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Effects of phosphorus on C—C, C—O, and C—H bond rupture during acetic acid decomposition over Ru(0001) and P_x-Ru(0001)

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ABSTRACT

Investigation of the conversion of acetic acid (a model oxygenate) on well-defined metal and metal phosphide surfaces provides insight to the reasons for the high selectivities of transition metal phosphide (TMP) catalysts for hydrodeoxygenation of bio-oils. Temperature programmed reaction (TPR) of acetic acid isotopologues on pristine Ru(0001) and a P modified Ru(0001) surface, representative of the Ru_2P (111) facet, show an identical sequence of elementary steps for acetic acid decomposition. The inclusion of P atoms in the surface does, however, lead to electronic changes of the Ru atoms and increase activation barriers for C—O, C—C, and C—H bond scission by values of ~5–10 kJ mol^{-1}. The differences increase the prevalence of C—C bond rupture over C—O bond rupture by a factor of two (determined in TPR measurements). Based on the changes in product selectivity and the relative changes in activation energies for C—C and C—O bond rupture, these results indicate that the addition of P atoms will increase selectivities toward C—O bond rupture during high temperature, hydrotreating catalysis, which matches reported HDO selectivities that are greater on TMP catalysts than on the corresponding metallic nanoparticles. These results provide fundamental insight to the reasons for the greater selectivity for C—O bond rupture.

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1. Introduction

Biomass is an alternative carbon source that can be used to produce fuels and chemicals with greenhouse gas emission lower than those associated with the conversion of fossil carbon sources [1]. Pyrolysis reactions convert biomass into crude bio-oil; however, bio-oil has a low pH (e.g., 2–3) due to a significant content of acetic and formic acids, which corrode storage vessels [2] and lower the heating value of the bio-oil [3–6]. These deleterious carboxylic acids (and other oxygenate compounds) may be eliminated from bio-oil by hydrodeoxygenation (HDO), which increases the chemical stability and decreases the oxygen content of the bio-oil. In addition, selective C—O bond rupture and hydrogen transfer reactions during hydrogenolysis can also produce platform chemicals (e.g., furfural, hydroxymethylfurfural (HMF) and levulinic acid) [7] and fuel additives on catalysts such as transition metal phosphides (TMP; e.g., PdP [8], MoP [9], CoP [10], WP [10], FeP [10], Ni_2P [11] and Ru_2P [12]). For instance, Ni_2P [11,13] and Ru_2P [12] selectively cleave hindered C—O bonds without facilitating C—C bond rupture [14], which differs significantly from the selectivity

patterns of the unmodified transition metal catalysts. As an example, hydrogenolysis of furan over a Ru/SiO$_2$ catalyst leads to a combination of C—C and C—O bond rupture reactions that produce C_3 hydrocarbon products with selectivities of nearly 90% [12]; however, Ru_2P/SiO$_2$ primarily cleaves C—O bonds to produce 83% C_4 hydrocarbons [12]. Predictions from density functional theory (DFT) calculations and surface science studies [15–17] suggest that the inclusion of phosphorus (P) atoms within transition metal surfaces may alter product selectivities due to the formation of Lewis acid sites, potential changes in reaction mechanisms due to this added catalytic function, and the dilution of metal ensembles. The method by which P atoms may change energetic barriers for bond rupture events (e.g., C—H, C—O, and C—C bond) that occur at transition metal sites during hydrogenolysis, however, remains unclear [6,12,18]. Clear understanding of the effect of P atoms on reaction mechanisms and the activation barriers during oxygenate conversion may assist the development of improved TMP catalysts with greater activity and selectivity toward specific C—O bonds. Notably, such selectivity patterns could enable the production of high value chemicals (e.g., primary alcohols, aldehydes, and olefins) from biomass.

We previously showed the effect that P atoms have on molecular chemisorption on the Ru(0001) surface and on the activation energies for C—H and C—O bond rupture during formic acid (i.e.,

DCOOH) decomposition [19]. The results demonstrated that P atoms decrease binding energies of small molecules (e.g., CO, NH$_3$) to surface Ru atoms and increase barriers to cleave the C—O bond more than the C—D bond of deuterated labeled formate (DCOO*). Together these changes suggest that coordination of P atoms to surface Ru decreases the extent of electron exchange and back donation between Ru and adsorbates, which is consistent with DFT calculations for Ni$_2$P(0001) [20]. Calculations based on the reactive molecular beam scattering experiments of DCOOH, onto a clean (i.e., *abundant) P modified Ru(0001), show that the addition of P atoms increases the C—O bond rupture energy barrier by 28 kJ mol^{-1} and C—D bond rupture energy barrier by 11 kJ mol^{-1}. In addition, the DCOOH scattering experiments as a function of temperature (400–800 K) over P$_x$-Ru(0001) showed C—D bond scission is preferred over C—O bond at temperatures less than 500 K, however, the higher activation energy for C—O bond scission leads to greater selectivity to this pathway as the surface temperature increases beyond 500 K. This trend is consistent with results showing an increase in C—O bond rupture selectivity in HDO of 2-methyltetrahydrofuran on Ni$_2$P compared to Ni [21].

