price filter

The price of the catalyst is always an important consideration in industry due to the need for large-scale production. In this section, we have used simple interpolation estimation to calculate the price of the metallic alloys, A_3B , composed by A and B elements. Reference prices of pure metals were taken from website chemcool [40] and the estimated prices for A_3B alloys were given in Table S4 of the supplementary information. We assume that the estimated prices of each alloy only depend on the composition ration of A and B elements, while we do not consider the costs for preparation. To exclude alloys containing relatively expensive metals, we set the cutoff price of alloys as $\$2000 \text{ kg}^{-1}$, illustrated in Fig. 6(b). Black stars denote the considered alloys with prices higher than $\$2000 \text{ kg}^{-1}$, while yellow stars in the volcano plot denote the alloys with prices lower than $\$2000 \text{ kg}^{-1}$. After screening by rate, selectivity, and price, only 39 alloys were left in the volcano plot, listed in Table 1. It should be noted that other elementary reaction steps steps than what we consider in this analysis might influence the reaction over some of these alloys. For instance, the direct C-O bond scission might be relevant over highly oxophilic metals.

From our prediction of alloys screening for the anhydrous CH_2O production from CH_3OH , we propose several bimetallic alloy candidates, which can provide experimentalists an alternative for future research in to catalytic CH_3OH dehydrogenation to produce anhydrous CH_2O .

Table 1: The screened alloys with the TOFs of CH_2O production $\geq 10^{-1} \text{ s}^{-1}$, selectivity toward CH_2O production ≥ 0.7 , and price $< \$2000 \text{ kg}^{-1}$.

$\text{Co}_3\text{Zr}/\text{AA}, \text{AB}$	$\text{Zn}_3\text{V}/\text{AA}$	$\text{Cd}_3\text{Y}/\text{AB}$	$\text{Pb}_3\text{Sc}/\text{AB}$	$\text{Zr}_3\text{Pb}/\text{AB}$
$\text{Ti}_3\text{La}/\text{AA}, \text{AB}$	$\text{Zn}_3\text{Y}/\text{AA}$	$\text{Co}_3\text{W}/\text{AB}$	$\text{Pb}_3\text{Y}/\text{AB}$	$\text{Zr}_3\text{Sb}/\text{AB}$
$\text{Fe}_3\text{Al}/\text{AA}$	$\text{Zn}_3\text{Zr}/\text{AA}$	$\text{Cu}_3\text{Al}/\text{AB}$	$\text{Sb}_3\text{Y}/\text{AB}$	$\text{Zr}_3\text{Sn}/\text{AB}$
$\text{Zn}_3\text{Fe}/\text{AA}$	$\text{Ag}_3\text{Al}/\text{AB}$	$\text{Ga}_3\text{Hf}/\text{AB}$	$\text{Sn}_3\text{Sc}/\text{AB}$	
$\text{Zn}_3\text{Hf}/\text{AA}$	$\text{Ag}_3\text{Y}/\text{AB}$	$\text{Hf}_3\text{Bi}/\text{AB}$	$\text{Sn}_3\text{Y}/\text{AB}$	
$\text{Zn}_3\text{Mo}/\text{AA}$	$\text{Al}_3\text{Cu}/\text{AB}$	$\text{Hf}_3\text{Sb}/\text{AB}$	$\text{Sn}_3\text{Zr}/\text{AB}$	
$\text{Zn}_3\text{Nb}/\text{AA}$	$\text{Bi}_3\text{La}/\text{AB}$	$\text{Hf}_3\text{Sn}/\text{AB}$	$\text{Ti}_3\text{Sc}/\text{AB}$	
$\text{Zn}_3\text{Ni}/\text{AA}$	$\text{Bi}_3\text{Sc}/\text{AB}$	$\text{Ni}_3\text{V}/\text{AB}$	$\text{Ti}_3\text{Y}/\text{AB}$	
$\text{Zn}_3\text{Ti}/\text{AA}$	$\text{Bi}_3\text{Y}/\text{AB}$	$\text{Pb}_3\text{La}/\text{AB}$	$\text{Zr}_3\text{Bi}/\text{AB}$	

4. Conclusions

We have demonstrated that binding energies of reaction intermediates and transition state energies for each elementary reaction can be accurately scaled with only two descriptors, E_{CHO} and E_{OH} , for dehydrogenation of CH_3OH on stepped (211) surfaces.

Based on these two descriptors, a microkinetic model performed with piecewise adsorbate-adsorbate interactions is used to estimate the reaction rates and selectivities. Our results show that the maximum TOFs of CH₂O production do not change, while the shape of the volcano becomes broad after the interactions are included due to the change of coverage for CH₃O* and surface free sites. Most of the stepped (211) metallic surfaces such as Au, Pt, Pd, Rh, Ru, Ni, Fe, and Co are located in the region of low selectivity towards CH₂O, while Zn, Cu, and Ag are located near the region of boundary between high and low selectivities. Based on the estimated microkinetic model on the stepped (211) pure metals, we use two descriptors (E_{CHO} and E_{OH}) to predict the rates and selectivities, as well as estimate the stabilities and prices for a large number of transition metal alloys. Finally, we propose several candidates for the production of anhydrous formaldehyde.

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