Here, we use a combination of temperature programed reaction (TPR) and reactive molecular beam scattering (RMBS) of a series of acetic acid isotopologues (i.e., perhydrogenated, perdeuterated, and with selective ^{13}C labeling) to probe how the presence of P atoms influences the binding energy of adsorbates and energy barriers for C—H, C—O, and C—C bond scission within acetic acid on Ru (0001) and P modified Ru(0001) surfaces. The mechanism for acetic acid decomposition on single crystal metal surfaces (e.g., Pd(1 1 1) [22], Pt(1 1 1) [23], Cu(1 0 0) [24], Cu(1 1 0) [25], Ni (1 1 1) [26], Ni(1 1 0) [27], and Al(1 1 1) [28]) involves dehydrogenation to form acetate (CH$_3$COO*) and atomic hydrogen (H*) [29], followed by the decomposition of acetate by either C—C bond cleavage to form CO$_2$, C* and 3H* or by C—O bond cleavage followed immediately by C—C bond cleavage to form CO, adatom oxygen (O*), C* and 3H*. TPR measurements of isotopically labeled acetic acid (e.g., CH$_3$^{13}COOH) on Ru (0001) and P$_x$-Ru(0001) surfaces (where x is the ratio of P atoms to Ru atoms) show that the elementary steps for acetic acid conversion remain constant (Scheme 1), but that the addition of P atoms to Ru(0001) increases the temperature at which acetate decomposes by increasing barriers for both C—O and C—C bond rupture.

Additionally, P atoms increase barriers for C—H bond rupture within CH$_3$* dehydrogenation following acetate decomposition (Scheme 1). We estimate the energy barrier for C—C bond rupture by the reaction of acetate with an adjacent unoccupied Ru site (*) since an unoccupied site is required to assist in C—C bond rupture; this has previously been used to describe the rate of acetate

decomposition as a function of acetate intermediate coverage (θ_{AC}) and unoccupied metal sites (*) coverage on other surfaces (e.g., Pd(1 1 0) [30], Ni(1 1 0) [31,32], Rh(1 1 1) [33], and Rh (1 1 0) [34]). We calculated that P atoms increase the intrinsic activation energy for C—C bond rupture by 7 kJ mol^{-1} during acetic acid decomposition, similar to the 10 kJ mol^{-1} increase observed in C—H bond rupture on formic acid decomposition over P modified Ru(0001) [19]. The increase in the C—C bond rupture energy barrier during acetic acid decomposition is consistent with an electronic effect on the active site for the reaction, specifically, a small charge transfer from Ru to P likely reduces the extent of electron back donation toward the anti-bonding orbital of the acetate intermediate and increases the barrier for C—C bond cleavage. Similar changes are seen for C—H and C—O bond rupture, however, small differences in these values lead to significant differences in the selectivity toward CO and CO$_2$ during acetate decomposition, which suggest that the addition of P atoms increases activation energies for C—O bond rupture more than for C—C bond rupture in acetate decomposition. The changes in product selectivity and activation energies for bond rupture are consistent with comparisons between transition metal catalysts and the corresponding TMP catalysts published previously and provide fundamental insight to the reasons for the greater selectivity for C—O bond rupture on TMP.

2. Materials and methods

All experiments are conducted within a custom-made ultrahigh-vacuum (UHV) system, and the details of the UHV system have been described previously [19]. Briefly, the UHV contains four chambers of which Chambers 1 and 2 comprise of a separable high vacuum section used to generate a molecular beam to dose molecules onto the sample surface for TPR and RMBS experiments. Chamber 3 provides differential pumping and assists in collimating the molecular beam. Chamber 4 has a base pressure of ~1×10^{-10} Torr and contains the Ru(0001) sample (Surface Preparation Labs, 99.999% purity, 12 mm diameter and 2 mm thick) on which all experiments are performed. The Ru(0001) single crystal is mounted by a 0.30″ diameter molybdenum wire (ESPI, 3N8) to 0.25″ thick high purity Cu electrical feedthroughs. The sample temperature is controlled over the range of 100–1500 K (measured by a type K thermocouple) using a combination of cooling with liquid nitrogen and resistive heating. Chamber 4 also contains instruments for low energy electron diffraction (LEED; PHI, 15–120), Auger electron spectroscopy (AES; Perkin-Elmer, 10–155), and quadrupole mass spectrometry (QMS; Extrel 500 HT). The Ru (0001) single crystal is mounted on an XYZ translator (U.H.V. Instrument, 3000-400-2-2-2), which in turn, is attached to a
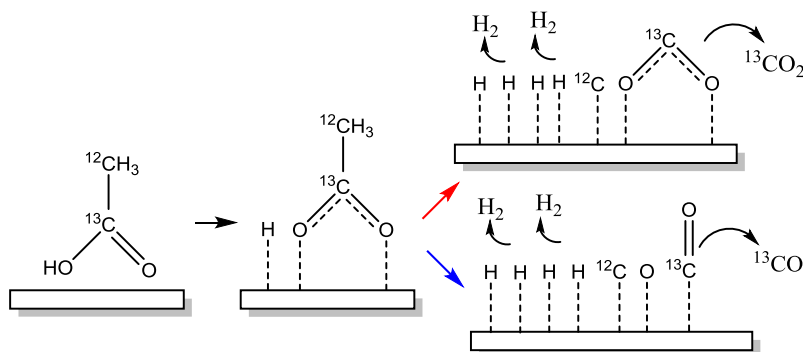
Scheme 1. Illustration of acetic acid decomposition over transition metals. Red arrow represents acetate decomposition pathway via C—C bond rupture to produce CO$_2$, while blue arrow represents decomposition pathway initiated by C—O bond rupture to produce CO.